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Studies on the formation of lead titanate by solid state reaction from PbO and TiO_2

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Abstract

Reaction between PbO and TiO_2 mixed in the stoichiometric ratio for the preparation of $PbTiO_3$ has been followed using DTA and XRD techniques. Studies reveal that the reaction is initiated at approximately 800 K. Samples heat-treated at 875 K showed the characteristic X-ray pattern for crystalline $PbTiO_3$ and, on the basis of dielectric constant measurements, a Curie transition temperature of 765 K. SEM micrographs also showed a single phase sample with well defined grains. The samples were also characterized by ac resistivity measurements. The DTA curve showed an exothermic heat effect in the temperature range 835–1020 K corresponding to the formation of lead titanate. The Curie transition in the compound so formed could be observed as another exothermic peak at 783 K in the cooling cycle. Simultaneous TG measurements confirmed that both heat effects were unattended by changes in sample weight.

Keywords: DTA; Dielectric constant; Lead titanate; Temperature of formation; X-ray diffraction.

1. Introduction

The stoichiometry of lead titanate is known to be an important factor for ensuring good electrothermal properties [1–3]. Generally, the method adopted for its preparation involves the heating of a mixture of lead oxide and titanium oxide above 1275 K [4], a temperature significantly above the melting point of lead oxide, which usually leads to Pb-deficient $PbTiO_3$ [2]. In order to minimize lead loss and thereby obtain

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stoichiometric lead titanate and its solid solutions with other oxides, different preparative methods are adopted, for example sol–gel and other chemical processing techniques [5–7]. All these techniques are aimed at reducing the temperature of preparation of the compound even though they are more involved and complicated in approach than the solid–solid reaction method. In this context, a systematic study of the reaction between lead oxide and titanium oxide is of interest. As part of this programme, we have undertaken the study of this reaction using X-ray diffraction, thermoanalytical and other related techniques. Our results conclusively prove that lead titanate can be prepared by a conventional solid-state approach at a lower temperature than that reported in literature. The reaction leading to compound formation starts at about 800 K, where the vapour pressure of lead oxide is not significant [8]. Hence, lead titanate prepared at or close to 875 K is less likely to be non-stoichiometric owing to loss of load. The low-temperature-formed $PbTiO_3$ samples were characterized by X-ray diffraction, DTA, SEM, dielectric and electrical resistivity measurements. The results of these investigations are reported in this paper.

2. Experimental

The o xide was prepared by the solid-state reaction of thoroughly ground mixtures of guaranteed reagent (GR) grade powders of PbO and TiO_2 (rutile) taken in the required stoichiometric ratio. The ground mixture was heated in air at temperatures varying from 775–1275 K for different periods as detailed in Table 1. Product formation and completion of the reaction were identified by X-ray diffractometry (XRD) using a Philips PW 1710 diffractometer employing CuK_α radiation.

The thermoanalytical measurements (DTA and TG) were carried out on a Netzsch model STA 409 thermobalance with Pt/Pt–10% Rh thermocouples as temperature sensors. The set-up was suitably modified for automatic data acquisition and process-

Table 1
Heat treatment given to stoichiometric mixtures of PbO and TiO_2

Sample	Temperature in K	Duration in h	Remark
A	–	–	Initial mixture after grinding
B	800	26	$PbTiO_3$ formed, X-ray peaks were not sharp
C	850	7	Similar to B
D	875	2	Well crystallized $PbTiO_3$ X-ray pattern
E	1075	2	Similar to D
F	1275	1.5 cooled to 825 K at 5 K min^{-1} and furnace cooled.	Poorly crystallized
G	F reheated to 875	2	Comparable with D

ing. Specimen holders made from recrystallized alumina were used. Calibration measurements using NIST/ICTAC-certified reference materials (Nos. GM-758 and 760) indicated the temperature accuracy to be within ± 5 K in the temperature range 400 K (transition in potassium nitrate) to 1083 K (transition in barium carbonate). Measurements were made on stoichiometrically mixed and ground powder (100 mg) of PbO and TiO_2 at the heating rates of 5 and 10 K min^{-1} in a static air environment.

