Ferroelectric and high-low spin transition by MEM using single-crystal and X-ray emission to 100GPa
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Many AB2O3 spinels transform to post-spinel structures without decomposition. Three structures of CaMn2O4 (Pmnab), CaFe2O4 (Pnma) and CaTi2O4 (Bbmm) have been reported as post-spinel phases. Structure studies were conducted under high pressure using SR. CaMn2O4 transforms to CaTi2O4 type structure at about 30GPa. MnO6 octahedron is distorted by the Jahn-Teller effect induced from Mn2+ (3d4) in the octahedral site. X-ray emission study at APS has been executed to discloses high-low spin transition of CaMn2O4 up to 100GPa. The spin transition gradually proceeds from 50GPa and then mixed spin states at 80GPa. Low-spin state is confirmed at 85GPa. A new phase is found by powder diffraction at 82 GPa. This structure (Pnam) is produced via martensitic transformation by displacing atoms in every three layers perpendicular to the c-axis. Four independent sites of Mn atoms yield the different spin transition pressures. PbTiO3 tetragonal perovskite structure (P4mm) at ambient conditions transforms cubic (Pm3m) at about 12GPa, which induces the transition from ferroelectric to paraelectric. Electron density distribution analysis is performed by maximum entropy method (MEM) using single-crystal diffraction intensities up to 12GPa taken at PF and up to 35GPa by two-circle diffractometer with IP at APS. Pressure dependence of the static dipole moment is elucidated by charge density analysis. MEM provides the split atom model of Ti and oxygen atoms in the direction to the c-axis and in the cubic phase no more splitting was observed. The split is generated from the statistical distribution of atoms or domain structures. The split becomes gradually smaller with increasing pressure. This is an intrinsic phenomenon in PbTiO3. Polarization in PbTiO3 is partly canceled.

Keywords: X-ray emission spectroscopy, maximumentropy method, ferroelectrics

Piezoplastic distortion of PbBi2S6, a reversible phase transition with migration of chemical bonds
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The compound PbBi2S6 was investigated by X-ray diffraction on single crystals in diamond-anvil cell between 0.0001 and 10.5 GPa. It undergoes a first-order phase transition at hydrostatic pressure between 3.7 and 4.9 GPa. The space group symmetry changes from Bbmm to Pbnm and the unit-cell volume decreases by 4 %. The transition is strongly anisotropic, with a contraction along one of the crystal axes by 16% and expansion along another one by 14%. This is the first recorded example of a piezoplastic phase transition, a displacive pressure-induced phase transition with a systematic shearing of atomic planes and migration of chemical bonds in the structure. In the case of PbBi2S6, the transition is achieved by the change of the archetypal architecture of the structure-building modules from a PbS-like to the SnS-like arrangement and a loss of mirror planes on the contact surfaces of modules. The phase transition is reversible with a preservation of the single crystal, which is a result of the stereochemical influence and migration of the s lone electron pairs of Pb and Bi.

Keywords: high pressure, single crystal diffraction, compression behaviour

Phase transition in AgInTe2 under high pressure
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