

vertices and through the edges, $[\text{OCu}_{2.5}]_{\infty}^{3+}$ ($\text{Cu}_5\text{O}_2(\text{PO}_4)_2$); layers of six-fold rings formed by tetrahedra connected through the vertices with variable up and down orientation of free vertices, $[\text{OCu}_{1.5}\text{Pb}]_{\infty}^{2+}$ ($\text{Pb}_2\text{Cu}_3\text{O}_2(\text{NO}_3)_2(\text{SeO}_3)_2$); layers of fedotovite couples connected through the common vertices, $[\text{OCu}_2]_{\infty}^{2+}$ (dolerophanite $\text{Cu}_2\text{O}(\text{SO}_4)$); frameworks $[\text{OCu}]_{\infty}^{\infty}$ (tenorite CuO), $[\text{OCu}_2]_{\infty}^{\infty}$ (cuprite Cu_2O) and frameworks of cuprite type in Cu_2O (SeO_3).

The average length of the bond O-Cu in the tetrahedron $[\text{OCu}_4]$ increases from 1.916 Å for free vertices to 1.940 Å for vertices common to two tetrahedra, and 1.96 for vertices common to four tetrahedra (tenorite). Angles of bonds Cu-O-Cu take values mainly in the interval of 95-125°.

Tetrahedra $[\text{OCu}_4]$, polyions and compounds containing these tetrahedra may be formed from volcanous gases, self-igniting dumps of coal basins, blast furnaces and oxygen converters, and from the liquid phase in hydrothermal and other processes. Such complexes can preserve information on the structure of crystallization environment.

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LATTICE MISFIT IN MICAS AND THE GROWTH BENDING PROBLEM. By A. G. Shtrukenberg*, Y. O. Punin and E. N. Kotelnikova, Crystal Genesis Laboratory, University of St. Petersburg, Russia.

The origin of micas with sphere bending of basal plane is part of the general problem of growth curvature of crystals. Complex investigation of phengite-muscovite from Urals amazonstone pegmatites has been performed to find out the connection between mica bending and chemical deformation of crystal lattice.

Goniometer research has shown sharp oscillations of crookedness in growth direction of crystals, with a trend diverging from the law of inheritance of crookedness. Geometry of bending and degree of deformation are different in various growth sectors for faces of various simple forms. This is the evidence of growth origin of bending and also of changeability of bending factor with time.

Variations of cell dimensions within the volume of the crystal have been determined by the X-ray powder diffraction method. They have been compared with local changes of chemical composition obtained by microprobe analysis. Linear correlation of lattice parameters (a and b) with iron content and of d_{001} with rubidium content has been found. Some increase of the parameter and d_{001} in growth sector (110) in comparison with those (001) sector has been revealed. Cation composition and lattice parameters of investigated crystals vary strongly within the crystal. The most significant variations have been observed for b parameter and estimated to be 1% of the mean value.

Data received prove the existing hypotheses to be insufficient. High polytype homogeneity ($2M_1$) of crystals excludes bending because of coherence syntactic coalescence of polytypes. Random character of cell dimensions variations excludes the existence of constant moment on growth front. However existing differences in lattice parameters are sufficient for formation of mosaic structure. Mosaic structure of (110) growth sector confirms this proposal. A new mechanism of the bending of crystals is being sug-

gested. The bending of crystals is the consequence of geometrical selection of systematically misorientated 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 $\text{Mg}_3\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot 4\text{H}_2\text{O}$ (HT) in serpentinite is of importance since it is responsible for many properties of this material, as well as being acid absorbent and catalyst carrier of practical use in cement and metal corrosion technology, for studies of different geological processes. The determination of HT in natural mixtures by XRD is beset with problems of X-ray amorphous serpentinite, of 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 serpentinite and other minerals—is present (Moroz T., Arkhipenko 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 ν_3 vibrations of CO_3 ions (at 1375 cm^{-1}) and ν Si-O(Si), Si-O(Mg) vibrations (at $980\text{-}1060\text{ cm}^{-1}$), the former being absent in serpentinite, the latter in HT. Calibration is required by another established method (DTA, microchemistry) and the accuracy of the calibration is $\pm 10\%$. 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 crystallochemical estimation of natural HT from different deposits in mixture with chlorite 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.

