

P20.03.06*Acta Cryst.* (2008). A64, C608**Ferroelectric and high-low spin transition by MEM using single-crystal and X-ray emission to 100GPa**Takamitsu Yamanaka¹, Takahiro Kuribayashi^{1,5}, Ho-kwang Mao¹, Russel J Hemley¹, Jinfu Shu¹, Hanns P Liermann², Weng Yang², Yu-ming Xiao², Premek Dera³, Wendy Mao⁴¹Carnegie Institution of Washington, Geophysical Laboratory, 5251 Broad Branch Road NW, Washington, DC, 20015-1305, USA, ²HPCAT Argonne National Laboratory, ³GSECARS Argonne National Laboratory, ⁴School of Earth Science, Stanford University, ⁵Department of Earth Science, Graduate School of Science, Tohoku University, E-mail : t.yamanaka@kce.biglobe.ne.jp

Many AB₂O₄ spinels transform to post-spinel structures without decomposition. Three structures of CaMn₂O₄ (*Pmab*), CaFe₂O₄ (*Pnam*) 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 Mn³⁺ (3d⁴) in the octahedral site. X-ray emission study at APS has been executed to disclose 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, maximum entropy method, ferroelectrics

P20.03.07*Acta Cryst.* (2008). A64, C608**Piezoplastic distortion of Pb₃Bi₂S₆, a reversible phase transition with migration of chemical bonds**

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The compound Pb₃Bi₂S₆ 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 Pb₃Bi₂S₆ 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 s² lone electron pairs of Pb^{II} and Bi^{III}.

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

P20.02.09*Acta Cryst.* (2008). A64, C608**Anomalous compression behaviour of GdPO₄-monazite**Oliver D Tschauner¹, Przemyslaw Dera², Barbara Lavina^{1,2}, Lauren Borkowski^{1,2}¹University of Nevada Las Vegas, High Pressure Science and Engineering Center, Department of Physics, 4505 Maryland Parkway, Las Vegas, Nevada, 89514, USA, ²University of Chicago, GSECARS, S Cass Ave., Argonne, Illinois 94682, USA, E-mail : olivert@physics.unlv.edu

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 ABO₄. 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 GdPO₄ 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

P20.03.10*Acta Cryst.* (2008). A64, C608-609**Phase transition in AgInTe₂ under high pressure**Thiti Bovornratanaraks¹, Komsilp Kotmool¹, Malcolm I McMahon², David J Ruffolo³¹Chulalongkorn University, Physics, Phayathai Road, Patumwan, Bangkok, Bangkok, 10330, Thailand, ²School of Physics and Centre for Science at

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The structural phase transformations in the chalcopyrite semiconductor AgInTe₂ have been studied up to 10 GPa on both pressure increase and decrease. The experiment were carried out using angle-dispersive X-ray diffraction with synchrotron radiation and an image plate. The diffraction patterns of AgInTe₂ at ambient pressure reveal two coexisting phases: the first has the chalcopyrite structure while the second has a zinc blende like structure. On pressure increase both phases transformed at 3-4 GPa to a cation-disordered structure with spacegroup Cmcm, the atomic coordinates of which $v=0.75$ for Ag or In and $v=0.25$ for Te - correspond to a NaCl-like structure. On pressure increase the Cmcm phase was stable up to at least 10.25 GPa. On pressure decrease, the chalcopyrite phase started to reappear at 0.55 GPa, and the Cmcm phase disappeared completely at ambient pressure. In addition to the experimental study, we have also performed density functional theory calculations. The calculated transition pressure from the chalcopyrite phase to the Cmcm phase is 4.08 GPa, and the calculated atomic positions in the Cmcm phase are in excellent agreement with those determined experimentally.

Keywords: diamond anvil cells, X-ray diffraction, *ab-initio* calculations

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High-pressure behavior of iron-nickel phosphides and its implications for meteorites and Earth core

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Minerals with composition (Fe,Ni)_xP, are rare, but important accessory phases present in iron, and chondrite meteorites. The occurrence of these minerals in meteoritic samples is believed to originate either from the equilibrium condensation of protoplanetary materials taking place in solar nebulae or from crystallization processes in the cores of parent bodies. Fe-Ni phosphides are considered an important candidate for a minor phase present in the Earth core, and at least partially responsible for the observed core density deficit with respect to pure Fe. We report results of high-pressure high-temperature single-crystal X-ray diffraction experiments with a range of materials belonging to the (Fe,Ni)_xP family, including Fe₃P, Fe₂P, and Ni₂P. A new phase transition to the Co₂Si-type structure (allabogdanite) has been found in Fe₂P at 8.0 GPa, upon heating. The high-pressure phase can be metastably quenched to ambient conditions at ambient temperature, and then, if heated again, transforms back to barringerite. Contrary to the recent reports, we find Fe₃P to remain stable in the schreibersite structure up to at least 60 GPa and 2000 K. Our results indicate that the presence of allabogdanite in meteoritic samples places two important constraints on the thermodynamic history of the meteorite. First, it imposes a minimum pressure and temperature for the formation of the Fe₂P, and additionally rules out any higher temperature low pressure alterations. If present in the Earth core, Fe₂P will have the allabogdanite rather, than barringerite structure. Crystal chemical

trends in the compressibility and thermal expansion of (Fe,Ni)_xP compounds, as well as polymorphic transition paths are analyzed in the context of the Earth's core composition and properties.

Keywords: Earth core, phase transitions, high pressure

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High-pressure and low-temperature charge density study of Pr_{1-x}Ca_xCoO₃ by SR powder diffraction

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The Pr_{1-x}Ca_xCoO₃ system exhibits a phase transition from a conductive to an insulating state with decreasing temperature under high pressure. The transition has found in the very narrow region of $x \sim 0.5$ at ambient pressure. Similar transition has also found in the wide x region under high pressure. No indication of this kind of transition has been observed in other species of R and A in the R_{1-x}A_xCoO₃ system (R = rare earth elements; A = Ca, Ba and Sr). The structural change through the pressure-induced phase transition under high pressure has never been determined. To investigate the structural change and the role of Pr and Ca in the pressure-induced phase transition, we carried out the high-pressure and low-temperature structural study of Pr_{0.7}Ca_{0.3}CoO₃ by the synchrotron radiation (SR) powder diffraction. The phase transition from a conductive to an insulating state has been found above 1.0 GPa for Pr_{0.7}Ca_{0.3}CoO₃ by the electrical resistivity measurement. The SR powder diffraction data of Pr_{0.7}Ca_{0.3}CoO₃ were collected at SPring-8 BL10XU beamline. The sample pressure and the temperature were controlled by the He-gas flow type cryostat combined with a He-gas driven diamond anvil cell (DAC). A change of the diffraction pattern indicating the structural phase transition was observed around 100 K at 1.3 GPa. The electron charge density distributions and the crystal structures were determined by the MEM/Rietveld analysis. It was revealed that the covalency of Pr/Ca-O bond is increased in the low-temperature phase. This fact implies that the Pr 4f-O 2p orbital hybridization contributes to the stabilization of the low-temperature insulating phase.

Keywords: high pressure, charge density, Co oxides

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Synthesis and structure of new platinum hydrides at high pressure

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