Thermal expansion studies on ferroelectric materials

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Abstract. Thermal expansion data is reported over a wide temperature range (80–800 K) for $BaTiO_3$ (BT) and $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN), belonging to different classes of the ferroelectric materials. The sharp structural phase transitions of BT result in lowering of the thermal expansion coefficient (α) at the transitions which is proportional to the change in polarization at the transitions. In PFN, a relaxor ferroelectric, lowering of α is spread over a wider temperature range across the dielectric maxima.

Keywords. Thermal expansion; ferroelectrics; relaxors; $BaTiO_3$; $Pb(Fe_{1/2}Nb_{1/2})O_3$; electric polarization.

1. Introduction

The magnetic and electric contribution to the thermal expansion of solids is well understood through Grüneisen parameter (Krishnan *et al* 1979). Extensive work on the effect of magnetic transition on thermal expansion has led to the development of invar alloys. The magnetostriction effects result in low thermal expansion coefficient, α, in these alloys and, hence, these materials are extensively used in electrical feed-through in ceramic/glass seals. There have not been many reports hitherto describing contribution to the thermal expansion arising from ferro- or antiferroelectric transitions.

$BaTiO_3$ (BT) is a well-known ferroelectric material which exhibits three structural phase transitions (Megaw 1947). The transitions of rhombohedral–to–orthorhombic, orthorhombic–to–tetragonal and tetragonal–to–cubic occur at 183, 273 and 403 K respectively. These transitions are reflected as sharp changes in the dielectric properties, electric polarization, etc. Early thermal expansion studies of $BaTiO_3$ also show discontinuity in $\Delta L/L$ plots at all the transitions (Kay and Vousden 1949; Rhodes 1951; Shirane and Takeda 1952). However, there is an inconsistency in the reported values of α at different crystal phases and phase transitions. According to Shirane and Takeda (1952), the α values were 5·2, 4·6, 6·5 and 9·8 × 10^{-6}/K in the rhombohedral, orthorhombic, tetragonal and cubic structures respectively. At the rhombohedral–to–tetragonal transition, they have observed an increase in α, while at the other two transitions it decreases.

Another class of ferroelectrics, called relaxor ferroelectrics, exhibit a broad dielectric maxima and the temperature of dielectric maximum (T_m) increases with the increase in measuring frequency. There is no identifiable structural change across the ferroelectric-like transition in these materials. The X-ray patterns of these materials can be indexed on cubic lattice even well below the T_m. Some authors have invoked rhombohedral unit cell with rhombohedral angle of 89·92° for a few materials. However, for all practical purposes, a pseudocubic unit cell is employed (Radhika *et al* 1996). The reason for the dielectric maxima in relaxor ferroelectrics is thought to be due to entirely a different phenomenon and is yet to be understood completely. A large number of

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lead-based complex oxides having perovskite structure $(Pb(B'B'')O_3)$ belong to this class of materials. Basically, in such materials, different valent cations occupy the same crystallographic site which builds up charge imbalance, resulting in polar nanodomains. Compositional inhomogeneity, superparaelectric behaviour and growth of polar regions are some of the reasons that have been proposed to explain the relaxor behaviour (Smolenskii 1984; Cross 1994; Tsurumi *et al* 1994). Generally, it is believed that the polar regions build up much above the T_m and grow with the decrease in temperature. The spontaneous polarization exists even above T_m and builds up slowly across the broad dielectric maxima region. These relaxor ferroelectrics are known to exhibit low thermal expansion in the region of broad dielectric maxima (Jang *et al* 1980; Nomura and Uchino 1982). Most of the relaxors have T_ms below room temperature and the systematic study of thermal expansion, especially much below their T_m, has not been reported.

We carried out thermal expansion measurements on normal and relaxor ferroelectrics using LVDT-based push-rod dilatometers developed in our laboratory. The thermal expansion coefficient and the known changes in polarization across the transitions of $BaTiO_3$ were correlated. We have attempted to use this correlation to get information about the nature of transition in the relaxor ferroelectric materials. In order to study the thermal expansion of relaxors, $Pb(Fe_{1/2}Nb_{1/2})O_3(PFN)$ with T_m of 385 K was selected. Although PFN does not exhibit the frequency dispersion of T_m, it shows a diffuse dielectric maxima and can generally be considered as a relaxor ferroelectric (Yokosuka 1993).

