

THE DIFFERENTIAL THERMAL ANALYSIS BEHAVIOR OF LEAD ZIRCONATE TITANATE MATERIALS

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ABSTRACT

Differential thermal analysis has been used to examine the reactions involved in the formation of lead zirconate titanate and related materials. The reaction of PbO and TiO₂ produced an exothermic peak near 600°C, while mixtures of PbO and ZrO₂ gave endothermic peaks at 760°C. Lead titanate and lead zirconate mixtures showed no evidence of reaction below 900°C. Evidence is presented which suggests that PbO and PbTiO₃ react in the vicinity of 750°C. For ternary mixtures of PbO, TiO₂, and ZrO₂, which lead to the formation of solid solutions of lead zirconate titanate, the thermograms indicate a complicated behavior between 600-800°C, depending on the ratios of the reactant materials. The results suggest that the calcination reaction to form lead zirconate titanate is a more complex process than has been recognized. Data on the various phase transitions for the lead zirconate titanate materials are also presented.

INTRODUCTION

Of considerable importance to electronics technology has been the development of ferroelectric and piezoelectric devices made from various mixtures of metal oxides with titania and zirconia¹. For example, certain solid solutions of lead zirconate titanate can be made into ceramic devices with very desirable piezoelectric characteristics, having electromechanical coupling coefficients much larger than other piezoelectric materials². However, the basic electrical and mechanical properties of lead zirconate titanate (PZT) ceramics are strongly influenced by the chemical composition and thermal treatment of the materials used to form the ceramic bodies³. Of particular importance in the process is the calcination step, in which the basic reactions between the constituent metal oxides (PbO, TiO₂, and ZrO₂) take place. It has been found that certain lots of metal oxide mixtures produce rather different electro-mechanical characteristics from other lots which have nominally the same composition³. Thus, to better understand the factors affecting the variability of the final products, a systematic study of the calcination reaction seemed warranted.

Reaction schemes and phase diagrams for the PZT system have been reported, largely on the basis of X-ray diffraction methods⁴⁻⁹. These studies usually have centered on the final sintered ceramic materials. Investigations of the calcination process by wet chemical and X-ray analysis of the products have also appeared^{10,11}. We felt that differential thermal analysis (DTA) could provide a convenient analytical method for the examination of the calcination process, since the high temperature reactions could be directly studied. In addition, some of the reactant and product phases might have thermal activity that would provide convenient identification of the substances involved. This report is a summary of a systematic study using DTA of the materials and reactions involved in the formation of calcines of lead zirconate titanate and related compounds.

EXPERIMENTAL

The DTA curves were obtained using a DuPont Model 990 system. The cells used with the system were the standard DSC cell, the 850°C cell, and the high temperature (1600°C) cell, with air flowing at about 50 ml min⁻¹ through the cells. The majority of experiments were done with the DSC and 850°C cells, using Al pans in the DSC runs, and Pt-lined quartz tubes for the higher temperature scans.

The PbO used in the studies was fumed litharge obtained from TAM Division of National Lead Company, Buffalo, N.Y. Electronic grade ZrO₂ and TG grade TiO₂ were also obtained from TAM. Samples for DTA experiments were prepared by direct weighing and mixing with a procelain mortar and pestle. Ten to 30 mg samples were normally employed for the DTA experiments. Several quenching experiments were performed in which mixed samples were placed in a Pt-boat in a high temperature furnace with a quiescent air atmosphere.

X-ray powder diffraction patterns were obtained for a number of samples. The patterns were taken either directly on the residues from DTA scans, or on samples prepared in the furnace.

