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Ferroelectric and high-low spin transition by MEM using single-crystal and X-ray emission to 100GPa

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Many AB_2O_4 spinels transform to post-spinel structures without decomposition. Three structures of $CaMn_2O_4$ (*Pmab*), $CaFe_2O_4$ (Pnam) and $CaTi_2O_4$ (*Bbmm*) have been reported as post-spinel phases. Structure studies were conducted under high pressure using SR. $CaMn_2O_4$ transforms to $CaTi_2O_4$ type structure at about 30GPa. MnO6 octahedron is distorted by the Jahn-Teller effect induced from Mn^{3+} (3d4) in the octahedral site. X-ray emission study at APS has been executed to discloses high-low spin transition of $CaMn_2O_4$ 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 martensic 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. $PbTiO_3$ tetragonal perovskite structure (*P*4*mm*) at ambient conditions transforms cubic (*Pm*3*m*) 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 $PbTiO_3$. Polarization in $PbTiO_3$ is partly canceled.

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

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Piezoplastic distortion of $Pb_3Bi_2S_6$, a reversible phase transition with migration of chemical bonds

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The compound $Pb_3Bi_2S_6$ 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 $Pb_3Bi_2S_6$ 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^2 lone electron pairs of Pb^{II} and Bi^{III}.

Keywords: phase transitions and structure, high-pressure phase transitions, piezoplastic phase transition

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Anomalous compression behaviour of $GdPO_4$-monazite

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We present the first compression study of monazite. This study is also one of the first single crystal diffraction studies to above 40 GPa and illustrates that single crystal data collected over such an extended pressure range provide volumetric data of sufficient accuracy to constrain K0' as well as they allow for distinguishing between different forms of EOS such as the Birch-Murnaghan- and Rydberg-potential based EOS. The monazite structure is common at high pressure among ionic compounds of stoichiometry ABO_4. However, there are no compression studies to above 1 GPa on monazite itself in spite of the fact that this mineral is an abundant carrier of Th and lanthanides in the Earth as well as the importance of the monazite structure at high pressure. Our experiments were conducted on flux-grown single crystal specimens of $GdPO_4$ loaded in a helium pressure medium. Diffraction data were collected at beamline 13 BMD at the APS with 45 keV primary beam energy and an IP detector. Images were collected at different omega angles and upon oscillation of omega. The GSE-ADA and RSV software by P.Dera was used for peak fitting and indexing. Typically 140 to 180 reflections were observed and indexed. The reduction of volume remains almost linear over this whole pressure interval with a slight negative curvature above 30 GPa. This decrease in compressibility and the almost linear behaviour over a 20% of volume compression are rather unexpected: A small K0' is typical for materials with high bulk modulus (> 200 GPa) while monazite has a bulk modulus of 82 GPa. We discuss this unexpected finding with respect to a) the compression mechanism in monazite, b) validity of different EOS such as continuum-theory - and Rydberg- or Morse-potential based EOS.

Keywords: high pressure, single crystal diffraction, compression behaviour

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Phase transition in $AgInTe_2$ under high pressure

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