

**[s11.m1.p7]** A single-crystal X-ray study on the low-temperature phase transitions in leonite-type compounds. B. Hertweck\*, T. Armbruster\*\*, E. Libowitzky\*, \*Institut für Mineralogie und Kristallographie, Universität Wien – Geozentrum, Althanstraße 14, A-1090 Wien, Austria. \*\* Laboratorium für Chemische und Mineralogische Kristallographie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland.

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Leonite-type structures ( $C2/m$  at room temperature), i.e., the minerals leonite,  $K_2Mg(SO_4)_2 \cdot 4H_2O$ , mereiterite,  $K_2Fe(SO_4)_2 \cdot 4H_2O$ , and the synthetic compound  $K_2Mn(SO_4)_2 \cdot 4H_2O$ , are composed of  $SO_4$  tetrahedra and  $MeO_6$  octahedra ( $Me = Mg, Mn, Fe$ ), assembled in the form of  $Me[(H_2O)_4(SO_4)_2]^{2-}$  units, which are interconnected by large K cations in [9]- or [10]-coordination and H bonds of the  $H_2O$  molecules.

Previous structure investigations have shown that one of the sulphate groups is disordered at room temperature<sup>1</sup>. Refinements of single-crystal X-ray data<sup>2</sup>, and optical and thermodynamical data<sup>3</sup> of leonite, mereiterite and the synthetic Mn-analogue at ambient and low temperatures indicate that the dynamic disorder freezes to an ordered structure ( $I2/a$ ) at low temperatures. Upon further cooling, the ordered arrangement in Mg- and Mn-leonite switches to another polytype ( $P2_1/a$ ) with a different sulphate ordering scheme.

Both low-temperature phases are in a subgroup relation to the room temperature phase ( $C2/m$ ), but do not show supergroup/subgroup relations with each other. The cell dimensions increase linearly with increasing temperature, except for the  $a$  lattice parameter, which is decreasing. At the  $P2_1/a \rightarrow I2/a$  first order phase transition of Mg- and Mn-leonite the temperature dependencies of the  $a$  lattice parameter and the  $\beta$  angle show a discontinuity, i.e., a sudden increase of  $\sim 0.014 \text{ \AA}$  for  $a$  and a decrease of  $\sim 0.05^\circ$  for  $\beta$ . With increasing temperature the  $h+k+l = \text{odd}$  X-ray reflections of the  $P2_1/a$  phase, contradicting the  $I$ -centered cell, disappear suddenly at the  $P2_1/a \rightarrow I2/a$  phase transition. The  $h+k = \text{odd}$  (with  $l = \text{odd}$ ) X-ray reflections of the  $I2/a$  phase, contradicting the  $C$ -centered cell, decrease in intensity with increasing temperature and disappear at the  $I2/a \rightarrow C2/m$  order-disorder phase transition. Skipping the intermediate  $I2/a$  phase, the  $h+k = \text{odd}$  reflections of mereiterite at the  $P2_1/a \rightarrow C2/m$  order-disorder phase transition appear similar to the  $I2/a \rightarrow C2/m$  phase transition, but with an additional discontinuity in the temperature dependence of the  $a$  lattice parameter, i.e., an anomalous increase starting 40 Kelvin below the measured<sup>3</sup> temperature of the phase transition.

[1] Srikanta, S., Sequeira, A. and Chidambaram, R. "Neutron diffraction study of the space group and structure of manganese-leonite,  $K_2Mn(SO_4)_2 \cdot 4H_2O$ .", *Acta Cryst.*, (1968), B24: 1176 – 1182.

[2] Hertweck, B., Giester, G. and Libowitzky, E. "The crystal structures of the low-temperature phases of leonite-type compounds,  $K_2Me(SO_4)_2 \cdot 4H_2O$  ( $Me=Mg, Mn, Fe$ ).", *Am. Mineral.*, submitted.

[3] Hertweck, B., Libowitzky, E. and Giester, G. "Phase transitions in leonite-type compounds.", *Beih. Eur. J. Mineral.*, (1999), 11: 104.

**[s11.m1.p8]** Crystal structure formation of silicates in accordance with the mechanism of matrix assembly. G.D.Ilyushin, L.N.Demianets, *Institute of Crystallography of RAS, Leninsky pr.59, Moscow 117333, RUSSIA.* E-mail: Ilyushin@mail.ru

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The mechanism of crystal structure formation of silicates, on the basis of equivalent involvement of all primary structural units (PSU), is not designed till now. In  $? ?$ -silicates  $Me_xSi_yO_z$  such PSU's are  $[? ?_4]$  tetrahedra and  $[? ?_n]$  polyhedra ( $n=6-9$ ,  $Me=Me(2+)$ ,  $Me(3+)$ ,  $Me(4+)$ ). We suggested the model of a matrix assembling the structure when each of crystallographically independent PSU takes part in creation of crystal structure. The solution of the set problem is possible only at a subpolyhedral level of structural self-organization. The following results were obtained:

1. The combinatorial-topological model of an initial stages of subpolyhedral structure units (SSU) formation for  $? ?$ -silicates is constructed for the systems consisted of tetrahedra  $[? ?_4]$  and polyhedra  $[? ?_n]$ . One-bound monomer  $\{[? ?_n]+[? ?_4]\}$  can develop with the formation of the simplest chain SSU-precursors only on six topologically different channels. In two cases from 6, chain dimers (two monomers with one joint apex) can form two topologically different types of two-bound ring dimers. All 8 topological dimers of composition 2 ( $[? ?_n]+[? ?_4]$ ) are discussed as informative dimers (i-dimers) carrying the information on the SSU symmetry.

2. The 67 symmetrically different versions of dimer structures are found theoretically on base of space group analysis (i.e. 67 variants of geometric realization of dimers in crystal structure). The distribution of 67 dimer structures on 8 i-dimer types is described.

3. The method of identification of the channel of SSU evolution is developed on the base of method of crystal-structural intersection of symmetry groups  $G$  of phases. The rules for the selection of basic SSU from the set of probable SSU are defined (?) in a unit cell, all symmetrically possible SSU are built within the framework of group symmetry  $G$ ; (?) the indexes of a connectedness of SSU are defined for transformation of dimers into tetramers and tetramers into octamers; (?) the basic SSU with a maximal connectedness are chosen. The further transfer of basic dimer to higher level of structural organization (from dimer- to tetramer- and from tetramer- to octamer-level) is inspected by a symmetry and connectedness between dimers.

The model of matrix assembly of 35 structural types (ST) of silicates is constructed for the systems  $? ? ? -SiO_2$  ( $M? - Mg, Ca, Sr, Ba$ ; 16 ST),  $M?_2O_3 - SiO_2$  ( $Me - Sc, Y, TR$ ; 13 ST),  $M?O_2 - SiO_2$  ( $M? - Zr, Hf, Ce, Th, U$ ; 1 ST, zircon  $ZrSiO_4$ ). Structure invariants of basic SSU (dimers) consisted of  $[SiO_4]$ -tetrahedra and  $[? ?_n]$ -polyhedra are found and their structural derivants (tetramers and octamers) are built. The specific feature of the silicate formation from melts is the formation of structure invariant as four-polyhedral ring dimers possessing a point symmetry (-1). Such phases belong to major rock-forming families (zircon, olivine, apatite, tortveitite).