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CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 69-15

THE EFFECTS OF SOME ADDITIVES ON THE PROPERTIES OF LEAD ZIRCONATE-TITANATE CERAMICS

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COPY NO. 1

FEBRUARY 20, 1969

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SUMMARY OF RESULTS

Ten different oxides were added, generally at the 0.5 wt % level, to lead zirconate-titanate of two compositions, and the effects on the electromechanical properties of the lead zirconate-titanate ceramics were determined. Calcium oxide produced effects that could be interpreted as being due to a shift of the tetragonal/ rhombohedral boundary to a higher zirconate/ titanate ratio. Nickel oxide and Cr_2O_3 decreased the dielectric constant and high-field loss, and increased the mechanical quality factor. Niobium pentoxide increased the poled dielectric constant in the higher-titanate material. The site at which the added cation substituted (Pb site or Ti, Zr site) could generally be inferred from the loss or gain of lead oxide during the reaction of the additive. Interpretation of the results was complicated by variations in density and in grain size among samples with different additives.

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INTRODUCTION

The effects of the addition of small quantities of various oxides to lead zirconate-titanate ceramics have been extensively studied during the past ten years. These studies have been fairly intensive for some additives while, for others, the reported studies are incomplete for one or more of a number of reasons. For example, in some cases, results on control samples without additions were not reported, additions were made at only one level, additives were not made to compositions on both sides of the rhombohedral/tetragonal boundary, or densities and grain sizes were not reported.

The purpose of the present rather cursory investigation was to review the effects of ten additives, studies on many of which have already been reported in the literature. In particular, a comparison of the effects of additions made to tetragonal and to rhombohedral materials was desired. If an additive changes the zirconate/titanate ratio of the rhombohedral/-tetragonal boundary, then opposite effects on both the dielectric constants and the coupling factor would, in general, be expected when the addition is made to materials that lie on opposite sides of the boundary. Such behaviour is anticipated since both the dielectric constants and the coupling factor have maximum values at or very close to the tetragonal/rhombohedral boundary in unmodified materials(1, 2). If the additive has an effect other than simply changing the position of the rhombohedral/tetragonal boundary, then the changes in properties should be qualitatively the same whether the addition is made to either a tetragonal or rhombohedral material.

It should be noted that the cursory examinations made during the course of the present investigation are not likely to lead to definitive conclusions, but should indicate phenomena that are worth investigating in greater detail. A fairly intensive investigation of the effects of Fe_2O_3 additions on the properties of lead zirconate-titanate ceramics was undertaken and has been reported separately(3).

EXPERIMENTAL PROCEDURES

Two calcined lots of spray-dried, co-precipitated mixed hydroxides (or hydrated oxides) of lead, zirconium and titanium were selected for use as the materials to which the additions were made. The precipitates had been prepared by Mr. V. M. McNamara, Extraction Metallurgy Division, Mines Branch, by procedures described previously(4). These materials were known from previous work(2, 5) to give ceramics with the compositions 51.8 mole % $PbZrO_3$/ 48.2 mole % $PbTiO_3$ (tetragonal) and 53.7 mole % $PbZrO_3$/ 46.3 mole % $PbTiO_3$ (rhombohedral). The spray-dried powders had been calcined at 700°C for 30 min. and for 1 hour, respectively*. The appropriate quantity of additive was mixed with the calcined powder in an agate mortar, and the mixed powder was pressed into three 1-inch-diameter disks. These disks were sintered along with a control disk without additive. Two lead zirconate disks were included to provide a lead oxide atmosphere in the furnace. The samples were heated at 250 deg C per hr to 1260°C and held at this temperature for 2 hours (53.7 % $PbZrO_3$ material) or 3 hours (51.8 % $PbZrO_3$ material). Any weight change that took place during sintering was noted. The sintered disks were lapped to a standard size and electroded by sputtering with gold.

Electromechanical properties were determined before poling and, subsequently, 24 hours after poling in an oil bath at 100°C. The methods used have been described previously(6) and are in accordance with accepted procedures(7). Dielectric constants (K before poling and K_{33}^{T} after poling) and dissipation factor (tan δ) at low field were determined at 1 kHz using a General Radio capacitance bridge, Model 716C. The radial coupling factor (k_p) was determined from measurements of the resonance and antiresonance

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*Powders calcined under these conditions would be expected to have specific surface areas of about 7 m^2/g.

