

Distribution of Local Structures in Lead-free Relaxor Ferroelectrics: (Bi_{1/2}Na_{1/2})TiO₃-BaTiO₃ Investigated with ²³Na NMR

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The structural features underlying the relaxor state and its electrical properties are still not fully understood, mainly due to the small magnitude of structural distortions and their lack of long coherence length. If one aims at a deeper understanding of relaxor ferroelectrics, characterization techniques sensitive to the local scale are highly desirable. Solid-state nuclear magnetic resonance (NMR) is a technique that fulfills these requirements but has been too little explored in the materials science community. Hence, we applied NMR to investigate structure-property relations in complex perovskites with formula (100-x)(Bi_{1/2}Na_{1/2})TiO₃-xBaTiO₃ (BNT-xBT) as a function of barium content and electric state.

By comparing ²³Na NMR spectra of BNT-xBT samples before and after electric poling, we reveal the coexistence of cubic and non-cubic phases for relaxor compositions. The cubic phase content, which may reach up to 25% for BNT-6BT, disappears after the establishment of ferroelectric order by electric poling, while the remaining phase exhibits barely any change in its local symmetry.

Furthermore, the shape of ²³Na 3QMAS NMR spectra indicates the non-cubic phase exhibits a disordered local structure characterized by a distribution of a specific spectral parameter (EFG). DFT calculations demonstrate this parameter is mostly influenced by tilting of oxygen octahedra. This fact indicates BNT-xBT materials present octahedral tilt disorder, which cannot be explained by the coexistence of two tilt systems. Moreover, the extent of disorder varies as a function of barium content and shows a correlation to frequency dispersion in ε(T). This fact suggests that octahedral tilting disorder is a local structural feature concurrent with the relaxor behavior in BNT-xBT materials.