

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

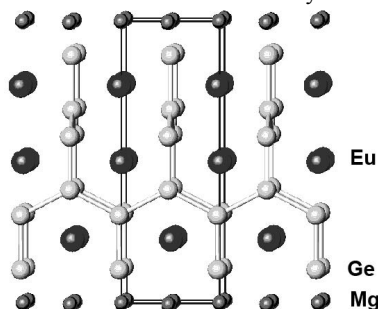
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#### Synthesis and Crystal Structure of the New Zintl Phase $\text{Eu}_3\text{Mg}_2\text{Ge}_6$

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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  $^{1-}_4[\text{Ge}_6^{10-}]$  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

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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

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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