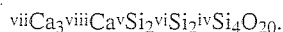


**PS08.00.22 STRUCTURE AND CRYSTAL CHEMISTRY OF  $\text{CaSi}_2\text{O}_5$  SYNTHESIZED AT 1500 °C AND 10 GPa: A NEW HIGH PRESSURE CALCIUM SILICATE WITH FIVE-COORDINATED SILICON.** Y. Kudoh<sup>1</sup>\*, M. Kanzaki<sup>2</sup>, <sup>1</sup>Institute of Mineralogy, Petrology, and Economic Geology Faculty of Science, Tohoku University, Sendai 980, Japan, <sup>2</sup>Department of Inorganic Materials, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan

Crystal structure of  $\text{CaSi}_2\text{O}_5$  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  $\text{Ca}_{1.02}\text{Si}_{1.99}\text{O}_5$  by E.P.M.A. analysis and  $a=7.243(2)$  Å,  $b=7.546(4)$  Å,  $c=6.501(4)$  Å,  $\alpha=98.57(5)^\circ$ ,  $\beta=95.18(4)^\circ$ ,  $\gamma=69.60(3)^\circ$ ,  $V=329.5(3)$  Å<sup>3</sup>, yielding the density value, 3.55 g/cm<sup>3</sup>. 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  $R_w=9.4\%$  with isotropic temperature factors. The crystal structure is closely related to that of titanite,  $\text{CaTiSiO}_5$ . The formula of unit cell contents is:



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.

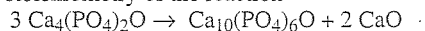
**PS08.00.23 ON THE CRYSTAL STRUCTURE OF APATITE.** Ann-Kristin Larsson<sup>a</sup>, Angel Landab<sup>b,c</sup>, <sup>a</sup>Research School of Chemistry, Australian National University, <sup>b</sup>Inorganic Chemistry 2, University of Lund, Sweden, <sup>c</sup>Present address: Dpto. Q. Inorganica, F.C.C. Quimicas, Universidad Complutense, 28040 Madrid, Spain

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 calcium phosphates and  $\text{CaO}$ .

The oxygen array of hydroxyapatite is described as a cyclic translation of an fcc lattice, as has been used to describe wightmanit and fluoborite<sup>2</sup>. Three-octahedra wide monolayers of edge-sharing oxygen octahedra are infinitely extended along  $\langle 110 \rangle_{\text{fcc}}$  ( $= \langle 001 \rangle_{\text{apatite}}$ ). 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  $\text{PO}_4$  tetrahedra (due to the small and highly charged  $\text{P}^{5+}$  ions).

HREM experiments showed the presence of slabs of  $\text{CaO}$  ( $\text{O}$  forms an fcc lattice) growing coherently in between slabs of apatite ( $\text{Ca/P}=1.67$ ). The apatite/ $\text{CaO}$  crystallites were formed from crystallites of tetracalcium phosphate ( $\text{Ca/P}=2$ ) 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  $\text{CaO}$ .

The stoichiometry of the reaction



suggests the formation of oxyapatite instead hydroxyapatite explaining the apparent p3 symmetry observed in the  $\langle 001 \rangle$  images of the apatite slabs.

<sup>1</sup>Kay, M. I., Young, R. A. & Possner, A. S (1964) *Nature*, **204**, 1050.

<sup>2</sup>Hyde, B. G. & Andersson, S. (1988) *Inorganic Crystal Structures*, John Wiley & Sons, New York.

**PS08.00.24 PREPARATION AND STRUCTURAL CHARACTERIZATION OF THE  $\text{PrBa}_2\text{Cu}_4\text{O}_8$  COMPOUND.** T.J. Lee\*, \*C.H. Chou, J.C. Huang<sup>§</sup>, C.H. Cheng<sup>§</sup>, S.R. Sheen<sup>#</sup>, and M.K.Wu<sup>#</sup>. \*Department of Physics, <sup>§</sup>Department of Chemistry, <sup>#</sup>Materials Science Center, National Tsing Hua University, Hsinchu, Taiwan 30043, ROC

The compound  $\text{PrBa}_2\text{Cu}_4\text{O}_8$  has been prepared under ambient oxygen pressure. The crystal structure of  $\text{PrBa}_2\text{Cu}_4\text{O}_8$  has been refined from X-ray powder diffraction data ( $\text{CuK}\alpha=1.5418\text{Å}$ ) by the Rietveld technique and confirms this compound has the 124 structure. At 300 K, the refined crystal data for  $\text{PrBa}_2\text{Cu}_4\text{O}_8$  are: orthorhombic system, space group Ammm,  $a=3.8897(2)\text{Å}$ ,  $b=3.9041(2)\text{Å}$ , and  $c=27.323(1)\text{Å}$ .  $M_r=1595.49$ ,  $V=414.92\text{Å}^3$ ,  $Z=1$ ,  $D_x=6.39\text{Mg m}^{-3}$ . The structure were refined with 30 parameters to  $R_w=6.02\%$ ,  $R_p=4.02\%$  for 4501 step intensities and  $R_b=8.0\%$ ,  $R_f=5.24\%$  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  $\text{YBa}_2\text{Cu}_4\text{O}_8$ .

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**PS08.00.25 HYDROTHERMAL SYNTHESIS AND CRYSTAL STRUCTURES OF GALLIUM AND INDIUM PHOSPHATES.** Kwang-Hwa Lii, Institute of Chemistry, Academia Sinica, Taipei, Taiwan, ROC

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 SYNTHESIS AND CRYSTAL STRUCTURES OF TWO NOVEL GALLOARSENATES:  $\text{Cs}_2\text{Ga}_3(\text{AsO}_4)_2(\text{As}_3\text{O}_{10})$  and  $\text{Cs}(\text{GaOH})_2\text{H}(\text{AsO}_4)_2$ .** Kuan-Jiuh Lin and Kwang-Hwa Lii, Institute of Chemistry, Academia Sinica, Taipei, Taiwan, R.O.C

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,  $\text{Cs}_2\text{Ga}_3(\text{AsO}_4)_2(\text{As}_3\text{O}_{10})$  and  $\text{Cs}(\text{GaOH})_2\text{H}(\text{AsO}_4)_2$ .

Crystals of  $\text{Cs}_2\text{Ga}_3(\text{AsO}_4)_2(\text{As}_3\text{O}_{10})$  were grown from a flux. It crystallizes in the monoclinic space group C2/c with  $a=27.0360(7)$ ,  $b=5.1074(2)$ ,  $c=12.5112(4)\text{Å}$ ,  $\beta=93.86(1)^\circ$ ,  $V=1723.7(2)\text{Å}^3$ ,  $Z=4$ ,  $R=0.035$  for 1486 independent reflections with  $I > 3.0\sigma(I)$ . The framework consists of  $\text{GaO}_6$  octahedra,  $\text{GaO}_5$  square pyramids,  $\text{AsO}_4$