DEPARTMENT OF
MINES AND TECHNICAL SURVEYS
MINES BRANCH

SYMPOSIUM ON THE PREPARATION AND PROPERTIES OF LEAD ZIRCONATE-LEAD TITANATE PIEZOELECTRIC CERAMICS

FOREWORD BY I. F. WRIGHT

MINERAL PROCESSING DIVISION

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FOREWORD

by

I. F. Wright*

Polycrystalline ceramics for electronic applications have conventially been made by the blending of various oxides, calcining and grinding this mixture to a fine powder, and pressing and sintering this powder into the desired shape. The electrical and electronic properties of the final shape are primarily dependent on the chemical composition of the material, but may be modified to a degree, either unfavourably or favourably, by the presence, respectively, either of unwanted impurities or of minor deliberate additives. The electrical properties of the shape are also dependent on other physical properties such as density and grain size. In manufacture and in the majority of research work that has been done on such materials, neither the initial mixing nor the calcining is ever complete, nor have the problems of optimizing the sintered density and of controlling the grain growth during sintering been thoroughly investigated. Consequently, much of the published information concerning such ceramics may be as much a function of the manufacturing technique as of the basic chemical composition itself. Such a state of affairs results not only in a lack of reproducibility on the production line, but presents an expensive and often inadequate method of evaluating the individual oxides for use in the manufacture of any particular ceramic composition or shape.

In the investigations described in this series of papers, which have been partly supported by the Canadian Defence Research Board under E.C.R.D.C. Research Project C-73, the solid-solution series lead zirconate-lead titanate, such as is used in transducer applications, was selected for consideration. The feasibility of producing intimate mixtures of oxides by wet chemical techniques has been demonstrated. The reproducibility of these mixtures with their compositions lying within the limits of accuracy of present analytical techniques has been shown. These analytical procedures are described, as are also the results of a phase study of the $PbO-ZrO_2-TiO_2$ system at 1100°C. The effects of certain common impurities and of certain fabrication parameters are also described.

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The system $PbO-ZrO_2-TiO_2$ at 1100°C

Foreword by I.F. Wright*

by A. Hubert Webster **
Ronald C. MacDonald **
Wm. S. Bowman ***

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ABSTRACT

The system $PbO-ZrO_2-TiO_2$ has been examined with particular emphasis on the sub-solidus phase relationships at 1100°C. The $PbZrO_3-PbTiO_3$ solid solution series has been found to exhibit smaller deviations from the ratio $\frac{PbO}{ZrO_2 + TiO_2} = 1$ than had been previously reported. Zirconium dioxide containing titania in solid solution, the compound $ZrTiO_4$ and titania have been found to co-exist with various ranges of the $PbZrO_3-PbTiO_3$ solid-solution series. Zirconia can take up to about 14 mol % of titania into solid solution. The general form of the diagram, however, agrees with the results of previous work by Ikeda et al.[5]

Introduction

Certain compositions in the lead titanate-lead zirconate solid-solution series show ferroelectric properties. Ceramic shapes, made from these ferroelectric compositions, when subjected to a high electric field, acquire piezoelectric properties and, hence, are of practical interest as electromechanical transducers.

The lead titanate-lead zirconate solid solution has been extensively studied [1,2,3] and [4]. This solid solution has a perovskite-type structure, cubic at high temperatures. Below the ferroelectric Curie temperature (490°C to 230°C, depending upon composition), lead titanate and solid solutions rich in lead titanate are distorted slightly from cubic to tetragonal symmetry. Except for a small range near lead zirconate itself, in which the solid solution is antiferroelectric and has orthorhombic structure, compositions richer in lead zirconate show rhombohedral symmetry. It is those compositions near the tetragonal-rhombohedral boundary that show the most enhanced ferroelectric properties.

A study of the $PbO-ZrO_2-TiO_2$ system, in which the lead titanate-lead zirconate solid-solution series occurs, was reported by Ikeda

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and co-workers[5] after preliminary work in this investigation had begun. Since (a), the system is of considerable technical interest, (b), somewhat different procedures in sample preparation were used, and (c), certain discrepancies were found with the published work, it was decided to continue the investigation. The present paper represents the results of these studies.

Experimental procedures

Compositions for study were prepared by co-precipitation from mixed solutions of the constituents, lead, zirconium, and titanium, in nitric acid solution. Aqueous ammonia, together with a small quantity of ammonium bicarbonate, was used as the precipitating agent. Using the co-precipitated material, it was possible to achieve reactions without the prolonged firing times that would have been required, in certain instances, had the constituents used been mixed powders of the component oxides. Solutions were prepared by dissolving lead oxide (Fisher Certified Reagent) and zirconyl nitrate (Anachemia C.P.) in nitric acid. Titanium dioxide (Baker's Analysed Reagent) was dissolved in concentrated sulphuric acid with added ammonium sulphate, and the hydroxide precipitated with ammonia, and redissolved in nitric acid. Hydrogen peroxide was added to complex the titanium and to stabilize the stock solution. The solutions were standardized, and mixed as required.

The precipitates were calcined at 650°C, crushed, pressed to half-inch diameter pellets, heated to 1100°C in air and held at this temperature for one hour. The pellets were then withdrawn from the furnace and air-cooled to room temperature. Each sample pellet sat upon a thin disk of its own composition. Another disk, also of the same composition, was placed on top of the sample pellet. This procedure was adopted to minimize loss of lead oxide from the samples. The pellets so protected were held in an alumina sagger.

Each sample was examined by X-ray diffraction using a 114.7 mm diameter Debye-Scherrer camera with Cu Kα radiation. Selected samples were also examined by chemical analysis, by differential thermal analysis, or by optical microscopy. Semi-quantitative spectrographic analysis indicated that the principal impurities were Mg, Ca and Si, associated with the zirconium, and Al, associated with the titanium, at levels of about 0.1 to 0.3%.

TABLE 1

Comparison of nominal compositions of selected samples with compositions after firing, as determined by chemical analysis

Component	Mole %		
	PbO	ZrO_2 (1)	TiO_2
Nominal	30.0	21.0	49.0
By Analysis (2)	30.0	21.4	48.6
Nominal	50.0	25.0	25.0
By Analysis (2)	50.5	24.9	24.6
Nominal	53.0	24.4	22.6
By Analysis (2)	51.8	25.0	23.2

(1) Any HfO_2 present included with ZrO_2: (2) Normalized to (PbO + ZrO_2 + TiO_2) equals 100%.

Experimental results

(i) Compositions examined: A comparison of nominal compositions with the results of chemical analysis are shown in Table 1.

As indicated in this table, the nominal compositions agreed with the analytically determined compositions to within 0.5 mole % or better in those samples that had PbO contents of 50 mole % or less. Hence, for samples with 50 mole % PbO or less, it was assumed that the final compositions were the same as the nominal compositions. Samples that were prepared to contain over 50 mole % PbO were found by analysis to be deficient in PbO after firing. The lead oxide was probably lost as vapour or as liquid that drained from the pellet during firing at 1100°C. All samples nominally containing over 50 mole % PbO that are reported in this investigation, were analysed chemically to determine their true compositions.

The phases found by X-ray diffraction examination, at room temperature after air cooling, are indicated in Figure 1. The proposed sub-solidus phase relationships, deduced from these determinations are also shown in Figure 1. It will be noted that the structures indicated for the lead titanate-lead zirconate solid-solution series, tetragonal, rhombohedral, and orthorhombic, are room-temperature structures. Above the Curie temperature, this solid-solution series exhibits cubic symmetry over the whole range of composition.

(ii) The lead titanate-lead zirconate solid-solution series: The boundary between the tetragonal lead titanate-rich solid solution and

the rhombohedral lead zirconate-rich solid solution was found to occur at a

$$\frac{PbZrO_3}{PbZrO_3 + PbTiO_3}$$ ratio of 0.53 ± 0.01.

Values of this ratio found previously include 0.54 ± 0.005 by Ikeda et al.[5] and 0.55 ± 0.025 by Jaffe et al.[2]. The orthorhombic solid solution at the $PbZrO_3$ end of the series appears to extend from $PbZrO_3$ to about 8 mole % $PbTiO_3$ in $PbZrO_3$.

The $PbTiO_3$-$PbZrO_3$ solid solution has been reported to show deviations from the stoichiometric ratio $\frac{PbO}{ZrO_2 + TiO_2} = 1$ [5]. Compositions with decreasing PbO content, for ZrO_2/TiO_2 ratios of 1/1 and 1/3, show a decrease in the tetragonal "a" cell edge as the PbO content falls below that required by the stoichiometric ratio. This effect is a result of the occurrence of zirconia (with some TiO_2 in solid solution) together with a $PbTiO_3$-$PbZrO_3$ solid solution having a $PbTiO_3/PbZrO_3$ ratio higher than that given by the TiO_2/ZrO_2 ratio of the gross composition of the sample. Such changes in cell edge have not been observed on samples of $PbTiO_3$-based and $PbZrO_3$-based compositions with deficiencies of PbO. In these cases, a change of TiO_2/ZrO_2 ratio is, of course, not possible. These changes in cell edge can be used to estimate the low-PbO limit of the lead titanate-lead zirconate solid-solution series by the graphical method indicated in Figure 2. Little change in lattice parameter was observed with $\frac{PbO}{ZrO_2 + TiO_2}$ ratios greater than 1.

These estimations of the limit of PbO deficiency which are plotted in Figure 3 are probably correct to about ± 0.04 in the ratio $\frac{PbO}{ZrO_2 + TiO_2}$ The upper-PbO limit of solid solution had to be estimated from the appearance of the PbO (orthorhombic) phase in the X-ray diffraction examination of the samples. This method of detection of PbO is probably quite sensitive on account of the high atomic

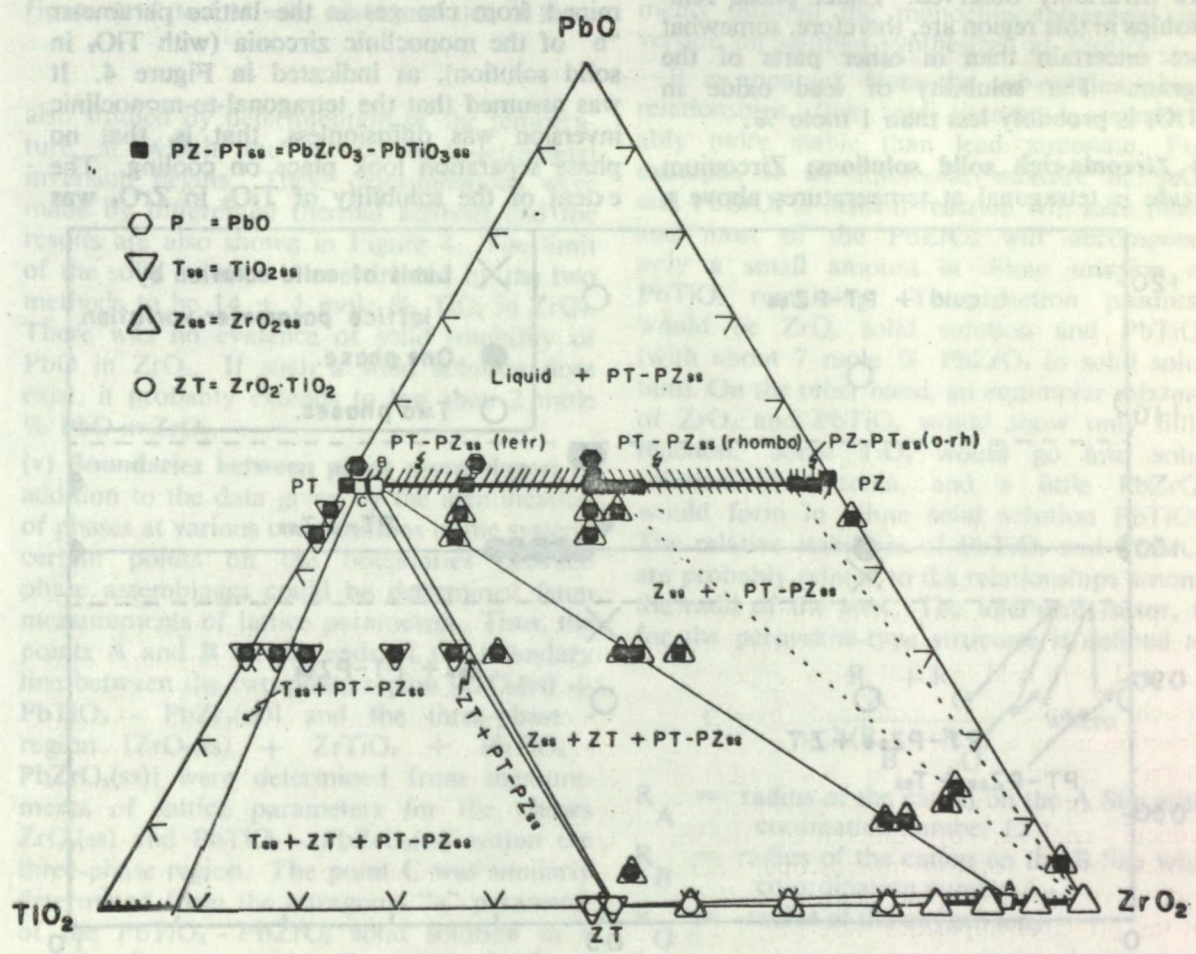

Figure 1

Sub-solidus phase relationships in the system PbO-ZrO_2-TiO_2 at 1100°C. Compositions in Mole percent. Note: PT-PZss is cubic at 1100°C. Structures indicated are those observed at room temperature.

number of lead. Confirming evidence for the occurrence or absence of a lead oxide was obtained by the examination of polished sections of crushed samples, mounted in "Araldite" resin. The lead oxide phase could be distinguished by its orange-brown colour under reflected light. The upper limit of the $\frac{PbO}{ZrO_2 + TiO_2}$ ratio for single-phase lead titanate-lead zirconate solid solution was estimated as 1.08 ± 0.04 and the lower limit as 0.96 ± 0.04. Ikeda et al.[5] indicated ratios of about 1.07 and 0.85, respectively, near the tetragonal-rhombohedral boundary.

(iii) The compound $ZrTiO_4$: The compound $ZrTiO_4$ (or $ZrO_2.TiO_2$) is relatively difficult to form at 1100°C from the mixed oxide powders[6]. This difficulty was largely overcome by preparing the samples from co-precipitated hydroxides. However, in all samples near the $ZrO_2.TiO_2$ composition, very faint lines of either ZrO_2 or TiO_2, or both, were invariably observed. Exact phase relationships in this region are, therefore, somewhat more uncertain than in other parts of the diagram. The solubility of lead oxide in $ZrTiO_4$ is probably less than 1 mole %.

