Enhanced piezoelectric response near the morphotropic phase-boundary in lead-free $(Na,Bi)TiO_3$-$BaTiO_3$

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Lead-free $Na_{1/2}Bi_{1/2}TiO_3$ (NBT) piezoelectrics have received much attention due to environmental concerns associated with traditional lead-containing piezoelectric compounds [1-5]. Structural investigations by x-ray diffraction (XRD) and neutron diffraction have revealed a morphotropic phase boundary (MPB) in the NBT-x%BaTiO3 (NBT-x %BT) solid solution for 6<x< 7, where piezoelectric coefficients as high as 480 pC/N have been reported [6]. The behavior as function of composition (x) and temperature is summarized in the phase-diagram of figure 1. The NBT-BT system exhibits a MPB around x=6%, between the R and T phases. This overall behavior is reminiscent of that seen in lead-containing compounds such as $Pb(Mg_{1/3}Nb_{2/3})O_3 - PbTiO_3$ (PMN-PT) and $Pb(Zn_{1/3}Nb_{2/3})O_3 - PbTiO_3$ (PZN-PT), which have been thoroughly studied owing to their good piezoelectric properties. However, the fundamental properties and microscopic mechanisms leading to the large piezoelectric response of NBT-BT have been much less studied. In addition, *there is a fundamental difference between the lead-based compounds, in which cation disorder is on the B-site of the ABO_3 perovskite structure, while the lead-free NBT-BT exhibits cation disorder in the A-site*. The impact of this fundamental difference on the lattice dynamics and the ferroelectric properties are currently not well understood.

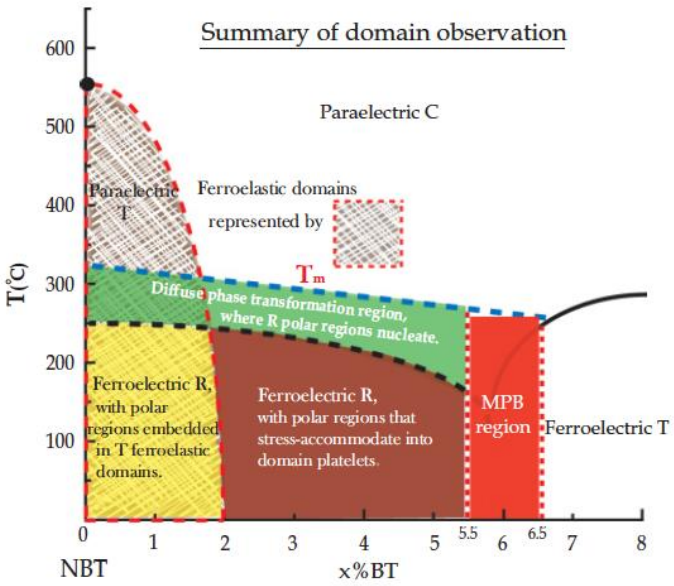

Figure 1 Phase-diagram of NBT-x %BT (from [5]).

Neutron diffuse scattering and inelastic scattering measurements are powerful techniques to unravel the microstructure and mechanisms underpinning the bulk piezoelectric behavior [7,8]. A recent study of neutron diffuse scattering comparing NBT and PMN reported both similarities and differences in the geometry of the diffuse scattering and the morphology of polar nanoregions [7]. This study found prominent ridges in the elastic diffuse scattering intensity contours that extend along <110>, with the same zone dependence as in PMN and other lead-based relaxors. These ridges disappear gradually on heating above the cubic-to-tetragonal phase transition temperature, T_{CT} = 523°C. It was concluded that <110>-oriented ridges are a relaxor-specific property. In addition, further ridges were also identified, which are perhaps more related to those seen in $BaTiO_3$ and $KNbO_3$, and could be related to either correlated off-centerings or anisotropic transverse acoustic phonons. This latter point remains to be elucidated.

In this experiment, which will start on Dec 15, we will focus on compositions x=4% and 6%, corresponding to the ferroelectric R phase and the MPB region, respectively (Fig. 1).

We propose to measure the phonon dispersions in single-crystals of NBT-x%BT across the morphotropic phase boundary, and correlate our results with diffuse scattering measurements, as well as piezo-force and electron microscopy measurements, to identify changes in lattice dynamics associated with the large piezoelectric response at the MPB.

We will focus on low-energy optic and acoustic phonons, which are the dominant contributors to the diffuse scattering signal. Specifically, we will map the TA and TO branches. The TO ferroelectric mode is expected to dip to very low energies at the zone center, although it can be quite steep. For this reason, we plan to use two incident energies Ei=27meV and Ei=15meV, which are both free of prompt-pulse contamination on HYSPEC, and have favorable neutron flux. The higher Ei will enable us to access phonon dispersions in Brillouin zones (0,0,2), (1,1,1), and (2,2,0), while the lower Ei will enable high resolution in (1,1,1).

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