Evidence for pressure induced 'morphotropic like' phase transition with concomitant octahedral tilting and emergence of a 'reentrant ferroelectric' phase in super-tetragonal phase of $0.5BiFeO_3$-$0.5PbTiO_3$ solid solution system

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Pressure induced structural phase transitions in oxide perovskites have received enormous interest as it can be utilized to tune many physical properties like piezoelectric coefficients, resistivity and ferroelectric polarization etc. $PbTiO_3$ (PT) is one such model compound whose high pressure behavior is a topic of extensive research in recent years because of its technological importance in the electronics industry as the end member of most of the commercial piezoelectric compositions [1]. However, the structural phase transition sequence of PT at high pressures has remained controversial with two entirely different propositions. As per the first principles calculations of Wu & Cohen [2] and subsequent experimental studies [3], pressure can induce polarization rotation in tetragonal ferroelectric PT much in the same way as the composition does in the morphotropic phase boundary (MPB) based commercial piezoelectric solid solution systems. First principles calculations of Kornev and his co-workers [4] present a completely different picture whereby PT undergoes a pressure induced antiferrodistortive (AFD) structural phase transition, albeit with decreasing tetragonality, until a 'pseudo-cubic' like non-ferroelectric phase appears which is followed by the emergence of a reentrant ferroelectric phase at still higher pressures. However, the evidence for AFD superlattice reflections were not observed at moderate pressures. In an attempt to address these controversies, we present here results of a high pressure structural phase transition study on a tetragonal composition of $PbTiO_3$ solid solution containing 50% $BiFeO_3$ (PT-0.5BF) using synchrotron x-ray diffraction measurements carried out at P02.2 Extreme Conditions beamline of PETRA III at DESY. We have chosen this tetragonal solid solution composition to enhance the AFD instability [5]. We have shown that even at quite moderate values of pressure (~2.15 GPa), the tetragonal P4mm phase of PT-0.5BF system transforms to monoclinic Cc phase which permits MPB type rotation of ferroelectric polarization vector as well as oxygen octahedral tilting induced by a concomitant AFD transition (see Fig. 1). This is the first observation of superlattice reflections in PT based system at the theoretically predicted moderate pressures. On increasing the pressure further, the monoclinic distortions and the ferroelectric polarization start decreasing acquiring a pseudo-cubic character at intermediate pressures as expected on the basis of Samara's criterion [6] (see Fig. 2). After a critical value of pressure (~7 GPa), they start increasing which suggests another phase transition which is isostructural in nature. Oxygen octahedral tilting provides an efficient mechanism for accommodating volume reduction in this reentrant ferroelectric phase. Our results show that the DFT based predictions of both the groups [2,4] are correct in parts but none of the two provides the complete picture. Our results not only resolve the existing controversies but also provide an insight towards designing of new environmentally friendly Pb-free piezoelectric compositions.

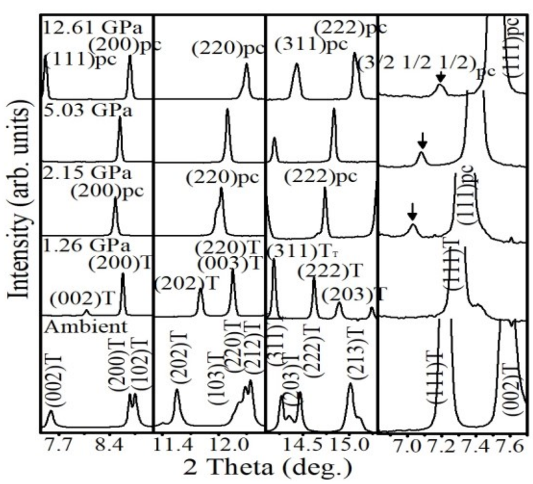

Figure 1. Evolution of characteristic perovskite reflections and (3/2 1/2 1/2)pc superlattice reflection with increasing pressure.

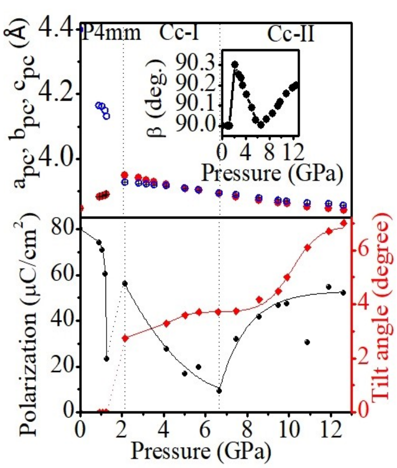

Figure 2. Variation of pseudo-cubic unit cell parameters, spontaneous polarization and tilt angle with pressure [5].

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