

**08.2-23** THE CRYSTAL STRUCTURE OF THE TERNARY OXIDE  $\text{Li}_2\text{Ca}_4\text{Si}_4\text{O}_{13}$ . By L.E. Rendon-DiazMiron, M.E. Villa-fuerte-Castrejon, Instituto de Investigaciones en Materiales, Universidad Nacional Autonoma, Mexico 20 D.F., and C. Campana, Nicolet XRD Corp., Cupertino, CA 95014, U.S.A.

Four stable new ternary compounds had been reported in the system  $\text{Li}_2\text{O}-\text{CaO}-\text{SiO}_2$  (A.R. West, J. Am. Ceram. Soc. (1978) **61**, No. 3-4) but no crystal chemistry was done on them. We grew crystals of the  $\text{Li}_2\text{Ca}_4\text{Si}_4\text{O}_{13}$  phase of optimum size for crystal structure analysis. Single crystal diffraction diagrams show the material to be triclinic,  $\overline{P1}$ ,  $a = 10.4503 \pm 0.0027$ ,  $b = 8.2312 \pm 0.0025$ ,  $c = 7.1700 \pm 0.0021$ ,  $\alpha = 77.713 \pm 0.024$ ,  $\beta = 90.056 \pm 0.023$ ,  $\gamma = 109.249 \pm 0.022$ . The structure was solved using 2166 observed reflections. Full matrix least squares refinement with anisotropic temperature factors was terminated when  $R = 0.038$  and  $R_w = 0.041$ . In this structure the silicon in tetrahedral coordination forms two types of anions: a  $(\text{Si}_3\text{O}_{10})^{4-}$  unit like a zig-zag chain, and a  $(\text{SiO}_4)^{4-}$  unit. The coordination polyhedra of the lithium is also a tetrahedron, but distorted, and joins together the two silicon anions, forming two-dimensional layers. The calcium has a distorted cube-like coordination polyhedron that links the silicon-lithium layers.

**08.2-24** COMPOUND FORMATION AND CRYSTAL CHEMISTRY IN THE SYSTEM  $\text{Li}_2\text{O} - \text{ZrO}_2 - \text{SiO}_2$ . By Patricia Quintana, Universidad Nacional Autónoma de México, División de Estudios de Posgrado, Facultad de Química, Ciudad Universitaria, México 20, D.F., México and Anthony R. West, Chemistry Dept., Aberdeen University, Meston Walk, Old Aberdeen, Scotland, Great Britain.

The new ternary compound  $\text{Li}_2\text{ZrSi}_5\text{O}_{15}$ , found in the system  $\text{Li}_2\text{O} - \text{ZrO}_2 - \text{SiO}_2$ , has a monoclinic unit-cell of dimensions  $a = 11.121(6)$ ,  $b = 10.146(6)$ ,  $c = 11.235(7)$  Å,  $\beta = 100.26(6)^\circ$  and space group  $P2_1/n$ . Its crystal structure appears to be closely related to that of Zektzerite,  $\text{LiNaZrSi}_5\text{O}_{15}$ .

In the system  $\text{Li}_2\text{O} - \text{ZrO}_2$  nine lithium zirconate phases have been prepared, five of which are new. One of the new phases is a high temperature polymorph of  $\text{Li}_4\text{ZrO}_4$  and the others are metastable phases. The thermal behaviour and reaction pathways of formation of the new phases were studied and their X-ray powder patterns are reported.

**08.2-25** CRYSTAL STRUCTURES OF SOME METAL SACCHARINATES. By G. Jovanovski and B. Kamenar, Faculty of Chemistry, University of Skopje and Faculty of Science, University of Zagreb, P.O. Box 153, 41001 Zagreb, Yugoslavia.

The crystal structure of sodium saccharinate 2/3 hydrate (1), magnesium disaccharinate heptahydrate (2), tetraaquadisaccharinatomanganese(II) dihydrate (3), and disaccharinatomercury(II) (4) have been examined by X-ray analysis based upon the intensity data collected on an automatic diffractometer. In structure (1) two  $\text{Na}^+$  ions have C.N. six being surrounded by O atoms from water molecules, CO and  $\text{SO}_2$  groups from saccharinates, the third  $\text{Na}^+$  ion has also C.N. six but realized by five O atoms from the same groups and by one saccharinato N atom. The Na to O distances vary from 230.4 to 279.6 pm. In (2)  $\text{Mg}^{2+}$  ion is octahedrally surrounded by five O atoms from water molecules and one O atom from CO group. The Mg to O distances range from 203.0 to 211.3 pm. In (3) Mn atom is in the centre of symmetry and has octahedral coordination being bonded to four water-oxygen atoms and two saccharinato-nitrogen atoms. The Mn-O distances are 216.2 (2x) and 221.9 (2x), while Mn-N amounts to 228.1 pm (2x). In the unit cell of (4) there are two independent molecules, both with digonal characteristic coordination of Hg atoms. In one the Hg-N bond lengths are 203.8 and 205.0 pm, while in the other 202.9 and 205.8 pm, respectively. The N-Hg-N angles are  $167.0^\circ$  and  $175.4^\circ$ , respectively. In (1), (2) and (3) water molecules participate in hydrogen bonding with saccharinate ions. The saccharinate ions are planar with bond lengths and angles within expected values. The structures have been refined to R values of (1) 0.039, (2) 0.038, (3) 0.028 and (4) 0.062.

**08.2-26** MERCURY(II) COMPOUNDS WITH HIGH COORDINATION NUMBERS. By K. Aurivillius and C. Stålhandske, Inorganic Chemistry, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund 7, Sweden.

In mercury(II) compounds two-coordination is prevalent. In the coordination to O, Hg is in most cases linearly or almost linearly bonded at the short distances 2.0-2.2 Å. There are, however, often 3-5 more ligands at 2.4-2.9 Å, implying considerable weaker interactions. Four- and six-coordination for Hg(II) are rather unusual and coordination numbers higher than six have so far been reported only for  $\text{K}_3[\text{Hg}(\text{NO}_2)_4]\text{NO}_3$  (Hall & Holland, Inorg. Chim. Acta (1969) **3**, 235; Power et al, Inorg. Nucl. Chem. Lett. (1972) **8**, 809), containing  $[\text{Hg}(\text{NO}_2)_4]^{2-}$  ions. The eight oxygen atoms of the four nitrite groups form a highly distorted square antiprism around Hg with Hg-O bonds of 2.39-2.57 Å; the average value is 2.48 Å.

Eight-coordinated Hg has now also been found in the two Hg(II) bromates  $\text{Hg}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{K}_2\text{Hg}(\text{BrO}_3)_2(\text{NO}_3)_2$ . A preliminary X-ray study of  $\text{Hg}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$  has shown that Hg is bonded to two water molecules [ $\text{Hg}-\text{O}_w$  2.33, 2.34 Å] and four bromate groups [ $\text{Hg}-\text{O}$  2.42-2.72 Å] (Fig. 1); the average Hg-O bond being 2.48 Å. A neutron diffraction study is planned and the result will be presented at the congress.

In  $\text{K}_2\text{Hg}(\text{BrO}_3)_2(\text{NO}_3)_2$  the eight-coordination for Hg(II) is obtained by bonds to two nitrate [ $\text{Hg}-\text{O}$  4x2.589 Å] and four bromate groups [ $\text{Hg}-\text{O}$  4x2.434 Å] (Fig. 1) with an average Hg-O bond length of 2.50 Å.