

$P6_3mc$) 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)

Keywords: perovskite, phase transition, Jahn-Teller

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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.

Keywords: X-ray diffraction, realgar and pararealgar, photochemistry

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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)

and containing no secondary phases. The Knoop indentation hardness tests showed that the hardness of NPD is as high as 120-130 GPa, which is equivalent to or even higher than those of single-crystal diamonds. High temperature hardness tests using Knoop indenters prepared from NPD specimens demonstrated that the hardness of NPD at high temperatures ($>800\text{ }^{\circ}\text{C}$) is about 2 times higher than those of single-crystal diamonds. The extremely high hardness is believed to be due to the blocking effect of dislocation movement (development of plastic deformation) at grain boundaries. The data from wear tests using a diamond wheel indicated that the wear rate of NPD is less than one-tenth of those of conventional polycrystalline diamond containing metal binders. These salient characteristics permit us to apply the large NPD to a wide field of industrial and scientific applications such as high-precision cutting tools, abrasion-resistant materials, optical windows, high-pressure anvils and so on.

Keywords: diamond, high pressure, nanostructures

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Crystal structure and lattice dynamics of high-pressure scandium trihydride

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In contrast to yttrium and rare-earth trihydrides, scandium trihydride is thermally unstable at ambient conditions and forms only under high hydrogen pressure [1]. Now scandium trihydride and trideuteride powder samples are synthesised under high pressure of gaseous hydrogen or deuterium and studied by neutron diffraction at ambient pressure and 95 K. Scandium trihydride is studied by inelastic neutron scattering at 20 K in the energy range 4-250 meV and compared to yttrium trihydride. The neutron diffraction investigation shows that hydrogen in ScH₃ occupies distorted tetrahedral and octahedral interstitial positions in the hexagonal close-packed metal lattice with the axial ratio of $c/a = 1.815$, which is typical of the YH₃ and HoH₃ structures. The displacements of the octahedral hydrogen atoms in ScH₃ demonstrate no ordering therefore the ScH₃ structure is described within space group $P6_3/mmc$. Inelastic neutron scattering shows that this is the symmetry of the mean lattice whereas the local structure is similar to that of yttrium and holmium trihydrides.

[1] I.O. Bashkin, E.G. Ponyatovskii, M.E. Kost, *phys. stat. sol. (b)*, 87 (1978) 369

Keywords: neutron structure analysis, metal hydride structures, high-pressure synthesis

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The structural study in Pd₂Mn alloy

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Pd-Mn alloy system has complicated phases and structures. It presents α_1 , β_1 , β_2 , and β_3 phases among 20-60 at. % Mn. There are few reports on the β_2 phase (Pd₂Mn), so that more detailed X-ray experiment should be performed for understanding of the structural characteristics. We have made a slice of multicrystal Pd-Mn alloys, which have 31.2, 33.4, and 34.7 at. % Mn. All the samples are quenched into ice water from 800°C after heated for two days, and then annealed from 600°C after heated for one month. Rietan-2000 is used to analyze the diffraction data for both quenched and annealed samples. Quenched samples show fcc structures and are considered to be in disorder states. The 33.4 at. % Mn sample annealed from 600°C is confirmed to be in β_2 phase, in which the space group is $Pnma$, and the atomic positions are Mn (1/8, 1/4, 1/12), Pd (I) (1/8, 1/4, 5/12), and Pd (II) (1/8, 1/4, 3/4), by the Rietveld analysis fitness of $R_{wp}=2.75$, and $S=1.46$. However, the atomic positions from our experiments are Mn (0.157, 0.25, 0.098), Pd (I) (0.148, 0.25, 0.416), and Pd (II) (0.083, 0.25, 0.757), a little shifted from the ideal positions. These shifts are considered to be from the distortions against the nearest Mn-Mn or Pd-Pd atom pairs. Our previous research shows in disordered states, a Pd or Mn atom tends to have an unlike nearest neighbour atom. The nearest neighbour's distances are 3.11Å for Mn-Mn, 2.81Å for Pd-Pd, and 2.60Å for Mn-Pd atoms pairs. The 31.2 and 34.7 at. % Mn samples annealed from 600°C present two phases of β_2 and DO₂₃. The in-situ diffraction measurements and the DSC thermal analysis are also on plan for understanding the process details of order-disorder phase transition.

Keywords: X-ray diffraction, alloy phases, Rietveld analysis

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Crystal structure and thermal property of ionic liquid-H₂O mixtures

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By simultaneous X-ray diffraction and DSC (Differential Scanning Calorimetry) method, crystal structure and thermal property of ionic liquid (IL)-H₂O mixtures were investigated. The IL used in this study is N,N-diethyl-N-methyl-N-2-methoxyethyl ammonium tetrafluoroborate. H₂O concentration, x , are 0.0 - 12.0 mol% H₂O. Anomalous phase diagrams are obtained both on cooling and heating. In-situ observations were performed using 3 kW X-ray generator (RINT-Ultima 3, Rigaku Co., Japan). On cooling, pure IL is crystallized at -30 °C. Two kinds of crystal structures (orthorhombic and monoclinic) are determined. With increasing H₂O concentration, crystallization temperature, T_c , decreased up to 6.66 mol%. At 6.66 mol%, no exothermal peak was observed on cooling. In addition, no Bragg peaks appeared. A pure amorphous state is realized at 6.66 mol%. Above 6.66 %, two phase coexistence of amorphous and crystal were formed. Therefore, 6.66 % (x_c) is regarded as the crossover point. On heating, cold crystallization occurred above x_c with the distinct exothermal peak on DSC measurements. The cold crystallization temperature, T_{cc} , was almost constant ($x_c < x < 12\%$). Crystal structures are the same ($0 < x < 12\%$). Moreover, no peak broadening of Bragg reflection appeared along the radial direction. At x_c , crystallization was completely suppressed on cooling. "Two dynamic components" in Raman spectrum suggest the two different