Diffuse phase transition in perovskite ferroelectrics

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Received 25 February 2000; accepted 23 December 2000

A mathematical model to estimate quantitatively the size of microregions with compositional fluctuations that affect the ferro-paraelectric phase transitions is presented. The ferro-paraelectric transition in $(Pb_{1-x}Ca_x)(Co_{0.5}W_{0.5})_{0.04}Ti_{0.96}O_3$ ceramics has been studied by measuring the dielectric permittivity as a function of temperature at different frequency. Experimental results show that with the increase in Ca-content width of the ferro-paraelectric transition region broadened while phase transition temperature decreases. Also this theoretical model has been applied to the present ceramic system.

Recent developments have established that ferroelectrics are important materials for electronic devices. Most technologically important ferroelectrics are oxides with perovskite structure having general formula $ABO_3$. The major stimuli for the development of these materials, either in the form of solid solution or dopant additions, have been the prospect of improving performance characteristics compared to the simple perovskite since they are having highly tolerant structure that allows their dielectric properties to be controlled by variable modifications either at A-site or B-site. The complex perovskites, $(A'A''...A''')B_3O_3$ and/or $(A'B'B''...B''')O_3$ are very interesting for both practical applications and scientific research. This complexity, which is statistically greater fluctuations in composition, some times led to increase the width of ferro-paraelectric transition region (i.e. transition broadening). These transition broadening is very common occurrence in solid solution and other disordered structures. Therefore, multiple ion occupation of A and/or B sites cause deviation from Curie-Weiss behaviour, where the transition temperature ($T_C$) is not sharp but physical properties change rather gradually over a temperature range and is known as diffuse phase transition (DPT).

DPT phenomena so far have been successfully explained by two widely quoted theories: Smolenskii's compositional fluctuation theory and Fritzberg's polarisation (structural) fluctuation theory. Smolenskii's compositional fluctuation theory has been based on the assumption that there exist spatial variations in composition such that the transition temperature is different in different regions and the size of microregions is 10~100 nm. Both the composition and spontaneous polarisation are considered to be constant in a particular microregion, but it may vary from one microregion to another. If the Curie point of the ferroelectric material is sensitive to the concentration of the two types of cations in the solid solution, each microregion will posses its own Curie point and the usual sharp temperature dependence of dielectric constant. Macroscopically one would observe a broad envelope of all these local transitions giving rise to diffuse or smeared response for dielectric constant. The degree of diffuseness will depend upon the composition fluctuation and the sensitivity of the Curie point on the compositional change in the solid solution.

The quantitative evaluation of compositional fluctuations in the binary solid solution having perovskite structure has been derived based on the assumption that there is no ordering of A or B site atoms. Ganesh and Goo extrapolated this mathematical technique for ternary solid solution. In the present investigation an attempt has been made to present a general mathematical model that can estimate quantitatively the size of microregions with compositional fluctuations which is responsible for broadening in transition region. This theoretical model is applicable to the perovskite binary, ternary, quaternary, etc. systems and has been tested, in this paper, on ferroelectric $(Pb_{1-x}Ca_x)(Co_{0.5}W_{0.5})_{0.04}Ti_{0.96}O_3$ ceramics.

Modified lead titanate having general formula $(Pb_{1-x}Me_x)(B_{0.3}W_{0.7})_{0.04}Ti_{1.2}O_3$ where $Me = Ba$, Sr, Ca
and B = Co, Ni, Mn are the potential candidates for their use in piezoelectric and/or pyroelectric applications\textsuperscript{14-27}.