For measurements of electrical resistivity and dielectric constant, pellets (12 mm diameter and approximately 2 mm height) were prepared from the stoichiometrically mixed powders of PbO and TiO_2. The mixtures were first heated to 825 K, for 4 h, re-ground and subjected to uniaxial cold compaction followed by sintering in air for 16 h at 875 K (sample H) and 1075 K (sample I), respectively. These samples were found to be very porous and fragile. To improve the hardness, the samples were prepared by adding 0.5% PVA binder to the initially heated mixture, compacting as above and sintering for 16 h at 875 K (sample J) and 1075 K (sample K), respectively. The details of the samples are given in Table 2. In order to ensure good electrical contact, silver paste was applied to both sides of the pellets and cured.

Dielectric constant and electrical resistivity were measured from room temperature to 875 K using a Genrad 1689 LCR meter at a frequency of 100 kHz under stepwise isothermal conditions.

The microstructures of the sintered pellets were examined by scanning electron microscopy (SEM) using a Jeol microscope, model 330 A.

3. Results and discussion

The TG–DTA curves recorded at a heating rate of 10 K min^{-1} for an equimolar mixture of lead oxide and titanium oxide are shown in Fig. 1. The initial mixture showed weight loss accompanied by endothermicity at 575–675 K and hence was heated to 700 K and cooled back to room temperature before subjecting it to TG–DTA measurements. Even after their pretreatment, the samples showed a weight loss of about 0.15% and a broad endothermic peak in the temperature range 375–675 K, presumably because of loss of carbon dioxide and moisture picked up while cooling in the furnace. The TG curve did not show any other significant weight change step. The DTA curve recorded at a heating rate of 10 K min^{-1} showed an exothermic peak in the

Table 2
Sintering conditions employed for the preparation of pellets (sintering time 16 h)

Sample	Binder	Temperature in K	Remark
H	No	875	Porous and fragile
I	No	1075	Similar to H
J	0.5% PVA	875	Density 6.46×10^3 kg m^{-3}
K	0.5% PVA	1075	Density 6.61×10^3 kg m^{-3}

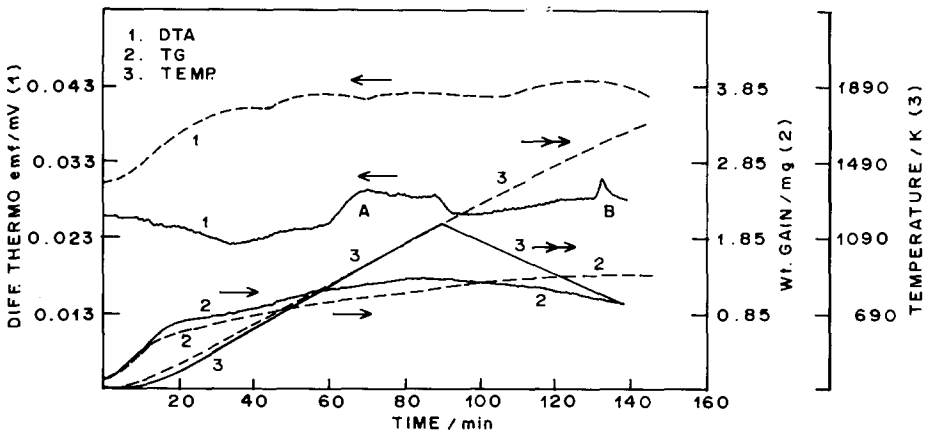

Fig. 1. TG–DTA curves of a stoichiometric mixture of PbO and TiO_2 at a heating rate of 10 K min^{-1}. —— Sample run, - - - - Blank run.

temperature range 848–1020 K (peak A). This peak is shown on an expanded scale in Fig. 2, made possible with the help of a noise filter incorporated in the software used for data processing [9]. A similar measurement carried out at a heating rate of 5 K min^{-1} showed a smaller exothermic DTA peak corresponding to the formation of the compound in the temperature range 833–983 K. The TG curve in the corresponding temperature range showed no weight change indicating that the reaction is either of a solid–liquid or solid–solid type. However, from the phase diagram available in the literature for the system PbO–TiO_2, there is no liquid phase below 1111 K at any composition [10]. The cooling curve indicates an exothermic transition in the temperature range 750–800 K (peak B, Fig. 1) with a peak temperature of 783 K. The well known crystallographic–ferroelectric transition temperature of lead titanate at 763 K [4] is within the temperature range of this DTA peak and lends credibility to the suggestion that lead titanate has already been formed before 1150 K, the maximum

