

meanwhile a covalent nature could be observed between Al and O.

[1] Xu C. N., *Encyclopedia of Smart Materials*, 2002, **1**, 190. [2] Liu Y., Xu C. N., *Appl. Phys. Lett.*, 2004, **84**, 5016.

Keywords: Rietveld structure analysis, maximum-entropy method, luminescent compounds

P.10.02.22

Acta Cryst. (2005). A61, C372

RE₆Ni₂In (RE = Gd, Tb, Dy, Ho, Lu) – The New Representatives of Ho₆Co₂Ga Structure Type

Yaroslav Galadzhun^a, Mariya Dzevenko^a, Vasyl' Zaremba^a, Julia Stepień-Damm^b, Yaroslav Kalychak^a, ^a*Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Ukraine.* ^b*W. Trzebiatowski Institute of Low Temperature and Structure Research, Wrocław, Poland.* E-mail: galadzh@mail.lviv.ua

The compound Ho₆Ni₂In was synthesized in an arc-melting furnace under an argon atmosphere and special heat treatment was applied for the growth of single crystals. Intensity data were collected by use of a KM-4 CCD diffractometer with graphite monochromatized MoK α radiation. The structure was refined by direct methods with anisotropic displacement parameters for all atoms using SHELX-86 and SHELXL-97 programs: sp.gr. *Immm*, $a = 9.319(2)$, $b = 9.523(2)$, $c = 9.930(2)$ Å, $Z = 4$; $R1 = 0,0401$, $wR2 = 0,0891$ for 581 reflections with $I > 4\sigma(I)$. The 2(a) site shows mixed occupancy Ni_{0,64(4)}In_{0,36(4)}.

Atom	Site	x	y	z	U _{eq} , Å ²
Ho1	8(n)	0.2912(1)	0.1840(1)	0	0.0140(3)
Ho2	8(m)	0.3032(1)	0	0.3222(1)	0.0107(3)
Ho3	8(l)	0	0.1963(1)	0.2232(1)	0.0200(3)
Ni1	4(j)	1/2	0	0.1226(4)	0.0136(8)
Ni2	4(g)	0	0.3603(5)	0	0.0179(9)
In	2(c)	1/2	1/2	0	0.0103(6)
M	2(a)	0	0	0	0.020(2)

The structure of the Ho₆Ni₂In compound belongs to the Ho₆Co₂Ga structure type [1]. Isostructural compounds were found also with Gd, Tb, Dy, and Lu.

[1] Gladyshevskii R., Grin Yu., Yarmolyuk Ya., *Dop. AN URSSR*, 1983, (2), 70.

Keywords: crystal structures, rare-earth compounds, indium compounds

P.10.04.1

Acta Cryst. (2005). A61, C372

White Phosphorus: The Equation of State and Pressure-Induced Transitions

Joseph M. Zaug^a, Simon M. Clark^b, Martin Kunz^b, Raymond Jeanloz^c, ^a*Lawrence Livermore National Laboratory.* ^b*Lawrence Berkeley National Laboratory.* ^c*University of California at Berkeley.* E-mail: zaug1@llnl.gov

We conducted angle dispersive x-ray powder diffraction measurements of hydrostatically compressed white phosphorus, P₄, to determine the equation of state and pressure dependant thermal expansion coefficients. We discovered a pressure-induced change in the powder pattern at ambient temperature. In addition, we have preliminary data that partially details the melting curve of P₄. Our condensed fluid state diffraction results will be used to deduce radial structure factor information. Our measurements were conducted on the new California high-pressure science observatory BL12.2.2 (<http://xraysweb.lbl.gov/bl1222/HOME.htm>) located at the Advanced Light Source at Lawrence Berkeley National Laboratory. An externally heated and membrane driven diamond anvil cell was employed to confine samples at controlled pressures and temperatures.

Ambient condition white phosphorus exists as a bcc crystalline solid with a I-43m space group. Upon increasing pressure, P₄ transforms at approximately 2.5 GPa to the orthorhombic black allotrope with a Cmca space group. The exact allotropic transition pressure depends most likely on the magnitude of shear forces present within the sample. For example, temperature annealing seems to extend the pressure stability of the bcc phase to nearly 6 GPa. When

heated to modest temperatures, P₄ transforms, upon increased pressure, to what we describe as an amorphous black phase.

