vested. The bending of crystals is the consequence of geometrical selection of systematically misoriented blocks, derived by lattice misfit strains.

PS-08.04.35 ESTIMATION OF HYDROTALCITE IN SERPENTINITES BY X-RAY DIFFRACTION AND IR SPECTROSCOPY.

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The amount of hydrotalcite Mg₃Al₆(OH)₁₆CO₃·₄H₂O (HT) in serpentinite is of importance since it is responsible for many properties of this material, as well as being acid absorber and catalyst carrier of practical use in cement and metal corrosion technologies for studies of different geological processes. The determination of HT in natural mixtures by XRD is beset with problems of X-ray amorphous serpentine, preferred orientation and disorder in minerals. These reasons prevent to use the X-ray method alone to estimate HT content in mixtures, because often more than one crystal type—usually several serpentine and other minerals—is present (Moroz T., Arkipenko D., Geol. Geophys., 1991, 2, 58). The development of a simple and convenient IR spectroscopic method for quantitative determination of HT in serpentinite is based on measurements of the relationship between intensities of IR vibrations of CO₃ ions (at 1375 cm⁻¹) and Si-O(Si), Si-O(Mg) vibrations (at 980–960 cm⁻¹), the former being absent in serpentine, the latter in HT. Calibration is required by another established method (DTA, autorheochromy) and the accuracy of the calibration is ±10%. The intensity and position of carbonate-related absorption defines the amount of interlayer carbonate and the local environments of the anions, and gives information about the cation order-disorder in octahedral sheets. The method appears to be applicable to crystallo-chemical estimation of natural HT from different deposits in mixture with chloride and talc, for checking on the separation of fine fraction and determination of structural regularities of hydrotalcite after T, P treatment.

PS-08.04.36 STRUCTURAL PECULIARITIES OF PHASE TRANSITION ANATASE - RUTILE.


In nature there are three polytypic modifications of TiO₂: anatase -D2h, z=4; brookite - D4h, z=8; rutile D4d, z=2. It is known that anatase and brookite on heating transform to rutile. Methods of X-ray diffraction and vibration spectroscopy have been used. X-ray anomalous intensities ("AnI") of different hkl reflections depending on temperature and heating conditions have been observed. The differences have been registered in IR and Raman-laser spectra as well. Lab IR - study of sorption of oleic acid on anatase, brookite and rutile structures showed essential differences. On the other hand X-ray analyses of samples of anatase and rutile from agid deposits registered "AnI" also i "markings" of phase transition, bipyramidal anatase forms were substituted by rutile. Samples of rutile with "AnI" from differ-
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PS-08.04.37 COPPER PHOSPHATES: LIBETHENITE Cu₄(PO₄)₂(OH) AND Cu₃Mn(PO₄)₂(OH)₂ SYNTHESIS AND CRYSTAL STRUCTURES.

By O. V. Yakubovich, Lomonosov State University and O. K. Melnikov, Inst. of Crystallography, Moscow, Russia. Crystals of two copper phosphates have been prepared by the hydrothermal method and characterized by complete X-ray single crystal structure determination; libethenite Cu₄(PO₄)₂(OH)₈, a=8.072(2), b=8.403(4), c=5.898(3) \( \AA \), \( \beta = 90^\circ \); \( \rho_{as} = 2.91 \text{ g/cm}^3 \); \( R = 0.097 \), \( R_w = 0.058 \), \( \chi = 1.28 \pm 0.14 \text{ refl.} \). Cu₃Mn(PO₄)₂(OH)₂, \( a=5.883(3), b=7.556(5), c=5.334 \) \( \AA \), \( \beta = 101.33(3), \beta = 105.80(3), \gamma = 108.42(3)^\circ \), \( P_1 \), \( Z=2 \), \( \rho_{as} = 2.70 \text{ g/cm}^3 \); \( R = 0.030 \), \( R_w = 0.033 \), \( \chi = 1.26 \pm 0.17 \text{ refl.} \). A new compound Cu₃Mn(PO₄)₂(OH)₂ with Cu²⁺ and Mn²⁺ cations in the same crystal were received for the first time. The basis of both structures is formed by a framework of octahedra and five-vertex polyhedra of Cu and Mn (N₅). All vertices of PO₄ tetrahedra are shared with the framework polyhedra. Peculiarities of Cu²⁺ polyhedron geometry are analyzed. The positions of the hydrogen atoms are located. A refinement of the hydrogen position in libethenite allowed to confirm a bifurcated hydrogen bond suggested earlier (Gordon A. J. C.). Min. 1798, 16, 153-157. It is shown that libethenite is a member of structures with triangular nets in the projection along the axis of 3n A. The BM sequence order and cause stacking faults. BM sequences may be described by sequences of BM- or BM-pair symbols. (Note: Further text on the page is not completely visible.)

Fig. 1. Scheme of a BM quadruple NH₁₁H. The octahedra are projecting into rhombi, circles indicate B atoms.


The structural variations of oxybates M₄B₄O₁₂ (M = Mg, Mn, Fe) considered by Bovin et al. (Acta Cryst., 1981, A37, 28-35) according to slip and twinning mechanisms may be completely explained by the OD nature of two alternating kinds of layer building modules (BM) (Fig. 1) parallel to the slip and twin planes and having symmetry Pm 2/m (2) and P1 2/m (1). α-operators 2 or 3 transforming a BM into itself are relating adjacent BM unambiguously while BM may be in two opposite orientations. The BMS may be denoted as H and N (11). BM pairs NH = h, HN = q, NI = d, HI = p are symmetrical and, hence, energetically equivalent (Dornberger-Schiff, Grundzüge einer OD Theorie, Berlin, 1964), and slight fluctuations in crystallization conditions and media composition may change the

PS-08.04.39 CRYSTALLOGRAPHIC STUDY OF A SERIES OF POLYMORPHIC OXYGEN CLUSTERS. By M.C. Zhao, T. Q. Huang, S.W. Zhang, Y.G. Wei & Y.Q. Tang, Department of Crystallography, Peiking University, Beijing, 100871, P.R. China.

Polyoxomolecules are important for elucidating the biological and catalytic functions of metal chelating clusters, a special type of chemistry seems to be related to redox and mixed valence clusters. If molybdate(VI) and tungstate(VI) are reduced in acid solution under Na₂ atmosphere, the resultant solution will be oxidized after exposure to air, and leads to the formation of novel and remarkable anions. With that we call TiO₂ Reconstituting (ROH) method, we have successfully synthesized a series of different types of heteropolyanions including three new type of high-nuclearity of clusters. The type and characteristics of these structures are:

1. Kang-type anions: \( \{\text{VW}_{11}\text{O}_{30}\}^{7-} \), space group \( P-\text{I}4 \text{~m} \text{~m} \), a=22.35(2), b=12.01(1), c=37.93(1), \( R = 0.054 \); 2. (VW₆O₁₈)²⁻, space group \( P-\text{I}4 \text{~m} \text{~m} \), a=31.07(3), \( R = 0.054 \).