2. Experimental

$BaTiO_3$ was prepared by the oxalate route (Clabaugh *et al* 1956). $BaCl_2 \cdot 2H_2O$ and $TiOCl_2$ were reacted with oxalic acid at 346 K to get a precipitate of barium titanyl oxalate. The precipitate was then dried and heated at 1173 K for 7 h. The PVA binder was added to the powder and pelletized. The pellets were sintered at 1623 K for 4 h.

$Pb(Fe_{1/2}Nb_{1/2})O_3$ was prepared using a Columbite route using respective oxides as the starting materials. $FeNbO_4$ was prepared by mixing the oxides and reacting at 1273 K for 4 h. It was then mixed with PbO and reacted at 1173 K for 1 h. The powder was pelletized and sintered at 1273 K for 1 h in lead-rich atmosphere (Radhika *et al* 1996).

Materials characterization was done by X-ray diffraction and dielectric measurements. Powder X-ray diffraction patterns were recorded on SCINTAG diffractometer at a scan speed of $2°/min$. Dielectric constant and $\tan \delta$ were measured at frequencies from 100 Hz to 1 MHz, using HP4194A impedance/gain phase analyzer from room temperature to 473 K.

Thermal expansion measurements were carried out on these samples of length of about 10 mm from 80 K to 800 K on dilatometers developed indigenously (Umarji *et al* 1997). The high-temperature dilatometer (HTD) can be used from room temperature to 1150 K, whereas, the low-temperature dilatometer (LTD) can be used from 77 K to 400 K. In both HTD and LTD, change in length of the sample was transferred to the magnetic core of the linear variable differential transformer (LVDT) by the quartz tube. The displacement was measured by monitoring the induced voltage changes in LVDT, which were produced by the movement of the magnetic core. An EG&G PAR 5210

lock-in-amplifier (LIA) was used to detect the signal from LVDT. The primary coil was excited by the internal oscillator of the LIA at 1·831 kHz and 0·75 V. The in-phase signal was detected on 1 mV and 3 mV scales for HTD and LTD respectively. Both the dilatometers were calibrated by measuring OFHP copper (SRM-736) and high purity aluminium samples.

The dilatometers working at a heating or cooling rate of 2 K/min have a sensitivity of $\Delta L/L = 2 \times 10^{-6}$ for sample length of 10 mm and accuracy of 5% in the measured thermal expansion coefficients. The output of LIA and the thermocouple output through DMM-196 were acquired by a PC via the IEEE-488 bus. The data was collected for every 90 sec and was averaged for 10 sec. The data was then corrected for the contribution from the quartz tubes and the plots of $\Delta L/L$ vs temperature and the derivative curve of $\Delta L/L$, i.e. α (thermal expansion coefficient) vs temperature were plotted.

3. Results and discussion

The room temperature X-ray diffraction pattern of BT could be indexed on tetragonal lattice. PFN was completely perovskite with a pseudocubic lattice. BT shows ferro-electric transition (T_c) at 403 K. The dielectric constant (ε) and $\tan\delta$ values of BT at room temperature were 2000, 0·03 with a ε_{max} of 8000 at 120 Hz. PFN shows a broad dielectric maxima of about 14000 at 100 Hz at 385 K.

The thermal strain ($\Delta L/L$) recorded for BT during heating cycle is shown in figure 1a. The strain is calculated with respect to L at room temperature. The exact overlapping of data taken, using HTD and LTD in the temperature range 300–400 K, confirms the reliability of data, calibration of the dilatometers and the analysis procedure adopted. The four structural regions separated by the three transitions are clearly seen as change of slope in $\Delta L/L$ curve. This is more evident in the α vs temperature curve (figure 1b). The average values of α were 3·4, 5·85, 7·55 and $12·88 \times 10^{-6}$/K in the rhombohedral, orthorhombic, tetragonal and cubic structures respectively. A systematic increase in α with temperature is expected. The temperatures at which α dips agree well with the temperatures of known phase transitions of BT.

The plot of $\Delta L/L$ with temperature recorded, while ramping up the temperature for PFN, is shown in figure 2a. At first glance, the curve appears to be consisting of two parts: a low-thermal expansion and a high-thermal expansion region. The transition from one region to another is gradual. The high temperature X-ray diffraction data also indicates a small increase in the cell parameters up to 400 K and a rapid increase thereafter (Sai Sundar and Umarji 1995). This gradual change in the thermal strain has been observed in $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$ and a solid solution of $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $PbTiO_3$ (Nomura *et al* 1975; Jang *et al* 1980).