(iv) Zirconia-rich solid solutions: Zirconium dioxide is tetragonal at temperatures above a transition which occurs between 1000°C to 1200°C[7] during heating; below this inversion temperature, ZrO_2 is monoclinic. The extent of solid solution of TiO_2 in ZrO_2 was determined from changes in the lattice parameter "b" of the monoclinic zirconia (with TiO_2 in solid solution), as indicated in Figure 4. It was assumed that the tetragonal-to-monoclinic inversion was diffusionless, that is, that no phase separation took place on cooling. The extent of the solubility of TiO_2 in ZrO_2 was

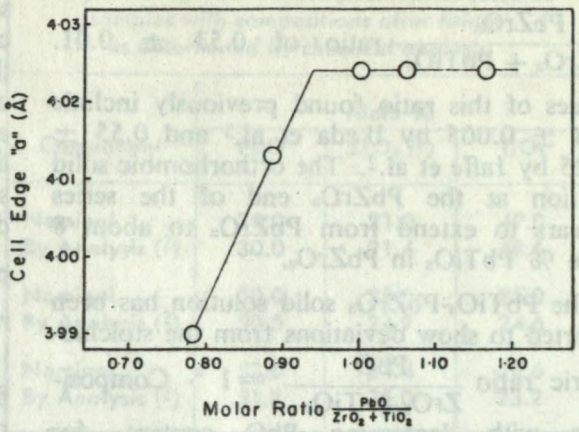

Figure 2. Variation of tetragonal "a" cell edge with changes in the molar ratio

$$\frac{PbO}{ZrO_2 + TiO_2} \cdot \text{Molar ratio } \frac{ZrO_2}{ZrO_2 + TiO_2} = 0.50.$$

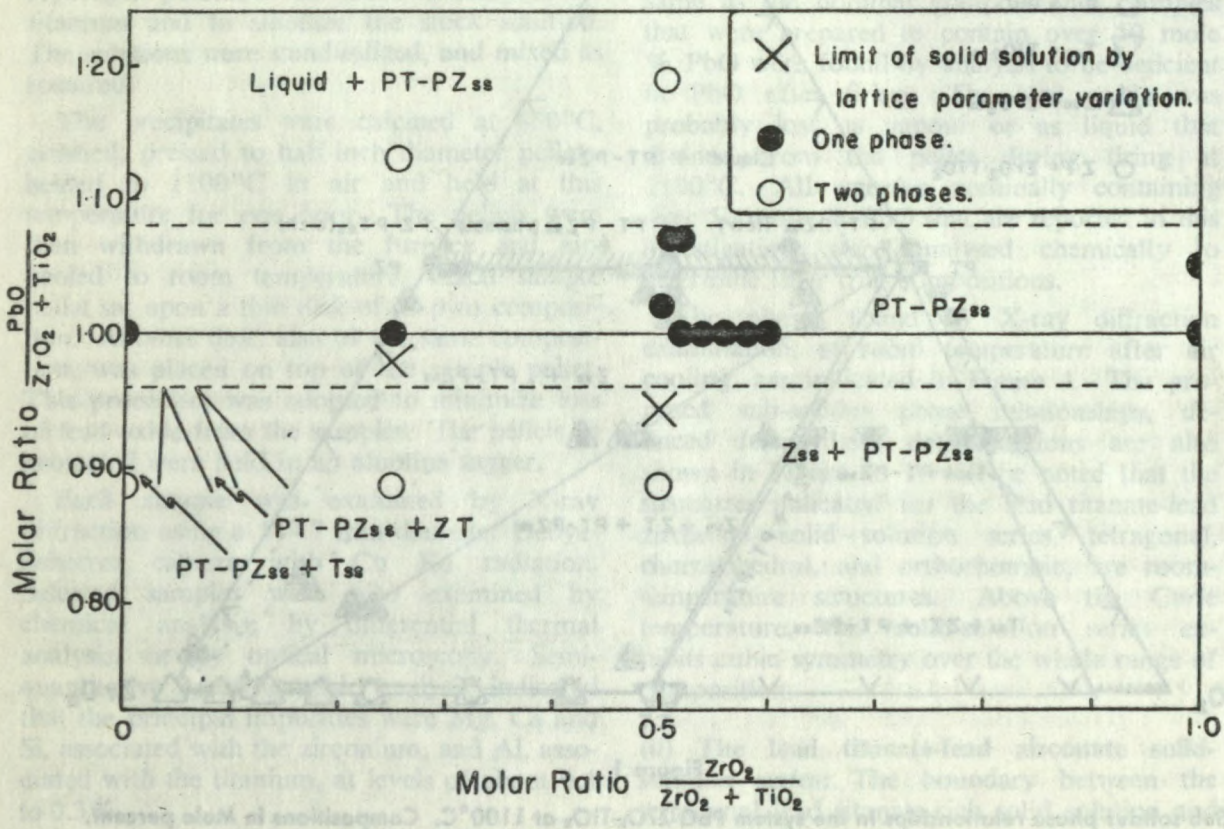

Figure 3. Deviation of Lead Titanate-Lead Zirconite solid solution from the stoichiometric molar ratio

$$\frac{PbO}{ZrO_2 + TiO_2} = 1$$

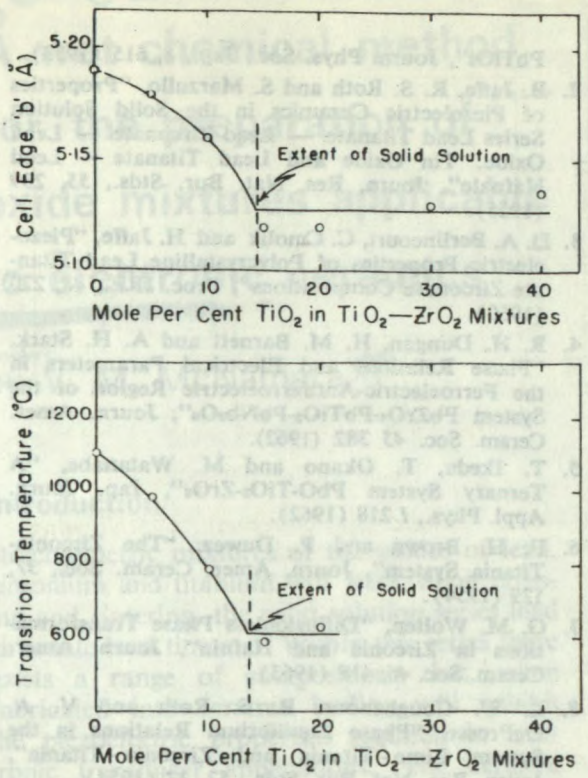

Figure 4. Extent of solid solution of TiO_2 in ZrO_2.

also studied by determination of the temperature at which the monoclinic-to-tetragonal inversion begins. These determinations were made by differential thermal analysis and the results are also shown in Figure 4. The limit of the solid solution was estimated by the two methods to be 14 ± 1 mole % TiO_2 in ZrO_2. There was no evidence of solid solubility of PbO in ZrO_2. If such a solid solution does exist, it probably extends to less than 2 mole % PbO in ZrO_2.

(v) Boundaries between phase assemblages: In addition to the data given by the identification of phases at various compositions in the system, certain points on the boundaries between phase assemblages could be determined from measurements of lattice parameters. Thus, the points **A** and **B** on the ends of the boundary line between the two-phase region [ZrO_2(ss) + $PbTiO_3$ - $PbZr_3$(ss)] and the three-phase - region [ZrO_2(ss) + $ZrTiO_4$ + $PbTiO_3$ - $PbZrO_3$(ss)] were determined from measurements of lattice parameters for the phases ZrO_2(ss) and $PbTiO_3$ - $PbZrO_3$(ss) within the three-phase region. The point **C** was similarly determined from the tetragonal "a" parameter of the $PbTiO_3$ - $PBZrO_3$ solid solution in a sample whose composition lay within the three-phase region [TiO_2(ss) + $ZrTiO_4$ + $PbTiO_3$ - $PbZrO_3$(ss)].

The solubility of ZrO_2 in TiO_2 was estimated to be about 8 mole % by interpolation of the data given by Brown and Duwez[6].

General discussion

The sub-solidus phase relationships in the system PbO-ZrO_2-TiO_2 at 1100°C, as determined in the present investigation, agree quite well with the "reaction diagram" given by Ikeda et al.[5] It was found that the non-stoichiometry of the $PbTiO_3$-$PbZrO_3$ solid solution, in terms of the ratio $\frac{PbO}{ZrO_2 + TiO_2}$ was less than that reported by Ikeda, and that the solid solution of TiO_2 in ZrO_2 extended considerably further than shown by Ikeda. The extent of TiO_2 solubility in ZrO_2 found in the present investigation (14 mole %) is considerably less than the 38% indicated by Coughanour, Roth, and DeProsse[8] for the solidus temperature of 1820°C. The lower solubility at 1100°C is not surprising. Brown and Duwez[6] also reported a solubility of about 40% based on dilatometric measurements through the monoclinic-tetragonal inversion on samples synthesized at 1760°C.

It is apparent, from the sub-solidus phase relationships, that lead titanate is considerably more stable than lead zirconate. For example, if an equimolar mixture of TiO_2 and $PbZrO_3$ is heated, reaction will take place and most of the $PbZrO_3$ will decompose, only a small amount in dilute solution in $PbTiO_3$ remaining. The reaction products would be ZrO_2 solid solution and $PbTiO_3$ (with about 7 mole % $PbZrO_3$ in solid solution). On the other hand, an equimolar mixture of ZrO_2 and $PbTiO_3$ would show only little reaction. Some TiO_2 would go into solid solution in zirconia, and a little $PbZrO_3$ would form in dilute solid solution $PbTiO_3$. The relative stabilities of $PbTiO_3$ and $PbZrO_3$ are probably related to the relationships among the radii of the ions. The tolerance factor, t, for the perovskite-type structure is defined as

$$t = \frac{R_A + R_O}{\sqrt{2}\,(R_B + R_O)} \quad \text{where}$$

R_A = radius of the cation on the A Site with cordination number 12

R_B = radius of the cation on the B Site with co-ordination number 6

R_O = radius of the oxygen ion.

This tolerance factor has an "ideal" value of unity for the closest packing of ions in the perovskite-type structure. The value of t is 0.84 for $PbZrO_3$ and 0.88 for $PbTiO_3$[9].

The manner in which the excess lead oxide enters the perovskite structure is subject to some conjecture. Possibly Pb^{4+}, which has an ionic radius close to that of Zr^{4+}, enters the lattice on the B sites.

Figure 1 indicates that solid solutions of $PbTiO_3$-$PbZrO_3$ near the tetragonal-rhombohedral boundary are in equilibrium with zirconium dioxide. This equilibrium is consistent with the common use of zirconia as a setter material for the firing of lead zirconate-titanate ceramics.

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A wet chemical method for the preparation of oxide mixtures applicable to electronic ceramics

by V. M. McNamara

ABSTRACT

A method is described for effecting the complete co-precipitation of the basic carbonates or hydroxides of lead, zirconium and titanium from a stoichiometric, acid-nitrate solution of the metals. The acidic solution containing the metal nitrates is sprayed onto the surface of dilute ammonium nitrate solution. Ammonia gas diluted with nitrogen is used to maintain the pH of the neutralizing solution above seven. This procedure results in the instantaneous neutralization of the individual droplets, thus each particle of precipitate has the desired stoichiometry. The effects of pH, temperature and agitation method are discussed and the spray technique described. Methods used for washing, settling and drying the precipitate are also described and evaluated.

The method yields, with good reproducibility, powders that are non-segregrating with respect to the components and are of high purity. Upon calcination at 650°C the powders react completely to give the solid solution lead zirconate-lead titanate.

Introduction

Stoichiometric mixtures of the oxides of lead, zirconium and titanium will yield, upon pressing and sintering, the solid solution series lead zirconate-lead titanate. Within this series there exists a range of compositions that, when fabricated into ceramic bodies, will exhibit the piezoelectric properties required in electronic transducer applications. The ceramic feed material should approach four nines purity, and must be homogeneous and of uniformly small particle size, preferably submicron. Any compromise in these specifications results in a ceramic with low density and inferior electro-mechanical properties. The most promising compositions fall within the range 50 to 55 mole per cent lead zirconate, although an expanded range of 40 to 70 mole per cent lead zirconate is of considerable interest. Certain properties of these ceramic bodies may be modified by the addition of minor quantities of other metal oxides such as those of strontium, iron, niobium or the elements in the lanthanide series.

The commercially available lead zirconate-titanates are prepared by mechanically mixing oxides of Pb^{++}, Zr^{4+} and Ti^{4+}. The existing method of preparation has not produced unmodified material that exhibits, in full measure, the desired fabricating and electrical characteristics. Nor indeed do production lots always duplicate the acceptable properties of previous lots and, consequently, wastage is considerable.

The aim of this project was the development of a chemical precipitation process that would be applicable to quantity production of homogeneous, high purity, reproducible precipitates, and the evaluation of the advantages of producing such material for electronic ceramic manufacture. This paper discusses the method developed for producing the precipitates. The evaluation of this ceramic material is reported in another publication by Webster, Weston and Craig of the Mines Branch[1]. It was hoped that a study of the electromechanical properties of ceramic bodies fabricated from the precipitates would provide an integrated area of new knowledge.

The chemical method presented in this paper yields specific ceramic compositions by the co-precipitation of lead, zirconium and titanium from a nitrate solution of the desired stoichiometry. Chemically pure or reagent grade chemicals were used as source material. Trace impurities in the source chemicals used may be undesirable, and it might become necessary in the future to obtain more uniform reagents of extreme purity. However, the emphasis in the present work has been on obtaining homogeneity, reasonable purity and closely-controlled composition for the product.

In the present process wet methods of chemical analysis were utilized to control the composition of the precipitation feed solution, and to determine the stoichiometry of the final product. The modified analytical methods that enabled the required accuracy and precision

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to be met were developed at the Mines Branch and are described and evaluated by J. C. Ingles et al.[2]

Experimental procedures

Overall process: The preparation of mixed oxide compositions by the wet chemical method began with the selection of suitable high purity source chemicals. Quantities were weighed out to yield sufficient product for adequate evaluation. The eight steps required in the preparation of the dry ceramic powder are as follows:

1. Preparation of clarified nitrate stock solutions of each of the metals that were involved in the ceramic compositions, and determination of metal content.

2. Blending of a composite nitrate solution containing the major components in the desired stoichiometric relationships, which were verified by analysis. If lesser quantities of certain metal oxides were to be incorporated into the ceramic in order to modify the properties of the material, the soluble nitrate salts of these metal oxides could be added to the composite solution.

3. Precipitation of the components by neutralization of the blended metal nitrate solution using controlled addition of ammonia, or alternatively, ammonia and carbon dioxide dispersed separately. The metals were quantitatively precipitated as hydrated oxides, hydroxides or basic carbonates[3].

4. Washing of the precipitate, batchwise, with demineralized water made slightly ammoniacal.

5. Dewatering the precipitate slurry by settling and decantation (thickener), partial filtration and repulping, or centrifuging.

6. Production of a dry homogeneous powder by means of spray drying the thickened precipitate slurry, or filtration of the thickened precipitate and drying the filter cake under vacuum. The spray dryer used in this work was a Nerco-Niro "Utility Unit" rated at 100 pounds of water evaporated per hour and fired by propane gas. The dry precipitate was sampled for chemical analysis to confirm stoichiometry, and for semi-quantitative spectrographic analysis to determine the approximate degree of purity. Figure 1 indicates the above procedural steps for the preparation of lead zirconate-titanate precipitates.

Two further steps were required in order to process this material to the point at which it could be fabricated into components. These two operations were not part of the investigation performed by the author but are listed for continuity as:

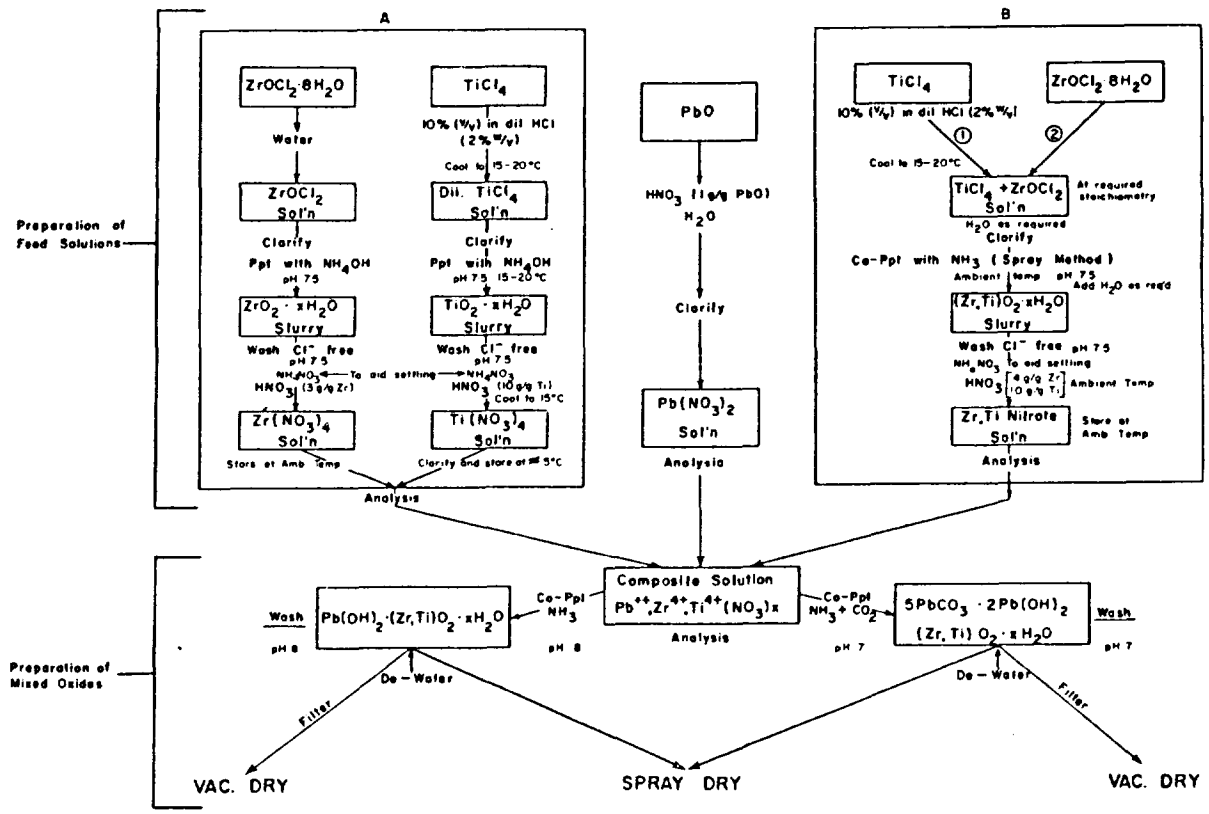


Figure 1. General flowsheet

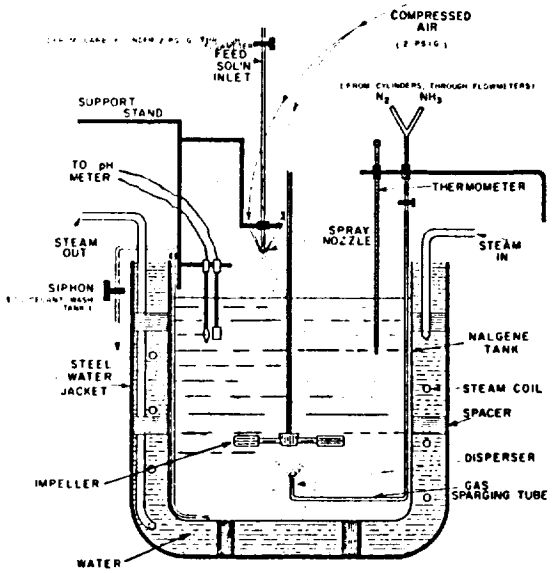


Figure 2. Batch co-precipitation equipment.