Table 1

Additions Made to Lead Zirconate-Titanate Powders

Additive	Level	Form of Addition	Source
CaO	0.3 wt %	$CaCO_3$	Mallinckrodt reagent
SrO	0.5 wt %	$SrCO_3$	Ppt from $SrCl_2$ solution
BaO	0.5 wt %	$BaCO_3$	B and A reagent
NiO	0.5 wt %	Nickel carbonate*	B and A reagent
Cr_2O_3	0.5 wt %	Cr_2O_3	B. D. H.
CoO	0.5 wt %	Cobaltous carbonate*	B and A reagent
La_2O_3	0.4_3 wt %	Lanthanum oxide*	Fairmont Chemical CP
Bi_2O_3	0.5 wt %	Bi_2O_3	B. D. H.
Ta_2O_5	0.5 wt %	PbO + Ta_2O_5**	Fansteel Metallurgical Corp.
Nb_2O_5	0.5 wt %	PbO + Nb_2O_5**	Ppt from nitrate solution

Notes: *Conversion factor to oxide determined by loss on ignition or by analysis. The lanthanum oxide was found to be partially hydrated.

**1 mole PbO added for each mole of oxide.

frequencies. The change in capacitance with field,

$$\Delta C = \frac{C_h - C_\ell}{C_\ell} \times 100\%,$$

where C_h = capacitance at a field of 2 kV/ cm (rms)
C_ℓ = capacitance at low field (10 V/ cm),

and dissipation factor under a 2 kV/ cm rms field, were determined using a specially constructed bridge. The mechanical quality factor (Q_m) was calculated from the resonance resistance, capacitance, and resonance and antiresonance frequencies. Mean grain diameters were determined on etched polished sections by the intercept method, and were taken as equal to $1.5\,\bar{\ell}$, where $\bar{\ell}$ = (length of arbitrary line)/(number of grains intersected)(8). Twenty lines, each intersecting 10 grains were measured.

The ten oxide additions made to each lead zirconate-titanate powder are listed in Table 1, together with the level, form, and source of the additive.

EXPERIMENTAL RESULTS

(1) Weight Changes During Sintering

For disks with non-volatile additives, any difference in the weight change during sintering from the weight change found for the control disks may be attributed to loss or gain of lead oxide. If the added element substitutes in the lead site of the perovskite-type lattice, a loss of PbO should occur. If, on the other hand, substitution in the titanium-zirconium site takes place, an accretion of PbO should occur. Other mechanisms of PbO loss or gain are also possible and, in some cases, the situation may be too complex to draw meaningful conclusions.

The weight changes attributable to loss or gain of lead oxide are shown in Table 2. The observed weight changes were adjusted to correct for the weight changes found with the control samples and for any known volatile constituents in the added material (e. g., CO_2 in carbonates).

Table 2

Weight Changes Due to Loss or Gain of Lead Oxide During Sintering

Added Oxide	Weight Change Attributable to PbO Loss (-) or Gain (+) (%)		Expected Weight Change (%)	
	51.8 mole % $PbZrO_3$ material	53.7 mole % $PbZrO_3$ material	Substitution on Pb Site	Substitution on Ti, Zr Site
CaO	-1.2	-1.4	-1.2	-
SrO	-1.0	-1.2	-1.1	-
BaO	-0.7	-0.7	-0.7	-
NiO	+0.5	+0.9	-	+1.5 ($1PbO \equiv 1NiO$)
Cr_2O_3	+2.3	+3.0	-	+1.5 ($2PbO \equiv 1Cr_2O_3$) +2.2 ($3PbO \equiv 1Cr_2O_3$)
CoO	+1.8	+2.8	-	+1.5 ($1PbO \equiv 1CoO$) +2.3 ($3PbO \equiv 1Co_2O_3$)
La_2O_3	-0.7	-0.7	-0.6 ($1La_2O_3 \equiv 2PbO$) -0.9 ($1La_2O_3 \equiv 3PbO$)	-
Bi_2O_3	-0.4	-0.5	-0.5 ($1Bi_2O_3 \equiv 2PbO$) -0.7 ($1Bi_2O_3 \equiv 3PbO$)	-
Ta_2O_5	+0.1	+0.2	-	0 ($1PbO \equiv 1Ta_2O_5$) +0.25 ($2PbO \equiv 1Ta_2O_5$)
Nb_2O_5	+0.2	+0.5	-	0 ($1PbO \equiv 1Nb_2O_5$) +0.4 ($2PbO \equiv 1Nb_2O_5$)

