P6/mmc and 80K (P6/mmc --- Cmcm). In the P6/mmc phase, the V(1) O₈ octahedron form trimers with a regular triangular shape, below 80K they distort into isosceles triangles [1]. Below 64.2K, NaV₆O₁₁ they distort into isosceles triangles [1]. Below 64.2K, NaV₆O₁₁ while the V(3)O₅ polyhedron shrinks on compression. In addition, the reaction mechanism underlying the photoinduced linkage isomerization of discrete arsenic-sulfur clusters in the realgar form of tetraarsenic tetrasulfide (alphα-As₄S₄) 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 As₅S₈ 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 As₅S₈ 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 realgar form. 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.


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

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_A study of the octahedral tilting / cooperative Jahn-Teller transition in (Sr₀.₉Ce₀.₁)MnO₃_

Christopher J. Howard¹, Zhaoxing Zhang¹, Brendan J. Kennedy¹, Motohide Matsuda², Michihiro Miyake³

¹University of Newcastle, School of Engineering, University Drive, Callaghan, NSW 2308, Australia, ²Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW, 2234, Australia, ³School of Chemistry, The University of Sydney, NSW, 2006, Australia, ⁴Graduate School of Environmental Science, Okayama University, 3-1-1 Tsushima-Naka, Okayama 700-8530, Japan, E-mail: chris.howard@newcastle.edu.au

Previous room temperature measurements on the system (Srᵢ₋ₓCeₓMnO₃) (Mn⁺⁺ᵢ-ₓMn⁺⁺ₓ)O₅⁺ have shown a Jahn-Teller distortion of the MnO₆ octahedron, which is significant at x=0.1 (10% of the active Mn⁺⁺ ion) but diminishes, somewhat unexpectedly, as the concentration of Mn⁺⁺ is increased [1]. We have explored the effect further through comparative variable temperature diffraction studies on (Srᵢ₋ₓCeₓMnO₅) (Mn⁺⁺ᵢ-ₓMn⁺⁺ₓ)O₅⁺ and (Srᵢ₋ₓCeₓMnO₅) (Mn⁺⁺ᵢ-ₓMn⁺⁺ₓ)O₅⁺ - the former contains a JT active ion (Mn⁺⁺) whereas the latter does not. Both compounds show a transition from a cubic structure in Pm-3m (no tilting) to a tetragonal structure in P4/mmm (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 both cases. 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 MnO₆ octahedra below the transition observed. The reason that the JT distortion appears to diminish with increasing (Mn⁺⁺) concentration is not yet understood.


Keywords: perovskite, phase transition, Jahn-Teller

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_Direct atomic scale observation of photoinduced isomerization of realgar to pararealgar_

Petré Makreski¹, Panče Naumov²,³, Gligor Jovanovski²,³

¹SS Cyril and Methodius University, Faculty of Science, Institute of Chemistry, P.O. Box 162, Arhîmedova 5, MK-1001, Skopje, Macedonia, ²Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, 565-0871, Osaka, Japan, ³Macedonian Academy of Sciences and Arts, P.O. Box 428, MK-1001 Skopje, Macedonia, E-mail: petremak@junona.pmf.ukim.edu.mk

The 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°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

Igor O. Bashkin1, Vladimir E. Antonov1, Vladimir K. Fedotov1, Thomas Hansen2, Salavat S. Khasanov1, Alexandre S. Ivanov2, Ireneusz Natkaniec3

1Institute of Solid State Physics RAS, Institute of Solid State Physics RAS, Chernogolovka, Moscow district, 142432, Russia, 2Institut Laue-Langevin, BP 156, 38042 Grenoble Cedex 9, France, 3Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Moscow district, 141980, Russia, E-mail: bashkin@issp.ac.ru

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 contains 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°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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The structural study in Pd2Mn alloy

Yin Suo1, Rokuro Miida2, Toetsu Shishido3, Ken-ichi Ohshima1

1University of Tsukuba, Institute of Materials Science, Tsukuba, Ibaraki, 305-8573, Japan, 2Center of General Education and Humanities, Tokyo University of Science, Chino, 391-0292, Japan, 3Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan, E-mail: suoin@hotmail.com

Pd-Mn alloy system has complicated phases and structures. It presents α1, β1, β2, and β3 phases among 20-60 at. % Mn. There are few reports on the β2 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 β2 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 Rwp=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 neighbouring atom. The nearest neighbour’s distances are 3.11Å for Mn-Mn, 2.81Å for Pd-Pd, and 2.60Å for Mn-Pd pairs. The 31.2 and 34.7 at. % Mn samples annealed from 600°C present two phases of β2 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

**P08.06.47**


Crystal structure and thermal property of ionic liquid-H2O mixtures

Yusuke Imai1, Takehumi Goto1, Yosuke Michishita1, Hiroshi Abe1, Yukihiro Yoshimura2, Hitoshi Matsumoto1

1National Defense Academy / Japan, Materials Science and Engineering, g45031@nda.ac.jp, Yokosuka, Kanagawa, 239-0811, Japan, 2Department of Applied Chemistry, National Defense Academy / Japan, Yokosuka, Kanagawa, 239-0811, Japan, E-mail: g45031@nda.ac.jp

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%. Above 6.66 %, two phase coexistence of amorphous 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°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: neutron structure analysis, metal hydride structures, high-pressure synthesis

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Crystal structure and thermal property of ionic liquid-H2O mixtures

Yasuyuki Imaj1, Takehumi Goto1, Yosuke Michishita1, Hiroshi Abe1, Yukihiro Yoshimura2, Hitoshi Matsumoto1

1National Defense Academy / Japan, Materials Science and Engineering, g45031@nda.ac.jp, Yokosuka, Kanagawa, 239-0811, Japan, 2Department of Applied Chemistry, National Defense Academy / Japan, Yokosuka, Kanagawa, 239-0811, Japan, E-mail: g45031@nda.ac.jp

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, Tc 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 % (x0) is regarded as the crossover point. On heating, cold crystallization occurred above x0 with the distinct exothermal peak on DSC measurements. The cold crystallization temperature, Tc0, was almost constant (x0 < x < 12 %). Crystal structures are the same (0 < x < 12 %). Moreover, no peak broadening of Bragg reflection appeared along the radial direction. At x0, crystallization was completely suppressed on cooling. “Two dynamic components” in Raman spectrum suggest the two different