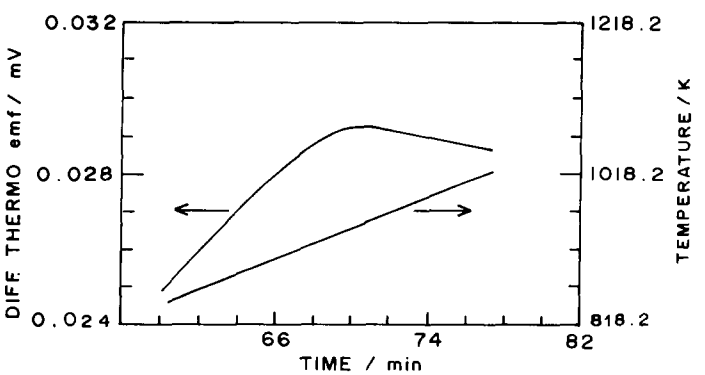

Fig. 2. DTA curve for the formation of lead titanate at a heating rate of 10 K min^{-1}.

temperature attained by the mixture in the TG–DTA studies. The higher value of the Curie temperature observed may be due to the difference in the densities [7]. These facts point to the conclusion that $PbTiO_3$ has been formed according to the reaction

$$PbO(s) + TiO_2(s) \longrightarrow PbTiO_3(s) - \Delta H \quad (1)$$

in the temperature range 850–1025 K where the DTA curve for the oxide mixture showed an exothermic peak in the heating mode.

The results of X-ray diffraction measurements supported the above conclusion that $PbTiO_3$ is formed at approximately 835 K. The X-ray diffraction studies were carried out on equimolar mixtures of PbO and TiO_2 heat-treated in a furnace under the conditions given in Table 1. The XRD patterns of the various heat-treated mixtures are shown in Fig. 3. These figures clearly indicate that the reaction between PbO and TiO_2 to form $PbTiO_3$ is initiated at 800 K (sample B). The difference of about 35 K between the initiation temperature of the reaction as observed from X-ray diffraction measurements and that from DTA studies is understandable in view of the different modes of heating adopted in the two studies. Dynamic methods like DTA and TG usually give a higher temperature of initiation of reaction than static (isothermal) methods because of the presence of temperature gradients in the specimen holder assembly of the former. The temperature of initiation of reaction derived from DTA measurements at the lower heating rate of 5 K min^{-1} was, in fact, approximately 15 K less than that derived from the DTA curve recorded at a heating rate of 10 K min^{-1}.

The X-ray diffractogram for the mixture held isothermally at 1275 K (sample F) for 90 min, cooled to 825 K at the rate of 5 K min^{-1}, and then furnace-cooled showed poor crystallinity, indicative of non-stoichiometry in the resulting lead titanate. The same specimen when annealed in air at 875 K for 2 h (sample G), however, showed a well characterized X-ray diffraction pattern matching that of crystalline $PbTiO_3$ [11, 12]. This may be because of better ordering of vacancies formed at high temperature [2]. Such intermediate annealing steps were not necessary for $PbTiO_3$ formed at 875 or 1075 K, all of which showed well defined X-ray diffraction patterns, characteristic of crystalline $PbTiO_3$.

Fig. 4 shows the variation of the estimated dielectric constant of sample J as a function of temperature. Because the samples were very porous and fragile, precise values of the dielectric constant cannot be obtained. It is, nevertheless, seen that at room temperature the dielectric constant is about 50. It increases slowly to a value of 80 at approximately 650 K, thereafter increases sharply to a maximum value of about 650 at ca. 765 K (Curie temperature) and above this temperature it decreases. The proportionate rise in the dielectric constant and the observed Curie temperature are in very good agreement with those reported in the literature [12, 13]. The measurements carried out on samples J and K sintered at different temperatures (Table 2) have not shown much variation in the magnitude of the dielectric constant and its temperature-dependence. This observation is in accordance with the reported nature of this oxide indicating that the ceramic body will break down while cooling below the Curie temperature because of the anisotropy in the crystal structure of the oxide above and below the transition temperature and hence densification by sintering at high temperature becomes ineffective [14].