7. Calcination of the dry powder at a temperature sufficient to achieve the desired reaction to form the solid solution.

8. Comminution of the calcine in a Trost Jet Mill to a submicron particle size required for subsequent fabrication of high density ceramic components.

Preparation of the precipitation feed solution: In the preparation of stock solutions of the individual components, it is desirable to utilize compounds that are readily soluble in water or dilute acid. Each of the solutions of metal salts then must be converted into one system that is stable and relatively non-corrosive. In this work the nitrate system was chosen, although the chloride system was considered and discarded for the following reasons.

(a) The susceptibility of stainless steel equipment to chloride attack.

(b) The appreciable loss of lead into discarded solutions when washing precipitates free of chloride ion.

(c) The necessity of eliminating chloride ion from the precipitates. When a nitrate system is employed, the precipitates need not be washed free of nitrate ion.

(d) The low solubility of lead chloride. A typical composite chloride precipitation feed solution contained 3 grams per litre total oxide equivalent at ambient temperature or 12 grams per litre at 60°C. A composite nitrate precipitation feed solution, by comparison, contained approximately 60 grams per litre total oxide equivalent at ambient temperature.

Lead oxide was readily converted to soluble lead nitrate with diluted nitric acid. The oxides of $Zr^{4}+$ and $Ti^{4}+$, however, are most difficult to solubilize and are not useful as source material for this process. Consequently, in most of this work zirconium oxychloride and titanium tetrachloride were used as source chemicals of these metals. The conversion of zirconium oxychloride to the nitrate form, as shown in Figure 1, was accomplished by precipitating hydrated zirconium oxide, with ammonia, from a water solution of the salt, washing the slurry free of chloride ion by multiple decantations with demineralized water and redissolving the hydrated oxide in nitric acid. A zirconyl nitrate (Hf$<$100 ppm) is now available commercially.

Titanium tetrachloride was the most suitable source of titanium, although titanium sulphate nonahydrate was used extensively in early stages of this investigation. Water soluble titanyl salts were not available commercially. Titanium tetrachloride, if handled with caution, was readily soluble in dilute hydrochloric acid (2% w/v) and was subsequently converted to a dilute solution of titanium nitrate in a manner similar to that used to prepare zirconium nitrate solution.

Clarification of the solution was required whenever a source chemical was dissolved. This rapid step removed small but significant quantities of insoluble impurities.

Pure titanium solutions are unstable and hydrolyze readily. It was found beneficial to add H_2O_2 (1 ml/g Ti) to the clarified titanium nitrate solution and to store this solution at about 35°F. Furthermore, the lower the concentrations of titanium, and of free nitric acid, the longer the titanium nitrate solution could be stored without hydrolysis.

It was found that if the major portions of titanium and zirconium were prepared as a composite solution and stored at ambient temperature the titanium did not hydrolyze as readily. However, it was noted that preparations of composite solutions containing more than 50 mole per cent titanium dioxide equivalent had limited stability as compared to a similarly prepared and stored solution of greater than 50 mole per cent zirconium dioxide equivalent. The method of preparing the composite zirconium-titanium solution is shown in Figure 1 (B). The titanium tetrachloride was carefully dissolved in 2% (w/v) hydrochloric acid, with cooling of the mixture to ambient temperature, or lower. The zirconium oxychloride was then dissolved in the dilute titanium tetrachloride and the resulting solution was clarified by filtration. The two components were co-precipitated as hydrated

oxides at ambient temperature by the spray technique (Figure 2). The precipitate slurry was washed free of chloride ion, thickened by settling or centrifuging and dissolved in nitric acid at ambient temperature. Batches of zirconium-titanium nitrates may be prepared at widely varying stoichiometric relationships and blended as desired to any intermediate composition.

Titanium nitrate solutions containing 10 grams Ti per litre, even when stabilized with H_2O_2 and stored at temperatures of 0 to 5°C, tended to hydrolyze over a period of several weeks. On the other hand zirconium-titanium nitrate solution containing approximately 5 grams Ti per litre and 11 grams Zr per litre was stored for several months at ambient temperature with no evidence of hydrolysis.

The compounds that were used as source material for this investigation are specified in Table 1 where the results of semi-quantitative spectrographic analyses done on these compounds are also tabulated. The most undesirable contaminant is silica, which is an impurity common to most reagents. In addition to that present in the source chemicals, silica is readily accumulated from equipment and unclean surroundings during processing. Consequently, the use of glass processing equipment was avoided, and all tanks were kept well covered and free of dust. Alumina is an equally undesirable impurity. Magnesia is not quite so harmful to the electromechanical properties of transducer material. Calcium, iron, manganese and copper are recorded because their oxides consistently reported in the final product and so reduced the overall purity of the lead zirconate-titanate.

Zirconium oxychloride and titanium tetrachloride are involved in the preparation of about one third of the product by weight. These compounds were the sources of most of the impurities. There were indications that, when precipitates were prepared and then redissolved, with solution clarification also involved, there was a stubstantial improvement in purity (Table 1) with respect to the more undesirable elements.

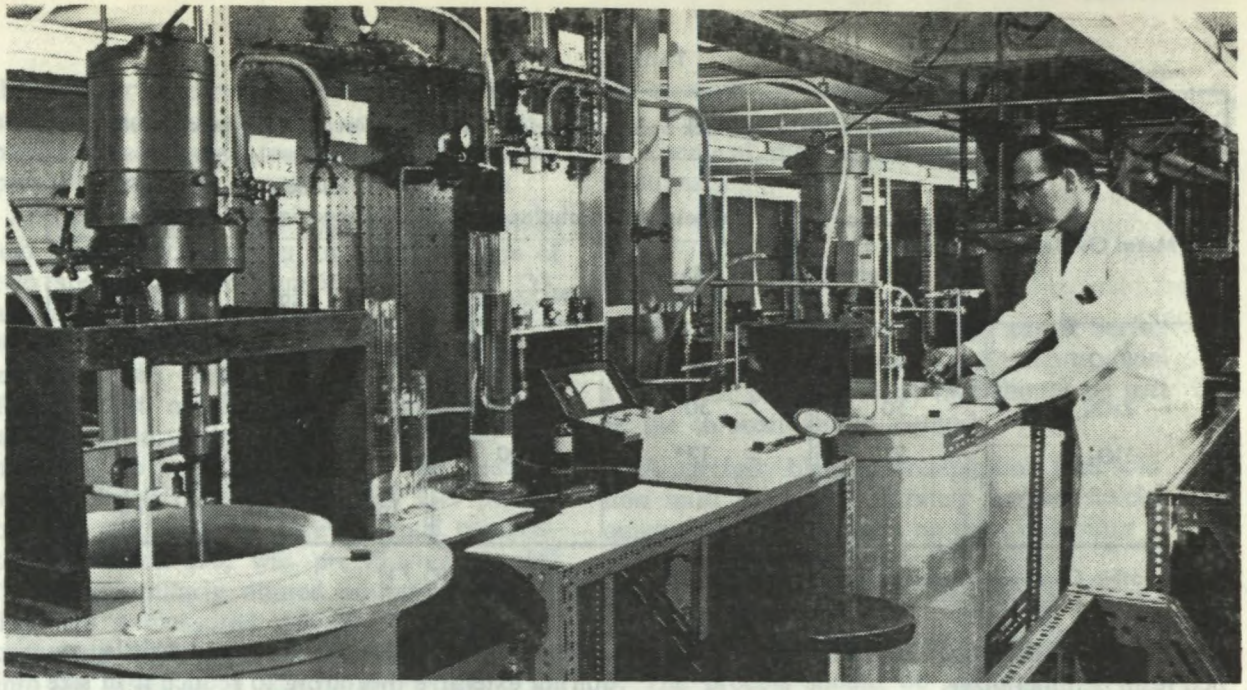
Co-precipitation of lead, zirconium and titanium as hydrated oxides: Figure 2 shows, diagrammatically, the technique used to precipitate simultaneously the metals from a stoichio-

TABLE 1

Semi-Quantitative Spectrographic Analyses
source material

Chemical	Source		Elements (ppm)									
			Si	Fe	Al	Mg	Ca	Mn	Cu	Pb	Zr	Ti
PbO	F		Tr	200	ND	Tr	ND	ND	20	—	ND	ND
$PbCO_3$	F		Tr	100	Tr	200	200	Tr	Tr	—	ND	ND
$Pb(OH)_2$ ppt.	PbO	A	ND	ND	ND	20	ND	50	50	—	30	ND
	Dissolve in HNO_3 - Filter, Evap. to dry.		ND	ND	ND	ND	ND	ND	Tr	—	20	ND
$ZrOCl_2 \cdot 8H_2O$	NL		500	200	50	70	ND	ND	Tr	ND	—	ND
$ZrO_2 \cdot x H_2O$ ppt.	$ZrOCl_2 \cdot 8H_2O$	NL	400	300	100	20	ND	50	40	80	—	50
	Dissolve in HNO_3 - Filter, Evap. to dry.		Tr	400	70	80	ND	4	Tr	Tr	—	ND
$Ti(SO_4)_2 \cdot 9H_2O$	F		500	200	40	200	200	Tr	Tr	ND	ND	—
$TiO_2 \cdot x H_2O$ ppt.	$TiCl_4$	A (1)	60	ND	ND	ND	ND	ND	50	Tr	ND	—
		(2)	200	ND	ND	80	ND	ND	100	ND	50	—
	$TiCl_4$	F	200	30	Tr	300	ND	5	50	40	ND	—

F = Fischer Scientific Co. Ltd: A = Anachemia Chemicals Ltd: NL = National Lead Co., Titanium Alloy Mfg. Div:
ND = not detected: Tr = trace



Co-precipitation of hydrated oxide compositions for use in the manufacture of electronic components.

metrically-blended solution. This procedure involves atomization of the acidic aqueous nitrate solution of the metals onto the surface of a relatively large volume of solution, which is initially very dilute alkaline ammonium nitrate, gradually increasing in salt concentration (i.e., NH_4NO_3) and in solid content (the precipitate) as precipitation proceeds. The precipitate slurry is under control in regard to:

(a) Temperature; normally held at 55-60°C by use of an external heating jacket.

(b) pH; held within the range 7.0 to 8.0 by control of ammonia gas flow rate through a disperser located at the bottom of the reaction tank, immediately below the impeller.

(c) Agitation of the bulk solution (slurry) and dispersion of the precipitant; accomplished by mechanical stirring and nitrogen gas sparging via the disperser. The volume of nitrogen used was usually one-half to one times the ammonia gas flow rate.

(d) Retention time; by control of the solution feed rate and the siphon rate for slurry withdrawal, or by vessel size (siphoned slurry flowed into the first batch decantation tank).

(e) Slurry density; since the slurry was subsequently washed by decantation, there was no necessity of obtaining maximum density of slurry in the precipitation vessel. Furthermore, thickened hydroxide slurries were not amenable to efficient agitation in the precipitation vessel.

Retention time and slurry density were not controlled at specific values. Agitation was sufficient to give thorough and rapid mixing within the precipitation vessel. The aim of this co-precipitation method was the quantitative precipitation of the metals contained in each minute droplet of feed solution with such rapidity that there is virtually no opportunity for selective precipitation to occur.

Precipitate washing and drying: The object of precipitate washing was the removal of the major portion of the ammonium nitrate from the slurry. A side effect of washing the precipitate was the conversion of some of the basic lead nitrate to lead hydroxide by hydrolysis, thus effecting an additional reduction in the nitrate content of the final product.

Most hydroxide precipitates, and the present group is no exception, are difficult to wash on a pan filter; filtration rates are very low. In addition, the filter cake does not submit to uniform repulping. Therefore, in most of this work precipitate washing was accomplished by batch decantation using water made slightly ammoniacal. Reasonable efficiency required some control over settling rates by the use of an organic flocculating agent. The agent used in this work was Separan and was added very slowly, with gentle mixing, as a 0.05% solution in just sufficient quantity to give a clear supernatant liquid and a satisfactory settling rate. Water used for washing was demineralized before use by passing it through a commercial water treatment unit, which included

TABLE 2

Metal Oxide Equivalent in Process Stock Solutions and in a Blended Precipitation Feed Solution

Metal Oxide	Max. Conc. Obtained in Stock Soln (g/1)	Process Stock Solutions		Blended Solution of Composition $Pb(Zr_{0.52}Ti_{0.48})O_3$		
		(g/1)	NO_3(g/1)		(g/1)	NO_3(g/1)
PbO	300	170	65		38.4	
ZrO_2	50	30*	50		11.3	
TiO_2	27	17*	100		6.8	
				Total	56.5	73

* Alternative Composite Stock Solution contained 14.6 g ZrO_2/1; 8.8 g TiO_2/1.

an activated carbon filter followed by a mixed-bed resin demineralizer.

Two variations in procedure for obtaining a de-watered filter cake were tried experimentally. They were:

(a) Removal of the water in the filter cake with repeated displacements of acetone or, alternatively, methyl hydrate which was in turn displaced by ether.

(b) Displacement of a large portion of the water in the filter cake with methyl hydrate followed by azeotropic distillation of the remaining water with benzene at 80°C.

The precipitate filter cake, when oven-dried at 110°C, became very hard and brittle, requiring extensive mortaring to reduce it in size to pass a 20 mesh Tyler screen. Drying of the precipitate under low vacuum at 35°C resulted in a more readily pulverized material but was time consuming. Alternatively, spray drying of the settled and decanted precipitate slurry was rapid and resulted in uniform free-flowing spherical particles.

Tables 2, 3, 4, and 5 are presented to give specific examples of operating procedures and conditions. Table 2 shows the metal nitrate concentrations of typical stock solutions that were used to prepare the precipitation feed solution. The values shown as maxima are

TABLE 3

Operating Conditions for the Co-precipitation Method

Batch Number		D3	D4
Batch Size	lb Oxides	5.86	3.49
Precipitation Tank Data			
Initial Volume*	Litres	130	65
Temperature	°C	55	55
pH		8	7
Siphon Withdrawal Rate	ml/min	240	270
Total Precipitation Time	hrs	2.83	1.75
Precipitate Wash			
Total Volume of Water**	Imp. Gal.	310	180
Number of Decantations		4	3
Feed to Spray Dryer			
Solids	Per Cent	3.1	4.2
NO_3 Content in Water	g/1	0.26	0.31

*Demineralized water containing an added quantity of NH_4NO_3 (1/2 g/1) to facilitate pH control at start up.

**Demineralized water adjusted to same pH value used in precipitation control.

the highest concentrations prepared in this study. Also shown is the composition of a blended precipitation feed solution, which was prepared from the process stock solutions.

