

$P6_3mc$) and 80K ($P6_3mc \rightarrow Cmc2_1$). In the $P6_3mc$ phase, the V(1) O_6 octahedra form trimers with a regular triangular shape, below 80K they distort into isosceles triangles [1]. Below 64.2K, NaV_6O_{11} exhibits a uniaxial magnetic anisotropy [2]. We performed low-temperature (down to 8 K at 10^{-4} GPa) and high-pressure (up to 8.06 GPa at 298 K) powder and single-crystal x-ray diffraction in the home laboratory and at different synchrotron sources and could confirm the stability of the $Cmc2_1$ phase from 80 to 8 K. The high pressure data show that the hexagonal lattice is stable at least to 8.06 GPa at $T = 298$ K. The refinement of the single-crystal data based on symmetry mode analysis indicates the $P6_3/mmc \rightarrow P6_3mc$ phase transition below 1 GPa. The volume of the V(1) O_6 octahedron is almost independent of the pressure. The V(2) O_6 octahedron expands, while the V(3) O_6 polyhedron shrinks on compression. In addition, the V(2)-V(2) distance shrinks. These observations indicate possible pressure-induced electron transfer from the V(3) to the V(2) cations. Symmetry mode analysis may serve as an aid for the restricted refinement of diffraction data with a small reflection-to-parameter ratio. As high-pressure data generally suffer from this problem, the potential of this method will be explored.

[1] Y. Kanke et al., J. Solid State Chem. 112, 429, 1994.

[2] Y. Uchida et al., J. Phys. Soc. Jpn. 60, 2530, 1991.

Keywords: phase transitions, mixed-valence transition-metal compounds, high-pressure crystallography

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A study of the octahedral tilting / cooperative Jahn-Teller transition in $(Sr_{0.8}Ce_{0.2})MnO_3$

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Previous room temperature measurements on the system $(Sr^{2+_{1-x}}Ce^{3+}_x)(Mn^{4+_{1-x}}Mn^{3+}_x)O_3$ have shown a Jahn-Teller distortion of the MnO_6 octahedron that is significant at $x=0.1$ (10% of the active Mn^{3+} ion) but diminishes, somewhat unexpectedly, as the concentration of Mn^{3+} is increased [1]. We have explored the effect further through comparative variable temperature diffraction studies on $(Sr^{2+_{0.8}}Ce^{3+_{0.2}})(Mn^{4+_{0.8}}Mn^{3+_{0.2}})O_3$ and $(Sr^{2+_{0.8}}Ce^{3+_{0.2}})(Mn^{4+_{0.8}}Co^{3+_{0.2}})O_3$ - the former contains a JT active ion (Mn^{3+}) whereas the latter does not. Both compounds show a transition from a cubic structure in $Pm-3m$ (no tilting) to a tetragonal structure in $I4/mcm$ (with tilting) at about 400°C - this transition appears to be of tricritical form. The tilt angle and its temperature dependence are the same in each case. There is no evidence for a separate cooperative JT transition in the title compound - the effect of the JT is simply to lead to elongation of the MnO_6 octahedra below the transition observed. The reason that the JT distortion appears to diminish with increasing (Mn^{3+}) concentration is not yet understood.

[1] Sundaresan *et al.*, Eur. Phys. J. B14, 431 (2000)

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Direct atomic scale observation of photoinduced isomerization of realgar to pararealgar

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The reaction mechanism underlying the photoinduced linkage isomerization of discrete arsenic-sulfur clusters in the realgar form of tetraarsenic tetrasulfide (α - As_4S_4) to its pararealgar form was studied on a natural specimen of the mineral with in situ single-crystal X-ray photodiffraction [1]. The technique provided direct atomic-resolution evidence of formation of intermediate As_4S_5 phase in which half of the realgar molecule is retained in its envelope-type conformation, while the other half is transformed by effective switching of positions of one sulfur and one arsenic atom. The initiation and propagation stages of the process are studied under light and dark conditions, during and after photoexcitation with polychromatic visible light. In the light reaction stage, the interatomic and cell parameters averaged over the crystal volume and photoexcitation time remain almost unchanged. The residual electron density features are indicative for formation of a small amount of As_4S_5 clusters, which at this stage do not affect the overall crystalline order. In the dark reaction stage, a set of self-sustainable autocatalytic reactions results in strong and nearly isotropic expansion of the unit cell. The structure in the dark stage represents direct evidence of formation of pararealgar which was obtained in yield of about 5% in the single-crystal of realgar. The cell expansion is due to increased mole ratio of clusters of pararealgar relative to realgar and to increased intercluster separation. Due to lattice incompatibility, a higher content of the product results in progressive decrease of crystal quality.

[1] P. Naumov, P. Makreski, G. Jovanovski, Inorg. Chem. 46 (2007) 10624-10631.

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Characterization of large nano-polycrystalline diamond synthesized by direct conversion of graphite

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High-purity nano-polycrystalline diamond (NPD) up to 5 mm in diameter and 8 mm in thickness with no cracks or contaminations has been successfully synthesized through direct conversion from graphite under a pressure of 15 GPa and a temperature of 2300 °C. A high-purity isotropic graphite rod was used as the starting material. The HPHT condition was generated with a large-sized Kawai-type multi anvil apparatus. The NPD obtained by this method was found to have a light brownish color and are highly transparent. The brownish color is ascribed to a continuous absorption similar to that of natural brown diamond crystal. TEM observations and XRD analyses revealed that the NPD consists of nano-diamond particles (<100 nm)