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Diffuse phase transitions in the $(Pb_xBa_{1-x})TiO_3$ system

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Diffuse phase transitions were observed in the solid solution $(Pb_xBa_{1-x})TiO_3$. By measuring the diffuseness of the paraelectric to ferroelectric transition as a function of composition in the solid solution $(Pb_xBa_{1-x})TiO_3$ the average size of the ferroelectric nuclei may be determined. Dielectric constant versus temperature curves were measured over the temperature range where the ferroelectric transition occurs. From these curves, the diffuseness of the transition was determined. The size of the microregions (Kanzig regions), which are responsible for the diffuse behaviour, was estimated to be between 2.5 and 4.0 nm. These microregions are the ferroelectric nuclei and hence this allows the measurement of the ferroelectric nuclei size. © *1998 Kluwer Academic Publishers*

1. Introduction

The paraelectric to ferroelectric phase transition is typically a sharp transition. Gradual or diffuse phase transitions have been observed in complex perovskites [1, 2], which are perovskites with more than one type of cation in at least one crystallographic site. It has been suggested that the statistical composition fluctuations in the ferroelectric nuclei, which occur if crystallographically equivalent sites are occupied randomly by different cations [3], is the reason for the diffuse characteristics of the normally sharp transitions. The study of ordered complex perovskites shows that ordering of the cations causes a diffuse phase transition to become sharp and is consistent with the proposed model [4].

The diffuseness of the transition may be observed by measuring the dielectric constant versus temperature. A sharp transition will manifest itself by a sharp peak in the dielectric constant at the temperature of the transition. In the case of diffuse transitions, a broad peak is observed, indicating the transition occurs over a range of temperature. In a complex perovskite, the variation in transition temperature occurs due to the variation in the composition of the ferroelectric nuclei simply as a result of statistical fluctuations of the composition for a small volume. The variation in the composition of the nuclei depends on the volume of the nuclei. Therefore, the diffuseness of the phase transition is a means of measuring the average ferroelectric nuclei size.

Early studies for the $(Pb_xBa_{1-x})TiO_3$ system for compositions with $x = 0.25$, 0.50 and 0.75 indicated that a solid solution exists over the entire composition range and that all compositions were ferroelectric at room temperature with a diffuse paraelectric to ferroelectric phase transition [5, 6]. Therefore, the $(Pb_xBa_{1-x})TiO_3$ system is a potential system for studying systematically the effect of composition on the diffuseness of the phase transition.

In this study the diffuseness of the transition in the $(Pb_xBa_{1-x})TiO_3$ system was studied, where x was varied in 0.1 increments. The diffuseness was determined by measuring the dielectric constant versus temperature.

2. Experimental procedure

The compositions of the samples were (Pb_xBa_{1-x})-TiO_3, where x varied from 0.0–1.0 in 0.1 increments. These compositions refer to the relative amounts of oxides used in preparing the powder. Bulk processing of the perovskite powder was done with chemically pure PbO (99.5%), TiO_2 (99.7%), and $BaCO_3$ (99.5%). The powders were mixed by ball milling with alumina balls and distilled water (in the form of a slurry) for 5 h in a polyethylene container, and oven dried. The powder was then calcined in a covered alumina crucible at 850 °C for 5 h. After remilling again for 5 h followed by drying, the final product was ground with a mortar and pestle into a fine powder. The powders were then cold pressed at a pressure of 240 MPa (35 000 p.s.i; 10^3 p.s.i. $= 6.89\ \mathrm{N\,mm^{-2}}$) into discs 3 mm thick and 25 mm diameter. The compacts were then sintered in a covered alumina dish, packed with powders of the same composition in the temperature range 1250–1350 °C for 5 h. The sintering temperature was 1350 °C for $PbTiO_3$ and was decreased to 1250 °C for $BaTiO_3$.

X-ray samples were obtained by cutting a thin slice from the as-sintered samples and mechanically polishing with a final polish in 0.3 mm alumina slurry to give a smooth surface. Lattice parameters were measured by using a Rigaku X-ray diffractometer, with a CuK_α radiation source, operating at 35 kV and 50 mA.

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The samples for the dielectric measurements were obtained by cutting a thin slice from the as-sintered samples and mechanically polishing with a final polish in 0.3 mm alumina slurry to give a smooth surface, which was then coated with silver electrodes on both sides, using a Denton vacuum evaporator. The dielectric measurements were carried out by using an experimental set up that was specifically designed to carry out these measurements at high temperatures. A Keithley 3322 LCZ meter was used to measure the variation of dielectric constant with temperature with an applied field of IV r.m.s. (without any bias) and a sampling time of 480–600 ms.