RESULTS

The data obtained for the various combinations of PZT components can be conveniently arranged in categories of (a) single compounds, (b) binary mixtures, and (c) ternary mixtures. These results are summarized below:

Single components

Curves were obtained for the three oxides, PbO, TiO₂, and ZrO₂, in the range of from room temperature to about 1200°C. Only PbO showed measureable thermal activity in this range. There is the melting endotherm at about 880°C, but in addition there are two peaks which occur in the vicinity of 250-400°C. Usually, these peaks appear as two endotherms, with peak maxima near 255 and 380°C, but the shapes of the peaks vary somewhat depending on the sample and its history. (See Figs. 2 and 3

for typical peaks.) The processes responsible for these peaks are not completely clear. Oxidation of PbO has been reported to occur at slightly higher temperatures¹². However, the same thermograms are obtained in N₂ atmosphere as in air. If one repeats the DTA experiment on a once-cycled sample of PbO, there are no peaks. These data seem to indicate that the peaks are due to a metastable phase or compound which undergoes change in the 250–400°C range. Interestingly, the X-ray pattern before and after heating through the transitions was the same, the tetragonal pattern of yellow PbO. It would seem that some work is required to clarify the nature of these transitions.

Figure 1 shows the curves for lead titanate and lead zirconate, which were also of interest in this study. Both compounds show the expected Curie transitions, sharp endotherms at 230 and 485°C, respectively for PbZrO₃ and PbTiO₃. Lead titanate, in addition, shows an erratic endotherm at about 1250°C, which from the phase diagram² of PbTiO₃, should be the melting transition.

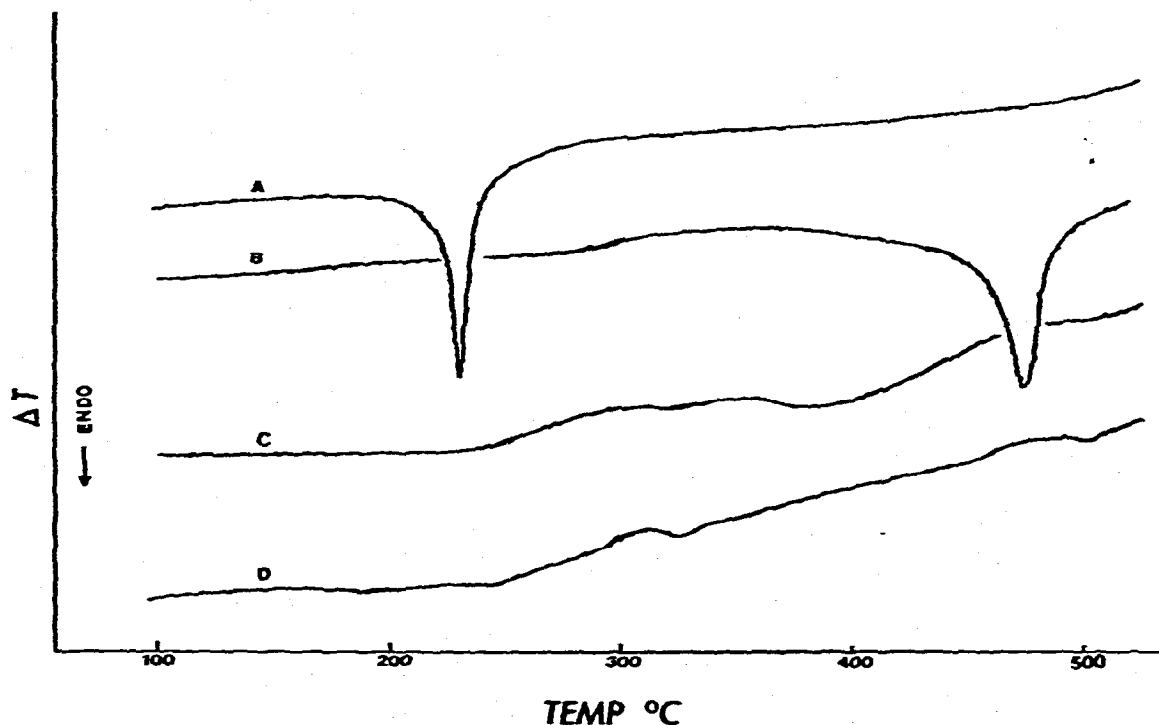


Fig. 1. Curves of PbZrO₃ (A), PbTiO₃ (B), Pb(Ti_{0.5}, Zr_{0.5})O₃ (C), and Pb(Ti_{0.8}, Zr_{0.2})O₃ (D) in temperature range of 100 to 500°C.

