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Microstructural Origin of Morphotropic Phase Boundary and Magnetic Ordering in the Multiferroic BiFeO3-PbTiO3

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Abstract : The morphotropic phase boundary (MPB) in the magnetoelectric (1-x)BiFeO3-(x)PbTiO3 has remained a matter of controversy ever since its discovery in 1964. The nature of the phase stabilized (single phase tetragonal or coexistence of tetragonal and rhombohedral phases) is very sensitive to the slight changes in the synthesis conditions. It thus remained an enigma as to what is the essential physical factor which is controlled by the slight difference in the synthesis conditions that finally determines, whether the phase formed will be single phase or coexistence of phases. In this paper, we demonstrate that the nature of the phase stabilized in this system is uniquely dependent on the crystallite size. The system is shown to exhibit features of abnormal grain growth (AGG) during sintering with abrupt increase in the grain size from ~ 1 micron to ~ 10 microns. The 10 micron grains exhibit pure tetragonal phase while the 1 micron grains exhibit coexistence of rhombohedral and tetragonal ferroelectric phases. The Rietveld analysis of powder neutron diffraction shows a paramagnetic to antiferromagnetic order transition inducing with crystalline size reduction from 10 micron to 1 micron. Since tetragonal phase is known to have paramagnetic order and rhombohedral phase has antiferromagnetic order in room temperature, this further strengthens our argument of size induced structure transition.

Keywords : size driven MPB, size driven magnetic ordering, abnormal grain growth, phase formation in BF-PT system
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