

08.4-15 THE X-RAY CHARACTERISTICS OF TAUSONITE, A NEW MINERAL OF THE PEROVSKITE GROUP

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Tausonite, SrTiO_3 , is of a perovskite type, its unit cell is primitive, cubic, space group $\text{Pm}\bar{3}\text{m}$. The single-crystal study does not reveal supplement reflection, which could indicate a pseudo-cubic symmetry of this mineral. The powder data from a diffractometer (DRON-3, $\text{CuK}\alpha$ - radiation) are identical to those of a synthetic SrTiO_3 . The double-line α_1 - α_2 is solving well, the halfwidth of reflections is comparable to that of quartz in close regions 2θ . The lattice parameters were obtained from a least-square refinement - $3.9048(1)\text{\AA}$. Taking into account the "ideal" cubic structure of tausonite, unit cell parameters help calculate the distance between atoms. The atom Sr is coordinated with 12 atoms O, and the Sr-O distance is 2.761\AA . The atom Ti is coordinated with 6 atoms O, and the Ti-O distance is 1.952\AA . Evidently tausonite is the first natural mineral in which the Ti-octahedra have the highest symmetry $\text{m}\bar{3}\text{m}$.

08.4-16 ON THE SIGNIFICANCE OF THE PHASE SIZE EFFECT FOR UNDERSTANDING THE PHENOMENA OF POLYMORPHISM AND POLYTYPOISM IN MINERAL CRYSTALS. By V.L.Tauson and M.G.Abramovich, A.P.Vinogradov Institute of Geochemistry, Irkutsk, USSR.

Considering the phase equilibria and thermodynamic properties of the small crystalline particles seems to be of great interest for mineralogy and crystallography since many of the minerals may occur in a dispersed state or indeed have passed through a microcrystal stage during their growth history. From the surface chemistry-state point equations are derived which describe the relationship between the shift of polymorphic equilibrium temperature and characteristics of size, habits and surface properties of crystals. These show a possibility for the phase size effect (PSE) in mineral crystals, that is to say the dependence of a phase transition point upon the crystal size. Experimental evidence for PSE in dispersed phases of ZnS and HgS is obtained. It is shown that the influence of crystal size on the $3\text{C} \rightarrow 2\text{H}$ tran-

sition in ZnS, at temperatures much lower than 1293 K (transition point in the bulk) is caused by the difference in specific surface free energies between 3C and 2H , being about 0.2 J/m^2 . The variations of the α - β transition point in HgS under annealing is presumed to be connected with the different particle size as well. The crystal polytypism could also be connected with the peculiarities of phase equilibria of small crystalline particles. From this an original mechanism for ZnS polytypes and microtwins formations in natural environments is proposed. It is based on the conception of PSE and presupposes the spontaneous accommodation of structure to the crystal size, constantly enlarging during the growth stage. The physicochemical consideration of the ZnS polytypism allowed to suggest the preference of structures having a higher percentage of cubic packing especially at elevated temperatures of the ore formation. The pure 2H -form could preferably occur under low temperature conditions.

08.4-17 ON THE STRUCTURAL RELATIONSHIP BETWEEN TWO POLYMORPHS OF $\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$. By R.M. Highcock, G.W. Smith and M.E. Vickers, BP Research Centre, Sunbury-on-Thames, Middx.

Two minerals with the above formula have been found at Leadhills, Scotland. They have been named leadhillite, which is monoclinic, space group $\text{P}2_1/\text{c}$, $a = 11.582(2)\text{\AA}$, $b = 20.809(3)\text{\AA}$, $c = 9.111(3)\text{\AA}$, $\beta = 90.48^\circ$, $Z = 8$ and macphersonite, orthorhombic, space group Pbca , $a = 9.227(2)\text{\AA}$, $b = 23.048(5)\text{\AA}$, $c = 10.368(4)\text{\AA}$, $Z = 8$. Both structures have been solved by direct methods from single-crystal diffractometer data. The severe effects of strong absorption ($\mu = 618\text{ cm}^{-1}$) have been investigated by applying semi-empirical, numerical and DIFABS correction procedures but the limitations inherent in all three methods have restricted refinement of the structures.

There are structural similarities between the two polymorphs. Both have alternating layers of carbonate and sulphate groups sandwiching the lead ions which are bridged by the hydroxyl groups. The difference between the structures lies in the relative positions of the cation and anion groups. A third polymorph, susannite also exists but so far good crystals are not available.

08.4-12 X-RAY AND NEUTRON-POWDER STUDY ON ENSTATITE. By H. Schrader, F. Frey and H. Boysen, Institut für Kristallographie und Mineralogie der Universität München, Theresienstr. 41, W-Germany.

Neutron powder diagrams of natural enstatite (MgSiO_3) from Bamble, Norway show a high diffuse background which is obviously caused by the incoherent scattering of hydrogen (talc?) and/or disorder within enstatite. The behavior of the diffuse background and the structural transformations of the (low) clino-, ortho- and protoenstatite by heat treatment was measured in the range from 300K up to 1470K and structure-refinements were carried out. X-Ray photographs of a single crystal enstatite at room temperature point out, that the material consists of ortho and clinoenstatite in a fine intergrowth with stacking faults which lead to diffuse streaks parallel to a^* . The scattered intensities of clino, ortho and proto superimpose in the powder diagram and change their contributions with various heat treatments. In any diagram only two polymorphs were simultaneously found and quantitatively separated by the Rietveld-technique: two diagrams with ortho and clino taken at room temperature from a natural crystal and from a tempered at 1470K and quenched crystal, further diagrams with ortho and proto taken at 1390K and 1470K. The relative volume ratio of the different polymorphs, the structural parameters, an analysis of the diffuse background and the time and temperature dependent transformation behavior will be given.