In the presence of the alkaline earth oxides (CaO, SrO, BaO) it was apparent that lead oxide had been expelled during sintering. It may be safely concluded, therefore, that the added divalent ions had entered the lead site, as would be expected.

The addition of NiO induces a weight gain attributable to accretion of PbO. It would appear that Ni enters principally into the Ti, Zr sites. However, the weight increase is only about one half of that expected. There may have been some volatilization of NiO or the solubility of NiO in the zirconate-titanate lattice may have been exceeded.

Chromium oxide definitely was volatile under the sintering conditions used, since the properties of the control samples were not as expected, but were intermediate between the expected properties and the properties of the Cr_2O_3-doped disks. It was evident, therefore, that chromium oxide had been transferred to the control samples through the vapour phase. The weight increase on sintering indicates that the Cr probably enters the Ti, Zr sites, but the magnitude of the increase is greater than expected. The explanation for this is not clear.

The presence of cobalt oxide also causes a weight increase. There is evidence, however, from microexamination of a polished section, that a molten intergranular phase had been present at the sintering temperature, and it may be assumed that this intergranular phase was a PbO-rich liquid for which PbO had been drawn from the furnace atmosphere.

The weight loss observed for samples with added La_2O_3 clearly indicates that the lanthanum replaced lead, but it is not certain whether 1 La replaces 1 Pb or whether 2 La replaces 3 Pb or whether both mechanisms of substitution were operative. Bismuth, also, appears to replace Pb but, in this case, there is also the possibility of Bi_2O_3 volatilization. The marked effects of the Bi_2O_3 on the electromechanical properties of the materials indicate, however, that an appreciable amount of bismuth must have remained in the ceramic.

Tantalum and niobium oxides were added with 1 mole of PbO for each mole of pentoxide. However, there appears to have been a further

Table 3

Mean Grain Diameters of Lead Zirconate-Titanate Ceramics (51.8 mole % Zirconate) with Various Additives

Addition	Mean Grain Diameter (μm)	Remarks
None	5.4	
CaO 0.3 wt %	6.2	
SrO 0.5 wt %	6.2	
BaO 0.5 wt %	6.1	
NiO 0.5 wt %	3.8	
Cr_2O_3 0.5 wt %	3.5	
CoO 0.5 wt %	4.1	Intergranular phase present
La_2O_3 0.43 wt %	17.1	Large pores; some pores "trapped" inside grains
Bi_2O_3 0.5 wt %	11.4	Large pores; some pores "trapped" inside grains
Ta_2O_5 0.5 wt %	16.6	Large pores; some pores "trapped" inside grains
Nb_2O_5 0.5 wt %	8.6	Large pores

increase in weight, indicating that perhaps more than one mole of PbO was required for each mole of pentoxide. It is clear that Nb and Ta enter the Ti, Zr sites of the lattice, as expected.

(2) Microstructures

The mean grain diameters, as determined from one disk for each additive, are presented in Table 3, together with some qualitative remarks on the microstructures. The microstructures appear to fall into three main groups. The alkaline earth oxide additions (CaO, SrO, BaO) may have increased the mean grain diameter slightly. The fourth-period transition-metal oxides (NiO, Cr_2O_3, CoO) decreased the mean grain diameter. On the other hand, metal oxides in which the valence of the added cation is one greater than the valence of the ion for which it substitutes, greatly increased the grain size. These oxides include La_2O_3 and Bi_2O_3, the cations of which substitute in Pb sites, and Nb_2O_5 and Ta_2O_5, the cations of which substitute in Ti, Zr sites. The sample to which CoO had been added showed an intergranular phase that appeared to have been molten at the sintering temperature.