Tables 3 and 4 show operating conditions and co-precipitation data for the production of two specific lots of precipitate. Batch D3, amounting to 5.86 pounds total oxides, represented a composition of 54 mole per cent lead zirconate, 46 mole per cent lead titanate. Precipitation of the three components was accomplished using ammonia gas, diluted with nitrogen, to maintain pH8 in the reaction vessel. Batch D4, amounting to 3.49 pounds of total oxides at the same nominal composition as Batch D3, was precipitated at pH7 by using similarly diluted ammonia gas. In Test D4 a measured quantity of ammonium carbonate solution was titrated continuously into the vessel as an additional precipitant for the lead.

Table 5 shows the importance of pH control on the efficiency of ammonia precipitation of the three major constituents and on the subsequent washing of precipitates. Clearly indicated is the necessity of controlling the pH at a sufficiently high value to prevent loss of lead to the discarded filtrate or to wash solutions. However, when carbonate is present as an additional precipitant as in Batch D4, the lead is completely precipitated at pH7. The precipitate may then be washed with water at pH7. The data given in Table 5 were obtained from preliminary bench work. Losses of lead to discard solutions in the preparation of larger batch lots such as D3 and D4 were of the order of <0.0001 grams per litre. Zirconium and titanium were not detected by chemical methods in any of the discard solutions.

Results

Chemical reproducibility — MR and R Series: There are three important requirements, from a chemical point of view, that should be met by the co-precipitation method:

1. A carefully blended precipitation feed solution must have an accurately known stoichiometry and this depends on the availability of precise analytical procedures.

2. The stoichiometry of this feed solution must report unchanged in the final product.

3. The process should be sufficiently flexible that some variations in the method could be tolerated without affecting reproducibility.

The key indications of the stoichiometry attained in the feed solution, or in the precipitate, are shown by two ratios. The ratio zirconia to zirconia plus titania indicates the proportion of the mixture that will ultimately become lead zirconate in the solid solution formed upon calcination. Therefore, one minus this ratio is the proportion representing lead titanate. The ratio lead oxide to zirconia plus titania indicates whether or not the lead contained in the mixture meets the stoichiometric requirement for the particular composition. Normally this relationship should equal exactly one.

TABLE 4

Co-precipitation of the Hydrated Oxides of Pb^{++}, Zr^{4+} and Ti^{4+} from an Acidic Nitrate Solution
Stoichiometry-Pb $(Zr_{0.54}\ Ti_{0.46})\ O_3$

Batch Number		D3	D4
Precipitation Feed Solution			
Volume	Litres	40.80	23.75
Analysis	g oxides/l	65.13	66.63
Flow Rate	ml/min	240	225
Precipitant			
NH_3:N_2 at 1:1	l/min	28.0	14.8
$(NH_4)_2CO_3$*	ml/min	Nil	45**
Reagent Consumption — lb/lb oxides	N_2	1.14	0.62
	NH_3	0.69	0.38
	$(NH_4)_2\ CO_3$	—	0.26

*8.6% solution.
**1.25 times the amount required to precipitate basic lead carbonate.

Table 6 presents a comparison of the stoichiometric ratios, based upon chemical analysis, for a series of lots wherein the compositions of the feed solutions ranged, nominally, from 50 mole per cent lead zirconate to 70 mole per cent lead zirconate. The lot sizes were constant and the feed solutions were of essentially constant metal content (21 to 24 grams total oxide equivalent per litre). The solution feed rate to precipitation was 120 ml per minute. Tap water was used to wash the precipitate slurry by batch decantation, prior to filtration and vacuum drying. This group of lots gave evidence that the stoichiometry of the feed solution did report in the final product to a satisfactory extent. This was observed from the percentage differences in the molar ratios, which were between ± 0.4 mole per cent for the ratio $ZrO_2/ZrO_2 + TiO_2$, and between -0.4 and $+0.8$ mole per cent for the ratio $PbO/ZrO_2 + TiO_2$. However, in this MR Series there was a large discrepancy, observed for all lots, in the computed values for the ratio lead oxide to zirconia plus titania compared to the nominal stoichiometry, which was expected to be $PbO/ZrO_2 + TiO_2 = 1.000$. The average values were 0.976 for the feed solution and 0.978 for the precipitate, which represents approximately a 2.3 per cent deficiency in PbO. Furthermore, better reproducibility, as indicated by the standard deviations, calculated for the seven batches, would be desirable. This MR Series represented the first attempt to determine stoichiometric reliability and the results indicated a requirement for improving the accuracy obtained in the compositing of the feed solutions by utilizing a more extensve system of adjustments, analysis, and re-adjustments, as well as improving upon the accuracy of the available methods of analysis for both solutions and precipitates.

Table 7 indicates the chemical reproducibility obtained in a series of seven similar batch precipitations (R1 to R7) when procedures had been improved mainly through the use of more precise analytical methods[2] and a more extensive sampling procedure. The composite solutions were prepared to represent 52.0 mole per cent lead zirconate, 48.0 mole per cent lead titanate. Test variations existed in respect to lot size (1 to 2¼ pounds), the oxide concentration in the composite feed solutions (15.6 to 26.4 g oxides per litre), and the rate of feed to the precipitation tank (R1 to R5 at 205 ml/min; R6 500 ml/min, R7 440 ml/min). Precipitate washing was done by batch decantation with demineralized water (pH 8) until the nitrate concentration in the wash solution was lowered to about one half gram per litre.

TABLE 5

Effect of pH in the Co-precipitation of Pb^{++} Zr^{4+} and Ti^{4+} from Acidic Nitrate Solution with Ammonia

	Control pH	Chemical analyses: g/l of discard soln.		
		PbO	ZrO_2	TiO_2
Filtrate	7.0	0.055	<.02	<.002
	7.5	0.010	<.02	<.002
	8.0	< .001	<.02	<.002
Filter Cake Wash	7.0	0.23	<.02	<.002
	7.5	0.12	<.02	<.002
	8.0	0.03	<.02	<.002

In this R Series good agreement was obtained between the stoichiometry of the feed solution and that of the dry powder, as shown by a comparison of the average values for the composition ratios (Table 7). Batchwise reproducibility is also acceptable as evidenced by the standard deviations from the means for the same four ratios. The closer relationships obtained in this series indicates the importance of precise chemical analysis.

Lot numbers 57 and 62 (Table 7) were produced to determine if similar process control was obtained where significant processing variations prevailed. The nominal compositions were chosen as 56.0 mole per cent lead zirconate and 54.0 mole per cent lead zirconate respectively. The variations were:

(a) The feed solution oxide contents for Lots 57 and 62 were from 1½ to 2 times the concentrations involved in the R Series feed solutions.

(b) The feed solutions for Lots 57 and 62 were dispersed into the precipitation tank via a laboratory-made pneumatic nozzle. The feed solutions for the R Series were dispersed via an industrial hydraulic nozzle (full cone spray pattern).

(c) The precipitates obtained in tests Number 57 and 62 were filtered, washed on the Buchner funnel, and vacuum dried, whereas for the R Series the washed precipitate slurries were spray dried.

(d) In Tests 57 and 62 the precipitation vessel contained all of the precipitate until completion of the neutralization of the batch of feed

solution, whereas the slurry in Lots R1 to R7 was continuously siphoned from the bottom of the tank to maintain a constant liquid level in the reaction vessel.

It can be seen from Table 7 that the reproducibility obtained in Tests 57 and 62 was as good as that obtained in the R Series. This indicates that the previously described process variations could be tolerated.

An evaluation of the fabrication and electromechanical properties of powder from Lots 57 and 62 has been reported by Weston (4). In general, it was found that the ceramic bodies produced from the two lots had electromechanical properties that were considered to be very good.

Comparison of some precipitation techniques and the effect of precipitate dewatering, washing and drying variables on reproducibility — D Series: The objectives in the preparation of this group of precipitate lots, designated the D Series, were:

1. To determine the effect on the final product composition and on the homogeneity of some variations in the precipitation method. The variables were (a) the separate precipitation of each component, followed by a mechanical mixing of the precipitates; (b) co-precipitation of the components with an ammonia-nitrogen gas mixture as was done in the previous series; and (c) co-precipitation of the components using ammonia-nitrogen mixture plus ammonium carbonate.

2. To compare, within each precipitation method, the effect on stoichiometry of spray drying the precipitate slurry versus vacuum drying of the precipitate filter cake.

3. To determine the effect on stoichiometry and the feasibility of using centrifuging or other means to thicken the precipitate slurry prior to spray drying.

Tables 8 and 9 show the test conditions and results for this series of precipitates. The stoichiometry for the series was, nominally, 54.0 mole per cent lead zirconate, 46.0 mole per cent lead titanate.

Procedures for the D Series: The first batch (D1) of precipitate was obtained by precipitating separately, at pH 8 and ambient temperature, carefully measured quantities of each of the stock solutions of the three components. The precipitations were simple batch neutralizations using ammonia. The three precipitates were transferred as slurries to one drum, thoroughly mixed by mechanical agitation, and a 0.05 per cent solution of a

TABLE 6

Co-precipitated Hydrated Oxides: Stoichiometry $Pb(Zr_{0.5}\ Ti_{0.5})\ O_3$ to $Pb(Zr_{0.7}\ Ti_{0.3})\ O_3$

Feed Soln: 21 to 24 g oxides/litre
Lot Size: 1⅓ lb oxides
Washing: Decantation
Drying: Vacuum (Filter Cake)

Lot No.	$ZrO_2/ZrO_2 + TiO_2$			Difference Mole %	$PbO\ ZrO_2 + TiO_2$		Difference Mole %
	Nitrate Feed Soln		Precipitate		Nitrate Feed Soln	Precipitate	
	Nominal	Calculated from Analyses			Calculated from Analyses		
MR1	0.500	0.502	0.499	—0.3	0.989	0.997	+0.8
MR2	0.510	0.507	0.511	+0.4	0.961	0.957	—0.4
MR3	0.530	0.527	0.523	—0.4	0.953	0.955	+0.2
MR4	0.550	0.554	0.553	—0.1	0.979	0.985	+0.6
MR5	0.600	0.596	0.592	—0.4	0.971	0.977	+0.6
MR6	0.650	0.640	0.643	+0.3	0.989	0.987	—0.2
MR7	0.700	0.690	0.693	+0.3	0.990	0.989	—0.1
				Average	0.975	0.978	
				Std. Dev.	±0.015	±0.016	

TABLE 7

Reproducibility of Dry Precipitate Stoichiometry
Co-precipitation Process

Lot No.	Oxide Recovery (lb)	Precipitate Handing Method	Analyses (g/l)			Stoichiometry			
			Feed Solution			Feed Solution		Dried Precipitate	
			PbO	ZrO_2	TiO_2	$ZrO_2/ZrO_2 + TiO_2$	$PbO/ZrO_2 + TiO_2$	$ZrO_2/ZrO_2 + TiO_2$	$PbO/ZrO_2 + TiO_2$
57	1.03	Filter, wash, Vac. dry	26.82	8.25	4.24	0.558	1.001	0.556	0.999
62	1.10	Decant. wash, Filter, Vac. dry	24.45	7.32	4.04	0.541	1.000	0.534	1.000
R1	1.09	Decant. wash, Spray dry	10.72	3.07	1.83	0.520	1.003	0.524	1.005
R2	1.02	"	10.77	3.09	1.85	0.520	1.000	0.525	1.014
R3	1.10	"	10.75	3.10	1.83	0.523	1.001	0.526	1.011
R4	2.18	"	11.87	3.42	1.98	0.524	1.003	0.526	1.003
R5	2.20	"	18.18	5.17	3.09	0.521	1.005	0.526	0.999
R6	2.20	"	10.74	3.06	1.83	0.520	1.005	0.524	0.998
R7	2.22	"	13.52	3.85	2.32	0.520	1.001	0.525	1.004
				Mean ± Std. Dev.		0.521 ± .002	1.002 ± 0.002	0.525 ± 0.001	1.004 ± 0.006

flocculating agent (Separan) was added. The precipitate was washed by decantation, free settled to a slurry containing 10 per cent solids, and the settled slurry divided into portions for spray drying, and for filtration followed by vacuum drying.

The second batch (D2) of precipitate was obtained by the co-precipitation method used to produce the MR and R Series precipitates. A blended nitrate solution containing 63.58 grams total oxides per litre was fed at the rate of 240 ml per minute through the spray nozzle. Precipitation was carried out at pH 8 and 55°C. The precipitate slurry was washed with water in an amount of 44 gallons per pound of total oxides and was initially divided into two portions representing one third and two thirds of the batch. The smaller portion (Lot D2-1) was centrifuged in a modified De Laval continuous unit operating at 12000 RPM and at a feed rate of two litres of slurry per minute. The centrifuge did not operate satisfactorily with this material, and produced an underflow discharge of only 7 per cent solids from a feed slurry containing 3 per cent solids. The larger portion of slurry was more extensively washed with an additional 76 gallons of water per pound of oxides and divided into two equal lots. One lot (D2-2) was centrifuged as above. Both centrifuged lots were spray dried. The remaining lot (D2-3) was filtered and vacuum dried.

The third (D3) precipitate batch was produced by the identical method and conditions used for the D2 preparation, which were detailed in Tables 3 and 4. The composite nitrate feed solution contained 65.13 grams total oxides per litre. This slurry was divided into three lots after precipitate washing by decantation. One portion of the washed, settled slurry was spray dried. The remainder was dewatered to 22 per cent solids by partial filtration and repulping; at this point the slurry was just fluid while being agitated mechanically. This thickened slurry was split into two portions, one spray dried, the other filtered, washed with methyl hydrate, and heated at 80°C under refluxing benzene until no further water was collected.

The final precipitate batch (D4) was co-precipitated under conditions specified in

Tables 3 and 4. The feed solution contained 66.63 grams total oxides per litre and was fed to the precipitation tank at the rate of 225 ml per minute. The addition of nitrogen-diluted ammonia enabled neutralization to proceed at pH7, while an 8.6 per cent solution of ammonium carbonate was added at the rate of 45 ml per minute. The precipitate was washed by decantation and divided into two equal lots in order to compare the effect of spray drying versus filtration and vacuum drying.

Results of the D Series: It may be observed (Table 8) that Lot D1-1 made by combining separately precipitated hydroxides, when spray dried, did not reflect the stoichiometry in all respects of the original mixture. The ratio $PbO/ZrO_2 + TiO_2$ was 0.978 compared to the value 0.999 expected. The portion (D1-2) which was vacuum dried did retain complete stoichiometric similarity with respect to the feed solution. The probable explanation is that these physically mixed precipitates segregated easily. There was, therefore, a problem in recovering material of the true composition from the spray dryer where there was a consistent 5 to 8% stack loss. The values marked F represented the composition of material recovered on a stack filter. This two per cent of the total lot shows very different stoichiometry from that of the main dryer product. Furthermore, the spherical shape and the density differences of the spray dried particles cause sampling difficulties.

Chemical reproducibility within the eight co-precipitated lots comprising Batches D2, D3 and D4 was essentially equal to that observed in the R Series. For the ratio zirconia to zirconia plus titania, standard deviations from the mean of ± 0.1 mole per cent for the R Series were obtained compared to ± 0.4 mole per cent for this D Series. For the ratio lead oxide to zirconia plus titania standard deviations of ± 0.6 mole per cent in each series was observed. It was expected that, in this D Series, the solution stoichiometry would reflect precisely in the product. That this was not accomplished is shown in the following comparison of the average values for the ratio $ZrO_2/ZrO_2 + TiO_2$ resulting from the R and D Series of precipitates, which were designed to test this requirement.

TABLE 8

Slurry Dewatering and Precipitate Drying — Effect on Stoichiometry
Washing of Precipitate by Batch Decantation

Batch No.	Oxides Recovered (lb)	Lot	Precipitate Slurry		Precipitate		Results of Analysis			
							Feed Solution		Precipitate	
			Dewatering Method	Per cent Solids	Drying Method	Per cent* of Batch	$ZrO_2/ZrO_2 + TiO_2$	$PbO/ZrO_2 + TiO_2$	$ZrO_2/ZrO_2 + TiO_2$	$PbO/ZrO_2 + TiO_2$
D1	5.23	1	Settle	10	Spray	53	0.539	0.997	0.540 0.533(F)	0.978 0.870(F)
		2			Vac.	43			0.539	0.999
D2	5.16	1	Centrifuge	7	Spray	34	0.541	1.004	0.529	0.972
		2	Centrifuge	8	Spray	28			0.530	0.969
		3	Settle	3.1	Vac.	29			0.526	0.970
D3	5.35	1	Settle	3.1	Spray	32	0.543	0.995	0.531	0.977
		2	Partial Filtration and Repulp	22	Spray	48			0.531	0.981
		3			Distil.	20			0.531	0.980
D4	3.29	1	Settle	4.2	Spray	46	0.534	0.998	0.522	0.986
		2			Vac.	46			0.523	0.980
					Average		0.539	0.999	0.528	0.977
					Std. Dev.		± 0.005	± 0.005	± 0.004	± 0.006

*Percentage totals for D1, D2, and D4 do not equal 100 since some precipitate slurry was withdrawn for settling and batch centrifuge tests.