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08.4-13 NATURAL AND SYNTHETIC OPALS : TRANSMISSION ELECTRON MICROSCOPY STRUCTURAL STUDY. By J.P. Gauthier, Laboratoire de Minéralogie, Université de Lyon I, 43 Bd du 11 Novembre 1918 - 69622 Villeurbanne Cédex, France.

Precious opal can be considered as a paracrystal when looking its regular structure, which consists in a close-packed stacking of spherulites of amorphous silica. The size of silica balls reaches several hundreds or thousands of angströms in diameter. Up to now, such ordered structures have been mainly investigated by means of reflection scanning electron microscope on fractured or polished and chemically etched surfaces or by conventional transmission on surface replicas. Here is presented a direct TEM observation achieved on ion-beam thinned opals.

Natural gem-opals show perfectly round balls with empty octahedral and tetrahedral vacancies. Some classical features of real crystals appear also in such close-packed stackings : punctual or planar defects, stacking faults, sometimes polytypism, grain boundaries, "amorphous" regions. Conversely, the silica balls of the synthetic precious opal seem slightly distorted (by compression) and the vacancies are filled with small spheres of an unidentified compound much more absorbent than the silica. Further analyses will be undertaken, allowing an open discussion on the synthesis of this opal. In addition, a piece of a common green opal has been thinned and observed in similar conditions. As seen on diffraction patterns and electron micrographs, it crystallizes into spheroids of different sizes. Some of them can be optically observed between crossed polarizers. They have a fibrous texture, radially grown from the nucleation centers.

08.4-14 SIX-COORDINATE SILICON: NEW HIGH PRESSURE SILICATES WITH THE BENITOITE AND WADEITE STRUCTURES. By B.A. Fursenko, Institute of Geology and Geophysics, USSR Academy of Sciences, Novosibirsk, 630090, USSR.

New "mixed-coordinate" compounds with silicon both in six-fold and four-fold coordinations; $\text{BaSi}[\text{Si}_3\text{O}_9]$ and $\text{Rb}_2\text{Si}[\text{Si}_3\text{O}_9]$ were synthesized at 30-40 kbar and 1000-1100°C. Two Ge-analogs of these compounds: $\text{BaGe}[\text{Si}_3\text{O}_9]$ and $\text{Rb}_2\text{Ge}[\text{Si}_3\text{O}_9]$ were synthesized at lower pressures (10 kbar at 1000°C). The powder diffraction patterns were successfully interpreted by analogy with $\text{BaTi}[\text{Si}_3\text{O}_9]$ (benitoite, sp.gr. $P6c2=D_{3h}^2$) and $\text{K}_2\text{Zr}[\text{Si}_3\text{O}_9]$ (wadeite, sp.gr. $P6_3/m=C_{6h}^2$). Rb-compounds are similar to the high pressure phases of $\text{K}_2\text{Si}[\text{Si}_3\text{O}_9]$ and $\text{K}_2\text{Ge}[\text{Si}_3\text{O}_9]$ first synthesized by N. Kinomura et al. (Mineral. Mag. (1975) 40, 40I). Six-fold coordination of silicon in benitoite structure type was not reported previously.

Lattice parameters of hexagonal HP-phases (Å)

	$\text{BaSi}[\text{Si}_3\text{O}_9]$	$\text{BaGe}[\text{Si}_3\text{O}_9]$	$\text{Rb}_2\text{Si}[\text{Si}_3\text{O}_9]$	$\text{Rb}_2\text{Ge}[\text{Si}_3\text{O}_9]$
a_0	6.4995(2)	6.5820(2)	6.7323(2)	6.7842(3)
c_0	9.3503(5)	9.5376(5)	9.5344(4)	9.6450(7)

The new synthesized compounds belong to a narrow circle of substances in which silicon adopts the six-fold coordination by oxygen at relatively low pressures (Liebau, Bull. Minéral. (1971) 94, 239). Their structure involves a peculiar framework built from corner-linked $[\text{SiO}_4]$ -tetrahedra (forming $[\text{Si}_3\text{O}_9]$ -rings) and $[\text{SiO}_6]$ -octahedra with Ba and Rb occupying the large cavities. Similarly to germano-germanates, one may regard these compounds as silico-silicates. Indeed they are closely related to corresponding Zr-, Hf-, Sn-, Ti- and Ge-silicates as it is confirmed by a regular variation of lattice constants in the series of isostructural compounds. Lattice parameters a_0 and c_0 decrease linearly with the six-coordinate cation radius (from Zr^{4+} to Si^{4+}). It can be visualized as contraction of $[\text{MO}_6]$ -octahedra, the rings of $[\text{SiO}_4]$ -tetrahedra being practically the same in dimension. Deviations from linear relationship in the case of $^{VI}\text{Si}^{4+}$ is accounted for by this cation being very small causing a drastic increase in repulsive forces between neighbour oxygen atoms in octahedron and preventing it from the further contraction.