According to the phase diagram of the PbO–TiO₂–ZrO₂ system⁷, solid solutions of Pb(Ti_x, Zr_{1-x})O₃ form continuously from pure PbTiO₃ to PbZrO₃. These intermediate solid solutions have Curie transitions which occur in the range of 230 to 485°C. We would expect then that endotherms would be observed for the Pb(Ti_x, Zr_{1-x})O₃ zirconate titanates in that temperature range. Figure 1 shows

several curves obtained for the solid solutions, compared with those of PbTiO_3 and PbZrO_3 . No very clear endothermic transitions are found. There are discontinuities in the heating curves (resembling second order transitions), but the actual transition temperatures and enthalpic effect are difficult to discern. It appears that either the transitions occur over very broad ranges of temperature, thus not giving sharp peaks, or the mechanism of the Curie transitions in the solid solutions is quite different from that of the pure titanate or zirconate. The formation of crystals of the solid solution phases has been found to be difficult⁷, so it may be that we are dealing here with rather small crystallites of variable composition. This could explain the rather non-descript thermal behavior of the solid solutions. Table 1 summarizes the data for the single component materials studied.

TABLE 1
DTA TRANSITIONS OF SOME PZT MATERIALS

<i>Compound</i>	<i>Observed transitions</i>	<i>Explanation</i>
PbO	250°C endo	None
	350–400°C endo	None
	880°C endo	Melting
PbTiO ₃	485°C endo	Curie temp.
	1250°C endo	Melting
PbZrO ₃	230°C endo	Curie temp.
	1100–1200°C endo	Decomp?
Pb(Ti _x , Zr _{1-x})O ₃ HH	230–480°C*	Curie temps?

* These transitions are broad and not clearly defined, but should be due to Curie transitions.

Binary mixtures

In order to better understand the reactions which occur in the ternary mixtures of PZT oxides, it is useful to have data on some of the possible binary mixtures. This section summarizes DTA studies on several of the two-component mixtures.

Curves were obtained for 1:1 mixtures of PbO and TiO₂. Three areas of thermal activity were found as shown in Fig. 2. The PbO peaks in the range 250–400°C were present, as expected. In addition, an exothermic peak with its maximum near 600°C appeared, and finally an erratic endotherm at 1250°C was found. A re-run of the same 1:1 sample up to 1000°C showed only one endothermic peak at 485°C, the Curie temperature of PbTiO₃. The curve can thus be interpreted that the solid state reaction occurs between PbO and TiO₂ at 500–650°C, with peak maximum around 600°C; and that the endotherm at 1250°C is the melting temperature of the PbTiO₃ formed in the reaction.

Figure 2 also shows the curve for a 1:1 mixture of PbO and ZrO₂. In addition to the PbO peaks there is an endotherm which peaks at 760°C. No other thermal activity was seen except a possible small broad endotherm above 1200°C. (It has been reported that PbZrO₃ decomposes near this temperature range.)⁴ Again, as with the