3. Results and discussion

3.1. Crystal structure

Both $BaTiO_3$ and $PbTiO_3$ have a tetragonal structure at room temperature with c/a ratios of 1.029 and 1.061, respectively [7]. In the present study, it has been verified that the crystal structure of $(Pb_xBa_{1-x})TiO_3$ remains tetragonal over the entire composition range $0 \leqslant x \leqslant 1.0$ consistent with previous reports [5]. The indexed X-ray diffraction peaks and their corresponding 2θ values were used to calculate the lattice parameters using the method given by Parrish and Wilson [8]. The lattice parameters a and c decreased and increased, respectively, with increasing lead content and were in agreement with linearly interpolating the a and c values for $PbTiO_3$ and $BaTiO_3$ (Fig. 1). The theoretical density increased with increasing lead content (Table I). The experimental density, ρ_{ex}, was always greater than 85% of the theoretical density, ρ_{th}. The cell volume ($V = a^2c$) did not show any significant trend over the measured. X-ray diffraction and electron diffraction did not reveal any cation ordering.

3.2. Dielectric measurements

The $(Pb_xBa_{1-x})TiO_3$ system exhibits a diffuse paraelectric–ferroelectric phase transition over the composition range $0.1 \leqslant x \leqslant 0.7$ (Fig. 2). The dielectric constant versus temperature curves could not be reliably measured for the compositions $x = 0.8$, 0.9 and 1.0, because the samples proved to be extremely brittle. The brittleness was due to the large c/a ratio creating microcracks in the ceramic upon transformation. The dielectric constant versus temperature curve may be suspect for the $x = 0.7$ composition for the same reason. It was observed that the Curie point varies linearly with composition (Fig. 3). None of the samples exhibited any relaxor behaviour because the dielectric constant versus temperature curves did not vary with frequency of the applied electric field.

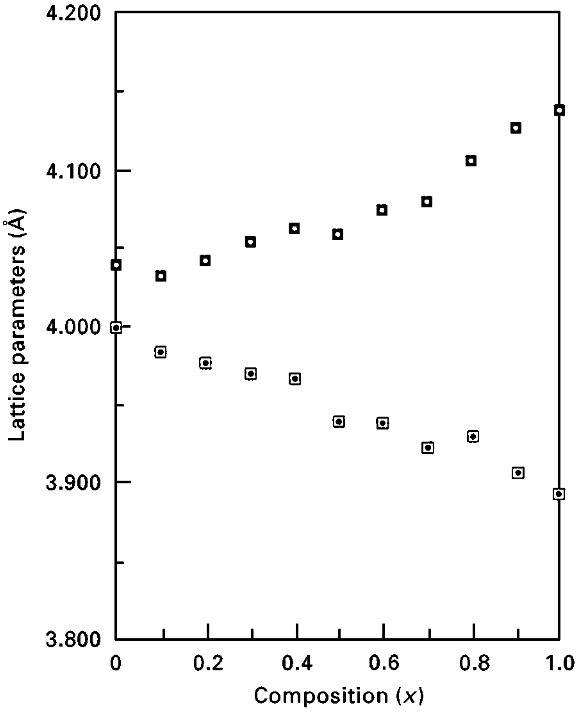

Figure 1 The variation of lattice parameters along the a- and c-axes with composition for tetragonal $(Pb_xBa_{1-x})TiO_3$.

Although the $(Pb_xBa_{1-x})TiO_3$ system forms a homogeneous solid solution in a macroscopic sense, there exist microregions that have compositions differing from the average composition and result in a diffuse phase transition. These microregions that have varying compositions have different local Curie temperatures. Smolenskii [1] reported a quantitative analysis of the influence of composition fluctuations on diffuse phase transitions for solid solutions of two

TABLE I Summary of sample properties for $(Pb_xBa_{1-x})TiO_3$

	x										
	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Molecular weight (g)	233.20	240.18	247.17	254.16	261.15	268.14	275.12	282.11	289.10	296.09	303.08
Sinter temperature (°C)	1350	1350	1330	1310	1310	1300	1290	1270	1270	1260	1250
a (nm)	0.3999	0.3984	0.3977	0.3970	0.3967	0.3939	0.3938	0.3922	0.3929	0.3906	0.3892
c (nm)	0.4039	0.4032	0.4042	0.4054	0.4063	0.4059	0.4075	0.4080	0.4106	0.4127	0.4138
c/a	1.0100	1.0120	1.0163	1.0211	1.0241	1.0304	1.0347	1.0402	1.0450	1.0565	1.0632
Cell volume (10^{-3} nm^3)	64.591	63.996	63.930	63.894	63.939	62.978	63.194	62.758	63.384	62.964	62.681
ρ_{th} (g cm^{-3})	6.009	6.231	6.419	6.604	6.781	7.068	7.228	7.463	7.572	7.807	8.028
ρ_{ex} (g cm^{-3})	5.613	5.677	5.761	5.859	5.973	6.134	6.264	6.919	7.145	7.284	7.585
ρ (%)	93.40	91.10	89.74	88.71	88.08	86.77	86.66	92.70	94.35	93.29	94.48
Curie point (°C)	120	164	211	259	299	340	372	403	–	–	–