(3) Electromechanical Properties

The results of measurements of the electromechanical properties of the disks, both with and without additions, are presented in Table 4 for the composition with 51.8 mole % $PbZrO_3$ and in Table 5 for the composition with 53.7 mole % $PbZrO_3$. The minimum differences considered significant were estimated at the 95% confidence level, using the "q" test(9) with a pooled standard deviation calculated from all groups of samples being considered. In cases where the standard deviation of the measurements of a property on a group of samples with a given additive was abnormally large, a separate test for significance was made.

In Table 5, the results for Nb_2O_5 additions are considered separately. This group of samples was sintered later than the others of the series, and some differences between the control disks for this group and the control samples for the main group were noted; the reason for these differences is not clear. Significant differences in this case were estimated

Table 4

Properties of Lead Zirconate-Titanate (51.8 mole % $PbZrO_3$-48.2 mole % $PbTiO_3$) Ceramics Modified with Small Additions of Various Oxides*

		Before Poling		After Poling at 30kV/cm for 10 minutes						
Addition	Density (g/cm^3)	K	tan δ (low field)	k_p	K^T_{33}	tan δ (low field)	tan δ ** (2kV/cm)	ΔC** (%)	Q_m	$f_r \cdot d$*** (kHz-m)
No addition	7.92	1158	0.0035	0.51	1418	0.0060	0.0513	22.6	291	2.14
CaO 0.3 wt %	7.83	1022	0.0020	0.44	1262	0.0045	0.0166	9.0	473	2.28
SrO 0.5 wt %	7.90	1167	0.0029	0.53	1506	0.0057	0.0528	24.2	304	2.17
BaO 0.5 wt %	7.88	1174	0.0030	0.53	1477	0.0063	0.0444	20.3	288	2.13
NiO 0.5 wt %	7.95	1090	0.0063	0.58	1157	0.0089	0.0493	21.2	353	2.15
Cr_2O_3 0.5 wt %	7.94	833	0.0090	0.49	879	0.0110	0.0175	6.3	522	2.32
CoO 0.5 wt %	7.81	658	0.083	0.36	613	0.045	0.0763	25.2	62	2.20
La_2O_3 0.43 wt %	7.56	1185	0.0112	0.37	1353	0.0132	0.1227	40.0	105	2.10
Bi_2O_3 0.5 wt %	7.52	1216	0.0101	0.34	1276	0.0105	0.1292	47.5	117	2.03
Ta_2O_5 0.5 wt %	6.91	1008	0.0071	0.31	1040	0.0105	0.1279	54.6	67	1.85
Nb_2O_5 0.5 wt %	7.28	1098	0.0146	0.50	1548	0.0146	0.1208	41.9	70	1.92
Minimum Difference Considered Significant		58	0.0014	0.08	120	0.0018	0.0146	7.6	46	0.04

Notes: *Results are averages of measurements on 14 control disks and 3 disks for each addition. Results considered significantly different from results on control samples are underlined.

**Determined after disks had been subjected to a field of 35kV/cm for 5 minutes.

***(Resonance frequency x disk diameter).

Table 5

Properties of Lead Zirconate-Titanate (53.7 mole % $PbZrO_3$-46.3 mole % $PbTiO_3$) Ceramics Modified with Small Additions of Various Oxides*

Addition	Density (g/cm^3)	Before Poling		After Poling at 35kV/cm for 5 minutes						
		K	tan δ (low field)	k_p	K_{33}^T	tan δ (low field)	tan δ (2kV/cm)	ΔC (%)	Q_m	$f_r \cdot d$ (kHz-m)
No addition	7.95	812	0.0059	0.52	679	0.0156	0.121	48	235	2.29
CaO 0.3 wt %	7.87	1100	0.0029	0.57	1022	0.0080	0.050	20	352	2.17
SrO 0.5 wt %	7.87	903	0.0053	0.55	702	0.0122	0.112	43	254	2.26
BaO 0.5 wt %	7.94	811	0.0064	0.49	699	0.0140	0.132	53	228	2.30
NiO 0.5 wt %	7.93	666	0.0065	0.44	652	0.0107	0.102	36	330	2.36
Cr_2O_3 0.5 wt %	7.92	632	0.0095**	0.47	564	0.0106	0.029	14	644	2.37
CoO 0.5 wt %	7.74	451	0.0337	0.26	438	0.0291	0.055	22	109	2.26
La_2O_3 0.4_3 wt %	7.86	928	0.0034	0.54	656	0.0078	0.109	52	297	2.23
Bi_2O_3 0.5 wt %	7.82	735	0.0057	0.48	610	0.0178	0.137	62	251	2.28
Ta_2O_5 0.5 wt %	7.87	764	0.0058	0.48	640	0.0104	0.150	90	254	2.27
Minimum difference considered significant		43	0.0013	0.05	63	0.0051	0.018	25	37	0.04
No Addition***	7.96	896	0.0082	0.50	759	0.0224	0.131	55	213	2.28
Nb_2O_5 0.5 wt %***	7.71	792	0.0086	0.44	677	0.0130	0.201	127	186	2.19