	$ZrO_2/ZrO_2 + TiO_2$		
	Solution	Precipitate	Av. Difference
R Series	0.521	0.525	0.4 mole %
D Series	0.539	0.528	1.1 mole %

The relationship lead oxide to zirconia plus titania was essentially equal to one for the R Series products. For the D Series precipitates the same ratio averaged 0.977, indicating a lead oxide deficiency of 2.3 mole per cent. There was no indication that the differences observed between feed solution and product stoichiometry, for the D Series, could be attributed to soluble losses. This deficiency can only be explained by assuming the feed solution analysis to be slightly in error. The precipitates were extensively analysed.

The results show that there was no significant effect on chemical reproducibility attributable to any of the three mehtods employed to dewater the precipitate, or to any of the three precipitate drying methods that were compared. This was to be expected if the precipitates were truly homogeneous and non-segregating.

Visual observations of spray dryer operation with slurry feeds ranging from 3 per cent solids to 22 per cent solids resulted in a request for particle size measurements on the dry products. It has been determined by optical microscopy that the volume-mean diameters were 9 ± 4 microns for dry particles resulting from a spray dryer feed at 3 per cent solids and 15 ± 7 microns for dry particles resulting from a spray dryer feed at 22 per cent solids[1].

The end point for adequate precipitate washing was arbitrarily chosen as approximately 0.3 grams soluble nitrate per litre of decant solution. As shown in Table 9 this quantity of wash amounted to about 50 Imperial gallons of water per pound of dry oxides and resulted in a nitrate content of about 3 per cent in the dry precipitate. Ammonia content of the dry precipitates was determined as less than 0.01%.

The portion of Batch D2 that was washed to the point at which the discarded decant

TABLE 9

Precipitate Wash by Batch Decantation
Demineralized Water: 0.05% w/w NH_3

Batch	Total Oxide Content in Slurry lbs	Lot No.	Wash Water		Nitrate Content		Method of Drying
			Volume Imp. Gal./ lb Oxide	Lead Content g Pb/1	Final Slurry (Sup. Liq.) g NO_3/1	Dry Ppt. % NO_3	
D1 Combined precipitates	5.51	1	49	0.00015	0.34	3.2	Spray
		2				2.9	Vac.
D2 Co-ppt. oxide hydrates	2.38	1	44	< .0001	0.46	3.6	Spray
	3.22	2	120	0.0005*	0.02	0.65	Spray
		3				0.60	Vac.
D3 Co-ppt. oxide hydrates	5.86	1				3.0	Spray
		2	54	0.0001	0.26	2.7	Spray
		3				0.85	Distil.
D4 Co-ppt. oxide hydrates & basic lead carbonate	3.49	1	52**	< .0001	0.31	3.2	Spray
		2				2.9	Vac.

*The additional 76 Imp. Gal. of water averaging 0.0005 grams lead per litre represents a loss equivalent to 0.06 mole % PbO.
**D4 wash water was adjusted to pH 7.

TABLE 10

Precipitate Slurry: Settling and Centrifuging Tests
Results of analysis on precipitate dried at 110°C.
Precipitate obtained from D-Series batches (decant washed)

Batch	Portion	Free Settling (Flocculant added*)				Centrifuging (2000 R.P.M.)		
		%	$ZrO_2/ZrO_2 + TiO_2$	$PbO/ZrO_2 + TiO_2$	CO_2, %	%	$ZrO_2/ZrO_2 + TiO_2$	$PbO/ZrO_2 + TiO_2$
D1 Combined precipitates	Top	26	0.540	0.652		27	0.501	0.744
	Centre	27	0.562	0.822		40	0.552	0.791
	Bottom	47	0.531	1.366		33	0.570	1.672
		100	0.542	1.034		100	0.544	1.059
D2 Co-ppt. oxide hydrates	T	30	0.535	0.965		35	0.532	0.957
	C	32	0.534	0.958		50	0.532	0.968
	B	38	0.532	0.958		15	0.531	0.963
		100	0.534	0.961		100	0.532	0.963
D2 Co-ppt. oxide hydrates adjusted to pH 7 bubbled with CO_2(2%)	T	27	0.534	0.958	4.04			
	C	36	0.528	0.967	4.14			
	B	37	0.530	0.965	4.12			
		100	0.530	0.964	4.11			
D4 Co-ppt. oxide hydrates & basic lead carbonate	T	26	0.523	0.978	8.70	45	0.525	0.877
	C	34	0.526	0.975	8.76	27	0.525	1.054
	B	40	0.525	0.975	8.83	28	0.525	1.052
		100	0.525	0.976	8.77	100	0.525	0.974

*Separan

water analysed 0.02 grams soluble nitrate per litre contained 0.65 per cent NO_3 as a spray dried powder. The resulting loss of lead in the decant solutions was determined as approximately 0.06 mole per cent and this loss would appear to reflect in the value 0.969 for the ratio $PbO/ZrO_2 + TiO_2$ (Table 8, D2-2) as compared to the mean value for this ratio of 0.977. There was no detectable loss of zirconium or titanium to any wash water. Analysis of all precipitation barren solutions showed them to be devoid of metal values. Lot D3-3 dry precipitate (Table 9) also contained a relatively small amount of nitrate. This was probably the result of the very slow water displacement wash with methyl hydrate that preceded azeotropic distillation.

Table 10 shows the results of an investigation designed to determine the degree of homogeneity of the precipitates obtained in the D Series test lots. Portions of precipitate were withdrawn from the washed slurries. Some portions were subjected to free settling while other portions were batch centrifuged. If segregation of components resulted from such treatment, then homogeneity would not necessarily be maintained throughout the processing steps leading to the dry product.

The free-settled slurry was siphoned off into three portions representing the top, centre, and bottom layers, which were filtered, dried and pulverized. The centrifuged precipitate was decanted free of solution, dried in the bottle, and the dry cake split into three portions (top, centre, bottom), which were pulverized.

The co-precipitated hydrated oxides (Table 10 D-2) showed no evidence of segregation. The ratios indicating stoichiometry were constant for all portions of settled or centrifuged slurry. Co-precipitated compositions containing basic lead carbonate (D4) did not exhibit a tendency to segregate upon free settling. The lead component did, however, preferentially settle when the precipitate was centrifuged, as observed from the variations in the lead oxide

to zirconia plus titania ratios. The zirconia-titania relationships were not altered. The mixtures of precipitates (D1) segregated under all conditions and all compositional relationships were affected. Precipitates that do not readily segregate are less susceptible to unpredictable changes in stoichiometry during the processing.

Since it was known that basic lead carbonate had better settling characteristics than lead hydroxide, a second portion of co-precipitated hydrated oxide slurry (D2) was adjusted to pH 7 while CO_2 gas (diluted to 2 per cent with air) was bubbled through a vertical tube containing the slurry. After two days the slurry was allowed to settle freely and portions were analysed as described above. Although there was appreciable conversion of lead hydroxide to basic lead carbonate, there was neither improved settling of the precipitate nor any effect on stoichiometry.

Discussion

There are a number of advantages that are inherent in the co-precipitation process that has been discussed in this paper. The precipitate particle consisted of a chemically-bound mixture of metal oxide hydrates when the only precipitant was ammonia, and consisted of a somewhat less tightly bound mixture of zirconium and titanium oxide hydrates and basic lead carbonate when the additional precipitant carbon dioxide was used. The components of the simultaneously co-precipitated material did not segregate during subsequent operations such as washing, settling and spray drying. Therefore the homogeneity and stoichiometry of the product were maintained. This was more desirable than the readily segregated physical blend of individually precipitated metal oxide hydrates.

The intimacy of the mix, resulting from the co-precipitation procedure, and the unusually reactive form of the dried precipitate enabled the calcining operation to be done at a considerably lower temperature than that required for the present commercial process. Because of the lower temperature used in calcining, it was possible to obtain more easily the required submicron particle size in the grinding step prior to sintering. The net result was that complete reaction and solid solution formation occurred at substantially lower temperatures and in less time than were required for finely ground mixtures of oxide powders[1].

The process should be readily amenable to continuous operation with control analysis performed on feed solutions, dry precipitates and calcined ceramic. Within the limits tested, neither the concentration of the components in the feed solution nor the flow rate of this solution to the precipitation tank had any effect upon the nature of the product. The concentrations in solution were limited by solubilities, optimum precipitate slurry densities, and by the instability of solutions containing titanium. Solution flow rates to the precipitation tank were subject to the capacity limitations of the equipment available. The retention time in the precipitation step and in the precipitate washing stages was varied over a wide range, but there was no evidence, from subsequent product evaluation, that the variations had an effect on the product.

The nitrate in the precipitate is believed to be represented as basic lead nitrate, $5\ Pb(OH)_2.Pb(NO_3)_2$[3]. Since the nitrate is readily decomposed upon calcination of the precipitate and appeared to cause no problems in fabricating the ceramic, it was decided that, for the present work, the ammonium nitrate should be washed out of the precipitate and that the resulting level of 2 to 5 per cent precipitate-bound nitrate would be quite acceptable for present evaluations. The quantity of water used to achieve this desired degree of washing had no adverse effect on the precipitate if the water was passed through an activated carbon filter and demineralizer before use. This water-treatment step was necessary to remove contaminants such as silica, iron, aluminum, magnesium and calcium, which would otherwise be precipitated with, or adsorbed on, the precipitate. A process disadvantage was the amount of washing required to remove the ammonium nitrate from the slurry. A small number of large slurry dilutions was required. The use of a larger number of smaller decantation washes was not beneficial because of the very slow settling rates for the precipitate, and the larger settled slurry volumes obtained in a tank of small cross-sectional area. When decanting wash solutions in which the concentration of nitrate is less than 0.2 gram per litre, settling difficulties increase and there is a possibility that discarded water may carry colloidal particles of all components as well as the soluble loss of lead reported in this paper (precipitate Lots D2-2 and D2-3). The use of a continuous centrifuge or, alternatively, continuous partial filtration equipment may allow efficient dewatering of the precipitate without permitting formation of caked material and with a reduced requirement for wash water.

In attempting to obtain a dry powder from gelatinous hydroxide-type precipitates, two

TABLE 11

Semi-Quantitative Spectrographic Analysis
Impurities in blended nitrate solutions & co-precipitated oxide hydrates
(Pb^{++}, Zr^{4+}, Ti^{4+})

Precipitation Test Series		Elements (ppm)						
		Si	Fe	Al	Mg	Ca	Mn	Cu
Evaporated Nitrate Feed Soln — Residue								
	MR 1 to MR 7	70	60	50	Tr	200	Tr	Tr
	R 1 to R 8	300	50	80	600	500	Tr	300
Dry Precipitates	No. 57	300	Tr	Tr	Tr	Tr	ND	30
	No. 62	300	Tr	90	Tr	ND	Tr	50
MR 1 to MR 7	Max.	2000	200	100	500	1000	Tr	40
	Min.	600	Tr	40	300	400	Tr	20
R 1 to R 8	Max.	300	100	100	100	Tr	10	300
	Min.	20	20	80	Tr	ND	5	Tr
D Series (10 lots)	Max.	300	300	20	100	40	10	400
	Min.	ND	Tr	ND	ND	ND	ND	40

ND = not detected: Tr = truce

factors must be considered. If the precipitate is filtered, washed and dried at 110°C, it will become very hard and brittle, requiring extensive grinding. However, removal of the water contained in the precipitate by displacements with alcohol or acetone was not practical because the precipitate cake contained 70-75 per cent water by weight. The cake also cracked readily when filtered on any type of Buchner funnel or pan filter and packing of the filter cake resulted in very low filtration rates. Acetone displacement washing on small lots did produce a readily pulverized dry material. Vacuum drying of the filter cake at low temperature was very time-consuming due to the large amount of water to be evaporated, but it did result in a friable dry precipitate. Both drying methods described above yielded material that was non-uniform in both size and shape.

As previously stated, spray drying the precipitate slurry yielded a product of very uniform size and shape. Spray dryer operation, with a single cyclone collector, resulted in a 92-95 per cent recovery of the oxides. All products that were either spray dried, or vacuum dried, contained from 88 to 93 per cent total oxides. The 12 to 7 per cent remainder was water of hydration plus either nitrate or carbonate in combination with the lead hydroxide. These diluents were volatilized during calcination of the precipitate. Spray drying of the precipitate slurry is rapid and represents a very satisfactory precipitate drying method.

The use of carbonate as an additional precipitant is relevant to the co-precipitation of strontium as a partial substitution for lead in future studies. This slurry settled more rapidly and to a somewhat higher slurry density than the slurries in which carbonate was not involved. The precipitate was less gelatinous, easier to filter and, when dried under vacuum, was more readily pulverized than were the precipitates containing no basic lead carbonate.

The precipitation of lead as basic lead carbonate in the work reported here has involved the addition of ammonium carbonate solution as a precipitant (Batch D4). In more recent development work the dispersion of carbon dioxide gas, diluted with nitrogen, has proven to be a very satisfactory method for producing the basic lead carbonate.

In order to set specific stoichiometric relationships for the precipitate, the precipitation feed solutions must be very accurately compositied. Assurance of a precise composition is obtained at the expense of considerable time

coupled with solution metal - concentration adjustments, are usually required. This disadvantage is gradually being reduced in severity by the development of more rapid methods of analysis.

The compositional ratio $ZrO_2/ZrO_2 + TiO_2$ of the ultimate fired ceramic is fixed by the relationship actually established in the preparation of the precipitate. The value for the ratio $PbO/ZrO_2 + TiO_2$ of the ceramic may be changed slightly from the value obtained in the precipitate by control of the lead atmosphere above the ceramic body when it is fired.

Product purity: Table 11 shows the results of semi - quantitative spectrographic analysis of evaporated residues of two composite feed solutions, and also records the maximum and minimum impurity levels for the three series of precipitates.

Indications are that lead zirconate-titanate compositions prepared by the precipitation method from reagent grade source chemicals are three nines pure or better.

The very appreciable contamination of the MR Series precipitates was attributable to the use of Ottawa tap water for precipitate washing. Consequently, demineralized water was used throughout the process for all subsequent production of precipitates.

For the R and the D Series precipitates, most of the individual lot spectrographic analyses were very close to the minimum values recorded in Table 11.

Reagent consumption: Table 12 presents a record of the materials that were consumed to produce one pound of lead zirconate-titanate dry powder by the co-precipitation method. The costs of the reagents are applicable to the purchase of source chemicals in 100 pound lots. The process is at the earliest stage of pilot plant development and minor economies are possible in some areas, particularly in respect to the quantity of diluent gas used during precipitation, and also in the method of washing and dewatering the precipitates. The lead, zirconium and titanium source chemicals accounted for $1.26 in the total cost of $3.00 per pound. Cheaper sources of the three major components would not result in any great economy. Estimates to cover costs

TABLE 12

Reagent Consumption in the Production of Dry Co-precipitated Oxide Hydrates
Basis: 1 lb $Pb(Zr_{0.54}\ Ti_{0.46})O_3$

Reagent	Pounds of Reagent								Cost, per lb. reagent $	Reagent Cost per lb. Cpd. $
	Preparation of Nitrate Solutions				Water Treatment Demineralization)	Precipitation	Ppt. Wash and Spray Dry	Total Reagent Consump.		
	PbO	ZrO_2	TiO_2	Sub-Total						
Final Product	0.684	0.204	0.113	1.00	—	—	—	—	—	—
PbO	0.684	—	—	0.684				0.684	0.65	0.445
$ZrOCl_2 . 8H_2O$	—	0.534		0.534				0.534	0.75	0.401
$TiCl_4$	—	—	0.268	0.268				0.268	1.56	0.418
HCl	—	—	0.027	0.027	0.704			0.731	0.175	0.128
HNO_3	0.677	0.410	0.677	1.764				1.764	0.380	0.670
NH_3	—	0.082	0.174	0.256		0.690	0.066	1.012	0.215	0.218
N_2	—	—	—	—		1.140		1.140	0.344	0.392
NH_4NO_3	—	—	0.535	0.535				0.535	0.350	0.187
Caustic (flake)	—	—	—	—	0.323			0.323	0.05	0.002
Liq. Propane	—	—	—	—			2.7	2.7	0.038	0.103
Water (Imp. Gal.)	0.5	19	18	37.5			53.5	91	0.034/100	0.031
									Total	$3.00

involved in process labour and analytical requirements have not been prepared in this work. Such expenditures, particularly for analysis, would considerably affect the total cost per pound of lead zirconate-titanate.

