PS08.00.22 STRUCTURE AND CRYSTAL CHEMISTRY OF $CaSi_2O_5$ SYNTHESIZED AT 1500 °C AND 10 GPa: A NEW HIGH PRESSURE CALCIUM SILICATE WITH FIVE-COORDINATED SILICON.

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Crystal structure of $CaSi_2O_5$ synthesized in a uniaxial, split-sphere, multi-anvil apparatus at conditions of 1500 °C and 10 GPa, has been solved and refined in noncentro-symmetric space group P1, using the X-ray diffraction data measured on a 35x71x71 micron single crystal. The composition (Z=4) and unit cell are $Ca_{1.02}Si_{1.99}O_5$ by E.P.M.A. analysis and a=7.243(2) Å, b=7.546(4) Å, c=6.501(4) Å, α=98.57(5)°, β =95.18(4)°, γ=69.60(3)°, V=329.5(3) Å^3, yielding the density value, 3.55 g/cm^3. The crystal structure was determined by Patterson method. Final agreement factors for 1973 Fo's observed up to $\sin\theta/\lambda$ =0.75 were R=8.0% and Rw=9.4% with isotropic temperature factors. The crystal structure is closely related to that of titanite,$CaTiSiO_5$. The formula of unit cell contents is:

$$^{vii}Ca_3{}^{viii}Ca{}^{v}Si_2{}^{vi}Si_2{}^{iv}Si_4O_{20}.$$

The structure consists the square pyramid fivefold coordination of silicon by oxygen. This is the first discovery about five-coordinated Si in an inorganic crystalline state.

PS08.00.23 ON THE CRYSTAL STRUCTURE OF APATITE.

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To investigate the bioinorganic interactions in bone and enamel, and to develop synthetic replacements, a thorough crystallographic understanding of the calcium phosphates involved is critical but far from achieved. (In accordance with "apatite" being Greek for "I deceive".) This contribution is to provide a useful crystal structure description of apatite, enlightening its relation to other calciumphosphates and CaO.

The oxygen array of hydroxyapatite is described as a cyclic translation of an fcc lattice, as has been used to describe wightmanit and fluoborite[2]. Three-octahedra wide monolayers of edge-sharing oxygen octahedra are infinitely extended along $<110>_{fcc}$ (= $<001>_{apatite}$). The central octahedral row contains empty octahedra and every second tetrahedron is filled with P. The outer octahedra are alternately empty or filled with Ca (at different heights in the different rows). The difference between this ideal and the real model can be accounted for by considering the contraction of the PO_4 tetrahedra (due to the small and highly charged P^{5+} ions).

HREM experiments showed the presence of slabs of CaO (O forms an fcc lattice) growing coherently in between slabs of apatite (Ca/P=1.67). The apatite/CaO crystallites were formed from crystallites of tetracalcium phosphate (Ca/P=2) inducing the phase transformation in the electron beam (JEOL 4000EX, Transmission Electron Microscope). The extra calcium was found as 2 or 3 octahedra thick intergrowths of CaO.

The stoichiometry of the reaction

$$3\ Ca_4(PO_4)_2O \rightarrow Ca_{10}(PO_4)_6O + 2\ CaO$$

suggests the formation of oxyapatite instead hyroxyapatite explaining the apparent p3 symmetry observed in the <001> images of the apatite slabs.

[1] Kay, M. I., Young, R. A. & Possner, A. S (1964) *Nature*, **204,** 1050.
[2] Hyde, B. G. & Andersson, S. (1988) *Inorganic Crystal Structures*, John Wiley & Sons, New York.

PS08.00.24 PREPARATION AND STRUCTURAL CHARACTERIZATION OF THE $PrBa_2Cu_4O_8$ COMPOUND.

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The compound $PrBa_2Cu_4O_8$ has been prepared under ambient oxygen pressure. The crystal structure of $PrBa_2Cu_4O_8$ has been refined from X-ray powder diffraction data (CuK-α=1.5418Å) by the Rietveld technique and confirms this compound has the 124 structure. At 300 K, the refined crystal data for $PrBa_2Cu_4O_8$ are: orthorhombic system, space group Ammm, a=3.8897(2)Å, b=3.9041(2)Å, and c=27.323(1)Å. Mr=1595.49, V=414.92 Å^3, Z=1, Dx=6.39 Mg m-3. The structure were refined with 30 parameters to Rwp=6.02%, Rp=4.02% for 4501 step intensities and Rb=8.0 %, Rf=5.24% for 536 reflections, "goodness of fit" S=1.74. Characterization of this compound by electrical resistivity and magnetization are also reported and compared with those of $YBa_2Cu_4O_8$.

