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DIFFERENTIAL THERMAL ANALYSIS OF SYNTHETIC INDIUM SULPHIDES PREPARED BY THE NEW BRUNSWICK RESEARCH AND PRODUCTIVITY COUNCIL

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EXTRACTION METALLURGY DIVISION

Mines Branch Investigation Report IR 69-64

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SUMMARY

Differential thermal analysis experiments were done on samples of three indium sulphides submitted by the New Brunwick Research and Productivity Council. The results from the sample containing free sulphur could not be resolved, but the results on the remaining two samples correlated the temperatures and compositions at which phase changes occur when the samples are heated. In_2S_3 is the most stable indium sulphide and InS appears to be the least stable. The stability of In_5S_6 is intermediate between that of In_2S_3 and InS. There are indications that In_6S_7 may exist, but its presence could not be confirmed.

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INTRODUCTION

In a telephone conversation on June 3, 1969, between Dr. D. Abbott of the New Brunswick Research and Productivity Council, and Dr. T.R. Ingraham of the Mines Branch, Dr. Abbott discussed one of the Council's research programs on the sulphides of indium. He indicated that the council was synthesizing a series of sulphides and that they wished to relate their thermal behaviour to composition.

As part of the program, they hoped to make an examination of the sulphides by differential thermal analysis. Prior to the delivery of a recently purchased DTA unit, Dr. Abbott requested that we make a preliminary survey on some of their specimens and that one of his staff be permitted to observe and participate in the experiments as part of a training procedure.

The proposal was submitted to Dr. K.W. Downes, Chief, Extraction Metallurgy Division, and with his concurrence, Mr. G. Ansell of the New Brunswick Productivity Council was present when the initial experimental work was done on June 9th and 10th.

Mr. Ansell obtained copies of the original experimental records. After his departure, samples were submitted for X-ray diffraction analysis. This report includes those results and an interpretation of the thermograms.

EXPERIMENTAL

Samples

Three samples of synthetic indium sulphide were submitted for study. The first was about 25 grams of a brownish coloured powder labelled In_2S_3. The second was about 10 grams of a maroon coloured material labelled InS. The third was about 10 grams of a black coloured material labelled In_6S_7. The materials were submitted for X-ray diffraction identification. The results are shown in Table I.

TABLE I

I D E N T I F I C A T I O N O F S A M P L E S *

Sample	R.P.C. Label	Composition	Reference
1 (brown)	In_2S_3	In_2S_3	ASTM No. 5-0729β 5-0731α
2 (maroon)	InS	InS	ASTM No. 5-0722
3 (black)	In_6S_7	In_5S_6	ASTM No. 5-0429

* From Internal Report EMT 69-9, by P. Bellanger, Mineralogy Section, Extraction Metallurgy Division.

The X-ray identification indicates that Sample 3 may be In_5S_6 rather than In_6S_7 as suggested by the Research and Productivity Council. The identification could not be unequivocally established because of the complexity of the patterns.

Apparatus and Procedure

Small silica cups were used to hold the samples. The sensing thermocouples were placed in wells at the base of the cups. The cups and thermocouples were contained in a closed boron nitride DTA cell that had been constructed to fit a Robert L. Stone Company Differential Thermal Analysis apparatus. The cell was flushed with dry argon during a run. The sample temperature and the differential temperature were recorded on a Moseley strip chart recorder. Sulphide samples weighing about one-quarter gram produced peak heights equivalent to about 20 microvolts. A chart speed of 0.1 inch/min was used. The samples were heated at a rate of 5°C/min.

At the end of a run, the samples were cooled to 500°C in an argon stream, and small specimens were removed for X-ray diffraction analysis.

RESULTS

Sample 1 (In_2S_3)

A satisfactory DTA pattern could not be obtained for the sample as it was submitted. During a DTA run the sample liberated sulphur continuously from 100°C to the end of the run at 883°C. Attempts to remove the excess sulphur by vacuum distillation at 500°C were not successful.

Sample 2 (InS)

The DTA pattern for the InS sample is shown in Figure 1. Only the section of the pattern obtained above 600°C is considered in this analysis. The first significant feature is the peak at 666°C. These are two possible explanations for its occurrence. It might be caused by the melting of a trace of the In-S eutectic in the sample or it might be a transition related

to the compound In_2S. In the absence of comparative runs with these materials, the more probable explanation of the peak cannot be suggested.

The principal feature on the pattern is the melting of InS at about 693°C. This recorded temperature is probably a few degrees above the true melting point of the material because of the rapid rate of heating the sample. The temperature suggested for the melting point in the Handbook of Chemistry and Physics is 692°C.