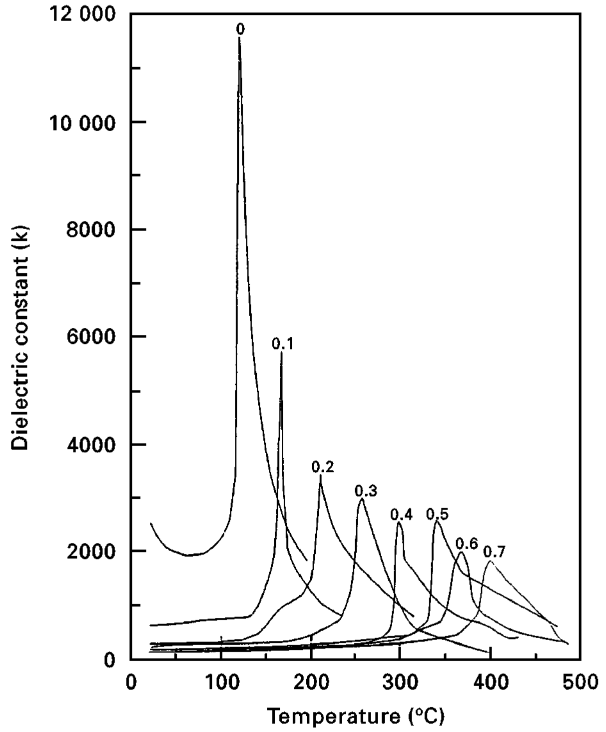

Figure 2 The variation of dielectric constant (at 10 kHz) with temperature for the $(Pb_xBa_{1-x})TiO_3$ system.

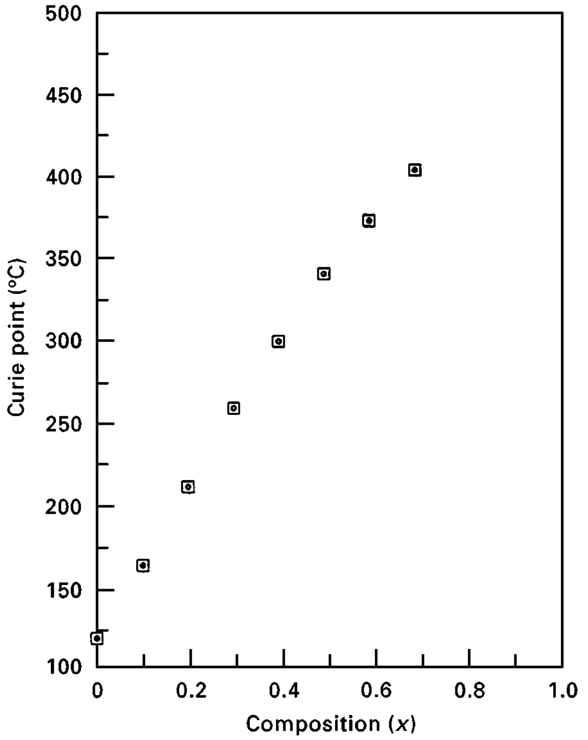

Figure 3 The variation of Curie point with composition for the $(Pb_xBa_{1-x})TiO_3$ system.

perovskite compounds. The size of these microregions is an important parameter that has not been experimentally measured. These microregions represent the minimum size for a ferroelectric nucleus in the paraelectric to ferroelectric transitions. By measuring the dielectric constant as temperature curves over a range of compositions for a given solid solution, the size of the microregions may be determined.

The relationship between the width of the dielectric constant versus temperature curve and the average size of the ferroelectric nuclei has been previously derived for both binary and ternary solid solutions [9]. The derivation of the relationship for the binary case will be briefly explained.

If a nucleus containing a total of n molecules of $A'BO_3$ and $A''BO_3$, in a solid with the macroscopic composition $A'_xA''_{1-x}BO_3$, the probability of finding m molecules of $A'BO_3$ for random occupation is given by

$$P(m) = \frac{1}{[2\pi nx(1-x)]^{1/2}} \exp\left[\frac{-n\xi^2}{2x(1-x)}\right] \tag{1}$$

where ξ is the difference between the macroscopic and microscopic concentrations and is given by $\xi = q - x$, where, $q = m/n$. At $\xi = 0, P(m)$ has a maximum. Hence, the value of ξ at half the maximum is given by