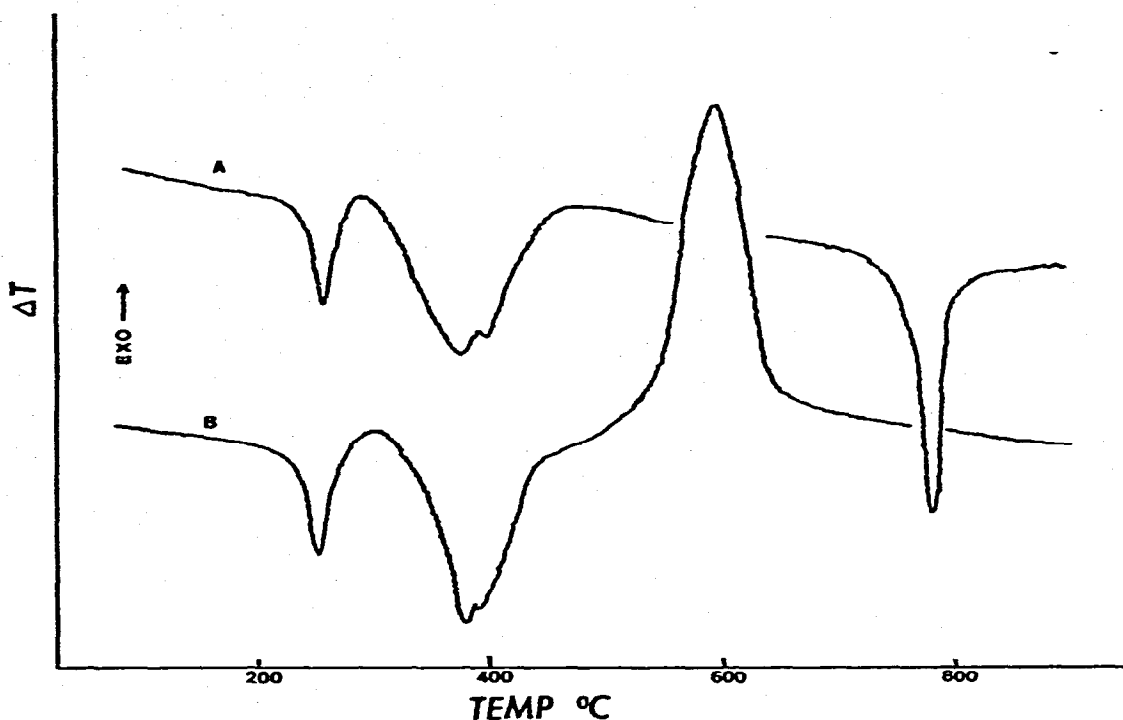


Fig. 2. Curves of binary mixtures of $1\text{PbO}+1\text{ZrO}_2$ (A), and $1\text{PbO}+1\text{TiO}_2$ (B), in temperature range 200 to 850°C .

PbTiO_3 reaction, a re-run of the DTA sample gives a single peak at 230°C , the Curie temperature for PbZrO_3 . It seems then that the endotherm at 760°C is the reaction peak for $\text{PbO}+\text{ZrO}_2$. In a separate experiment, a 1:1 mixture of PbO and ZrO_2 was placed in a Pt crucible at 650°C for 16 h, and no discernable PbZrO_3 was found in the residue. However, a $\frac{1}{2}$ -h heating in the furnace at 770°C produced virtually complete conversion to PbZrO_3 , as measured from the area of the Curie transition peak at 230°C . It is interesting and a bit puzzling that the PbO reaction with TiO_2 is exothermic, while for $\text{PbO}+\text{ZrO}_2$ the heat effect is endothermic.

It was of interest in the course of this study to determine if PbTiO_3 and PbZrO_3 react in the temperature range of calcination. A 1:1 mixture of the two showed no thermal activity other than the Curie transitions for the two components up to 850°C . A re-scan was essentially identical. However, a higher temperature scan to above 1100°C indicated a small, broad exotherm near 1000°C . The product of this high temperature scan showed neither Curie transition of the components, but rather gave the non-descript behavior typical of the solid solutions of PZT. It appears that below 850°C reaction between PbTiO_3 and PbZrO_3 is very slow if it occurs at all, but near 1000°C the reaction does proceed.

Another binary mixture was examined ($1\text{PbTiO}_3+0.5\text{ZrO}_2$), which was found to be of interest in the examination of mechanistic details of calcination. This mixture was examined to over 1100°C and no peaks other than the Curie transition of PbTiO_3 ,

were observed. Re-scans of the residues of these runs gave curves identical to the original. We are led to conclude that no reaction occurs between ZrO_2 and $PbTiO_3$ in the range of temperatures studied.

Two other binary mixtures were studied. The curve of $2PbO + 1TiO_2$ showed the expected transitions for PbO , and the reaction of $PbO + TiO_2$ (the $600^\circ C$ exotherm). But, in addition, two small endotherms appeared at 740 and $775^\circ C$ (see Fig. 3). The particular ratio of $2PbO : 1TiO_2$ was chosen because of the possibility that a Pb_2TiO_4 phase might form under these conditions. The existence of this phase has