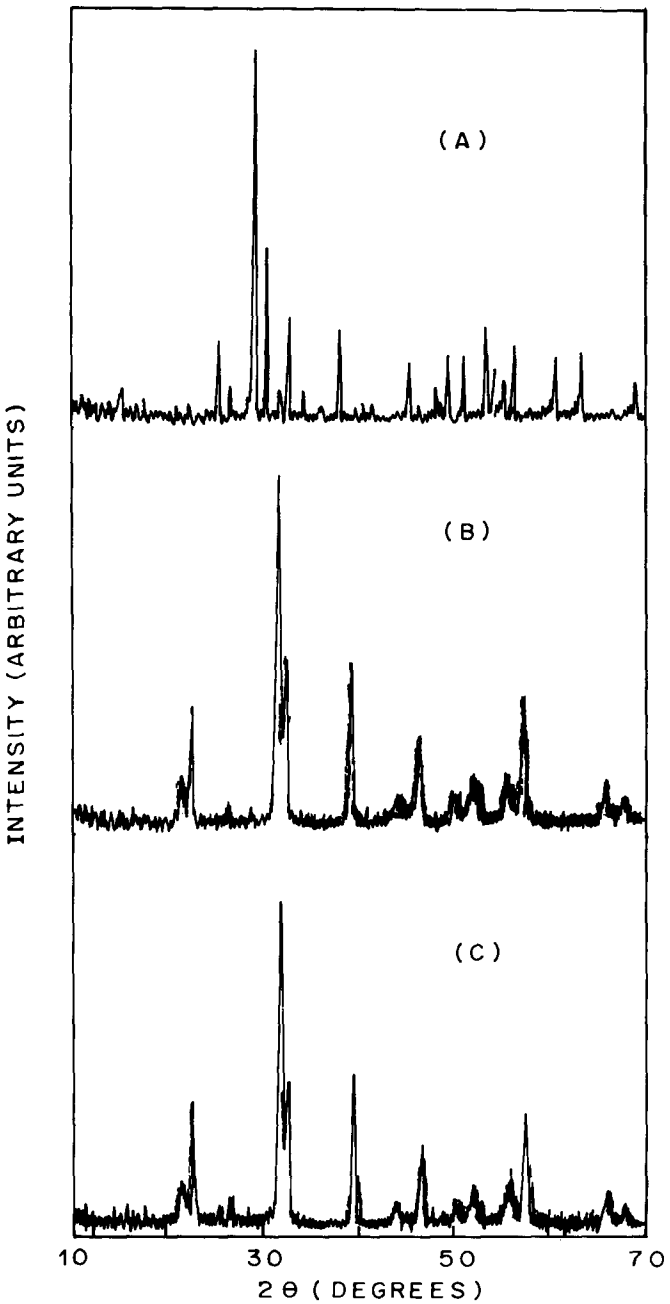

Fig. 3. X-ray diffraction patterns for the mixtures of PbO and TiO_2 heat treated as indicated in Table 1.