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PS08.00.25 HYDROTHERMAL SYNTHESIS AND CRYSTAL STRUCTURES OF GALLIUM AND INDIUM PHOSPHATES.

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Aluminophosphates have been extensively studied because they are known to be useful materials for catalysis and adsorption. Gallophosphates have also been synthesized to discover new open-framework materials. The replacement of aluminum by gallium yields both novel structure types and phases that are analogous to known aluminophosphates and aluminosilicates. Compared to the large number of aluminophosphates and gallophosphates synthesized and structurally characterized there is very scant information on indium phosphates in the literature. As part of a continuing study on the structural chemistry of phosphates containing mixed octahedral-tetrahedral frameworks, the phosphates and arsenates of Group 13 elements have also been examined. The synthetic methods are two-fold, *viz.* the high-temperature, high-pressure hydrothermal and the flux-growth methods. Hydrothermal synthesis involves the use of aqueous solvents or mineralizers under high temperature and high pressure to dissolve and recrystallize materials that are relatively insoluble under ordinary conditions. Small gold tubes, welded at both ends containing the reactants, are used in the pressure vessels. This presentation reports the results of hydrothermal synthesis and crystal structures of several new ternary gallium and indium phosphates.

PS08.00.26 SYNTHESES AND CRYSTAL STRUCTURES OF TWO NOVEL GALLOARSENATES: $Cs_2Ga_3(AsO_4)_2(As_3O_{10})$ and $Cs(GaOH)_2H(AsO_4)_2$.

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Microporous aluminophosphates have been extensively studied because of their potential sorption and catalytic properties. Numerous gallophosphates have also been synthesized to discover new open framework materials. The replacement of aluminum by gallium has yielded both novel structure types and phases that are analogous to known aluminophosphates and aluminosilicates. In contrast to the phosphates, much less galloarsenates have been reported. This poster presents the results of our exploratory synthesis and single-crystal X-ray structures of two novel galloarsenates,$Cs_2Ga_3(AsO_4)_2(As_3O_{10})$ and $Cs(GaOH)_2H(AsO_4)_2$.

Crystals of $Cs_2Ga_3(AsO_4)_2(As_3O_{10})$ were grown from a flux. It crystallizes in the monoclinic space group C2/c with a= 27.0360(7), b= 5.1074(2), c= 12.5112(4) Å, β= 93.86(1)°, V= 1723.7 (2) Å^3, Z= 4, R= 0.035 for 1486 independent reflections with $I > 3.0\ \sigma(I)$. The framework consists of GaO_6 octahedra, GaO_5 square pyramids, AsO_4

tetrahedra and the very rare triarsenate groups As_3O_{10} which together serve as building units to form an intersecting tunnel structure with the Cs^+ cations located at the intersections of tunnels. Crystals of $Cs(GaOH)_2H(AsO_4)_2$ were grown by a high-temperature, high-pressure hydrothermal method. It crystallizes in the monoclinic space group $P2_1/c$ with a= 4.6479(4), b= 6.051(1), c= 16.457(2) Å, β = 92.99(1)°, V= 462.2(1) Å^3, Z= 2, R = 0.045 for 929 independent reflections with $I > 2.5\,\sigma(I)$. The structure contains infinite chains of GaO_6 octahedra sharing trains edges. These chains are connected by arsenate groups to form layers in the ab-plane. The layers are linked by Cs^+ cations and hydrogen bonding.

PS08.00.27 RIETVELD REFINEMENT OF $Na_2CaMg(PO_4)_2$, $NH_4Al_3(SO_4)_2(OH)_6$.

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The structure analysis of $Na_2CaMg(PO_4)_2$ and $NH_4Al_3(SO_4)_2(OH)_6$ has been made by means of X-ray powder diffraction using Rietveld method.

The first compound is known as the mineral brianite(1) and it is structurally isomorphous with the mineral merwinite $Ca_2CaMg(SiO_4)_2$ (2). The other compound is structurally isomorphous with $KAl_3(SO_4)_2(OH)_6$ (3). None of these compounds has got an entry in ICSD or PDF-2 databases. Therefore, we have refined the structures of these minerals and prepared powder cards for them.The initial cell parameters were evaluated with TREOR 90(4) and the framework atom positions with temperature factors were taken from the literature. The theoretical powder patterns were calculated and their comparison with measured data undoubtedly confirmed isomorphism of solved structures.