**Experimental Procedure**

Ceramics \((\text{Ph}_{x} \text{Ca}_{1-x})[(\text{Co}_{0.5} \text{W}_{0.5})_{0.04} \text{Ti}_{0.96}]\text{O}_{3}\) with \(x = 0.10, 0.20, 0.24, 0.25, 0.30, 0.35\) and 0.40 have been prepared using solid reaction technique. The detailed procedure adopted for preparation are described elsewhere\textsuperscript{25,27}. The calcination and sintering temperatures are respectively 950°C/4h and 1100°C/2h. The completion of reaction and formation of desired compound was checked by the X-ray diffractometer (Rikagll Miniflex, Japan) with monochromatized CuK\(\alpha\) radiation \((\lambda = 0.15418\text{nm})\) in wide range of Bragg angles \((5° \leq 2\theta \leq 70°)\) with a scanning speed of \(2°\text{min}^{-1}\) at \(33°C\). The surface morphology of the ceramic samples was taken by Cambridge Stereoscan (S-180) scanning electron microscope. To measure the dielectric properties of the compounds, air drying silver paint was applied on both the large faces of the samples to serve as electrodes. Measurements of dielectric constant \((\varepsilon)\) and dielectric loss \((\tan\delta)\) were carried out as a function of temperature (26 - 300°C) at 1kHz and 10kHz using LCR Hi-Tester (HIOKI - Japan). To overcome the moisture effect on the electrical properties, the samples were preheated to 100°C to evaporate the moisture, if any, and then cooled to room temperature and then experiments were carried out.

**Mathematic Model**

Let us consider a general system of the type \((A_1', A_2', \ldots, A_n')\text{BO}_3\) or \((B_1', B_2', \ldots, B_n')\text{O}_3\) where \(x_i\) is the macroscopic composition of \(A_{x_i}\) or \(B_{x_i}\) and \(\sum_{i=1}^{n} x_i = 1\). The probability of finding \(m_1\) molecules of \(A_1'B_03\), \(m_2\) molecules of \(A_2'B_03\), ..., and \(m_{n-1}\) molecules of \(A_1'(n-1)B_03\) or probability of finding \(m_1\) molecules of \(AB'O_3\), \(m_2\) molecules of \(AB'O_3\), ... and \(m_{n-1}\) molecules of \(AB'(n-1)O_3\) or probability of finding \(m_1\) molecules of \(A'BO_3\), ... and \(m_{n-1}\) molecules of \(A'(n-1)BO_3\) in a microscopic volume containing a total number of \(N\) molecules of \((A_1'A_2'\ldots A_n')\text{BO}_3\) or \((A_1'B_1'\ldots B_n')\text{O}_3\) is given by

\[
P(m_1, m_2, \ldots, m_{n-1}) = \frac{N!}{\prod_{i=1}^{n-1} m_i! (N - \sum_{i=1}^{n-1} m_i)!} \left( \prod_{i=1}^{n-1} \left( \frac{x_i}{m_i} \right)^{m_i} \left( 1 - \sum_{i=1}^{n-1} x_i \right)^{N - \sum_{i=1}^{n-1} m_i} \right)^{1/2}.
\]

For example when \(n = 2\) represent binary system : \(A'\text{A}''\text{BO}_3\) or \(A'B'\text{BO}_3\), then equation (1) reduces to

\[
P(m_1) = \frac{N!}{m_1! (N - m_1)!} \left( x_1 \right)^{m_1} \left( 1 - x_1 \right)^{N - m_1}.
\]

when \(n = 3\) represent ternary system : \(A'A''A'''\text{BO}_3\) or \(A'B'B'''\text{O}_3\) equation (1) reduces to

\[
P(m_1, m_2) = \frac{N!}{m_1! m_2! (N - m_1 - m_2)!} \left( x_1 \right)^{m_1} \left( x_2 \right)^{m_2} \left( 1 - x_1 - x_2 \right)^{N - m_1 - m_2}.
\]

Similarly \(n = 4\) represents quaternary system and so on. Using Stirling’s approximation for large value of \(N\) we have

\[
N! = (2\pi N)^{1/2} (Ne)^N
\]

Using Eq.(4) in Eq.(1) we get

\[
P(m_1, m_2, \ldots, m_{n-1}) = \frac{\sqrt{N} (N - \sum_{i=1}^{n} \frac{1}{2} \left( \prod_{i=1}^{n} \left( x_i \right)^{m_i} \left( 1 - \sum_{i=1}^{n} x_i \right)^{N - \sum_{i=1}^{n} m_i} \right)^{1/2}} \prod_{i=1}^{n} \left( \frac{x_i}{m_i} \right)^{m_i} \left( 1 - \sum_{i=1}^{n} x_i \right)^{N - \sum_{i=1}^{n} m_i}.
\]