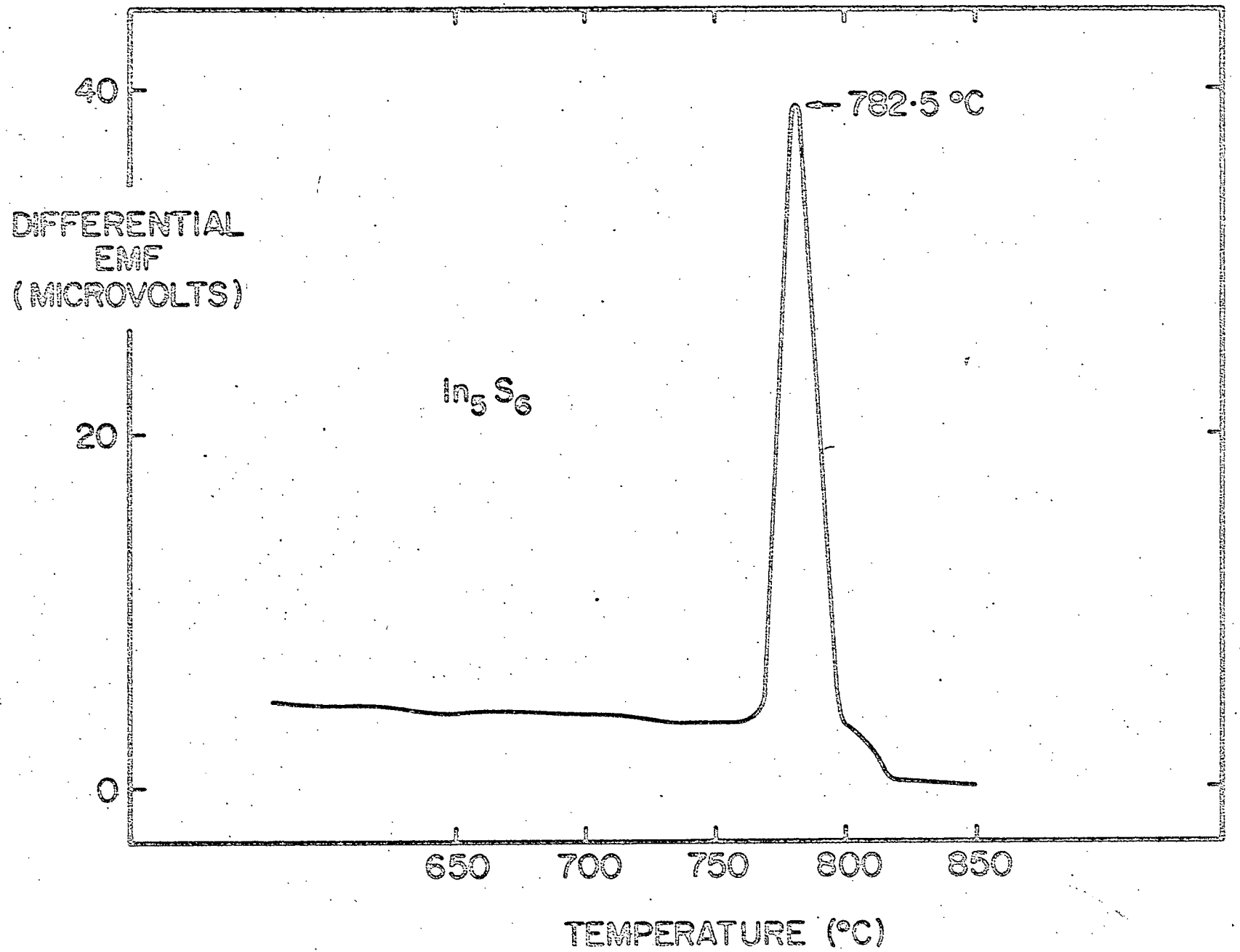
There are two additional secondary features on the pattern: a peak at 759°C and a shoulder at about 782°C. The shoulder at 782°C corresponds to the melting point of In_5S_6 as will be shown in Figure 2. The peak at 759°C cannot be surely identified, but it seems reasonable to suggest that it may be associated with a phase change in a compound having a composition intermediate between In_5S_6 and InS e.g. In_6S_7. The residue at the end of the run was a mixture of In_2S_3 and In_5S_6.

Sample 3 (In_5S_6)

The DTA pattern for the In_5S_6 sample is shown in Figure 2. The only significant feature is the melting of In_5S_6 at 782.5°C. The product recovered at the end of the run was a mixture of In_5S_6 and In_2S_3.