The X-ray data were collected on DRON-UM-1 powder diffractometer with CuKα radiation (7 - 120° 2ϕ range, 0.02° step size, 5 seconds per step). The Howard´s version DBWS 4.1(5) was used for the Rietveld refinement.The table 1. summarises final cell parameters and R factors for both structures.

Table 1.: Final cell parameters and R factors for both structures.

a(Å)	b(Å)	c(Å)	β(°)	V(A^3)	$R_{w\%}$
13.385(6)	5.204(1)	9.119(1)	90.78(2)	635.1(5)	8.12
7.007(1)	7.007(1)	17.616(1)	120.0	749.3(1)	10.55

(1) L. Fuchs et al., Geochim. Cosmoch. Acta 31, 1711 (1967)
(2) P. B.Moore & T. Araki, Am. Mineralogist, 57, 1355 (1972)
(3) S. Manchetti, Neus Jahrbuch fur Mineralogie, 406 (1976)
(4) P. E. Werner, Z. Krist., 120, 375(1964)
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PS08.00.28 QUANTITATIVE RELATIONS AMONG CRYSTAL STRUCTURES ZEOLITES OF NATROLITE - EDINGTINITE GROUP.

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The comparative quantitative evaluation of crystal structure similarity degree was applied to small group of zeolite minerals. A procedure of quantitative evaluation is based on the concept of mapping [1]. A derived structure (2) is called to be related to a basic one (1) if it can be mapped by a pair of matrices(A,S). A is a non-singular 3x3 matrix, S is a (3x1) column matrix. M=(A,S) is called the mapping of the relationship. The special computer program was created [2]. The type of symmetry relationship among more than 10 structures of natrolite-edingtonite-scolecite-thomsonit-kalborsite series was shown. There is a strong specific influence of cation type on the tetrahedral network. The influence of different cations (in row H-Na-K-Rb-Ca-Ba) on other atomic positions in the structure is quantitatively estimated. The role of water molecules was discussed.

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[2] Malinovsky Yu.A., Burzlaff H.,Rothammel W., Structure of Lovozerite Type - a Quantitative Investigation, Acta Cryst. B 49 (1992), pp.158-164

PS08.00.29 STRUCTURES OF $SrSiO_3$ AND $SrGeO_3$.

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I succeeded in synthesizing $SrSiO_3$ and $SrGeO_3$ single crystals The space group is C2/c and the crystal data are: a=12.305(4), 12.533(3)Å; b=7.129(2), 7.262(1)Å; c=10.861(2), 11.259(3)Å; β =111.60(2), 111.30(2)° for $SrSiO_3$ and $SrGeO_3$, respectively. Hilmer(1962) studied the crystal structure of $SrGeO_3$ by Weissenberg method and Nadezhina, Pobedimskaya, Ilyukhin, Nikishina and Belov (1977) studied it by four-circle diffractometer. According to my results, it may be said that Hilmer's crystal is same polymorph as mine but he misunderstood its unit cell. On the contrary, it is certain that Nadezhina's one is another polymorph having $SrGeO_3$ contents. I can summarized: (1) Both structures include the layers comprised by SiO_4 or GeO_4 three-membered rings and the layers comprised by SrO_8 polyhedra. (2) They are piled up along **c** direction alternately. (3) In viewpoint of the polytipic consideration, my crystals are classified into the 6-layers group which are studied by Yamanaka and Mori (1981).

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Nadezhina, T. N., Pobedimskaya, E. A., Ilyukhin, V. V., Nikishina, N. N. & Belov, N. V. Dokl. Akad. Nauk SSSR, **233**, 1086 (1977).
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PS08.00.30 CHARACTERIZATION OF UO^{2+}_2 EXCHANGE Y-ZEOLITE.

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The present study involves the incorporation of uranyl ion into Y-zeolite. The Na^+- UO^{2+}_2 exchange in the framework was measured by neutron activation analyses. The X-Ray diffraction patterns of the materials have been studied in order to understand the behavior of uranyl ions in the zeolite and in order to present the unknown crystal data.

The Y- zeolite framework distort in response to the cation present in the structure. Hence the position of the UO^{2+}_2 in the structure was inferred from powder X-Ray diffraction data.