Keywords: phosphorus, equations of state, phase transitions

P.10.04.2

Acta Cryst. (2005). A61, C372

X-ray Study of the Iridium-Osmium System

Ilya Korolkov, Sergey Gromilov, Kirill Yusenko, Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia. E-mail: x-vizor@yandex.ru

Os and Ir metals are of particular attention regarding their characteristics. For example, the osmium has the highest bulk moduli value of 462 GPa [1] among all other materials. Furthermore, Os and Ir possess the high values of density, melting temperature, etc. A phase diagram of Os-Ir system belongs to the peritectic type. Single-phase areas with the face-centered cubic (fcc) and hexagonal close packed (hcp) lattices are separated by a diphasic area.

In some cases, it is possible to obtain a non-equilibrium solid solution that is placed into the diphasic area. To get the single Ir_{0,5}Os_{0,5} phase we have thermalized a precursor complex [Ir(NH₃)₅Cl][OsBr₆] at 700°C in hydrogen atmosphere. Finally, according to X-ray analysis data, a single phase with the hcp lattice was obtained. After further heating up to 800°C for 24 hours in vacuum the sample became diphasic. The lattice parameters of the hcp phase are close to Ir_{0,5}Os_{0,5}. The lattice parameter of the fcc phase is close to the pure iridium.

Besides, we have obtained the Ir_{0,67}Os_{0,33} fcc phase from the [Ir(NH₃)₅Cl]₂[OsCl₆]Cl₂ complex by prolonged heating; another phases Ir_{0,5}Os_{0,5} (hcp, non-equilibrium), Ir_{0,75}Os_{0,25} (fcc) and Ir_{0,25}Os_{0,75} (hcp) were synthesized by thermolysis of salt solid solutions (NH₄)₂[OsCl₆]_(1-x)[IrCl₆]_x (0 ≤ x ≤ 1). For all of the phases we have calculated a "volume per atom" parameter. The calculated values fit a line that connects the values for pure iridium and osmium.

[1] Cynn H., Klepeis J. E., Yoo C. et. al., *J. Phys. Rev. Lett.*, 2002, **88**, 135701.

Keywords: platinum group, thermal study, X-ray analysis

P.10.04.3

Acta Cryst. (2005). A61, C372-C373

Crystal Phases in Glasses

Andrei Lysiuk, Institute of Geology Russian Academy of Sciences, Syktyvkar, Russia. E-mail: andra227@yandex.ru

We investigated crystal phases of fulgurite glasses. Fulgurites is a glassware tubular bodies, which formed after the melting of rocks by the hit of a lightning. The successful case was presented to us to study the structure and composition of two fulgurite fragments of Sonora desert (south of Mexico). Earlier we have studied the fulgurite from area of Nigoziro in Karelia, Russia, which was formed on a carbon-containing aleurolites. Thus an excellent opportunity has appeared to make the comparative analysis of fulgurites, formed on completely various geological breeds.

By data received with the help of X-Ray analysis the basic volume of all investigated fulgurite glasses is the X-Ray amorphous phase. For Mexican fulgurite it is a prevailing phase. Also we expose the heterogeneity of glasses which consists in combined presence of amorphous glassy matrix and crystalline formations with different composition: orthoclase, hematite, chlorite, pyrite.

By the micro-probe analysis we determined that the main mass of glassy fulgurite substance is a thickened Si-Al-Fe fusion. In the main mass of fusion the areas of almost pure glasses are distinguished. The simultaneous appearance of fragments as glassy such as residual quartz in fusion tells that the temperature of fusion in that zone was near the temperature of quartz melting, this is about 1700 C.

In the outlying districts of fulgurite iron contains by the higher portions. Here we find a great amount inclusions, mainly of Fe-Al composition. In the fulgurite glass we also find an inclusions of almost pure alloy which consists from the iron and aluminium with the small admixture of magnesia. That inclusions are characterised by the good crystallographic cutting. The presence of costal growing forms tells about the post-melting formation of this inclusions. Also we often meet inclusions of hematite Fe₂O₃. Its grains have the straight borders.