$$\exp\left[\frac{-n\xi^2}{2x(1-x)}\right] = \frac{1}{2} \tag{2}$$

This gives

$$\xi = \pm\left[\frac{x(1-x)\ln 4}{n}\right]^{1/2} \tag{3}$$

It is assumed that the Curie point changes linearly with composition, which is a good assumption because the fluctuations in composition being considered are very small. Hence $\xi = \nu(T - T_0)$, where T and T_0 are the Curie temperatures of the microscopic and macroscopic regions, respectively, and ν is a constant of proportionality, which is the slope of the plot of the Curie point as a function of composition. Therefore, the width at half maximum, Δ, of the peak in the ε versus T curve is given by

$$\Delta = \frac{C}{\nu}[x(1-x)]^{1/2} \tag{4}$$

where $C = [\ln(4/n)]^{1/2}$, x is the composition, n the number of unit cells, and Δ is as shown in Fig. 4a.

The size of the microregions is estimated by comparing the WHM (Δ) at different compositions with the above equation. Fig. 4b gives a plot of the theoretical curves and experimentally obtained data points for the WHM with composition. The theoretical curves are calculated for nuclei with 135 and 450 molecules. Theoretically one expects a maximum in the WHM for the 0.5 composition because at this composition there will be a maximum in the composition fluctuation for a nucleus of a given size. Although, in principle, it is possible to calculate the value of n and hence the size of the nucleus from a measurement of a single composition, the measurement over a range of compositions allows greater confidence that the diffuseness is cause by statistical composition fluctuation and that the proposed model for measuring the nucleus size is valid.

The data on the barium-rich side ($0.0 \leqslant x \leqslant 0.5$) follows the shape of the theoretical curve quite well. As

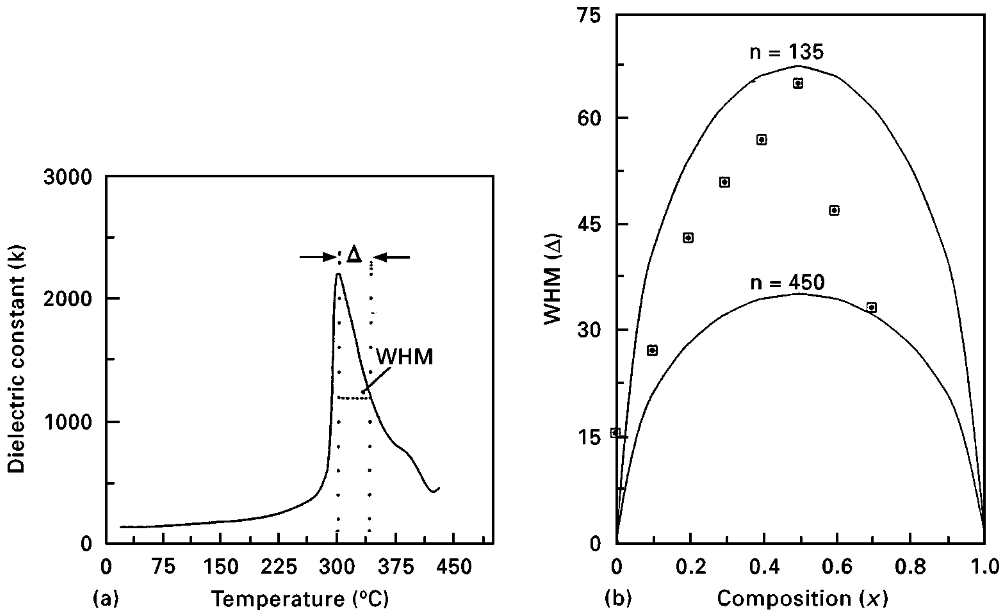

Figure 4 (a) Illustration of the width at half maximum (WHM), Δ; (b) theoretical and experimental variation of the width at half-maximum, Δ, for $(Pb_xBa_{1-x})TiO_3$.

mentioned previously the $x = 0.8$, 0.9 and 1.0 samples were brittle due to microcracks. It is certainly possible that the 0.7 and, to a lesser extent the 0.6, samples are also affected by the microcracking.

The value of n was found to lie between 135 and 450 which are the limiting curves for these compositions (Fig. 4b). From these n values, the average nucleus diameter was calculated to lie between 2.5 and 4.0 nm, using an average cell volume of 64×10^{-3} nm.

4. Conclusion

The measurements of dielectric constant versus temperature for the solid solution $(Pb_xBa_{1-x})TiO_3$ for x ranging from 0.0–0.7 show a diffuse transition. The diffuse transition did not exhibit any relaxor behaviour. The variation of the width-at-half-maximum of the peak in the dielectric constant versus temperature curve as a function of composition indicates that the diffuseness is caused by the statistical fluctuation in the composition of the ferroelectric nucleus. This allows the average feeroelectric nuclei size to be estimated. The diameter of the average ferroelectric nucleus is estimated to be between 2.5 and 4.0 nm.

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