A careful examination of the curve shows that it has three segments, although not well distinguished. However, this is more evident in the α vs temperature plot shown in figure 2b. The α slowly increases from $\sim 1 \times 10^{-6}$/K to $\sim 2 \times 10^{-6}$ K in the tempera-ture region 100–280 K before lowering to $\sim 0·5 \times 10^{-6}$/K in the temperature region of 300–360 K. Then it rapidly increases and saturates above 500 K to a value of 12×10^{-6}/K. It appears that the perovskite lattice has α of $1–3 \times 10^{-6}$/K at around 90 K and steadily reach a value of $\sim 12 \times 10^{-6}$/K at about 500 K. Any deviation from this could possibly be attributed to the ferroelectric phase transition.
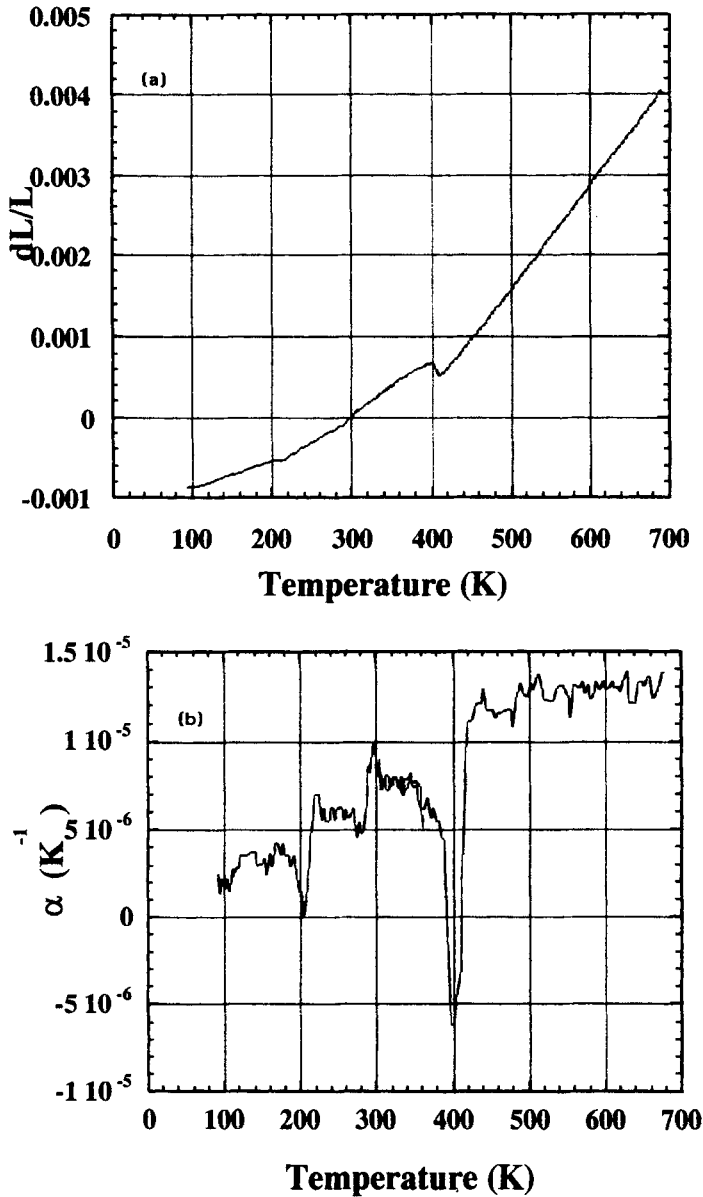
Figure 1. a. Plot of thermal strain, $\Delta L/L$ vs temperature of $BaTiO_3$ and b. plot of α, thermal expansion coefficient vs temperature for $BaTiO_3$.

We have attempted to qualitatively relate the changes in α with the phase transitions of BT in order to understand the nature of relaxor ferroelectrics.

