08.2-2   CRYSTAL STRUCTURES OF AZIDES CONTAINING TWO DIFFERENT METAL ATOMS. By H.Krischner,Technical University Graz,AUSTRIA.

Azide compounds containing two different metal atoms can be prepared from aqueous solutions in various compositions and structure types. Crystal structure analyses of more than twenty azides demonstrate some general principles.

Elements with higher electronegativity have the greatest influence on the structures. They form finite or infinite metal-azide complexes. The coordination polyhedra are often similar to those in the simple azides. The apparent radii of the azide groups vary between 1.25 Å and 1.65 Å and can be taken as clue to the bonding strenght. M-N-N-bond angles in finite complexes are about 120°.

Elements with lower electronegativity have various coordination numbers and are ionic bonded. M-N-N-bond angles vary between 80° and 180°and central nitrogen atoms of azide groups are sometimes located closer to the metal than terminal nitrogens. In potassium strontium azide hydrate both cations are distributed among identical lattice positions and form a series of solid solutions.

Azide groups are always coordinated with both terminal N-atoms to several metal atoms. The surroundings of the nitrogen atoms are irregular. N-N-bonds vary between 1.10 Å and 1.28 Å, the mean distance within azide groups amounts to 1.18 Å. The N-N-N-angles deviate somewhat from 180°.

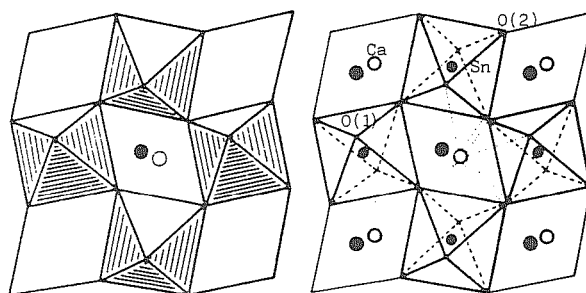Water is often situated beside azide groups within the coordination polyhedra.

Fig.1

for octahedra lying in the ab plane (Fig.1) and 148.23(30)° for those linked parallel to the c axis,and corresponding to Sn...Sn distances of 3.963 and 3.953 Å, respectively (mean value 3.958 Å).From these distances, the "one-angle" radius for Sn can be evaluated as 1.98 Å. The Ca atoms appears eight-coordinated, at the center of an irregular bicapped trigonal prism, with Ca-O distances of 2x2.791(4), 2x2.640(4), 2.414(6), 2x2.364(4) and 2.344(6) Å. These bonds are represented as dotted lines in Figure 1.

The coordinations numbers for aniones are: four for O(1)(with two Sn at 2.063 A and two Ca at distances of 2.344 and 2.414 Å) and five for O(2) (two Sn at 2.061 Å and three Ca at 2.364, 2.640 and 2.792 Å).

The SrSnO₃ crystals, whose orthorhombic unit cell dimensions would be approximately a ≈ 5.702 b ≈ 5.702 c ≈8.064 Å, are receiving our attention.

08.2-3   THE CRYSTAL STRUCTURE OF CaSnO₃. By A.Vegas, M.T. García-González*, M. Vallet-Regí** and J.M. González-Calbet**, Instituto Elhuyar, CSIC, Madrid, *Instituto de Edafología, CSIC, Madrid, **Dpto. Química Inorgánica, Universidad Complutense, Madrid, Spain.

SrSnO₃ and CaSnO₃ have been reported to have a perovskite-like structure, the former being cubic, with a=2aₚ (aₚ is the cell parameter of the parent cubic perovskite E2₁) (Müller and Roy, The major ternary structural families, Springer Verlag, Berlín (1974)) and the last, orthorhombic, with cell dimensions aₚ√2, 2aₚ, aₚ√2 (Coughanour, Roth and Fillmore, J. Research NBS (1954), 53, 201).

However, recent studies by electron diffraction and microscopy (Alario et al.(1983) unpublished results), suggest the existence of multitwinned crystals, in SrSnO₃, leading to a cubic symmetry arising from the superposition of three orthorhombic (slightly distorted cubic) nets. Thus, the same cell-type of CaSnO₃ (aₚ√2, 2aₚ, aₚ√2) must be assigned to SrSnO₃. To elucidate the differences between both structures and to confirm the results obtained by electron microscopy, we have undertaken their crystal structure determination. The structure of CaSnO₃ is presented below.

CaSnO₃, Pbnm, a=5.532(2) b=5.681(2) c=7.906(2)Å Z=4. The structure was solved from single crystal data, collected with Mo Kα radiation and corrected for absorption. Anisotropic refinement using the high-order reflexions (sin θ/λ >0.40 Å⁻¹) gave a final R=0.026.

The structure (Fig.1) is similar to that of CaTiO₃ and GdFeO₃, and its relation with the parent cubic structure (E2₁) has been well stablished (O'Keeffe and Hyde, Acta Cryst. (1977), B33, 3802). The SnO₆ octahedra are slightly compressed, with O-Sn-O angles from 87.65 to 92.35°, but with almost equal Sn-O bond-lengths (2.061-2.063(4) Å). The Sn-O-Sn angles are 146.65(30)°

08.2-4   STRUCTURAL ASPECTS OF THE PHASE TRANSITIONS IN TRICALCIUM SILICATE Ca₃SiO₅ (=C3S) Y. Takéuchi, F. Nishi, Mineralogical Institute, Faculty of Science, University of Tokyo, Hongo, Tokyo 113, and I. Maki, Department of Inorganic Materials, Nagoya Institute of Technology.

The crystal structure of the rhombohedral phase (Rh) of C3S, which is fundamental to those of the seven polymorphs of the material, has been determined based on a set of 371 diffraction intensities measured with aₒ single-crystal diffractometer at 1200°C [a=7.135(6) A, c=25.59(2) Å, R3m, Z=9 × Ca₂.₉₈Al₀.₀₄Si₀.₉₈O₅, R=10%]. Although the structure is similar to the reported rhombohedral average structure (<M>) (Jeffery, Acta Cryst. (1952) 5, 56) of the monoclinic superstructure of the MI phase, it is highly characterized by orientational disorder of the silicate tetrahedra: (a) a fraction, by 70%, of one of the three independent tetrahedra on the threefold axis points the -c, direction (a D orientation), while the remaining fraction points the +c direction (a U orientation), and (b) all tetrahedra are tilted in such a way that their apical bonds, otherwise on the threefold axis, slightly swing away from the threefold axis with Si's being kept in the axis.

The superstructure of MI has also been fully determined based on 3886 diffraction intensities [a=33.083(8) Å, b=7.027(2) Å, c=18.499 Å, β=94.12(2)°, Cm, Z=36 × Ca₂.₉₈ Mg₀.₁₁SiO₅, R=9.9%]. Fig.1 shows the arrangement of the silicate tetrahedra in a plane corresponding to the mirror plane passing through the origin and parallel to (110) of Rh; the broken lines trace the cell of <MI>. In terms of the orientational characteristics with respect to the subcell axes, the silicate tetrahedra may be classified into three categories: (1) those having fixed orientations, (2) those showing disorder in the two orientations U and D(U-D disorder), and (3) those showing U-D-G disorder, where G (Fig.1) represents