Now suppose \(\alpha_i = m/N\), where \(i = 1, 2, 3, \ldots, (n-1)\), represents the composition of micro volume, therefore

\[
P(m_1, m_2, \ldots, m_{n-1}) = \frac{N!}{\prod_{i=1}^{n} \left( \frac{x_i}{m_i} \right)^{m_i} \left( 1 - \sum_{i=1}^{n} x_i \right)^{N - \sum_{i=1}^{n} m_i}} \left( \prod_{i=1}^{n} \left( \frac{x_i}{m_i} \right)^{m_i} \left( 1 - \sum_{i=1}^{n} x_i \right)^{N - \sum_{i=1}^{n} m_i} \right)^{1/2}.
\]

If \(\alpha_i - x_i = \delta_i\), \(i = 1, 2, 3, \ldots, (n-1)\), then \(\delta_i\) represents the deviations of the microscopic composition from the macroscopic composition. Therefore, for binary
system \( \alpha_i - x_i = \delta_i \) while for ternary system \( \alpha_i - x_i = \delta_i \) and \( \alpha_i - x_2 = \delta_2 \) and so on. To see how the diffuseness varies with compositional fluctuations in a system for a given \( N \), one can plot \( P(m_1, m_2, ... m_{n-1}) \) as a function of deviation \( (\delta_i)^{9,13} \). In order to establish a relation between diffuseness that occur in \( P(m_1, m_2, ... m_{n-1}) = \delta_i \) plot with diffuseness occur in the peak region of dielectric \( (\varepsilon - T) \) plot, it is necessary to obtain the width at half maximum from the equation \( (6)^{13} \). It can be seen that \( P(m_1, m_2, ... m_{n-1}) \) is maximum when \( \delta_i \) are zero. Hence, substituting \( \alpha_i = x_i \) in equation \( (6) \) one has:

\[
P(m_1, m_2, ... m_{n-1}) = \frac{1}{2\pi N} \left( \prod_{i=1}^{n-1} x_i \right) \left( \prod_{i=1}^{n-1} x_i \right)^{-\frac{1}{2}}
\]

Therefore, the value at half maximum is given by:

\[
P_{\text{half max}}(m_1, m_2, ... m_{n-1}) = \frac{1}{4\pi N} \left( \prod_{i=1}^{n-1} x_i \right) \left( \prod_{i=1}^{n-1} x_i \right)^{-\frac{1}{2}}
\]

Equating eqs.\( (6) \) and \( (8) \) yield:

\[
\left( \prod_{i=1}^{n-1} x_i \right)^N \left( \prod_{i=1}^{n-1} x_i \right)^{-\frac{N}{2}} = \frac{1}{2}
\]

Let us assume that Curie temperature \( (T_C) \) varies linearly with small fluctuations in composition. Therefore, for a small change in composition \( (\delta x_i) \), the approximated Curie point \( (ACP) \) of the system, in general, is given by:

\[
T_C = \sum_{i=1}^{n} T_{C_i} x_i
\]

where \( T_{C_i} \) is the Curie temperature of ith molecule.

Now similar as in the case of binary\(^{26} \) if we have \( \alpha_i - x_i = g_i (T - T_C) \) \( \ldots (11) \)

where \( g_i \) are the proportionality constants, then \( 1/g_i = \partial T_C / \partial x_i \). If \( T - T_C = \Delta \), therefore,

\[
\alpha_i - x_i = \Delta (\partial T_C / \partial x_i) \quad \ldots (12)
\]

Substituting the values of \( \alpha_i \) in Eq. \( (9) \) then \( \Delta \) represents the width at half maximum with respect to \( T \) and is experimentally determined from \( \varepsilon - T \) plots.

Using the experimentally estimated \( \Delta \) in Eq. \( (9) \), one can obtain \( N \) and consequently the size of microregions.

**Results and Discussion**

The XRD-pattern analyses indicated that all specimens are of single-phase with perovskite-type tetragonal structure. The lattice parameters were estimated using a standard computer program (least squares refinement method). Experimentally observed and calculated \( d \)-values for these compounds were compared. A good agreement of calculated and observed \( d \)-values of all diffraction lines of different compositions suggest that there is no change in basic crystal structure between pure and modified form of \( \text{PbTiO}_3 \).