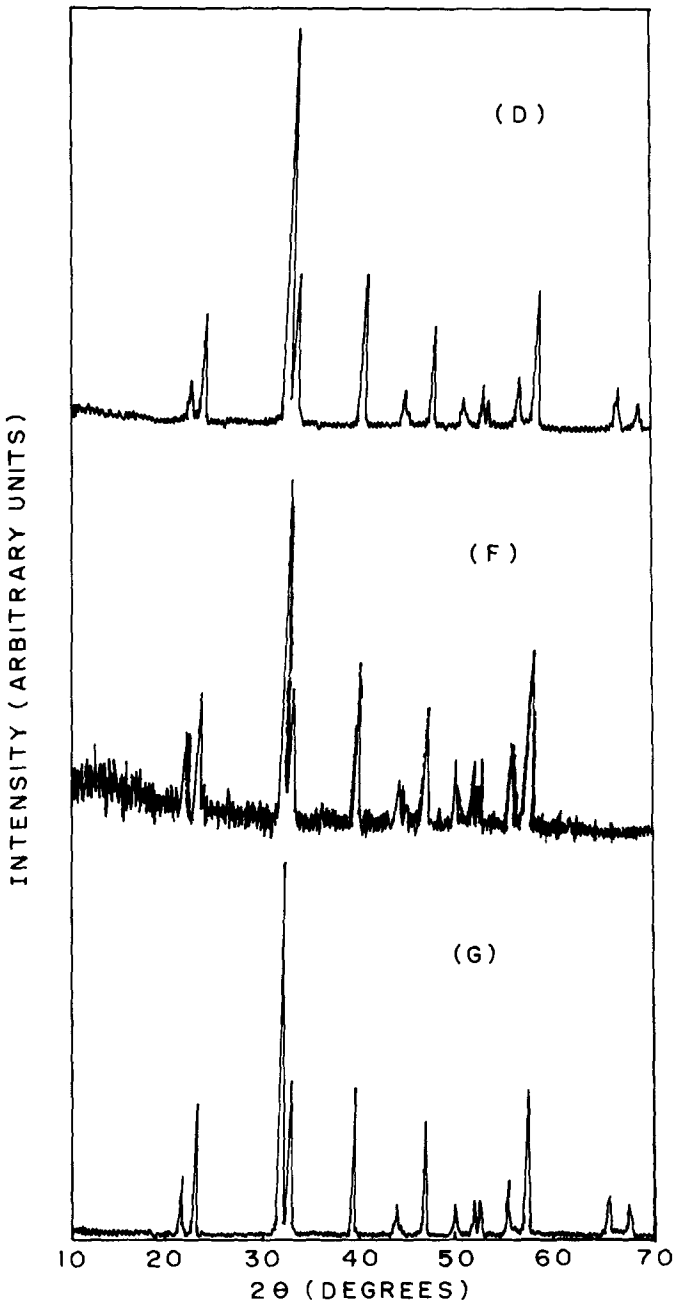

Fig. 3. (*Continued*)

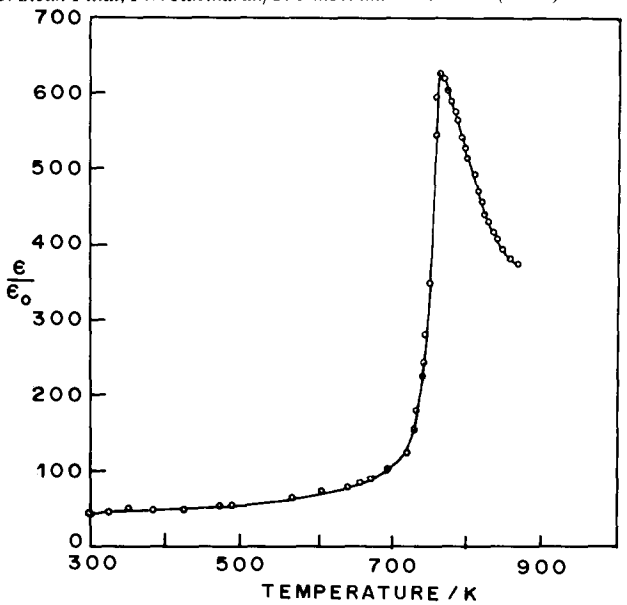

Fig. 4. Temperature-dependence of dielectric constant.

A typical SEM micrograph of sample J is given in Fig. 5. From the figure it is clear that the material heat-treated at 875 K appears to be single phase with an average grain size of 3 μm.

The ac conductivity (reciprocal of resistivity) measurements at 100 kHz for sample J are shown in Fig. 6. The room temperature conductivity was found to be approxi-

Fig. 5. SEM micrograph of sample J.