Conclusions

This investigation has dealt with the development of a chemical co-precipitation method for the production of powders having compositions that are applicable to the fabrication of lead zirconate-titanate electronic ceramics. Sufficient quantities of material were produced, batchwise, to allow evaluation of the process and the product. The results indicated that:

(a) The feed solution stoichiometry reported accurately in the product. This capability was established as being within the order of ± 0.4 mole per cent for the proportion of lead zirconate in the mixture, and within about ± 0.8 mole per cent for the stoichiometric requirement for lead oxide.

(b) Batches of powder were reproduced chemically at a particular stoichiometry. The results indicated that such reproducibility is possible to within ± 0.2 mole per cent for the ratio lead zirconate to total lead zirconate-titanate, and to within ± 0.6 mole per cent for the ratio of lead oxide to total zirconia plus titania.

(c) Chemical reproducibility of the product was achieved when variations in the processing steps were introduced. It was established that the following variables had no appreciable effect on reproducibility and production of a desired stoichiometry by co-precipitation with ammonia:

1. Batch size
2. Feed solution flow rate to the precipitation tank
3. Method used to de-water the precipitate
4. Quantity of wash water, up to 50 Imp. gal. per pound of oxides
5. Ageing of the precipitate (retention time at any step)
6. Precipitate drying method.

(d) Precipitate homogeneity was amply demonstrated for the co-precipitated oxide hydrates. Co-precipitated material containing basic lead carbonate remained homogeneous under all processing conditions except batch centrifuging.

(e) Most of the precipitates, when process water was demineralized, were considerably higher than three nines chemically pure $PbO.ZrO_2.TiO_2.xH_2O.yNO_3.zCO_2$.

(f) During the course of the investigation, the analysts achieved a high degree of confidence in the appropriate analytical methods applicable to control of composition throughout the process[2].

(g) Material from certain lots sintered to near-theoretical density and showed electromechanical properties that were considered very good[1].

This method for co-precipitating compositions suitable for electronic ceramic manufacture is considered to be amenable to, and undoubtedly useful in, the study of other oxide systems such as the various ferrite compositions and the barium titanates.

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Some ceramic and electrical properties of bodies fabricated from co-precipitated Lead-Zirconium-Titanium Hydroxide

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ABSTRACT

Co-precipitated lead-zirconium-titanium hydroxides, with and without the presence of carbonate, have been successfully fabricated into lead zirconate-titanate ceramic test pieces. The effects of certain processing variables during the precipitation and drying stages on the structural, chemical and electrical properties of the ceramic bodies are described. Some difficulties, encountered during preliminary work in this investigation and found to be caused by the presence of impurities, led to an examination of the effects of various constituents when added to the calcined precipitates prior to sintering. In particular, the presence of small amounts of fluorine and of alumina were found to be very detrimental to the electro-mechanical properties of the sintered ceramic body.

Introduction

The fabrication of piezoelectric ceramic pieces from co-precipitated lead-zirconium-titanium hydroxides has been shown to be feasible, as reported previously[1]. In this earlier report, the effects of some fabrication conditions on the properties of lead zirconate-titanate ceramics were discussed. It was shown that the densities of the sintered ceramics increased with increasing sintering temperature and sintering time, and that the electromechanical properties of the ceramics improved with increasing density. The various lots of co-precipitated lead-zirconium-titanium hydroxides, described by McNamara[2], provided an opportunity to investigate the effects of variations in precipitation and drying procedures on the electromechanical properties of ceramic disks fabricated from these powders.

Outline of Investigations

This paper comprises a description of two main investigations: (1) a comparison of a number of lots of powder, known as the D series, prepared to give nominally identical lead zirconate-titanate compositions, but differing in precipitation and drying procedures, and (2) an examination of the effects of a number of impurities added to one member of the preceding series, Lot D1. As a preamble, however, a short account is also given of an investigation of an earlier series of powders, the R series.

Comparisons were made by fabricating sample disks by cold pressing and sintering, and by evaluating the properties of these disks. The most significant properties of the materials prepared in this investigation are considered to be the dielectric constants and the planar electromechanical coupling factors of the disks after poling in a suitable d-c electric field, and the chemical composition, with special emphasis on the zirconate-titanate ratio and the excess or deficiency of lead. Information is also given on the density, grain size and structure of sample disks, and on the effective dielectric breakdown strength of the ceramics under the conditions encountered in poling.

Experimental procedures

1. Treatment of powders: The powders examined in this investigation have been described by McNamara[2]. Those powders that had been spray-dried consisted of small discrete spherical particles whose volume-mean diameters, as determined by optical microscopy, lay between 9 and 15 microns, depending upon the percentage of solids in the slurry fed to the spray drier; the standard deviations of the particle size distributions lay between ± 4 and ± 7 microns. The vacuum-dried precipitates had been crushed to pass a 20 mesh screen. The powders were amorphous to X-ray diffraction.

Part of each lot of powder was calcined at 700°C for ½ hour and the remainder left uncalcined. Differential thermal analysis indicated that all detectable reactions were completed by 650°C; X-ray diffraction indicated that only the lead zirconate-lead titanate solid solution was present in samples heated above this temperature.

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Both calcined and uncalcined powders were comminuted in a Trost Jet Mill, Model T X C. Two milled samples of the D series were examined by electron microscopy and the volume-mean diameter of the particles was determined to be about 0.1$_4$ microns. Except in the studies of the effect of impurities, for which only calcined powders were used, sample disks were prepared from both calcined and uncalcined powders in the investigations to follow.

2. Fabrication of disks: Disks were pressed from the milled material at 40,000 psi in a 1 in. diameter mould. A small amount of an aqueous solution of polyvinyl alcohol was used as a binder with the calcined material only. Four to six disks were set in a zirconia rack with lead zirconate disks at each end of the row to suppress the possible loss of lead oxide by volatilization. The zirconia rack was placed in an alumina tube set in an electrically heated furnace. The furnace was heated at 250 deg. C/hr to the desired firing temperature, with a flow of oxygen being maintained up to 1000°C. After being held at the firing temperature for 1 or 2 hours, depending on the investigation, the disks were allowed to cool overnight at the natural cooling rate of the furnace.

The sintered disks were ground and lapped to a uniform size, 1.84 cm diameter by 0.15 cm thick. Densities were determined on the lapped disks by weighing and dimensional measurement. Gold electrodes were applied to the faces of the disks by sputtering, and an air-drying conductive silver paste was painted on top of the gold.

3. Electromechanical measurements: The sample disks were generally poled in groups at 100°C in a bath of transformer oil. In the main, poling was continued for 10 minutes at

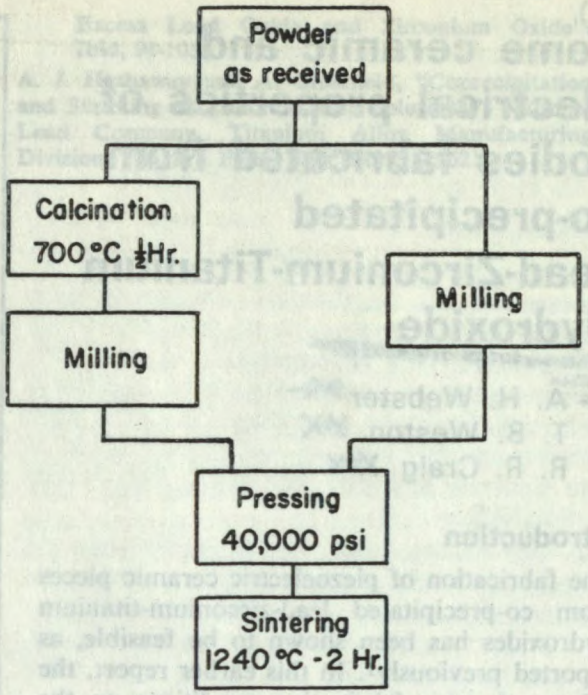

Figure 1. Fabrication of test specimens for D series lots.

30 kV/cm and subsequently for 5 minutes at 40kV/cm. Measurements were made 24 hours after poling in each case. In the D-series comparison studies, however, the disks were individually poled in silicone oil at the 40 kV/cm level. In the impurity studies, a special poling procedure, to be described later, was employed to permit a simultaneous study of dielectric breakdown.

Evaluation of the electromechanical properties was limited to those parameters most readily measured on samples in the form of circular disks, i.e., the dielectric constant K_{33}^{T}, the dissipation factor and the planar coupling factor k_p. A GR 716C bridge was used for the dielectric measurements at 1 kc, including

TABLE 1

Some properties of lead zirconate-titanate ceramics fabricated from R Series lots of powder

Lot No.	Mean Density g/cm^3	Molar Ratios		Poling	40kV/cm
		$\frac{PbO}{ZrO_2 + TiO_2}$	$\frac{ZrO_2}{ZrO_2 + TiO_2}$	k_p	K_{33}^{T}
R4	7.74	1.033	0.524	0.47	926
R5	7.77	1.028	0.521	0.54	874
R6	7.81	1.023	0.521	0.53	904
Mean	7.77	1.028	0.522	0.51	901
R7	7.54	1.022	0.521	0.34	844

Samples pressed at 40,000 psi, sintered at 1180°C for 2 hours, poled for 5 minutes at 40kV/cm and 100°C.

TABLE 2

Some non-electrical properties of lead zirconate-titanate ceramics sintered from D Series lots of powder

Lot No.	Powder Preparation	Sintered Density % Theor. (8.0 g/cm³)	Mole Ratios $\frac{PbO}{ZrO_2 + TiO_2}$	Mole Ratios $\frac{ZrO_2}{ZrO_2 + TiO_2}$	Mean Grain Diameter (microns)	Principal Phase
D2-1	slurry 7% solids spray dried	99.3	1.007	0.527	2.0	Tetrag
D2-2	slurry 8% solids spray dried	98.6	0.986	0.528	1.9	Tetrag
D2-3	filtered and vacuum dried	99.1	0.989	0.527	2.0	Tetrag
D3-1	slurry 3% solids spray dried	99.5	1.004	0.528	1.9	Tetrag
D3-2	slurry 22% solids spray dried	99.6	0.993	0.528	1.6	Tetrag
D4-1	carbonate ppt, slurry 4% solids, spray dried	99.0	1.013	0.523	2.0	Tetrag
D4-2	carbonate ppt, filtered & vacuum dried	98.9	0.996	0.522	1.8	Tetrag
Mean Std. Dev.		99.1 ±0.4	0.998 ±0.010	0.526 ±.003	1.9	
D1-1	combined ppts, slurry 10% solids, spray dried	99.4	0.998	0.536	2.4	Tetrag
D1-2	combined ppts, filtered & vacuum dried	99.3	1.002	0.533	1.9	Rhombo
D3-3	filtered & dried by distillation under benzene	99.4	1.009	0.528	2.3	Tetrag

Samples pressed at 40,000 psi, sintered at 1240°C for 2 hours.

those at fields of 1 kV/cm or more, for which a special arrangement of the bridge was employed. The planar coupling factor was determined by resonance-antiresonance measurements in accordance with the appropriate IRE Standards[3]. Sample resistivity was determined from two-terminal measurements with a megohmmeter, after two-minute electrification at 500 volts.

4. Chemical analysis: One sintered disk from each lot was analyzed for PbO, ZrO_2 and TiO_2 by the following method. A two-gram sample of the crushed disk was fumed with concentrated sulphuric acid and ammonium sulphate until decomposition was complete. The solution was diluted to 10%* H_2SO_4 concentration, boiled to dissolve the zirconium and titanium, cooled, and filtered to collect the $PbSO_4$. The sulphate residue was retreated to dissolve entrapped zirconium and titanium salts, and the filtrates were combined and made to a volume of 200 ml.

Zirconium was determined by taking an aliquot of the filtrate to dryness, dissolving the salts in 15% HCl, and following the standard mandelic acid procedure.

Titanium was determined by adding 30% H_2O_2 to a suitable aliquot of the filtrate solution and making up to volume while adjusting acidity to 10% H_2SO_4. The titanium concentration was measured colorimetrically by a differential technique.

The lead sulphate collected was decomposed with ammonium acetate and the lead precipitated as lead chromate. The lead chro-

*All acid concentrations are in per cent by volume.

mate was filtered through a Gooch crucible and weighed.

5. Microscopical and X-ray examinations: Grain sizes were estimated on selected disks, two from each lot in the case of the D series. Polished sections were etched with 0.2% HCl to which a trace of HF had been added. They were examined with a micrometer eyepiece, and the diameters of all grains intersected by the scale base line in each of three fields were measured.

X-ray powder diffraction patterns were taken on one disk from each lot. Copper K_a radiation was used with a 114.7 mm diameter Debye-Scherrer camera.

Comparison of powder lots of the R series

1. Introduction: The powder lots of the R series were nominally of the same composition and were precipitated and dried by uniform procedures. Spray-drying was carried out from a slurry containing 3% solids, as indicated by McNamara.[2]

When the first ceramic samples were made from these powder lots, the planar coupling factors were found to be much lower than expected for samples of this composition and density. At that time parts of Teflon were present in the Trost Jet Mill used for comminuting the powders, and preliminary studies of the effect of certain impurities indicated that these parts might constitute a source of fluorine contamination that was detrimental to the properties. When these parts were removed and replaced by polyurethane, the properties of ceramics made from the milled

TABLE 3

Some electromechanical properties of lead zirconate-titanate ceramics sintered from D Series lots of powder

Lot No.	Powder Preparation	Poling Field 30kV/cm. k_p	Poling Field 30kV/cm. K_{33}^T	Poling Field 40kV/cm. k_p	Poling Field 40kV/cm. % breakdown
D2-1	slurry 7% solids spray dried	0.43	1181	0.56	0
D2-2	slurry 8% solids spray dried	0.38	1146	0.49	83
D2-3	filtered and vacuum dried	0.37	1189	0.49	50
D3-1	slurry 3% solids spray dried	0.47	1149	0.54	33
D3-2	slurry 22% solids spray dried	0.46	1160	0.53	0
D4-1	carbonate ppt, slurry 4% solids, spray dried	0.50	1182	0.60	50
D4-2	carbonate ppt, filtered & vacuum dried	0.40	1209	0.55	33
Mean		0.43	1174	0.54	—
Std. Dev.	among lots	±0.05	±23	±0.04	
Std. Dev.	within lots	±0.03	±43	±0.02	
D1-1	combined ptts, slurry 10% solids, spray dried	0.42	906	0.49	17
D1-2	combined ppts, filtered & vacuum dried	0.52	809	0.55	17
D3-3	filtered & dried by distillation under benzene	0.38	1023	0.46	0

Samples poled at 100°C; 10 minutes at 30kV/cm, 5 minutes at 40kV/cm.

TABLE 4

Some effects of silica additions on properties of lead zirconate-titanate ceramics

Property	Lead Zirconate Titanate Lot No.	Control	with 0.5 wt% Silica
Coupling factor k_p (poled at 40kV/cm)	D1-1	0.53	0.38
	17-62	0.55	0.38
Average grain diameter (microns)	D1-1	1.1	3.1
	17-62	9	23
Weight change on sintering (per cent)	D1-1	—0.7	+1.5
	17-62	—0.6	+3.2

Lot D1-1, sintered 1240°C for 1 hour.
Lot 17-62 sintered 1225°C for 1 hour.

powders improved to the level indicated in Table 1.

2. Procedure: Preparation and testing of samples were in accord with the general procedures already described; all samples were fired at 1280°C for 2 hours. Both calcined and uncalcined powders were used in preparing the disks.

3. Results and discussion: As the lot numbers given in Table 1 indicate, there were originally seven members of the R series, but, because of the initial difficulties with fluorine contamination already mentioned, only four of these were evaluated completely. The figures given are averages based on the results from both calcined and uncalcined powders, since there seemed to be no systematic differences in the properties of disks fabricated from each. It is clear that satisfactory results were obtained from Lots R4, R5 and R6, after solving the problem of fluorine contamination, which will be discussed in greater detail later. The properties of Lot R7 are significantly poorer than those of the others, however, and the reasons for this are not yet clear.