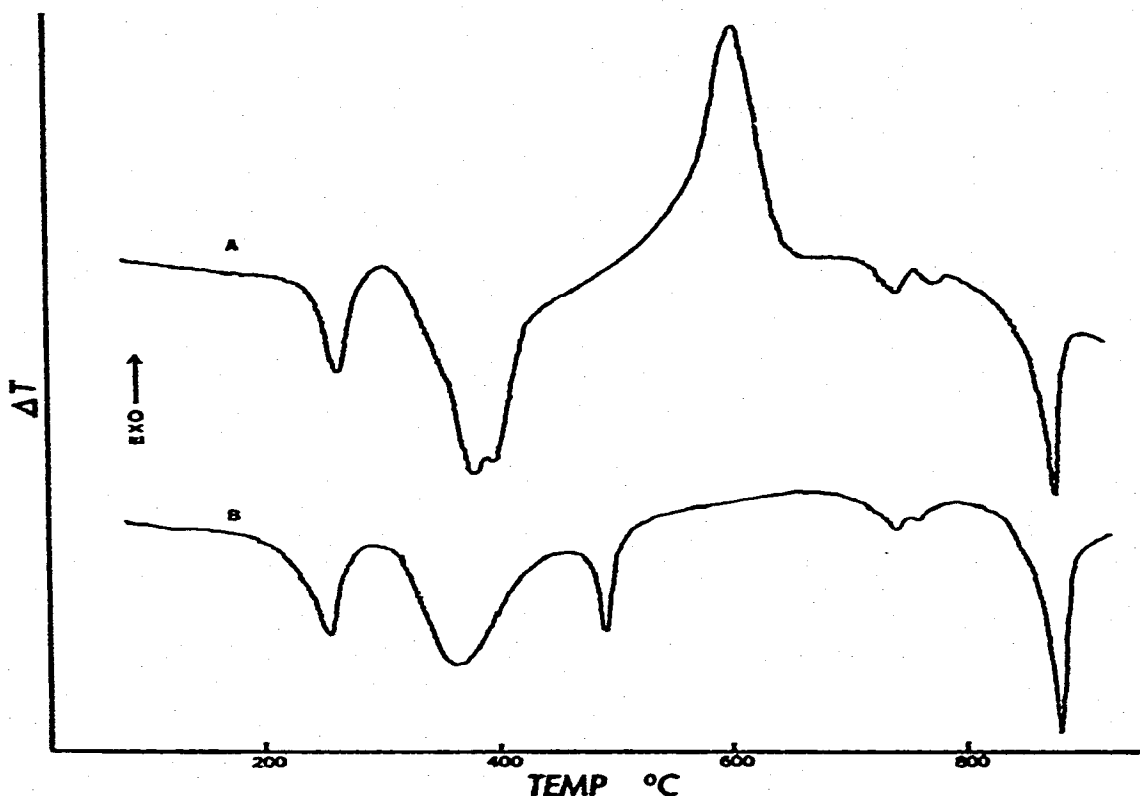


Fig. 3. Curves of binary mixtures of $1PbO + 0.5TiO_2$ (A), and $1PbTiO_3 + 1PbO$ (B), in temperature range 200 to $900^\circ C$.

been controversial, but has been reported in several studies^{13,14}. The two small endotherms are not seen in other mixtures of oxide reactants, but are seen in the curve of a 1:1 mixture of $PbTiO_3$ and PbO (see Fig. 3). A re-scan of the residues from either the $(2PbO + 1TiO_2)$ or $(PbTiO_3 + PbO)$ experiments gives the Curie transition peak of $PbTiO_3$, and the melting endotherm of PbO . However, the X-ray powder pattern of the residues shows $PbTiO_3$ and some other phase which is not PbO . Combining the X-ray evidence with the fact that the additional endotherms occur in the thermograms of these mixtures suggests that another compound is forming. But,

at this point it is not clear that Pb_2TiO_4 is the compound, and to what extent the additional compound actually forms.

