

for  $\text{Fe} \leq 0.1\%$  (higher than 60%), and is absent for  $\text{Fe} \geq 1\%$ . It is emphasized that the composition  $\text{Fe} = 0.5\%$  is crucial: because Ca- and Sr- samples are a mixture of apatite and triphosphate, while Ba-sample is 100% barium triphosphate. The accurate cell constant determination allows some considerations about  $a$  and  $c$  parameters dependence on chemical composition. Preliminary Mössbauer results indicate the presence of oxidic iron species and of substituted hydroxyapatite and phosphate in amounts that are function of both the iron amount in the starting material and the type of cation, in agreement with the X-ray powder diffraction data.

**Keywords:** apatites, Mössbauer spectroscopy, X-ray diffraction

#### P.10.02.18

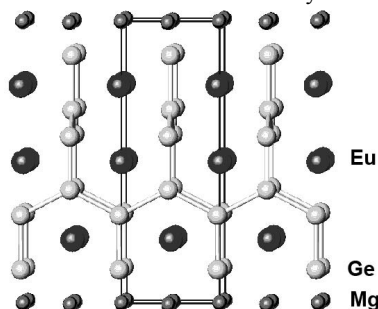
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#### Synthesis and Crystal Structure of the New Zintl Phase $\text{Eu}_3\text{Mg}_2\text{Ge}_6$

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The new Zintl phase  $\text{Eu}_3\text{Mg}_2\text{Ge}_6$  was prepared and structurally characterized. The compound crystallizes in the tetragonal space group  $P-4m2$  (No. 115) with  $a = 4.476(1) \text{ \AA}$  and  $c = 12.794(3) \text{ \AA}$ . The structure contains the novel Zintl anion  ${}^4_4[\text{Ge}_6^{10-}]$  with an infinitely branched chain of linked perpendicular zig-zag chains, related to sections of the  $\alpha\text{-ThSi}_2$  structure type.

The occurrence of diffuse scattering in the  $[0kl]$ -layer points to the presence of stacking faults. Different models for stacking faults were developed and discussed, favouring one possibility, which yields a good qualitative explanation of the diffuse scattering intensities [1] and also for the observed residual electron density.



[1] Proffen Th., Neder R.B., *J. Appl. Cryst.*, 1997, 30, 171.

**Keywords:** germanides, diffuse scattering, Zintl phase

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#### Metallic Clusters Interactions: Structures of $\text{Co}(\text{H}_2\text{O})_6\text{K}_2\text{M}_2\text{W}_4\text{O}_{19}\cdot x\text{H}_2\text{O}$ ( $\text{M}=\text{V}, \text{Nb}$ )

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The compounds  $[\text{Co}(\text{H}_2\text{O})_6]\text{K}_2\text{V}_2\text{W}_4\text{O}_{19}\cdot 3\text{H}_2\text{O}$  (**1**) and  $[\text{Co}(\text{H}_2\text{O})_6]\text{K}_2\text{Nb}_2\text{W}_4\text{O}_{19}$  (**2**) crystallizes respectively in the Orthorhombic system, space group  $\text{Cmcm}$  and the Hexagonal system, space group  $\text{R-3m}$ . The cell parameters for (**1**) are  $a=11.645(1)\text{ \AA}$ ,  $b=13.242(1)\text{ \AA}$ ,  $c=15.417(1)\text{ \AA}$ ,  $V=2377(3) \text{ \AA}^3$  with  $Z=4$  and  $a=9.887(2) \text{ \AA}$   $c=24.242(1) \text{ \AA}$ ,  $V=2052.4(2) \text{ \AA}^3$  with  $Z=4$  for (**2**). The structure of the anion  $[\text{M}_2\text{W}_4\text{O}_{19}]^{4-}$  ( $\text{M}=\text{V}$  or  $\text{Nb}$ ) is essentially that of Lindqvist<sup>[1]</sup>, the metals positions are disordered, occupancies of V or Nb and W were refined and are close to the theoretical values. The crystal structure shows that the oppositely charged polyhedral ions are arranged alternately and have their faces parallel to each other for maximal interactions (face-to-face interaction)<sup>[2]</sup>. The crystal (**1**) has large mono-directional channels along the  $[001]$  axis with a sectional area of  $10.23 \times 6.35 \text{ \AA}^2$  that are filled by cobalt. The crystal (**2**) has also mono-directional quasi squared channels along the  $[012]$  axis

with a sectional area of  $(4.52)^2 \text{ \AA}^2$  that are filled by cobalt.

[1] Lindqvist, *I. Ark. Kemi.*, 1952, 5, 247. [2] Son J., Kwon Y., *Inorg. Chem.*, 2004, 43, 1929-1932.

