Structure and properties in the $K_{0.5}Bi_{0.5}TiO_3$ - $BiFeO_3$ (KBT –BF) solid solution

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The perovskite compounds ABO_3 are one of the most common oxide structures and thus have been extensively studied. Indeed, they present a very large panel of interesting physical properties (ferroelectricity, piezoelectricity, superconductivity ...) [1]. Some of them also present magnetic properties and are thus potentially multiferroic. Multiferroic materials are widely investigated nowadays, because they constitute an exciting challenge in the field of physics and solid state chemistry. Among them, $BiFeO_3$ (BF) appears actually as one of the most interesting [2]. At room temperature, BF is a rhombohedral perovskite (R3c), presenting both ferroelectricity and an antiferromagnetic order (T_N = 640K). For a lot of perovskite materials, the formation of solid solutions is a classical way to modulate and control the physical properties. In the particular case of boundary between rhomboedral and tetragonal symmetry, like in PZT materials, a peculiar behavior is frequently evidenced, called "Morphotropic Phase Boundary" (MPB), for which the properties are improved, compared to those of pure compounds [1]. Since BF presents rhomboedral symmetry, such behavior could be expected by solid-solution formation with a tetragonal compound. For this purpose, we selected the $K_{0.5}Bi_{0.5}TiO_3$ (KBT) compound (space group P4mm), a lead-free material presenting interesting dielectric and ferroelectric - piezoelectric properties [3]. A KBT-BF solid solution is thus formed, corresponding to chemical substitution in both A-site and B-site of the perovskite lattice. For the BF-rich range of this system, a structural transformation from pseudo-cubic to rhomboedral symmetry was evidenced by Matsuo & al. around 60% BF [4] and considered as being a Morphotropic Phase Boundary. The compositions between 40 and 60% BF were assigned to pseudo-cubic symmetry but also presented ferroelectric properties. In addition, this study didn't report structural results for the tetragonal KBT-rich part of the solid solution. As a consequence, the structural evolution for this solid solution appears as not totally understood.

Thus the aim of the present work is (i) to investigate the structural evolution in the KBT-BF solid solution for a larger range of composition and (ii) to improve the understanding of the relationships between structure and properties. The structural evolution was investigated by X-ray diffraction and Rietveld analysis. The dielectric properties were studied on ceramic samples by impedance spectroscopy and measurement of the ferroelectric cycles. X-ray diffraction patterns confirmed that the mean lattice parameter increase with BF content, according to the ionic radii of K^+/Bi^{3+} (A-site) and Ti^{4+}/Fe^{3+} (B-site) ions . But Vegard's law is not followed, evidencing a non-continuous evolution. Rietveld analysis confirmed the progressive change from tetragonal to rhomboedral symmetry, according to reported results. Finally, the evolution of the properties was determined, confirming the structural evolution. This solid - solution appear thus as very interesting in order to improve the understanding of the structure / properties relationships for the Bi-based perovskite compounds.

References

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