Table 2 summarizes the data for the binary mixtures, and we see that the DTA behavior clearly indicates that reactions occur between some PZT components, and further that the positions of the peaks give information on the ranges of temperature

TABLE 2
DTA TRANSITIONS OF SOME PZT BINARY REACTION MIXTURES

<i>Mixture</i>	<i>Observed transitions</i>		<i>Explanation</i>
1 PbO + 1 TiO ₂	255°C	endo	PbO peaks
	400°C	endo	PbO peaks
	600°C	exo	Reaction to PbTiO ₃
	1250°C	endo	Melting of PbTiO ₃
1 PbO + 1 ZrO ₂	255°C	endo	PbO peaks
	400°C	endo	PbO peaks
	760°C	endo	Reaction to PbZrO ₃
1 PbTiO ₃ + 1 PbZrO ₃	230°C	endo	PbZrO ₃ Curie pt.
	485°C	endo	PbTiO ₃ Curie pt.
	1000°C	exo	Solid solution form
1 PbTiO ₃ + 0.5 ZrO ₂	485°C	endo	PbTiO ₃ Curie pt.
1 PbO + 0.5 TiO ₂	255°C	endo	PbO peaks
	400°C	endo	PbO peaks
	600°C	exo	PbTiO ₃ formation
	740°C	endo	?
	775°C	endo	?
1 PbTiO ₃ + 1 PbO	255°C	endo	PbO peaks
	400°C	endo	PbO peaks
	740–780°C	endo	?

to expect reactions to occur readily. It should be emphasized that the reaction endotherms and exotherms are obtained under dynamic conditions (normally scan rates of about $20^\circ\text{C min}^{-1}$), and thus the peak maxima depend somewhat on the scan rate. It was found, for example, that the reaction exotherm peak maximum for $\text{PbO} + \text{TiO}_2$ varied from 580 to 640°C for scan rates of 5 and $50^\circ\text{C min}^{-1}$, respectively. Thus, reactions carried out under equilibrium conditions may occur readily at temperatures somewhat below the peak maxima of the DTA scan. We have found for the PZT cases, however, that reactions carried out in a furnace at much lower temperatures than 50°C below the DTA peak maximum using the $20^\circ\text{C min}^{-1}$ scan rate do not occur very rapidly if at all. So, the peaks do serve as a useful guide to expected equilibrium reaction conditions.

Ternary mixtures

Under normal conditions the preparation of piezoelectric ceramics of PZT is accomplished by firing a calcined mixture of the oxides. The calcines are usually

prepared by heating the proper stoichiometric mixture of oxides at 800–900°C, and the solid solution of $\text{Pb}(\text{Ti}_x, \text{Zr}_{1-x})\text{O}_3$ is formed from the calcination reaction. It is of interest then to examine the DTA behavior of mixtures of the three oxides. Figure 4 shows the curves of mixtures of the composition, $1\text{PbO} + x\text{TiO}_2 + (1-x)\text{ZrO}_2$, with x varying between 0 and 1. The typical PbO peaks between 250 and 400°C are not shown in the diagrams since they are common to all of the curves. Starting with $x = 0$, we have the reaction peak for PbZrO_3 formation at about 760°C.