CONCLUSIONS

Differential thermal analysis of samples of InS and In_5S_6 show clearly defined phase changes that may be correlated with the established melting points of In_5S_6 (In_6S_7) and InS. There are two additional phase changes at 660°C and 759°C that have not been positively identified. The former may be associated with either a eutectic or with the compound In_2S, and the latter may indicate the presence of an unidentified sulphide phase.


40
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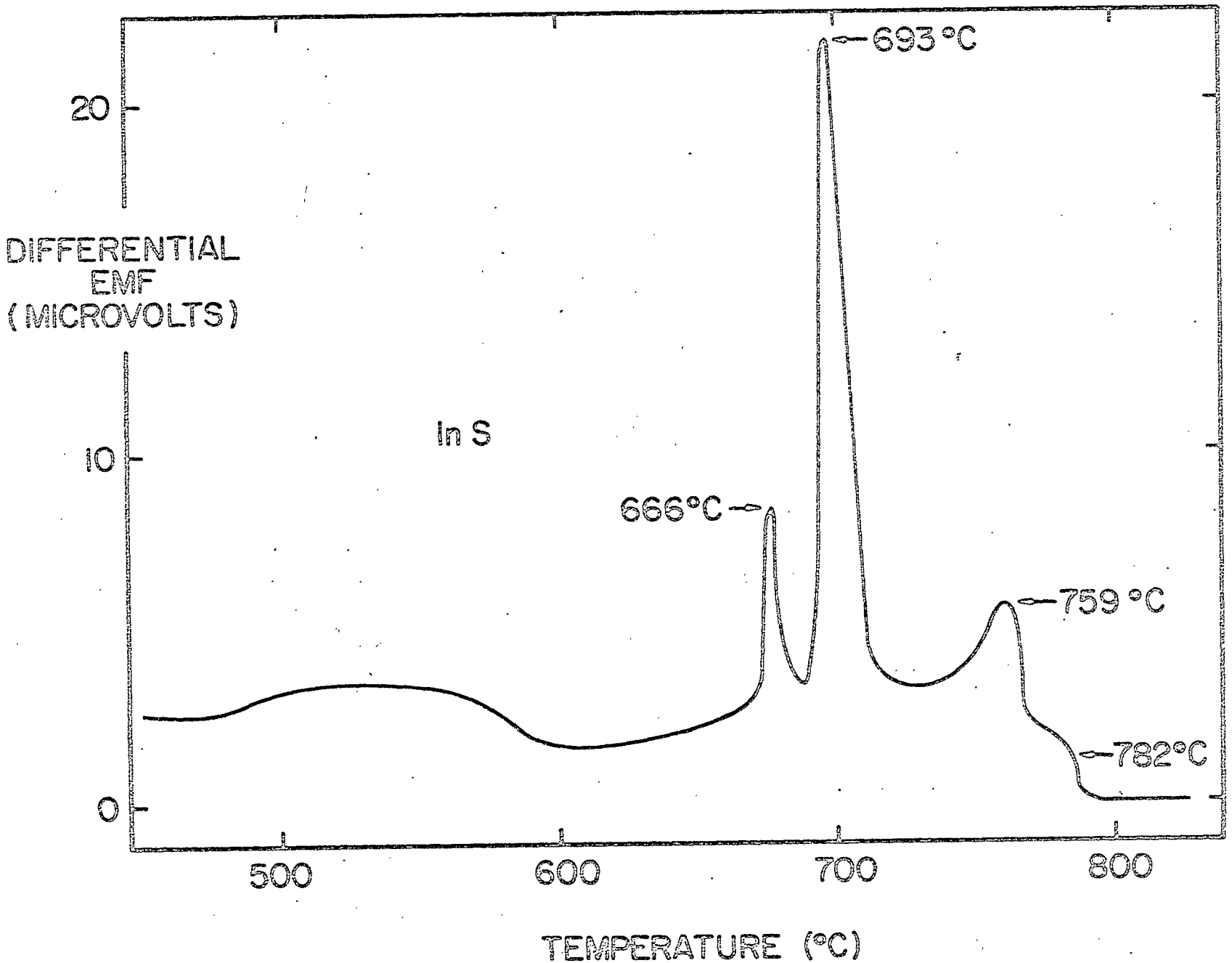
782·5 °C
In_5S_6
650
700
750
800
850
TEMPERATURE (°C)


693°C
20
DIFFERENTIAL
EMF
(MICROVOLTS)
In S
10
666°C
759°C
782°C
0
500
600
700
800
TEMPERATURE (°C)