Comparison of powder lots of the D series

1. Introduction: The powder lots of the D series were of nominally identical composition, but differed in the precipitation and drying procedures employed. Lots D2 and D3 were co-precipitated with ammonia, then subjected to various drying procedures as indicated in Table 2, including spray drying with various densities of slurry, vacuum drying, and azeotropic distillation under benzene. In the D4 lots, ammonium carbonate as well as ammonia was employed in the co-precipitation procedure, so that the lead was brought down as a basic lead carbonate rather than as the hydroxide. In the D1 lots, the three metal hydroxides were precipitated separately in different vessels, and then combined in the proper proportions to yield the desired stoichiometric ratios, as has already been described.[2] The main purpose of this investigation was to determine whether these differences in procedure had an appreciable effect on the properties of ceramics made from the powders.

2. Procedure: The preparation and testing of ceramic specimens was in accord with the general procedures described earlier in the paper. As indicated in Figure 1, a portion of each powder lot was calcined at 700°C, and the remainder uncalcined. Sintering was done at 1240°C for 2 hours. For each lot, 3 samples prepared from calcined powder and 3 from uncalcined powder were evaluated. The test specimens from a given lot were sintered in pairs, one calcined and one uncalcined, in three different cycles. The position of disks from a given lot was varied from cycle to cycle. Sample breakage, particularly among

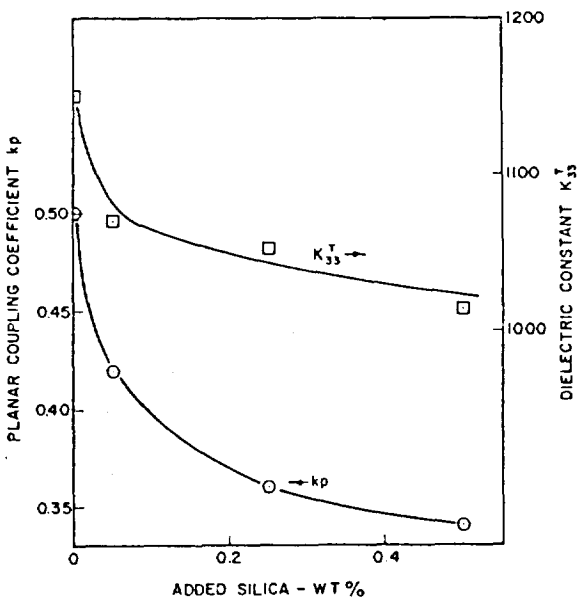

Figure 2. Effect of SiO_2 on planar coupling coefficient and dielectric constant (Lot D1-1, sintered at 1240°C for 1 hr., poled 36 kv/cm).

those made from uncalcined powder, necessitated some variations in this procedure.

3. Results and discussion: It is clear from Table 2 that ceramics of high density could be sintered from all of the powders. Except for higher breakage and increased shrinkage on firing, samples made from uncalcined powder exhibited no significant differences in properties from the others; the property values quoted in the tables are therefore averaged over all samples for each lot.

The mole ratios given indicate that the zirconate-titanate ratios agree well with the analyses on powders given by McNamara[2] and, with the exception of the D1 lots, are quite uniform. The ratio of lead oxide to zirconia plus titania indicates that the lead oxide content increased slightly on sintering. This could be the result of pick-up from the lead oxide atmosphere provided by the lead zirconate disks; the lead content appeared to be affected slightly by proximity to these disks. There are no significant differences in grain size or structure; all lots except D1-2 showed a preponderance of the tetragonal phase, but all of the compositions are very close to the rhombohedral-tetragonal phase boundary.

In Table 3, it is indicated that the average dielectric constant and the coupling factor at 40 kV/cm for the first seven lots are slightly higher than the best values previously published for an unmodified 52/48 composition ($KT_{33}=730$, $kp=0.53$).[4] There are significant differences between lots in coupling factor, though not in dielectric constant. Lots D1-1, D1-2 and D3-3 are separated from the others in Table 3 because of the wider differences exhibited; particularly significant are the lower values of dielectric constant for the D1 lots and the low coupling factor of D3-3.

The variations in breakdown strength, expressed as the percentage of samples breaking down by the end of the 40 kV/cm poling process, are especially noteworthy, particularly in view of the close similarity in processing between Lots D2-1 and D2-2, for example.

Despite the variations in properties discussed above, however, it should be emphasized that none of these variations can be related in any systematic way to whether spray or vacuum drying was used, to the density of the slurry, or to the presence or absence of carbonate in the precipitate.

Effects of certain impurities on the properties of lead zirconate-titanate ceramics

1. Introduction: A study was undertaken to determine the effects of small amounts of added impurities on the electromechanical properties of lead zirconate-titanate ceramics. The impurities chosen for study were those that might be expected to enter the material from the initial reagents or during the processing. It was hoped to determine which of these impurities must be controlled most rigorously and at approximately what levels they might be tolerated. It is known that there are certain additives, such as Nb_2O_5[5] and

TABLE 5

Some effects of fluorine additions on properties of lead zirconate-titanate ceramics

Property	Addition	Control	with Fluorine
Coupling factor k_p (poled at 40kV/cm)	PbF_2 (0.05 wt% F)	0.53	0.18
	CaF_2 (0.1 wt% F)	0.49	0.01
	Teflon (0.1 wt%)	0.49	0.05
Dielectric Constant K^T_{33}	PbF_2	1164	1179
	CaF_2	1162	(920)
	Teflon	1162	1007
Electrical Conductivity ohm^{-1} metre^{-1}	PbF_2	6×10^{-11}	12×10^{-11}
	CaF_2	2×10^{-11}	5×10^{-11}
	Teflon	2×10^{-11}	14×10^{-11}

Lot D1-1, sintered 1240° for 1 hour.

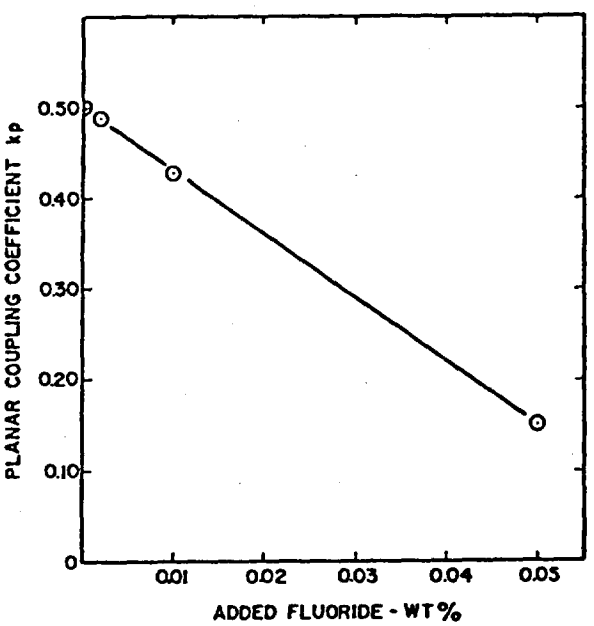

Figure 3. Effect of Fluoride (added as PbF_2) on planar coupling coefficient (lot D1-1 sintered at 1240°C for 1 hr. poled 36 kv/cm.).

Bi_2O_3 [6], that improve some of the electrical properties of lead zirconate-titanate ceramics, but the present investigation was not specificially designed to find other additives with beneficial effects.

The importance of a knowledge of the effects of impurities can be illustrated by considering certain difficulties encountered during examination of various lots of co-precipitated lead-zirconium-titanium hydroxides. One series of powders, described as the MR series by McNamara[2], had a high impurity content and showed almost negligible planar coupling coefficients after poling. All the impurities found in two lots from this series are included in the present study. Another series of powders, previously referred to as the R series, was first comminuted in a mill lined with Teflon; these samples also exhibited rather low planar coupling coefficients. When portions of the same lots were comminuted in a mill lined with polyurethane, the better properties quoted earlier, in Table 1, were obtained.

2. Procedure: The impurities to be studied were added to Lot D1-1 after it had been calcined at 700°C and milled. Silica was also added to a sample of Lot 17-62, after calcining at 650°C and milling. Mixing was carried out in an agate mortar. Most of the impurities were added either as the oxides or as the carbonates; sulphate, chloride, and phosphate were added in the form of standardized solutions of the respective acids. Fluorine was added as lead fluoride, and also, to a separately milled batch of powder, as calcium fluoride and as Teflon.

Sample disks were prepared and tested in the manner indicated previously; they were fired at 1240°C for 1 hour. In order to permit a study of dielectric breakdown during poling, the poling field was increased in 2 kV/cm steps, starting at 30 kV/cm, the voltage being applied for 5 minutes and turned off for 10 minutes before going on to the next step. The samples were withdrawn for evaluation at the 30, 36 and 40 kV/cm levels.

3. Results and discussion: From Figure 2 it can be seen that silica depresses both the dielectric constant and the planar coupling factor of the lead zirconate-titanate ceramics; the

TABLE 6

Effects of some additions on electromechanical properties of lead zirconate-titanate ceramics

Addition	Wt %	K_{33}^T	k_p	Dissip. Factor (at 1 kV/cm, 1 kc)	Breakdown Field (kV/cm)
None	—	1164	0.53	0.044	43
Al_2O_3	0.25	1093	*0.22*	0.032	43
CaO	0.25	1180	0.55	0.034	42
Na_2O	0.25	*736*	0.54	0.040	45
Sulphate	0.25 SO_3	1111	0.52	0.045	41
Chloride	0.25 Cl	1202	0.54	0.041	41
Phosphate	0.25 P_2O_5	1147	*0.46*	0.039	42
MnO_2	0.1	1174	0.53	0.044	42
V_2O_5	0.1	1037	*0.44*	0.040	42
CuO	0.1	*958*	0.53	0.034	42
NiO	0.1	*832*	*0.56*	0.034	42
None	—	1150*	0.50*	0.044	43
MgO	0.25	*769**	*0.43**	0.038	39

Lot D1-1, sintered 1240°C for 1 hour, poled 5 minutes at 40kV/cm and 100°C, except * poled at 36kV/cm.

Changes that appear significant are in italics.

effect seemes to be non-linear with concentration. Examination of polished sections of disks with added silica indicated the presence of an intergranular phase that appeared to have been molten at high temperature. Probably the silica formed a lead silicate flux; some of the lead oxide for this flux could have been drawn from the lead oxide atmosphere in the furnace, since the disks gained weight in sintering (Table 4). The grain growth indicated in Table 4 was probably facilitated by the flux. It is also likely that the presence of the intergranular phase is significant with regard to the reduction in planar coupling factor. The effect of silica is the same in the two lots of powder to which it was added.

The addition of lead fluoride produces a marked decrease in planar coupling coefficient; as shown in Figure 3, this decrease is proportional to the weight of additive. The results shown in Table 5 indicate that the addition of calcium fluoride or Teflon also produces a lowering of the coupling coefficient. It was observed that control samples, sintered together with disks to which fluoride had been added, also exhibited a deterioration in properties. Transfer of volatile fluoride in the furnace is indicated. The increase in electrical conductivity observed with increasing fluorine content may give an indication of the nature of the mechanism involved. The ionic radius of F^- (1.36A, Pauling's value) is very close to that of the O^{2-} ion (1.40A°). A substitution of F^- for O^{2-} would require a compensating valence change in one or more of the cations, probably titanium. The presence of a small content of Ti^{3plus} ions would be expected to increase the electrical conductivity by cation-cation electron transfer between Ti^{3plus} and Ti^{4plus}.

The effects of the other impurities are summarized in Table 6. It will be noted that the oxides* of sodium, copper, nickel and magnesium reduce the dielectric constant, whereas the presence of alumina, phosphate, vanadium pentoxide or magnesium oxide was detrimental to the planar coupling factor, the effect of alumina being particularly severe. Phosphate additions also appeared to produce a slight amount of grain growth and some increase in specimen weight during sintering; probably some lead phosphate was formed by reaction with lead oxide in the furnace atmosphere.

Calcium oxide, manganese oxide, sulphate and chloride appear to produce insignificant changes in properties at the levels indicated; it is probable that the latter two were volatilized at the sintering temperature.

The only additive having a significant effect on dielectric breakdown was magnesium oxide. Since none of the samples containing this additive survived to 40 kV/cm, property values after poling at 36 kV/cm are given in the table. Since thermal breakdown effects are significant under the conditions to which the samples are subjected during poling, the results of the breakdown tests will depend to a considerable extent on the method of mounting of the samples and the effectiveness of cooling. In this experiment, the samples were poled in groups of 16, and it is believed that the differences in treatment between individual samples were negligible. It would be difficult, however, to compare the results directly with those of other workers.

*It is assumed that the carbonates had decomposed to the oxides during sintering.

Summary

The electromechanical properties of ceramics fabricated from lots of co-precipitated powder did not appear to vary systematically with the following changes introduced in the co-precipitation and powder drying procedures:

(a) changes in pulp density of the slurry fed to the spray drier,

(b) changing from spray drying to filtering and vacuum drying,

(c) the use of carbonate as well as hydroxide as the precipitating agent.

The successful fabrication of disks from the carbonate precipitate is significant since certain common additives, such as strontium, would be most conveniently co-precipitated in the form of the carbonate. There were, however, variations in electromechanical properties from lot to lot that have not been correlated with changes in chemical composition, crystal structure, or grain size of the ceramic. On the other hand, certain powder preparation procedures did appear to affect adversely the electromechanical properties of the ceramics. These procedures were separate precipitation of the hydroxides, followed by mixing of these precipitates, and drying the precipitate by azeotropic distillation under benzene.

The presence of fluoride, alumina, silica, vanadium pentoxide or phosphate was shown to lower the planar coupling coefficient of the lead zirconate-titanate ceramics. The oxides of magnesium, copper, nickel, and sodium were shown to decrease the dielectric constant.

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Chemical determination of lead, titanium and zirconium in precipitates used for production of homogenous lead zirconate-lead titanate solid solutions

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ABSTRACT

Methods are described for the determination of lead, zirconium and titanium in precipitates containing all three of these elements as major constituents. Lead is determined by titration with EDTA, using Xylenol Orange as indicator, after isolation from the other constituents by a solvent extraction step employing sodium diethyl-dithiocarbamate. Titanium is determined by differential absorptiometry of the titanium-hydrogen peroxide compound, in the raffinate from the lead removal step. Zirconium is determined conventionally on a separate aliquot of the sample solution, by the gravimetric mandelic acid procedure, after prior removal of lead as sulphate.

Data on the precision and accuracy of the methods are also presented.

Introduction

An extensive program on the production of electronic ceramics is being carried out on an interdivisional basis within the Mines Branch, at Ottawa, under the sponsorship of the Defence Research Board. As its contribution to this program the Extraction Metallurgy Division has undertaken to prepare a series of mixed powders of specified closely- controlled composition, high purity and complete homogeneity, for conversion to the desired ceramic form. One phase of this work, involving the production of lead zirconate-lead titanate powders, has recently been described by McNamara and Gow.[1]

Because one of the aims of the overall program was to investigate the effects, on the electrical properties, resulting from minor changes in the molar ratios of the components, it was essential that the analytical laboratory not only establish the amounts of the respective elements but also provide an estimate of the precision with which the analytical values were known. The present paper presents a brief description of the analytical methods used and describes the experimental work carried out to define the limits of accuracy of these methods.

Procedure

Analytical methods: The analytical scheme for the determination of the three elements is outlined diagrammatically in Figure 1.

The sample, dried at 110°C, is first dissolved — using one of a variety of procedures depending on its previous history — and then diluted accurately to 500 ml at 20° ± 0.5°C. One aliquot is used for the lead and titanium determinations, and a second, larger aliquot is taken for the determination of zirconium.

Lead: The method used for the determination of lead is basically that of Kinnunen and Wennerstrand[2] as modified by Hitchen[3]. Lead is first separated from the other components of the mixture by extraction, as the diethyldithiocarbamate, from tartrate medium with chloroform. After removal of the organic components of the solvent extract, the lead is dissolved in acetate buffer and then is titrated with a standard solution of the sodium salt of ethylenediaminetetra-acetic acid, at pH 5.4, using Xylenol Orange as the indicator.