Notes: *Results are averages of measurements on 7 control disks and 3 disks for each addition. Results considered significantly different from results on control samples are underlined.

**Scatter in results for tan δ (before poling) with Cr_2O_3 addition was abnormally high, and the difference from the control group could not be considered significant.

***Results are averages of measurements on 3 disks. Poling conditions, 35kV/cm for 2 minutes.

using the "t" test(10). The results that are considered significantly different from results on control samples have been underlined in Tables 4 and 5.

The mean values of the sintered densities are given in Tables 4 and 5. The differences in density and in grain size between the control samples and the samples with additives will give rise to effects in addition to those produced by the presence of the additive. In general, a low density will be accompanied by low values for dielectric constants, coupling factors, and frequency constants(11). Also, larger grain diameters might be expected to be accompanied by somewhat lower dielectric constants and dielectric losses and by higher coupling factors and mechanical quality factors(12). Since the average grain diameters are, in most cases, above 4 μm, the grain-size effects should be relatively small.

Some comparisons indicated substantial, but not statistically significant differences; significant differences might be detected if larger additions were used or if more disks were examined.

DISCUSSION

(1) Alkaline Earth Oxides

The addition of SrO or BaO did not appear to make significant changes in the properties of the lead zirconate-titanate ceramics, except that the dielectric constant before poling was increased by SrO in the rhombohedral (53.7 mole % zirconate) material. This absence of significant effects is no doubt due to the relatively small quantities of the additives, which, in the case of Sr additions, replaced 1.6 at. % of the Pb and, in the case of Ba additions, replaced 1.1 at.% of the Pb. It is known that the replacement of Pb^{2+} (ionic radius, 1.32 Å)* by Ba^{2+} (ionic radius, 1.43 Å) shifts the tetragonal/ rhombohedral boundary towards higher titanate compositions(13), while the replacement of Pb^{2+} by up to 15 at.% Sr^{2+} (ionic radius, 1.27 Å) shifts the boundary towards higher zirconate compositions(14, 15).

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*Goldschmidt radii.

The replacement of 1.7 at.% of the Pb^{2+} by Ca^{2+} (ionic radius, 1.06 Å) also appears, from the data presented in Tables 4 and 5, to shift the boundary towards higher zirconate concentrations, since the dielectric constants (K and K_{33}^{T}) decrease for the tetragonal material and increase for the rhombohedral material on the replacement of Pb^{2+} by Ca^{2+}. Results reported by Kulcsar(15) for the substitution of Ca are also consistent with this postulated shift in the tetragonal/ rhombohedral boundary, since it was shown that the substitution of 5 and 8 at.% of Ca for Pb in $Pb(Zr_{0.53}T_{0.47})O_3$ appeared to change this material from rhombohedral($K/K_{33}^{T} > 1$) to tetragonal ($K/K_{33}^{T} < 1$). It appears, moreover, that the smaller Ca^{2+} ion has a more marked effect in producing this boundary shift than does the Sr^{2+} ion. Further investigation of the effects of Ca^{2+} substitution might be of interest in order to confirm the existence of the shift and its effects on the electromechanical properties of the lead zirconate-titanate ceramics. The substitution of Ca for Pb also appears to increase the mechanical quality factor, Q_m, and to decrease the high-field dissipation factor (tan δ) and the change of capacitance with field (ΔC), for both tetragonal and rhombohedral materials. These effects are due, in part at least, to the shift in the tetragonal/ rhombohedral boundary to higher zirconate compositions, since Q_m increases and tan δ and ΔC decrease in passing from the rhombohedral to the tetragonal compositions in unmodified lead zirconate-titanate(2).