The appearance of these inclusions allow us to estimate the temperature of the fusion which did not reach the temperature of hematite melting. Besides, in the glass, we find the inclusions of hematite with the tracks of partial fusion.

Appearance of a great amount skeleton formations with the composition such as FeO is an evidence of a great fusion cooling speed. Such structures forms because of dissociation on the stage of cooling.

Besides we find the numerous inclusions corresponding by structure to baddeleyite glass in the form of thin thready formations, specifying on processes of segregation proceeding in the time of hardening of fusion. These processes of segregation were not observed before in fulgurites. Also, inclusions of baddeleyite glass meets and as separate grains with crystallographic facet and with the raised contents of uranium. Besides there are aluminosilicate inclusions enriched with the titan and phosphorus. In such inclusions are widely used the clusters of ferrian composition.

Keywords: fulgurite, hematite, segregation

P.10.04.4

Acta Cryst. (2005). A61, C373

Synthesis and X-ray Study of [Pt(NH₃)₄](ReO₄)₂ Thermolysis Products

Andrey Zadesenets, Ilya Korolkov, Iraida Baidina, Sergey Gromilov, ^aNikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia. E-mail: zadesenez@ngs.ru

Catalysts based on the Pt and Re play an essential role in reforming processes. About 65% of all the produced rhenium is used for these needs. One of the methods to prepare catalysts is the thermolysis of inorganic complex salts, containing two required metals. In this work we have studied the precursor complex [Pt(NH₃)₄](ReO₄)₂ and obtained a solid solution Pt_{0.33}Re_{0.67}.

A synthesis of the precursor complex [Pt(NH₃)₄](ReO₄)₂, was held in the following way: 0.2 M water solutions of [Pt(NH₃)₄]Cl₂ and NaReO₄ were mixed at 50°C, then kept for an hour at room temperature. A white residue was separated and washed away with water and acetone. The yield is 75%. The crystal structure of [Pt(NH₃)₄](ReO₄)₂ was determined with a X8APEX Bruker diffractometer (MoK α -radiation, θ range 2.85–32.59°, 2007 independent reflections), R = 2.11%. Crystal data: a = 5.1847(6), b = 7.7397(8), c = 7.9540(9) Å, α = 69.531(3), β = 79.656(3), γ = 77.649(3)°, V = 290.19(6) Å³, space group P-1, Z = 1. This complex is isostructural to [Pt(NH₃)₄](TeO₄)₂ [ICSD Card 65-766]. The structure consists of the isolated complex [Pt(NH₃)₄]²⁺ and ReO₄⁻ ions.

The thermolysis of [Pt(NH₃)₄](ReO₄)₂ was carried out at 900°C in H₂ atmosphere for 7 hours. According to X-ray analysis, the product is a single phase solid solution Pt_{0.33}Re_{0.67}. It is based on the hexagonal close-packed rhenium structure. Crystal data of the solid solution: a = 2.764(2), b = 4.415(3) Å, V = 29.21 Å³, space group P6₃/mmc, Z = 2.

Keywords: platinum group, X-ray analysis, single-crystal structure analysis

P.10.04.5

Acta Cryst. (2005). A61, C373

Crystal Structure of KLiSO₄ at High Temperatures

Hyun Min Park, Yang Koo Cho, Su Jin Chung, *New Materials Evaluation Center, Korea Research Institute of Standards and Science, P.O. Box 102, Taejeon, 305-600 Korea.* E-mail: hmpark@kriss.re.kr

Above room temperature there are three modifications of KLiSO₄; i.e. phase I, II and III. Phase transitions temperatures between them are 435°C and 668°C respectively. The x-ray diffraction intensities of phase I at about 700°C and of phase II at about 600°C were collected on the CAD4 single crystal diffractometer equipped a self-made furnace. During collection of intensities data, a prominent decay of intensities was observed. The crystal structure of phase I is the tridymite derivatives with ordered arrangement of SO₄⁻ and LiO₄⁻ tetrahedra similar to that of phase III. The statistical data of the structure refinement for phase I with polar space group of P6₃mc was R = 0.057, Rw = 0.056 and S (goodness-of-fit) = 1.859. The crystals

of phase II usually exhibit misleading hexagonal twinned cell which is composed of three orthorhombic twin domains in the temperature range between 435°C and 668°C. An almost twin-free single crystal of Phase II was observed at the elevated temperature. The crystal structure of phase II was refined with this crystal is orthorhombic with the polar space group Pc2₁n. The final statistical data was R = 0.077, Rw = 0.073 and the S = 1.028 with ordered arrangement of atoms. This data was compared with that of the twinned crystal corrected with twin ratio and further discussed previously reported disordered model with the space group of Pmcn.

