

08.2-15 INTERSTITIAL CRISTOBALITE TYPE COMPOUNDS ( $\text{Na}_2\text{O}$ )<sub>0.33</sub>Na[AlSiO<sub>4</sub>]. By R. Klingenberg und J. Felsche, Fakultät für Chemie, Universität Konstanz, Postfach 5560, 7750 Konstanz, FRG.

A new series of interstitial compounds ( $\text{Na}_2\text{O}$ )<sub>0.33</sub>NaAlSiO<sub>4</sub> reveals cubic symmetry of the cristobalite type NaAlSiO<sub>4</sub>-carnegieite host lattice as concentrations of 0.01-0.33 Na<sub>2</sub>O are intercalated at elevated temperatures under closed system conditions 800-1100°C. The lattice expands correspondingly from  $a_0=7.3001(5)$  to  $7.3209(1)$  Å. The structure model of the end member ( $\text{Na}_2\text{O}$ )<sub>0.33</sub>NaAlSiO<sub>4</sub> shows unique (Na<sub>2</sub>O)-(Na<sub>2</sub>O) in the high temperature form of 3.17 Å from structure factor calculations based on X-ray powder diffraction data.  $6^{2/3}$  sodium atoms and  $1^{1/3}$  oxygens occupying the cage-like 12fold oxygen-coordinated position of space group F  $\bar{4}3m$  statistically form a diamond type sublattice in the high cristobalite type host lattice [AlSiO<sub>4</sub>]<sub>4</sub><sup>-1</sup>. Long-term annealing experiments (200 h, 100-600°C) indicate complex ordering mechanisms from super structure characteristics on X-ray GUINIER powder diffraction data.

At temperatures >1350°C intercalated Na<sub>2</sub>O is released under open system conditions with subsequent collapse of the NaAlSiO<sub>4</sub> host lattice from cubic to triclinic which is the regular symmetry of NaAlSiO<sub>4</sub>-carnegieites at temperatures <673°C.

Various single crystal growth experiments failed so far, unfortunately.

08.2-16 CRYSTAL STRUCTURE OF Na<sub>5</sub>Fe<sub>3</sub>(SO<sub>4</sub>)<sub>6</sub>O · 11H<sub>2</sub>O AND ITS RELATIONSHIPS WITH OTHER SIMILAR COMPOUNDS. By F. Scordari and G. Milella, Department of Geomineralogy, Bari University, 70121 Bari, Italy.

The title compound has been crystallized from a solution containing Na<sub>2</sub>SO<sub>4</sub> · 10H<sub>2</sub>O (3.4g) and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · nH<sub>2</sub>O (4.3g) at about 353 K. It is the Na-end member of some compounds obtained in the system K<sub>2</sub>SO<sub>4</sub>-Na<sub>2</sub>SO<sub>4</sub>-Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>-H<sub>2</sub>O (Scordari, B37, 312 (1981) and references therein). All their structures contain [Fe<sup>3+</sup>O(SO<sub>4</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>5-</sup> clusters. The nature of the monovalent cations, as the disorder involving some waters, hydronium and part of the alkaline, seems to be responsible of the different crystallochemical relationships between the clusters quoted above. This is reflected on the symmetry and on the stability of the salts.

The main crystal data for our compound are: Na(Na<sub>0.33</sub>, H<sub>2</sub>O<sub>0.67</sub>)<sub>12</sub>Fe<sub>3</sub>(SO<sub>4</sub>)<sub>6</sub>O · 3H<sub>2</sub>O, Cmcm,  $a = 15.015(4)$ ,  $b = 11.154(3)$ ,  $c = 18.385(4)$  Å,  $V = 3078.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 2.30$  (by flotation),  $D_x = 2.31$ ,  $M_oK\alpha$ ,  $\lambda = 0.7107$ ,  $\mu = 2.03$  mm<sup>-1</sup>, final  $R = 0.064$  for 1143 observed reflections.

08.2-17 X-RAY CRYSTALLOGRAPHIC STUDY OF HEXAKIS (PHENYLTHIO) CYCLOTRIPHOSPHAZATRIENE N<sub>3</sub>P<sub>3</sub>(Sph)<sub>6</sub>

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The structure of the title compound has been undertaken as part of a programme on the studies of cyclophosphazenes containing sulphur substituents.

The crystals are orthorhombic, space group P2<sub>1</sub>2<sub>1</sub>2 with two molecules in the unit cell of dimensions  $a = 19.392(2)$ ,  $b = 7.559(2)$  and  $c = 12.685(2)$  Å. The structure was solved by direct methods using visually measured intensities from photographic data and subsequently refined by least-squares with diffractometer data using anisotropic temperature factors to R-value of 0.029 for 1540 observed reflections.

The molecule lies on a two-fold axis. The phosphazene ring is planar. The structural features will be discussed and compared with those of N<sub>3</sub>P<sub>3</sub>Cl<sub>4</sub>(Sph)<sub>2</sub> and N<sub>3</sub>P<sub>3</sub>(OPh)<sub>6</sub> solved earlier.

08.2-18  $\alpha$ ,  $\gamma$  AND  $\beta$  PHASES OF LITHIUM IODATE BY NEUTRON SCATTERING AND NMR. By J.-M. Crettez, E. Coquet, Laboratoire d'Optique du Réseau Cristallin, UER MIPC, 6 Bd. Gabriel, 21100 Dijon, France, and J. Pannetier, J. Bouillot, Institut Laue-Langevin, 156X, 38042-Grenoble Cedex, France, and M. Durand-Le Floch, Laboratoire de Chimie Minérale D, Fac. Sciences, Avenue du Général Leclerc, 35042 Rennes, France.

Neutron powder diffraction patterns of ( $\gamma+\alpha$ ) and  $\beta$  lithium iodate samples are used to refine the structure of  $\gamma$  (at 488 K) and  $\beta$  (at 513 K) LiIO<sub>3</sub>. All three modifications are built up from Li<sup>+</sup> and (IO<sub>3</sub>)<sup>-</sup> pyramids but lithium is 6-fold, 5-fold and 4-fold coordinated to oxygen in the  $\alpha$ -,  $\gamma$ - and  $\beta$ -phases respectively. The study of IO<sub>3</sub> group displacements through the  $\alpha \rightarrow \gamma$  phase transition suggests that the  $\gamma$  phase structure is closely related to a mixed orthohexagonal description of the  $\alpha$  structure where both enantiomorphic forms of the hexagonal unit cell are present. The existence of a new  $\alpha'$  modification is postulated in view of neutron diffraction and NMR results. A simulation of the structure of hexagonal  $\alpha$ -LiIO<sub>3</sub> is also presented. Moreover, a kinetic study of the sequence of phase transitions on a neutron powder diffractometer has shown that the intermediate phase  $\gamma$  is always in equilibrium with either  $\alpha$  or  $\beta$  phases, and that the domain of stability of each phase depends on the particle size.