8.2.15  INTERSTITIAL CRYSTOBALITE TYPE COMPOUNDS
(Na₂O)₀.₃₃Na[Al₅O₁₈]·Na₂Oₐl₂O₅. By G. Klingenberg and J. Felsche, Fakultät für Chemie, Universität Konstanz, Postfach 5560, 7750 Konstanz, FRG.

A new series of interstitial compounds (Na₂O)₀.₃₃Na[Al₅O₁₈]·Na₂Oₐl₂O₅ reveals cubic symmetry of the cristobalite type NaAl₂O₅-carneigliite host lattice as concentrations of 0.01-0.33 Na₂O are intercalated at elevated temperatures under closed system conditions 200-1100°C. The lattice expands correspondingly from a₀=7.3001(5) to 7.3209(1) Å. The structure model of the end member (Na₂O)₀.₃₃Na[Al₅O₁₈] shows unique (Na₂O)₀.₃₃Na[Al₅O₁₈] in the high temperature form of 3.17 Å from structure factor calculations based on X-ray powder diffraction data. 67Na sodium atoms and 17/6 oxygens occupying the cage-like 12fold oxygen-coordinated position of space group P 4m statistically form a diamond type sublattice in the high cristobalite type host lattice [Al₅O₈]. Long-term annealing experiments (200 h, 1000-1000°C) indicate complex ordering mechanisms from super structure characteristics on X-ray Guinier powder diffraction data.

At temperatures >1380°C intercalated Na₂O is released under non equilibrated conditions with Na₂Oₐl₂O₅ collapse of the NaAl₂O₅-host lattice from cubic to triclinic which is the regular symmetry of NaAl₂O₅-carneigliite at temperatures <673°C.

Various single crystal growth experiments failed so far, unfortunately.

8.2.16  CRYSTAL STRUCTURE OF Na₅Fe₃(SO₄)₆O·11H₂O AND ITS RELATIONSHIPS WITH OTHER SIMILAR COMPOUNDS. By F. Scorza and G. Mizzali, Department of Mineralogy, Bari University, 70121 Bari, Italy.

The title compound has been crystallized from a solution containing Na₂SO₄·11H₂O·(3.4g) and Fe₂(SO₄)₃·nH₂O·(4.3g) at about 353 K. It is the Na₂-end-member of the compounds obtained in the system K₂SO₄·Na₂SO₄·Fe₂(SO₄)₃·nH₂O (Scordari, B37, 312 (1981) and references therein). All their structures contain [Fe²⁺SO₄]₃⁻·(H₂O)₃⁻ clusters. The nature of the monovalent cations, as the disorder involving some waters, hydronium and part of the alkali, seems to be responsible of the different crystallographic 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 is: Na₂(Na₂SO₄·11H₂O·(3.4g)·(FeSO₄)₃·(4.3g), Cam: a = 15.0151(6), b = 11.154(3), c = 18.385(4) Å, β = 3078.9. As, β = 4, Dm = 2.10 (by flotation), En = 2.317. MoKα, λ = 0.7107, μ = 2.03 mm⁻¹, Initial R = 0.064 for 1143 observed reflections.

8.2.17  X-RAY CRYSTALLOGRAPHIC STUDY OF HEXAKIS(PHENYLTHIO)CYCLOTRIPHOSPHAZETRINE N₃P₃(SPh)₆
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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 Pnma 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 N₃P₃Cl₄(SPh)₂ and N₃P₃(SPh)₆ solved earlier.


Neutron powder diffraction patterns of (γ + a) and δ lithium iodate samples are used to refine the structure of γ (at 488 K) and δ (at 513 K) LiI0₃. All these modifications are built up from L₄⁺ and (IO₃)⁻ pyramids but lithium is 6-fold, 5-fold and 4-fold coordinated to oxygen in the a-, γ- and δ-phases respectively. The study of IO₃ group displacements through the a- γ phase transition suggests that the γ phase structure is closely related to a mixed orthohexagonal description of the a structure where both enantiomorphic forms of the hexagonal unit cell are present. The existence of a new α' modification is postulated in view of neutron diffraction and NMR results. A simulation of the structure of hexagonal a-LiI0₃ is also presented. Moreover, a kinetic study of the sequence of phase transitions on a neutron powder diffractometer has shown that the intermediate phase γ is always in equilibrium with either a or δ phases, and that the domain of stability of each phase depends on the particle size.