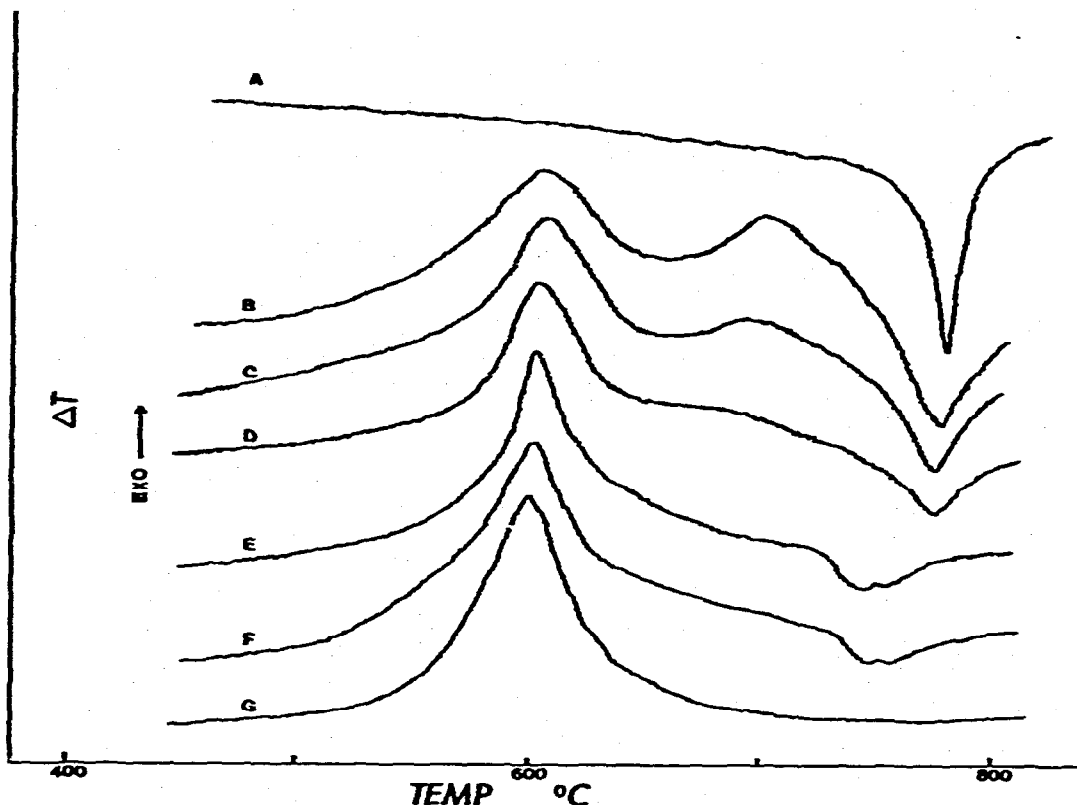


Fig. 4. Curves for ternary mixtures of $1\text{PbO} + x\text{TiO}_2 + (1-x)\text{ZrO}_2$ in temperature range 400 to 850°C. A, $X = 0$; B, $X = 0.2$; C, $X = 0.3$; D, $X = 0.5$; E, $X = 0.7$; F, $X = 0.8$; G, $X = 1$.

With the introduction of any titania, the curve in the 500–800°C range changes rather drastically. There is an exotherm at around 600°C, which is logical to associate with the formation of PbTiO_3 . Interestingly, there is also an exotherm at about 700°C in the composition low in titania. This peak seems almost completely gone at $x = 0.5$. In all of the curves studied, except the one for $1\text{PbO} + 1\text{TiO}_2 + (0)\text{ZrO}_2$, there is an endotherm in the region near 750°C. Re-scans of all of the intermediate mixtures shows that solid solutions have formed.

The explanation of these thermal events is a bit difficult. The formation of PbTiO_3 from the binary mixture of the oxides was found to be rapid and complete

by 650°C. So, if we assume this is so in the ternary mixture, by 650°C the PbO and TiO₂ will have reacted and any subsequent reaction between the remaining components will be with PbTiO₃ to form the solid solution. It was also found, however, in the study of the binary mixtures that PbTiO₃ does not react with either PbZrO₃ or ZrO₂ below 800°C, at least in the stoichiometric compositions. There appears to be either something unique about the ternary mixtures, or there are other intermediates formed which we have not characterized.

The intriguing possibility that an intermediate Pb₂TiO₄ phase forms which then reacts with ZrO₂ does not seem possible, since in the composition range where Pb₂TiO₄ would be most likely to form, $x = 0.2-0.5$, an exotherm is observed in the ternary mixture. This seems at odds with the observation that when mixtures of 2PbO + TiO₂ were reacted (see above), small endothermic peaks were found. The other interesting problem is the peak at around 750°C, which could be associated with the formation of PbZrO₃. Since PbTiO₃ and PbZrO₃ were found not to react to form a solid solution in this temperature range, the endotherm near 750°C must be due to another process. Thus, the combination of the exotherm at 700°C and the endotherm at 750°C point to a rather complex situation in which possible chemical intermediates are forming whose actual compositions change, depending on the value of x . Matsuo and Sasaki¹⁵ have suggested that the calcination of PZT oxides in the vicinity of 700°C yields a solid solution of different composition than when the temperature is 800°C. Although no explanation is given for this difference, his results are consistent with the possibility of a changing mechanism in the formation of the solid solution. Unfortunately, the Matsuo and Sasaki¹¹ study only examined one composition of PZT oxide mixtures. It would appear that more work is required to clarify the reaction sequence in the vicinity of 700–800°C.