(2) Transition-Metal Oxides (NiO, Cr_2O_3, CoO)

Nickel oxide, Cr_2O_3, CoO and Fe_2O_3 have been classified as "hardeners" by Thomann with regard to their effects on lead zirconate-titanate ceramics(16). The characteristic effects attributed to "hardener" additions include lowering the dielectric constant and dielectric loss and increasing the mechanical quality factor and the coercive field. The results shown in Tables 4 and 5 indicate that, for NiO and Cr_2O_3 additions at the 0.5 wt % level, there is a decrease in dielectric constant (both K and K_{33}^{T}) and in high-field dissipation factor and, also, an increase in mechanical quality factor. In two cases (the effect of NiO on the tan δ in the tetragonal material, and of

NiO on K_{33}^{T} in the rhombohedral), the changes, however, were not large enough to be considered significant on the basis of the present results. On the other hand, increases in low-field dissipation factors were observed for the tetragonal material on the addition of NiO and Cr_2O_3. The presence of Cr_2O_3 appeared to increase the frequency constant (resonance frequency x disk diameter).

The samples with added NiO and Cr_2O_3 had densities comparable to those of the control samples, but smaller grain sizes. The smaller grain size would tend to raise the unpoled dielectric constant and to lower the mechanical quality factor, effects contrary to those observed. Thus the changes can be attributed to the additives themselves rather than to differences in microstructures. The classification of NiO and Cr_2O_3 as "hardener" additions is supported by most of the results of the present investigation, the behaviour of the low-field dissipation factor being an exception.

The effect of CoO is anomalous, since this additive appeared to decrease the coupling factor and mechanical quality factor. Also, the decrease in dielectric constant was considerably greater than that obtained with any of the other additives. These effects may be associated with the presence of the intergranular second phase that appeared to have been molten at the sintering temperature. Furthermore, when CoO was added to the tetragonal material, it was found that the dielectric constant after poling (K_{33}^{T}) was less than the dielectric constant before poling (K). This behaviour is generally typical of a rhombohedral material, and, indeed, powder X-ray diffraction results indicated that such a sample with added CoO had a rhombohedral structure rather than a tetragonal one. It is possible that the composition of the solid phase at the sintering temperature may have been changed by solution in the molten phase. It was also observed that the electrical conductivity increased greatly with the CoO addition. Possibly this may be due to the formation of some trivalent cobalt, resulting in increased conductivity due to electrons hopping between divalent and trivalent cobalt ion sites.

(3) Other Additions (La_2O_3, Bi_2O_3, Ta_2O_5, Nb_2O_5)

The weight changes observed during sintering indicate that La and Bi substitute for Pb in the perovskite lattice, while Ta and Nb appear to substitute on the Ti, Zr sites. Such substitutions have generally been assumed on the basis of a comparison of ionic radii(16, 17). As a result of these substitutions, a lattice site apparently becomes occupied by an ion with a valency one greater than that of the ion that would normally occupy the site. It has been suggested that Pb vacancies are also formed, for example by a reaction that could be represented thus:

$$La_2O_3 + 3Pb(Ti,Zr)O_3 \rightarrow La_2\square(Ti,Zr)_3O_9 + 3PbO\uparrow$$

where $\square$ = a Pb-site vacancy. The presence of such vacancies has been invoked to explain the "softening" effect of these additives on lead zirconate-titanate ceramics(16, 17). The characteristics of the "softening" effect are an increase in dielectric constant and in dielectric loss and a decrease in mechanical quality factor. These characteristic changes, however, are not uniformly observed in the data of Tables 4 and 5. The presence of lead-site vacancies may increase diffusion rates in the solid and so contribute to the rapid grain growth observed in materials with these additives.

Alternatives to the above mechanism of substitution are possible. The example given above requires that 3 moles of PbO be displaced by each mole of La_2O_3, but the results in Table 2, although not conclusive, suggest the displacement of less than 3 moles of PbO for each mole of La_2O_3 added. In the latter case, presumably, fewer Pb vacancies would be formed.