Fig. 1 shows a decreasing trend in unit cell volume \((a^2 c)\) with the increment in \( \text{Ca}\% \). Also a decrease in tetragonality is observed with the increment in \( \text{Ca} \) content.

Fig. 2 shows the SEM-photograph for the ceramic \( \text{Pb}_{0.76} \text{Ca}_{0.24} \text{Co}_{0.02} \text{W}_{0.02} \text{Ti}_{0.96} \text{O}_3 \). The photograph contains a very few voids or cavities, suggest that the density of the material is high and all the particles are uniformly and homogeneously distributed. Average grain size is estimated to be about 2.4 \( \mu \text{m} \).

Fig. 3 shows the variation of \( \varepsilon \) at 1 kHz with the increment in temperature. As typical of normal
ferroelectrics, $\varepsilon$ increases gradually with increment in temperature up to the transition temperature ($T_c$) and then decreases. It is seen that the partial substitution of Pb$^{2+}$ by Ca$^{2+}$ decreases the value of $T_c$ (Fig.1), the value of $\varepsilon_{RT}$ and $\tan\delta_{RT}$ (RT denotes values at room temperature) increase while maximum value of $\varepsilon$ ($\varepsilon_{max}$) decreases, dielectric peak shifts towards lower temperature side and $\varepsilon$-$T$ curve flattens i.e. the phase transition becomes more diffuse. In other words, the ferro-paraelectric phase becomes more disordered. This can be explained on the basis of the fact that the delicate balance of short-range forces (favouring the non-polar cubic phase) and long-range Coulomb forces (favouring the ferroelectric state) makes the transition sensitive to defects (substitutions) that modify the short-range interactions and to carriers (e.g. photoelectrons) that screen the long-range field$^{29}$. The decrease in $\varepsilon_{max}$ implies that the substitution of Ca-ions reduces the dipole moment of the lattice and lowers the peak dielectric constant. In all the materials $\tan\delta_{RT}$ was found to be of the order of $10^{-2}$. The low $\tan\delta$ of this kind can be advantageous when improved detectivity is required. The increase in $\varepsilon_{RT}$ probably come from the decrease in Curie temperature due to Ca substitution for Pb. No shift in the dielectric maxima has been observed with the increment in frequency. 

Here the region around the dielectric peak is broadened, which is one of the most important characteristics of disordered perovskite type structure with diffuse phase transition (DPT) and does not follow the Curie-Weiss Law but exhibits the following type of temperature dependence$^{30}$:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{max}} = A(T - T_c)^\gamma$$

where $\varepsilon_{max}$ is the peak value of the dielectric constant and $\gamma$ is a critical exponent which lies in the range $1 < \gamma \leq 2$. $\gamma = 1$ represents ideal Curie-Weiss behaviour while between 1 and 2 indicate diffuse behaviour. Inset Fig.3 shows the variation of $\ln(1/\varepsilon - 1/\varepsilon_{max})$ with $\ln(T - T_c)$ for Pb$_{0.76}$Ca$_{0.24}$Co$_{0.02}$W$_{0.02}$Ti$_{0.98}$O$_3$ only at 1kHz. The graph shows almost linear behaviour as temperature changes. The value of exponent, $\gamma$, in expression (13) was estimated from the slope of the curves. We find $\gamma > 1$ for all cases and its value increases with increase in Ca content (Fig.1). In other words diffusivity increases with decrease in tetragonality. Value of $\gamma > 1$ imply diffuse phase transition$^{30}$ which may be due to compositional fluctuations where the local Curie points of different microregions are statistically distributed around the mean Curie temperature. It is possible to explain the results considering an increasing disorder on the arrangement of Pb$^{2+}$ and Ca$^{2+}$ ions at A-site, that should produce some kind of heterogeneities. The size of microregions, estimated with the help of the model and the experimental data, is found to be in the range of 20-30nm for the present ceramic system.

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Fig. 2—SEM picture of Pb$_{0.76}$Ca$_{0.24}$Co$_{0.02}$W$_{0.02}$Ti$_{0.98}$O$_3$ ceramic

Fig. 3—Variation of $\varepsilon$ with temperature of Pb$_{0.76}$Ca$_{0.24}$Co$_{0.02}$W$_{0.02}$Ti$_{0.98}$O$_3$ ceramic at 1kHz
References