It should be mentioned in concluding this section that several curves were obtained for ternary mixtures that were not stoichiometric with regard to the formation of solid solutions of the compositions Pb(Ti _{x} , Zr _{$1-x$})O₃. These curves gave the expected results that solid solutions formed along with phases which happen to be in excess. In the case where PbO was limiting, for example with a 1PbO:3TiO₂:3ZrO₂ mixture, only PbTiO₃ was found, as might be expected from the above observations.

CONCLUSIONS

In concluding this report, several comments should be made about the study of the calcination of PZT materials using DTA. The elucidation of some of the mechanistic details, i.e., that PbTiO₃ forms at 600°C when the three oxides are heated together, is consistent with other studies of the sequence of reactions that occur in calcination^{1,10,15}. But, in addition, the thermal behavior in the 700–800°C region seems to indicate a more complex situation than has previously been recognized. The results suggest that in the vicinity of 700–800°C the solid solutions could form by the reaction of PbTiO₃ with PbO and ZrO₂ in a sequence of steps which may be different

depending on the ratio of ZrO_2 to TiO_2 in the mixtures. The observation that the lead oxide-titania reaction is exothermic while the lead oxide-zirconia reaction is endothermic, as revealed in the thermograms, points out that the mechanistic details and thermodynamics of these reactions are rather subtle. Further work is in progress to try to understand some of these problems.

The analytical utility of DTA is clearly demonstrated in this work. The peaks for PbO , $PbTiO_3$, $PbZrO_3$, and the several reaction peaks can serve as both qualitative and quantitative probes for the various reactants of phases present. For example we have obtained curves for commercial calcine preparations of PZT which show the presence of unreacted PbO , and by virtue of the $600^\circ C$ exotherm indicate unreacted TiO_2 in the samples. The detection of a few mole percent of the PZT components should be possible under typical DTA conditions. The scans can be obtained quickly with virtually no sample preparation. DTA characterization could thus be used to meet the problems of raw materials variability, and provide a basis for the adjustment of manufacturing conditions to compensate for the materials variability.

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REFERENCES

- 1 B. Jaffe, W. R. Cook and N. Jaffe, *Piezoelectric Ceramics*, Academic Press, New York, 1971.
- 2 B. Jaffe, R. S. Roth and S. Marzallo, *J. Res. Nat. Bur. Stand.*, 55 (1955) 239.
- 3 G. G. Palmer, *Stable Lead Zirconate Titanate*, G. E. Report (DA-121-520), Sept. 1974.
- 4 T. Skeda, T. Okano and M. Watanabe, *Jap. J. Appl. Phys.*, 1 (1962) 218.
- 5 G. Shirane and A. Takeda, *J. Phys. Soc. Jap.*, 7 (1952) 5.
- 6 G. Shirane, K. Suzuki and A. Takeda, *J. Phys. Soc. Jap.*, 7 (1952) 12.
- 7 S. Fushimi and T. Skeda, *J. Am. Ceram. Soc.*, 50 (1967) 129.
- 8 K. H. Hardtl and H. Rau, *Solid State Commun.*, 7 (1969) 41.
- 9 K. Aukan, *J. Am. Ceram. Soc.*, 51 (1968) 577.
- 10 A. E. Robinson and T. A. Joyce, *J. Br. Ceram. Soc.*, 61 (1962) 85.
- 11 Y. Matsuo and H. Sasaki, *J. Am. Ceram. Soc.*, 48 (1965) 289.
- 12 C. A. Sorreil, *J. Am. Ceram. Soc.*, 56 (1973) 613.
- 13 I. N. Belyaer and A. K. Nesterova, *Zh. Obshch. Khim.*, 22 (1952) 396.
- 14 I. N. Belyaer, *Russ. J. Inorg. Chem.*, 15 (1970) 282.
- 15 Y. Matsuo and H. Sasaki, *J. Am. Ceram. Soc.*, 48 (1965) 289.