



Structured Diffuse Scattering and Polar Nano Regions in the Ba(Ti_{1-x}Sn_x)O₃ and Ba(Ti_{1-x}Zr_x)O₃ Relaxor Ferroelectric Systems

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The observation via electron diffraction of relatively sharp, $\mathbf{G} \pm \{001\}^*$ sheets of diffuse intensity arising from the large amplitude excitation of inherently polar, transverse optical modes of distortion in Ba(Ti_{1-x}Sn_x)O₃ (BTS), $0.1 \leq x \leq 0.5$, and Ba(Ti_{1-x}Zr_x)O₃, $x = 0.3$, samples, both at room temperature as well as liquid nitrogen temperature, show that the polar nano regions (PNR's) responsible for the observed dielectric behaviour of these relaxor ferroelectric materials correspond to the same highly anisotropic $\langle 001 \rangle$ chain dipoles as are characteristic of the normal ferroelectric end member BaTiO₃ itself. The role of the dopant Sn and Zr ions is not to directly induce PNR's but rather to set up random local strain fields preventing the condensation of long wavelength homogeneous strain distortion of the unit cell thereby suppressing transverse correlations of the $\langle 001 \rangle$ chain dipoles and the development of long range ordered ferroelectric state/s.

1. Introduction

Early transition metal d^0 cations in octahedral environments (such as *e.g.* the Ti⁴⁺ ion in the TiO₆ octahedra of BaTiO₃, KTiOPO₄ *etc.* or the Nb⁵⁺ ion in the NbO₆ octahedra of KNbO₃) have a well known susceptibility to moving off-centre in a correlated fashion giving rise to inherently polar ferroelectric materials and to paraelectric to ferroelectric phase transitions. The large peaks in dielectric constant accompanying these paraelectric to ferroelectric phase transitions are potentially very useful. A major drawback, however, is that such peaks are typically rather sharp and strongly temperature-dependent. For practical applications, it is necessary to broaden out these peaks in permittivity while still maintaining as high a magnitude as possible. The traditional way of achieving this is to chemically substitute inherently ferroelectric materials such as *e.g.* BaTiO₃ with appropriate dopants to give rise to so-called Relaxor Ferroelectrics (RFE's) such as Ba(Ti_{1-x}Sn_x)O₃ (BTS) or Ba(Ti_{1-x}Zr_x)O₃ (BTZ). Above a certain level of dopant ions, such relaxor systems exhibit a so-called "diffuse phase transition" (at T_m , see Fig.1 below), believed to be induced by compositional heterogeneity on the nanometer length scale, and hence maintain relatively high dielectric constants which do not vary too markedly over a much larger temperature range. The physical mechanism underlying these "diffuse phase transitions" (DPT's) has been of intense and continuing interest [1,2] ever since the pioneering work of Smolenskii [3].

2. Experimental

A series of Ba(Ti_{1-x}Sn_x)O₃, $x = 0.10, 0.20, 0.25, 0.30$ and 0.50 (labelled BTS10, BTS20, BTS25, BTS30, and BTS50 hereafter) powder samples as well as a Ba(Ti_{1-x}Zr_x)O₃, $x = 0.30$ (labelled BTZ30) powder sample were synthesized via conventional solid state reaction using reagent grade BaCO₃, SrCO₃, TiO₂ and SnO₂ or ZrO₂ as starting materials. The resultant samples were all single phase and metrically cubic. Powder samples were ground, pelleted and annealed at 1400 °C for 2h. The pellets were then polished on both sides and coated with

silver paste for dielectric measurements using a high precision LCR meter (HP4284A). Their relative density was typically > 95% while the average grain size was ≈ 1.0 μm .

3. Results

3.1 Dielectric measurements

Fig. 1 shows the measured temperature-dependent permittivities of the BTS10, 20, 25, 30 and 50 samples from room temperature up to 200°C. Note the systematic lowering of T_m and the broadening of the peak in permittivity at T_m with increasing Sn content. Note also that the peak in permittivity becomes noticeably frequency dependent for $x > 0.2$.