In BT, the magnitude of decrease in α appears to be directly related to change in polarization across the phase transitions. The spontaneous polarization changes in single crystal BT are $+9.5$, $+6$ and $-18\,\mu C\,cm^{-2}$ at rhombohedral–to–orthorhombic, orthorhombic–to–tetragonal and tetragonal–to–cubic transitions respectively (Jaffe *et al* 1971). Irrespective of the sign of the change in polarization, α decreases at all
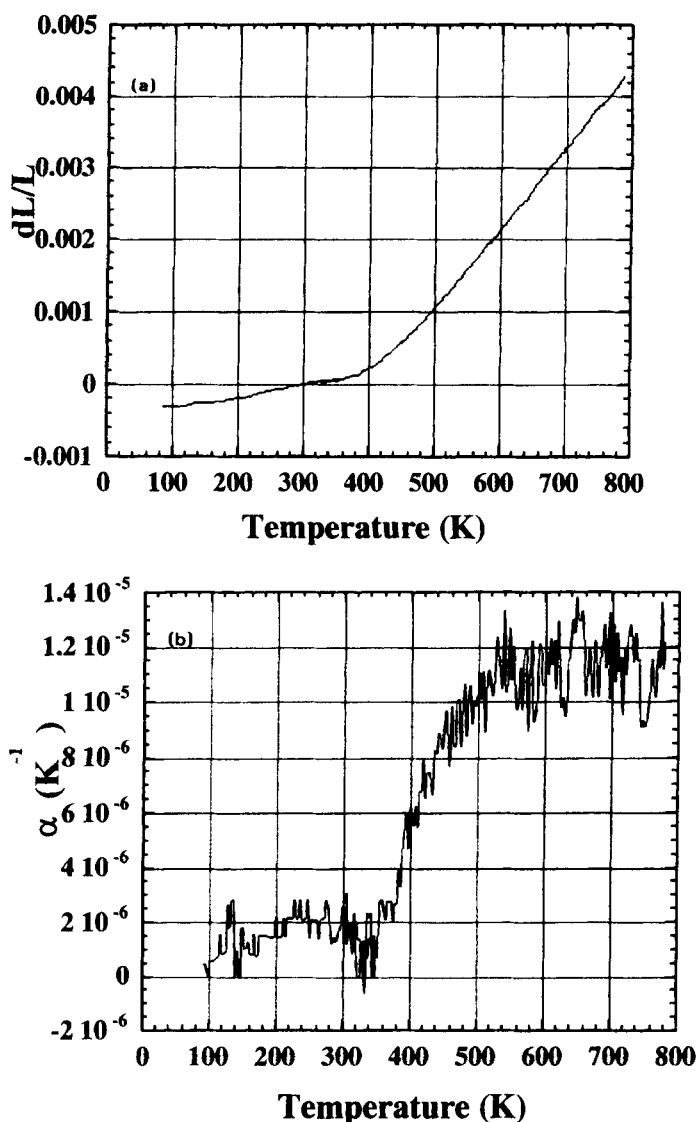
Figure 2. **a.** Plot of thermal strain, $\Delta L/L$ vs temperature of PFN and **b.** plot of α, thermal expansion coefficient vs temperature for PFN.

the three transitions. This indicates a P^2 or $|P|$ relation with α. During the first order transition, α gets affected over a very narrow temperature range (10 K) at the transition and the change is sharp.

Assuming a decrease in α to be directly related to changes in the polarization in a material, the behaviour of α of PFN indicates that the polarization changes at much higher temperatures. In case of BT, α remains $\sim 13 \times 10^{-6}$/K even about 20 K higher than T_c. In case of PFN, α starts decreasing at about 500 K, i.e. 120 K above T_m. This indicates that the polar regions develop at these temperatures in PFN. Direct evidence of polar regions in $Pb(Mg_{1/3}Nb_{2/3})O_3$ and other relaxor materials has been established

by TEM and hysteresis loop experiments (Cross 1994). However, the fact that α increases to $\sim 2 \times 10^{-6}/K$ at lower temperatures ($< 300\,K$), after attaining a low value at T_m, could be a suggestion of saturation of polarization. The total temperature region over which α deviates from the perovskite behaviour (500–300 K) indicates that the polar regions grow in this range, and, hence, a broad dielectric maxima is observed.

4. Conclusions

In summary, we have shown that α always shows a decrease at polarization changes in ferroelectric materials. Careful thermal expansion data of relaxor ferroelectric indicate polarization build up over a wide temperature range around T_m. Saturation of polarization is speculated at a point below T_m. The diffuse nature of ferroelectric phase transition is reflected in broad range of low α.

Acknowledgements

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