Studies carried out by Hitchen[3] have shown that only copper, nickel, zinc, cobalt, cadmium, antimony, tin, bismuth, manganese, and phosphate interfere in his procedure. His report has outlined methods for dealing with these interferences, but because in the present investigation none of the elements mentioned

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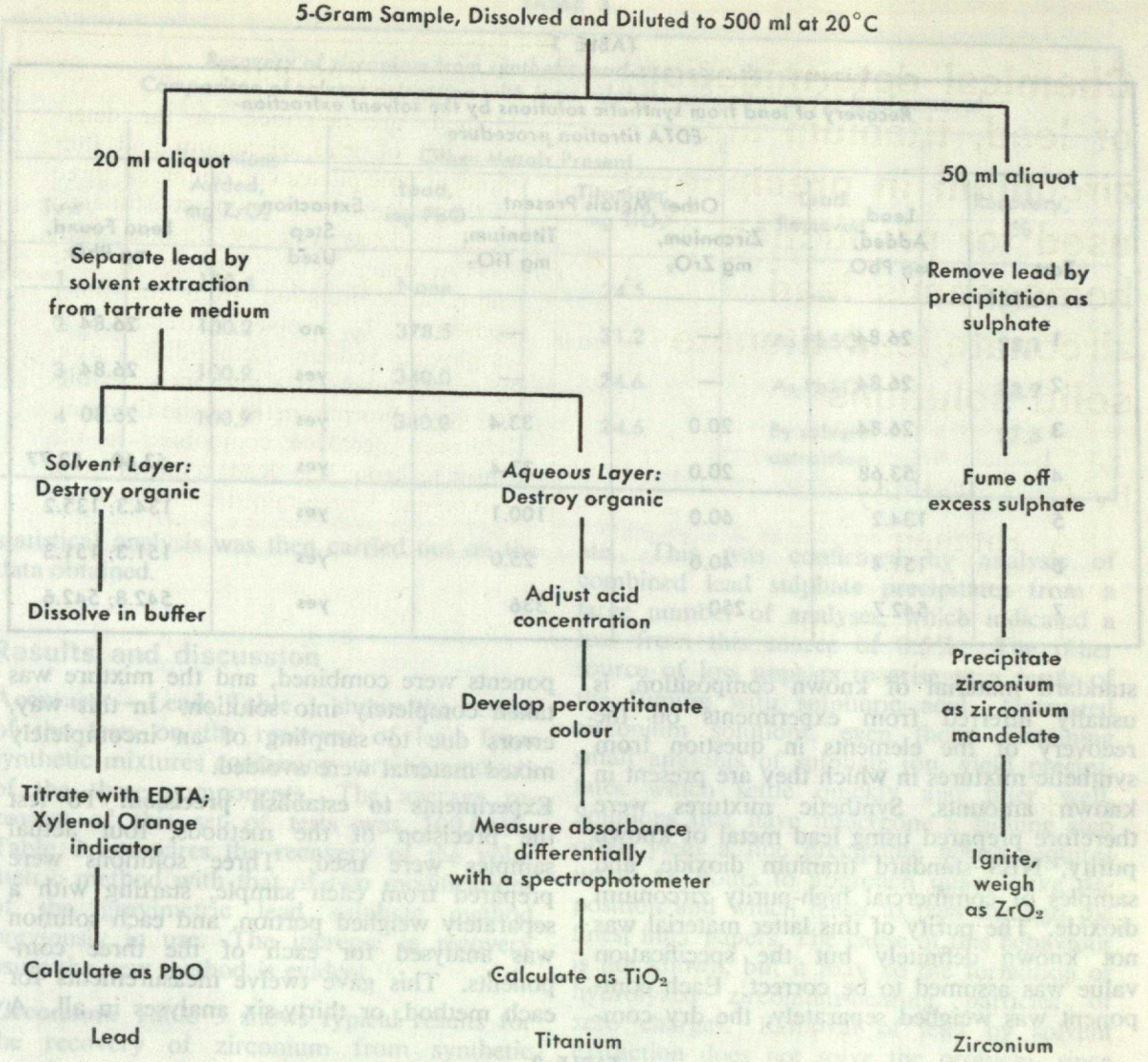

Figure 1. Analytical scheme for the determination of lead, titanium and zirconium in lead zirconate-lead titanate precipitates.

was expected to be present in the powders to be analysed, it was not considered necessary to take any special steps on this account.

Zirconium: Zirconium is determined by a conventional mandelic acid gravimetric procedure[4]. The solution is first fumed down with sulphuric acid to precipitate the bulk of the lead and the silica, which are filtered off. Zirconium is then precipitated from the filtrate with mandelic acid. The original precipitate is redissolved and the zirconium is precipitated again with mandelic acid to ensure complete removal of lead and silica.

Titanium: The aqueous extract resulting from the solvent extraction removal of lead, which contains all the titanium and zirconium present in the original aliquot, is treated with sulphuric and perchloric acids to remove the tartrate it contains. The colour of the titanium-hydrogen peroxide compound is then developed in the solution without removal of the zirconium. Colour development takes place in 20% sulphuric acid of closely controlled concentration; aliquots of standard solutions are taken with volumetric equipment that has been restandardized for use with this medium; and the colour of the sample is compared with that of the standards, using the high-precision (differential) absorptiometric technique of Neal[5]. The differential technique theoretically permits a tenfold increase in precision over methods using direct spectrophotometric measurement. The actual precision found (given later in this report) represents about a fourfold increase over that of the direct method.

Experiments to establish accuracy: The accuracy of an analytical method for a particular type of material in the absence of similar

TABLE 1

Recovery of lead from synthetic solutions by the solvent extraction-EDTA titration procedure

Test	Lead Added, mg PbO	Other Metals Present		Extraction Step Used	Lead Found, mg PbO
		Zirconium, mg ZrO_2	Titanium, mg TiO_2		
1	26.84	—	—	no	26.84
2	26.84	—	—	yes	26.84
3	26.84	20.0	33.4	yes	26.80
4	53.68	20.0	33.4	yes	53.60; 53.77
5	134.2	60.0	100.1	yes	134.3; 135.2
6	151.4	40.0	25.0	yes	151.3; 151.3
7	542.7	250	336	yes	542.8; 542.6

standard material of known composition, is usually inferred from experiments on the recovery of the elements in question from synthetic mixtures in which they are present in known amounts. Synthetic mixtures were therefore prepared using lead metal of known purity, NBS standard titanium dioxide, and samples of commercial high-purity zirconium dioxide. The purity of this latter material was not known definitely but the specification value was assumed to be correct. Each component was weighed separately, the dry components were combined, and the mixture was taken completely into solution. In this way, errors due to sampling of an incompletely mixed material were avoided.

Experiments to establish precision: To test the precision of the methods, four actual samples were used. Three solutions were prepared from each sample, starting with a separately weighed portion, and each solution was analysed for each of the three components. This gave twelve measurements for each method, or thirty-six analyses in all. A

TABLE 2

Determination of lead in intermediates used in the production of lead zirconate-lead titanate ceramics: Comparison of the volumetric procedure with conventional gravimetric procedures (Ref. 3)

Sample Solutions	Other Constituents Present			Lead Found, as PbO		
				Gravimetric Methods*		
	ZrO_2, g/l	TiO_2, g/l	NO_3, g/l	A, g/l	B, g/l	Present Method, g/l
1937	5.67	1.50	30.3	15.05; 15.03		15.25; 15.30
1938	1.35	3.18	26.0	8.93; 8.84		8.88; 8.88
2455	5.55	1.93	—		15.20; 15.17	15.25; 15.25
2456	5.57	1.58	—		14.06; 14.07	14.12; 14.09
Solids	%	%	%	%	% %	%
2121	17.0	10.24	0.53	63.06; 62.89		63.61; 63.46
2667	15.9	10.36	0.33	57.59; 57.59		57.73; 57.79

* *Gravimetric Methods:*
A. Precipitation and weighing as lead sulphate.
B. Same as A, but with electrolytic recovery of lead passing through into the filtrate.

TABLE 3

Recovery of zirconium from synthetic lead-zirconium-titanium mixtures: Comparison of solvent extraction with lead-sulphate precipitation for lead removal

Test	Zirconium Added, mg ZrO_2	Other Metals Present		Lead Removed	Recovery, %
		Lead, mg PbO	Titanium, mg TiO_2		
1	100.4	None	24.5	—	100.6
2	100.2	378.5	31.2	As $PbSO_4$	98.1
3	100.9	340.0	24.6	As $PbSO_4$	98.9
4	100.9	340.0	24.6	By solvent extraction	97.5

statistical analysis was then carried out on the data obtained.

Results and discussion

Accuracy — Lead: Table 1 shows the results of the tests on the recovery of lead from synthetic mixtures containing varying amounts of the three components. The average recovery of this set of tests was 100.04%. Table 2 compares the recovery of the volumetric method with that of two modifications of the gravimetric lead sulphate method previously in use. The increase in recovery using the new method is evident.

Zirconium: Table 3 shows typical results for the recovery of zirconium from synthetic samples. The slightly high result for Test 1 is probably due to incomplete removal of silica in the absence of lead. The low results in Tests 2 and 3 are due, at least in part, to co-precipitation of zirconium by lead sulphate. This was confirmed by analysis of combined lead sulphate precipitates from a large number of analyses, which indicated a loss from this source of 0.5%. The other source of loss appears to arise as a result of the fuming with sulphuric acid. Untreated zirconium solutions, even those containing small amounts of sulphate ion, yield precipitates which settle quickly and filter well. Solutions that have undergone a fuming step often yield a fine precipitate which requires up to 16 hours to approach quantitative deposition and which tends to pass through the finest filter papers. The cause of this behaviour is not known, but it may be the formation of hydrolyzed zirconium-bearing particles of zero charge[6]. Removal of lead by solvent extraction does not solve the problem, since the necessity of destroying the tartaric acid also involves a fuming step. Furthermore, silica must be removed, which requires a fuming step in any case. Work on alternative methods is proceeding, but in the meantime a

TABLE 4

Recovery of titanium from synthetic lead-zirconium-titanium mixtures: Comparison of lead-sulphate precipitation with solvent extraction for lead separation

Test	Titanium Added, mg TiO_2	Other Metals Present		Lead Removed	Recovery, %
		Lead, mg PbO	Zirconium, mg ZrO_2		
1	25.02	—	—	—	99.75
2	24.50	—	100.4	—	99.70
3	24.82	378.3	100.2	As $PbSO_4$	99.40
4	24.60	340.0	100.9	By solvent extraction	100.02

TABLE 5

Precision of the lead determination on lead zirconate-lead titanate precipitate samples

Sample No.	Lead as PbO, %			
	1	2	3	Average
R4	60.50	60.49	60.45	60.48
R5	59.95	59.94	59.96	59.95
R6	60.08	60.09	60.11	60.09
R7	60.45	60.49	60.53	60.49

Standard deviation = ± 0.026
Relative standard deviation = ± 0.044% of the amount present
Confidence limits, L_{95},
for the average of three determinations = ± 0.066

rigidly standardized procedure is used, and lack of quantitative recovery is corrected for, assuming a constant loss of 1% of the amount indicated by the analysis.

Titanium: Table 4 shows typical values for the recovery of titanium from synthetic mixtures, and it will be seen that a slightly higher recovery of titanium was obtained with the solution from which the lead had been removed by solvent extraction.

Precision: The data from the precision studies were evaluated statistically by the methods of Dean and Dixon[7]. The results of the analyses and of the statistical calculations are given in Tables 5 to 9.

Tables 5, 6 and 7 give the original analytical results for lead, zirconium and titanium respectively, and, in addition, the standard deviation, the relative standard deviation, and the 95% confidence limits for the reported percentage values of each of the three constituents.

The same statistical information, calculated for the mole percentages of the three constituents, is shown in Table 8. Table 9 shows the corresponding values for the molar ratios. It will be observed in these latter tables that the standard deviations tend to approach each other. This is due, of course, to the fact that the results of all three determinations enter into each calculation.

Finally, Table 10 compares the values

TABLE 6

Precision of the zirconium determination on lead zirconate-lead titanate precipitate samples

Sample No.	Zirconium as ZrO_2, %			
	1	2	3	Average
R4	17.50	17.49	17.47	17.49
R5	17.36	17.42	17.49	17.42
R6	17.46	17.43	17.44	17.44
R7	17.42	17.49	17.45	17.45

Standard deviation = ± 0.039
Relative standard deviation = ± 0.22% of the amount present
Confidence limits L_{95},
for the average of three determinations = ± 0.096

TABLE 7

Precision of the titanium determination on lead zirconate-lead titanate precipitate samples

Sample No.	Titanium as TiO_2, %			
	1	2	3	Average
R4	10.24	10.22	10.24	10.23
R5	10.19	10.19	10.18	10.19
R6	10.22	10.26	10.26	10.24
R7	10.24	10.26	10.26	10.25

Standard deviation = ± 0.013
Relative standard deviation = ± 0.13% of the amount present
Confidence limits, L95,
for the average of three determinations = ± 0.033

TABLE 8

Precision of the reported values of the elements, calculated as mole percentages for one lead zirconate-lead titanate precipitate sample (R4)

Element	Mole %, Average of Three Determinations	Standard Deviation of a Single Determination	Confidence Limits, L 95, for the Average of Three Determinations
Lead (as PbO)	50.089	± 0.036	± 0.09
Zirconium (as ZrO_2)	26.235	± 0.045	± 0.11
Titanium (as TiO_2)	23.700	± 0.032	± 0.08

TABLE 9

Precision of the reported values of the elements, calculated as molar ratios, for one lead zirconate-lead titanate precipitate sample (R4)

Ratios of Oxides	Molar Ratio, Average of Three Determinations	Standard Deviation of a Single Determination	Confidence Limits, L 95, for the Average of Three Determinations
$Pbo/ZrO_2 + TiO_2$	1.0035	± 0.0015	± 0.0038
$ZrO_2/ZrO_2 + TiO_2$	0.52561	± 0.00056	± 0.0014
$TiO_2/ZrO_2 + TiO_2$	0.47439	± 0.00071	± 0.0018

obtained in this study by the Chemical Analysis Section for the percentage composition of the sample with the values obtained in the Mineral Sciences Division's analytical chemistry laboratory. These values are also the average of triplicate determinations.

Conclusions

The methods described here have been successfully applied to the determination of the relative proportions of lead, zirconium and titanium oxides in powders used for the

TABLE 10

Interlaboratory comparison of the chemical analysis results for typical lead zirconate-lead titanate precipitate samples

Sample No.	Mineral Sciences Division Analytical Chemistry Laboratory*			Extraction Metallurgy Division Chemical Analysis Laboratory		
	Lead as PbO, %	Zirconium as ZrO_2, %	Titanium as TiO_2 %	Lead as PbO, %	Zirconium as ZrO_2, %	Titanium as TiO_2, %
R4	60.41	17.37	10.22	60.48	17.49	10.23
R5	59.97	17.21	10.20	59.95	17.42	10.19
R6	60.21	17.37	10.31	60.09	17.44	10.25
R7	60.56	17.44	10.33	60.49	17.45	10.25

*From Internal Report MS-AC-2113 of the Mineral Sciences Division, dated December 1, 1964.

production of electronic ceramics. Studies of accuracy and precision show that they are adequate for characterizing individual samples, and for differentiating between samples that vary only slightly in molecular composition. Of the three methods used, only that for zirconium appears to offer scope for significant improvement; experimental studies to this end are under way.

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APPENDIX

ELECTRONIC CERAMICS

ECRDC RESEARCH PROJECT C 73

Identification of Mines Branch Personnel

Advisory Committee

Mr. Ian F. Wright, MPD*, Chairman
Mr. W. A. Gow, EMD
Dr. N. F. H. Bright, MSD
Mr. J. G. Brady, MPD
Mr. V. A. McCourt, MPD

Operational	Function
Mr. V.M. McNamara, EMD	Pilot plant ceramic powder preparation
Mr. J. C. Ingles, EMD	Control analyses
Dr. A. H. Webster, MSD	Sintering and structural studies
Mr. V. A. McCourt, MPD	Lapidary and electroding
Mr. Ian F. Wright, MPD	Ceramic engineering
Mr. T. B. Weston, MPD	Electronic test methods and component evaluation
Mr. W. R. Inman, MSD	Wet chemical analytical methods and analyses
Dr. A. H. Gillieson, MSD	Spectrographic analyses
Dr. E. H. Nickel, MSD	Sample preparation for petrographic studies

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EMD - Extraction Metallurgy Division
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