The sintered densities for samples with the additives La_2O_3 Bi_2O_3, Ta_2O_5 and Nb_2O_5 are all low; on the other hand, the grain sizes are larger than those of the control samples. As a result, low dielectric constants might be expected. In spite of this, the values of the dielectric constant before poling (K) increased on the addition of Bi_2O_3 to the tetragonal material, and of La_2O_3 to the rhombohedral material, as would be expected for "softener" additives; but, for all other additions, the values of K decreased or showed no significant change. It would require further investigation to determine whether the decreases in dielectric constant (K) were due solely to the changes in density and microstructure. The value of the poled dielectric constant K_{33}^{T} increased only on the addition of Nb_2O_5 to the tetragonal material. Since this increase occurred in spite of low density and large grain-size, it probably represents a significant effect.

The mechanical quality factor decreased when the "softener" additions were made to the tetragonal material, but the addition of La_2O_3 to the rhombohedral material appeared to increase the mechanical quality factor, contrary to expectations. The high-field dissipation factor increased with doping, as expected, except for those cases where the changes were below the level considered significant. It is evident, therefore, that many exceptions to the expected effects of "softening" additions were observed. Some of these exceptions may have been due, at least in part, to low densities and perhaps to large grain-size. Another factor may have been an inhomogeneous distribution of the additive in the ceramic. Kulcsar(18) has reported increases in dielectric constant and dissipation factor on the addition of Nb_2O_5, Ta_2O_5, and La_2O_3 to $Pb(Zr_{0.54}Ti_{0.46})O_3$, as expected for "softening" modifiers. Haertling(19) has reported that the effects of Bi_2O_3 on lead zirconate-titanate ceramics are comparable to those of Nb_2O_5.

The manner in which these additions were made may have had an effect on the densities and grain sizes of the ceramics. If the additives had been homogeneously mixed into the starting material, for example by co-precipitation, densification might have been favoured over grain growth.

(4) Summary of Effects of Additives on Properties of Interest

The poled dielectric constant (K_{33}^{T}) increased when Nb_2O_5 was added to the tetragonal material and when CaO was added to the rhombohedral material. The latter effect was probably the result of a shift in the zirconate/titanate ratio at which the rhombohedral/tetragonal boundary occurs. The effect of the Nb_2O_5, however, was a specific effect of the additive.

The only significant increase in k_p was observed on the substitution of Ca for Pb in the rhombohedral material. This effect, also, was probably due to a shift in the rhombohedral/tetragonal boundary. The high-field dissipation factor and the change in capacitance with field consistently decreased, for both tetragonal and rhombohedral materials, on the addition of CaO and Cr_2O_3. The mechanical quality factor increased consistently on the addition of CaO, NiO, and Cr_2O_3.

ACKNOWLEDGEMENTS

The authors wish to thank Mr. V. M. McNamara, Extraction Metallurgy Division, for providing the co-precipitated powders used in this investigation; the members of the Preparation and Properties of Materials Section, Mineral Processing Division, for lapping and electroding the specimens; Mr. A. J. Hanson for assistance with the electrical testing, and Mr. R. L. Grenon for assistance with the ceramic fabrication.

This investigation forms part of a study of electronic ceramics under the general direction of Mr. I. F. Wright, whose encouragement and helpful discussions are gratefully acknowledged. The investigation was conducted under a Defence Research Board Contract, Project No. ECRDC C-73.

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APPENDIX

ELECTRONIC CERAMICS

ECRDC RESEARCH PROJECT C-73

Identification of Mines Branch Personnel
Advisory Committee

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

Operational

V. M. McNamara EMD	Pilot-plant ceramic powder preparation
J. C. Ingles EMD	Control analyses
Dr. A. H. Webster MSD	Sintering and structural studies
V. A. McCourt MPD	Lapidary and electroding
Ian F. Wright MPD	Ceramic engineering
T. B. Weston MPD	Electronic test methods and component evaluation
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
Dr. Sutarno	Ferrite program

*MPD - Mineral Processing Division
EMD - Extraction Metallurgy Division
MSD - Mineral Sciences Division

Ian F. Wright,
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