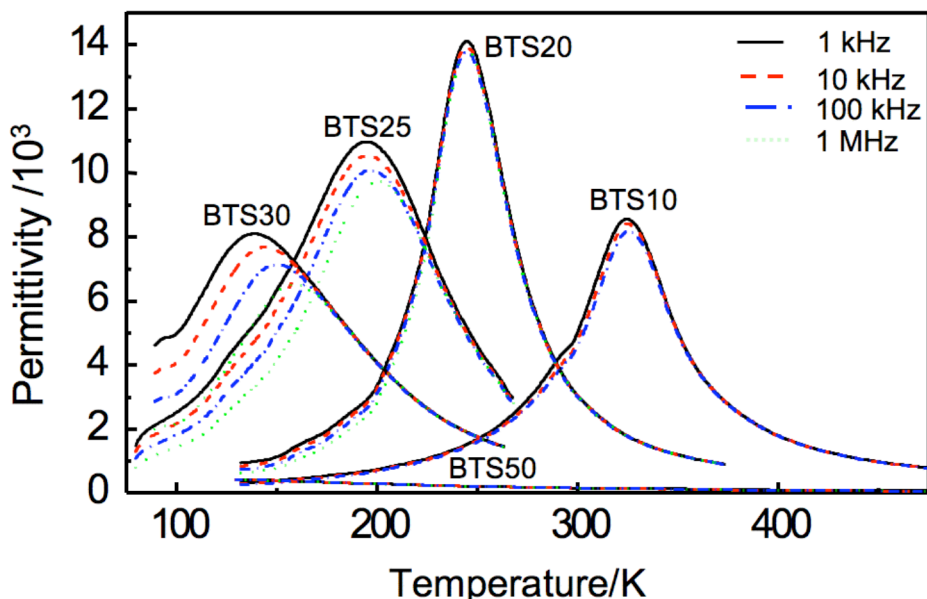


Fig. 1. Measured temperature-dependent permittivities of the BTS10, 20, 25, 30 and 50 samples from room temperature up to 200°C.

3.2 Electron Diffraction results

Very similar structured diffuse scattering, in the form of transverse polarized, quite sharp, $\{001\}^*$ sheets of diffuse intensity were observed right across the BTS, $x \neq 0.1$, solid solution as well as for the BTZ ($x = 0.30$) sample, both at room temperature as well as at low (liquid nitrogen) temperature (see Fig. 2).

Fig. 2. (a) $\langle -1, 5, 0 \rangle$ zone axis EDP of BTS10 at liquid nitrogen temperature. (b) a typical $\langle 1, 2, 0 \rangle$ zone axis EDP of BTZ30.



Note that the zero magnitude component of the individual $\mathbf{q} = \langle h k 0 \rangle^*$, h, k continuous, modulation wave-vectors (constituting these $\{001\}^*$ sheets of diffuse intensity) along the orthogonal $\langle 001 \rangle$ real space directions regardless of composition, *i.e.* regardless of the Ti/Sn or Ti/Zr composition ratio rules out the possibility of Sn/Ti or Zr/Ti compositional ordering being responsible for the the observed diffuse distribution. Rather characteristic extinction conditions associated with the diffuse distribution [4,5] *e.g.* the fact that $F(\mathbf{G} + \mathbf{q}) \sim 0$ at $(\mathbf{G} + \mathbf{q}) = [2, 1, 0 + \square]^*$, $[2, 1, 1 + \square]^*$, $[4, 2, 0 + \square]^*$ and $[4, 2, 1 + \square]^*$ *etc.* (see Fig.2b) require that these $\{001\}^*$ sheets of diffuse intensity arise from individual inherently polar, transverse optical, displacive modes of distortion giving rise to what are, in effect, 1-d PNR's (see [5] and Fig.3 below for details). Note that from the diffraction point of view, these polar displacive modes of distortion could be either static or dynamic in nature. Whether static or dynamic, however, the diffraction evidence clearly demonstrates extremely anisotropic, anti-correlated behaviour of the off-centre displacements of the Ti and O ions ultimately responsible for the observed dielectric behaviour of BTS.

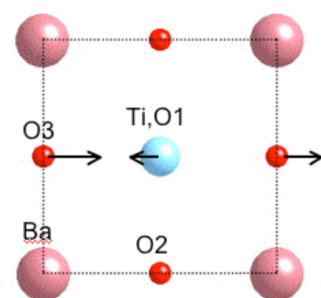


Fig. 3. Shows the 5 distinct ions per parent perovskite unit cell of BTS or BTZ: Ba at 0,0,0; $\text{Ti}_{1-x}\text{Sn}_x$ or $\text{Ti}_{1-x}\text{Zr}_x$ at $1/2, 1/2, 1/2$; O1 at $1/2, 1/2, 0$; O2 at $1/2, 0, 1/2$ and O3 at $0, 1/2, 1/2$ along with the relevant inherently polar displacive shifts along $\langle 100 \rangle$ deduced from extinction conditions associated with the observed diffuse distribution.

The diffuse phase transitions apparent in these BTS and BTZ samples (see Fig.1) are thus clearly not a result of a DPT into a long range ordered ferroelectric state below T_m but rather are a result of a dynamic freezing or glass-like transition [1,2] involving the slowing down of the dipolar dynamics of the 1-d PNR's implied by the existence of the structured diffuse distribution. This suggests that the prime role of the dopant ions is not to introduce the PNR's. Rather the role of the dopant ions appears to be to set up random local strain fields thereby suppressing homogeneous long wavelength strain distortion of the underlying cubic lattice, the transverse correlation of the pre-existing static 1-d PNR's (below T_m) and a transition into a long range ordered ferroelectric state.

Acknowledgments

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