High-pressure stabilized oxide perovskite structures

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Remarkable properties of the lead zirconate-titanate and other complex oxides with the perovskite-type structure motivated researchers to search for new ABO_3 compounds with the lone electron pair of *A*-site cation. It turned out that many very promising compositions containing Pb^{2+} or Bi^{3+} do not crystallize in perovskite structure at ambient pressure. Some of those compositions require elevated pressures to transform into the perovskite phase from a single-phase but less compact polymorphs; others form the perovskite compounds under high-pressure & high-temperature conditions only [1]. Beginning with the successful high-pressure synthesis of $BiMnO_3$ and $BiCrO_3$ [2] in the middle of sixties in the last century, a great number of simple and complex perovskite compounds with unique combinations of atomic orderings, oxygen octahedra tilts, atomic displacements and magnetic structures has been produced using the high-pressure & high-temperature technique. High-pressure stabilized Mn_2O_3 perovskite with Mn^{2+}/Mn^{3+} in *A*-sites and Mn^{3+}/Mn^{4+} in *B*-sites is one of most prominent recent examples [3]. The unique feature of this binary perovskite that all the *A*- and *B*-site cations can be magnetically and electrically active, thus leading to an interplay of multiple structural and electronic instabilities. Another outstanding example is Cu-substituted $BiMn_7O_{12}$ perovskite synthesized under high-pressure [4]. In the case of the particular (x=0.1) composition of the $BiCu_xMn_{7-x}O_{12}$ series, the competing interactions arising from the orbital ordering and the stereochemically active lone pair electrons result in the onset of the structural modulation with a complex helical ordering of electric dipoles.

We have recently demonstrated the phenomenon of annealing-stimulated irreversible transformations of the high-pressure stabilized phases (conversion polymorphism) [5] as a new and promising approach to produce novel multiferroic materials. In particular, it has been shown that conversion is the only way to stabilize some of the polymorphs in a bulk form and these polymorphs exhibit unique properties.

Here we report on reversible and irreversible transformations between metastable phases of the Bi-containing perovskite solid solutions $BiFeO_3$-$BiScO_3$, $BiFeO_3$-$BiCrO_3$ and $BiMg_{0.5}Ti_{0.5}O_3$-$BiZn_{0.5}Ti_{0.5}O_3$ below their decomposition temperature. New perovskite polymorphs with interesting combinations of ferroic orders are compared and discussed.

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