Keywords: KLiSO₄, structure analysis, high temperature

P.10.04.6

Acta Cryst. (2005). A61, C373

Ab initio Treatment of Minerals at Extreme Conditions

Daniel Y. Jung^{a,b}, Artem R. Oganov^b, ^aInstitut of mineralogy and petrology, Department of Earth science, ETH Zürich. ^bLaboratory of crystallography, Department of Materials, ETH Zürich, Switzerland. E-mail: daniel.jung@mat.ethz.ch

The mantle of the Earth extends from the depth of about 670 km to 2981 km. It consists mainly of MgSiO₃-perovskite, (Mg,Fe)O magnesiowüstite and CaSiO₃-perovskite. It is possible to calculate thermodynamic properties, structures and energetics of the separate minerals at extreme conditions of the mantle using *ab initio* methods, such as the density functional theory with the generalized gradient approximation (GGA) [1] and the projector augmented wave (PAW) method [2], which are included in the VASP [3] code. To get a better picture of the mantle it is necessary to not only look at chemically pure minerals, but to consider them as a solid solution, as it is the probable case in nature.

Using density functional theory the structure and the stability of the CaSiO₃ perovskite in the pressure range of the Earth's mantle (0-150 GPa) have been calculated [4]. Additionally we use the subregular solid solution model together with point defect calculations to model the solvus of the (Ca,Mg)-perovskite phase diagram at 25 GPa. This is a special case, because there is also a symmetry change from a tetragonal to an orthorhombic perovskite structure as you increase the concentration of Mg. This is the first work to treat this subject with *ab initio* methods.

[1] Perdew J.P., Burke K., Ernzerhof M., *Phys. Rev. Lett.*, 1996, **77**, 3865. [2] Blöchl P.E., *Phys. Rev. B.*, 1994, **50**, 17953. [3] Kresse G., Furthmüller J., *Phys. Rev. B.*, 1996, **54**, 11169. [4] Jung D.Y., Oganov A.R., *Phys. Chem. Mineral*, 2005, *in press*.

Keywords: (Ca,Mg)SiO₃ perovskite, Earth's mantle, solid solution

P.10.04.7

Acta Cryst. (2005). A61, C373-C374

Viscosity Measurements of Fe-FeS Melts under High Pressures

Ken-ichi Funakoshi, Akifumi Nozawa, *Japan Synchrotron Radiation Research Institute, SPring-8, Hyogo, Japan.* E-mail: funakosi@spring8.or.jp

The Fe-FeS melt is the important Earth's outer core material and its viscosity has been thought to be very low under high pressure and high temperature. Recent measurements of the Fe-FeS melt have showed the low viscosity values (~10⁻² Pa-s), however, the accuracies are not so good for determining the viscosity values. An x-ray radiography technique with synchrotron radiation is very useful for the falling sphere viscosity measurement, because it enables us in situ observation of the sinking process and determination of the reliable viscosity coefficient.

We measured the viscosities of Fe-FeS (Fe₇₃S₂₇, Fe₈₀S₂₀, Fe₉₀S₁₀) melts, combining the falling sphere method with the large volume press at the SPring-8. Precise viscosities have been obtained up to 9 GPa using Stoke's law. The pressure dependences of the viscosities are very small, however, the viscosities slightly increase with increasing pressures. The activation energies and the activation volumes have been determined from the dependences on pressure and temperature of the viscosities. The viscosities of the Earth's outer core have been calculated using the activation energies and the activation volumes of Fe₉₀S₁₀. The calculated viscosities of the Earth's outer core