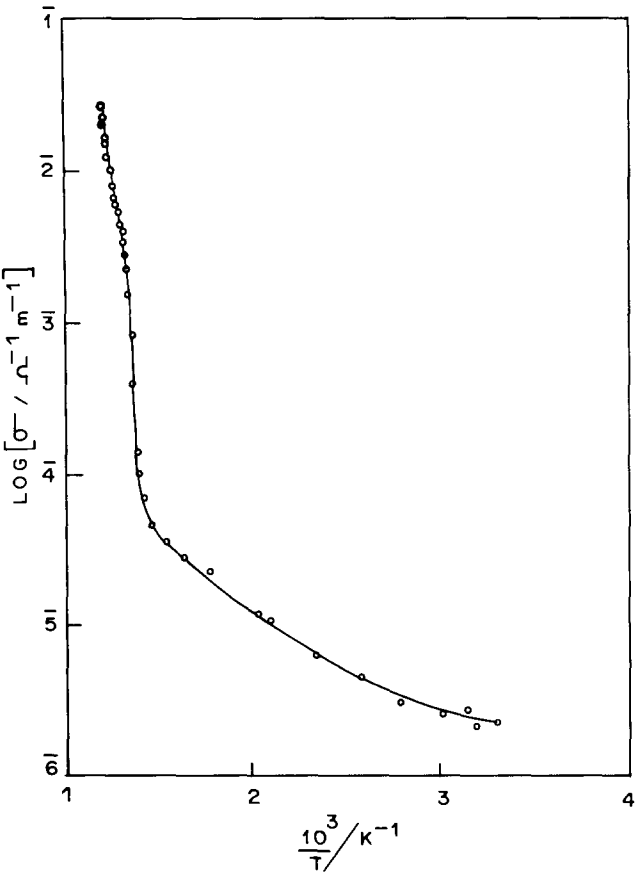

Fig. 6. Variation of ac conductivity with temperature.

mately $10^{-5}\,\Omega^{-1}\,m^{-1}$. It increases with increase of temperature and reaches a value of about $10^{-2}\,\Omega^{-1}\,m^{-1}$ above the Curie temperature. There is a sudden rise above 575 K. This conductivity behaviour is in agreement with that reported in literature [6, 13]. However, no decrease in conductivity was observed above the Curie temperature as reported by Bhide et al. in their studies on $PbTiO_3$ single crystals [13].

4. Conclusions

The exothermic reaction between lead oxide and titanium oxide has been observed to take place in the temperature range 833–1020 K using DTA. The compound prepared by heat-treating the oxide mixtures at 875 K showed a well characterized X-ray diffraction pattern for $PbTiO_3$ with a Curie temperature of 765 K. The results conclusively prove that lead titanate can be prepared by solid-state reaction of

a stoichiometric mixture of PbO and TiO_2 at 875 K, a temperature significantly lower than that reported in the literature (approximately 1275 K).

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References

[1] S. Shirasaki, Solid State Commun., 9 (1971) 1217.
[2] S. Shirasaki, K. Takahashi, H. Yamamura, K. Kakegawa and J. Mori, J. Solid State Chem., 12 (1975) 84.
[3] O.I. Prokopalo, Ferroelectrics, 14 (1976) 683.
[4] G. Shirane, S. Hoshino and K. Suzuki, Phys. Rev., 80 (1950) 1105.
[5] M.L. Calzada and J. De Frutos, J. Mater. Sci. 4 (1993) 83.
[6] J.P. Remeika and A.M. Glass, Mater. Res. Bull., 5 (1970) 37.
[7] K.K. Deb, Ferroelectrics, 99 (1989) 173.
[8] J. Drowart, R. Colin and G. Exsteen, Trans. Faraday Soc., 61 (1965) 1376.
[9] P.V. Ravindran, Personal communication, 1995.
[10] R.L. Holman, Ferroelectrics, 14 (1976) 675.
[11] H.E. Swanson, N.T. Gilfrich and G.M. Ugrinic, NBS Circular 539 (5) (1955) 39.
[12] G. Shirane and S. Hoshino, J. Phys. Soc. Japan, 6 (1951) 265.
[13] V.G. Bhide, K.G. Deshmukh and M.S. Hegde, Physica, 28 (1962) 871.
[14] K. Okazaki, Ferroelectrics, 41 (1982) 77.