**Keywords:** polyoxometalate structures, inorganic clusters, interactions

#### P.10.02.20

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#### Hydrogen Bonds in Triclinic $\text{MH}(\text{XO}_4)$ Compounds

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The crystal structure of triclinic  $\text{SrHAsO}_4$  was re-investigated from single crystal X-ray data. The strong reflections of the present investigation are in agreement with a former description [1]. However, additional weak superstructure reflections are responsible for a unit cell with four-fold cell volume. The non-standard space-group setting

$F\bar{1}$  ( $a = 14.697(3)$ ,  $b = 28.230(5)$ ,  $c = 14.920(3) \text{ \AA}$ ,  $\alpha = 95.20(3)$ ,  $\beta = 104.78(3)$ ,  $\gamma = 88.11(3)^\circ$ ,  $Z = 64$ ) was chosen to facilitate the comparison with  $\text{CaHPO}_4$  (monetite),  $\text{CaHAsO}_4$  (weilite),  $\alpha\text{-SrHPO}_4$ ,  $\text{NaHSO}_4$ , and  $\text{HgHAsO}_4$ . Their unit cells correspond with the average cell of  $\text{SrHAsO}_4$ . The arrangements of the  $M$  and  $X$  atoms ( $M = \text{Na}, \text{Ca}, \text{Sr}, \text{Hg}$ ;  $X = \text{S}, \text{P}, \text{As}$ ) compare well; their coordination figures are qualitatively maintained. Despite a structural analogy, isotropy is not verified. Essential differences are evident for the hydrogen bonds. The

parental structure has space group  $P\bar{1}$  ( $Z = 4$ ) and exhibits three crystallographically different hydrogen bonds. Only half of the H atoms p.f.u. forms conventional hydrogen bonds. Two hydrogen

bonds are restricted by  $\bar{1}$  symmetry ( $\text{O}\cdots\text{O} \geq 2.40 \text{ \AA}$ ). Distinct order phenomena in the structurally related compounds are observed. In  $\text{SrHAsO}_4$  the formation of a superstructure violates these inversion centres and all hydrogen bonds have distinct donor and acceptor atoms. However, some short contacts  $\text{O}\cdots\text{O}' \geq 2.47 \text{ \AA}$  are maintained. Financial support of the Austrian science foundation (FWF) is gratefully acknowledged (Grant P15875-N03).

[1] Nabar M.A., Dalvi A.P., *Bull. Soc. fr. Min. Crist.*, 1977, 100, 353.

**Keywords:**  $\text{MH}(\text{XO}_4)$ , hydrogen bonding, crystal chemistry of inorganic compounds

#### P.10.02.21

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#### Structural and Electron Density Studies of Stuffed Tridymite

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Stuffed tridymite materials,  $\text{MA}_2\text{O}_4$  ( $\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$ ) are one of the most important matrices for luminous materials because of easily introducing various dopant ions into the framework structure and can realize various luminous colours. Utilizing these matrices, we have developed newly functional materials, which show strong mechano-, electro-, and photo-luminescence in one material [1,2]. Their physical properties are largely related to the crystal structure because the luminescent properties are strongly sensitive to its local atomic configuration and the local polarization state around dopant ions. Therefore the structural study of these materials is important for controlling their mechanical, luminescent and optical properties.

We have determined the accurate structural parameters of  $\text{MA}_2\text{O}_4$  ( $\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$ ) by Rietveld refinements using high resolved powder diffraction data with synchrotron X-ray radiation (SPring-8 BL02B2). It was found that their structural features were strongly dependent on cation size. The shape of  $\text{AlO}_4$  tetrahedra that constitute of the framework structure was almost independent to the cation size meanwhile the void space around cation was variable, suggesting that the framework structure in stuffed tridymite may be easily deformed. Furthermore the charge density distribution was also calculated from the observed form factors  $F_o$  using the maximum entropy method (MEM), demonstrating that the cation ions were isolated ions

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

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#### RE<sub>6</sub>Ni<sub>2</sub>In (RE = Gd, Tb, Dy, Ho, Lu) – The New Representatives of Ho<sub>6</sub>Co<sub>2</sub>Ga Structure Type

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The compound Ho<sub>6</sub>Ni<sub>2</sub>In 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 $\alpha$  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<sub>0,64(4)</sub>In<sub>0,36(4)</sub>.

Atom	Site	x	y	z	U <sub>eq</sub> , Å <sup>2</sup>
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 Ho<sub>6</sub>Ni<sub>2</sub>In compound belongs to the Ho<sub>6</sub>Co<sub>2</sub>Ga 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

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

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We conducted angle dispersive x-ray powder diffraction measurements of hydrostatically compressed white phosphorous, P<sub>4</sub>, 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 P<sub>4</sub>. 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, P<sub>4</sub> 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, P<sub>4</sub> transforms, upon increased pressure, to what we describe as an amorphous black phase.

**Keywords:** phosphorus, equations of state, phase transitions

#### P.10.04.2

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#### X-ray Study of the Iridium-Osmium System

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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<sub>0,5</sub>Os<sub>0,5</sub> phase we have thermalized a precursor complex [Ir(NH<sub>3</sub>)<sub>5</sub>Cl][OsBr<sub>6</sub>] 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<sub>0,5</sub>Os<sub>0,5</sub>. The lattice parameter of the fcc phase is close to the pure iridium.

Besides, we have obtained the Ir<sub>0,67</sub>Os<sub>0,33</sub> fcc phase from the [Ir(NH<sub>3</sub>)<sub>5</sub>Cl]<sub>2</sub>[OsCl<sub>6</sub>]Cl<sub>2</sub> complex by prolonged heating; another phases Ir<sub>0,5</sub>Os<sub>0,5</sub> (hcp, non-equilibrium), Ir<sub>0,75</sub>Os<sub>0,25</sub> (fcc) and Ir<sub>0,25</sub>Os<sub>0,75</sub> (hcp) were synthesized by thermolysis of salt solid solutions (NH<sub>4</sub>)<sub>2</sub>[OsCl<sub>6</sub>]<sub>(1-x)</sub>[IrCl<sub>6</sub>]<sub>x</sub> (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

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#### Crystal Phases in Glasses

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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 Fe<sub>2</sub>O<sub>3</sub>. Its grains have the straight borders.