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In nature there are 3 polymorphic modifications of TiO_2 : anatase - D_{2h}^8 , $z=4$, brookite - D_{2h}^8 , $z=8$, rutile D_{2h}^8 , $z=2$. 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 agold deposit registered "AnI" also; "markings" of phase transition: bipyramidal anatase forms were substituted by rutile. Samples of rutile with "AnI" from differ-

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ent parts of the deposit have been registered also and they correlate with geological data in a good way. Thus solution of direct problem in lab has allowed to solve a "converse" problem: "to reconstruct" a scheme of natural influence on anatase and rutile structures by analysis of "AnI". Therefore the changing of sorption properties after T-influence is one of the reasons of coexistence of gold and other noble metals with TiO_2 .

PS-08.04.37

COPPER PHOSPHATES: LIBETHENITE $\text{Cu}_2(\text{PO}_4)(\text{OH})$ AND $\text{Cu}_{2.5}\text{Mn}(\text{PO}_4)_2(\text{OH})$ -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 $\text{Cu}_2(\text{PO}_4)(\text{OH})$, $a=8.071(2)$, $b=8.403(4)$, $c=5.898(3)$ Å, Pnm, $Z=4$, $\rho_{\text{calc}}=3.97\text{g/cm}^3$, $R=0.0397$, $R_w=0.0358$, $s=1.28$, 814 refl.

$\text{Cu}_{2.5}\text{Mn}(\text{PO}_4)_2(\text{OH})$, $a=8.883(3)$, $b=7.556(3)$, $c=5.334(1)$ Å, $\alpha=101.33(3)$, $\beta=95.80(3)$, $\gamma=108.62(3)^\circ$, P1, $Z=2$, $\rho_{\text{calc}}=4.27\text{g/cm}^3$, $R=0.0310$, $R_w=0.0327$, $s=1.26$, 1720 refl.

A new compound $\text{Cu}_{2.5}\text{Mn}(\text{PO}_4)_2(\text{OH})$ with Cu^{2+} and Mn^{2+} 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). All vertices of PO_4 tetrahedra are shared with the framework polyhedra. Peculiarities of Cu^{2+} 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 (Cordson A. Canad. Mineral., 1978, 16, 153-157). It is shown that libethenite is a member of structures with triangular nets in the projection along the axis of $3n$ Å.

PS-08.04.38 THE MODULAR INTERPRETATION OF OXYBORATE STRUCTURES.

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The structural variations of oxyborates M_3BO_5 ($M = \text{Mg}, \text{Mn}, \text{Fe}$) 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 twinning planes and having symmetries $\text{Pm } 2/m$ (2) and $\text{P1 } 2/m$ (1). λ -operations 2 or 2m transforming a BM into itself are relating adjacent BM_1 unambiguously while BM_2 may be in two opposite orientations. The BMs may be denoted as H and N (11). BM-pairs $\text{NH}=\text{b}$, $\text{HN}=\text{q}$, $\text{NH}=\text{d}$, $\text{HN}=\text{p}$ are symmetrically and, hence, energetically equivalent (Dornberger-Schiff, Grundzüge einer OD Theorie, Berlin, 1964), and slight fluctuations in crystallization conditions and media composition may change the

BM sequence order and cause stacking faults. BM sequences may be described by sequences of BM- or BM-pair symbols. Numbers of consecutive equal letters N, H, b, d, p or q compose numerical symbols like those of Zdanov. These symbols directly correspond to the zig-zag chains of light spots imaging B-positions in HREM patterns. Symbols 2 and 2m of the λ -operations acting in H-BMs when used in structure notations are attributed to the intervals between equal or mirrorly equal letters (e.g. as for bb, dd or bd). Therefore they play the same role as letters h and c for close packings. According to the distribution of these operations, there are only two MDO (simple) structures satisfying the homogeneity condition: those of pinakillite (P), $\dots 2.2.2\dots$ and ludwigite (L), $\dots 2m.2m.2m\dots$. The other periodic structures listed by Bovin et al. (1981) are inhomogeneous (complex) as mixtures of P and L. The ratio P/L being equal to the ratio of the numbers of 2 and 2m operations is 1:2, 1:1 and 2:1 for the hypothetical structure (HS) in Fig. 8 of (Bovin et al., 1981), orthopinakillite (OP) and takeuchiite (T) respectively. The modular system is considered with common axes $a_0 \sim 12.5$, $b_0 \sim 3.0$, $c_0 \sim 4.6$ Å (c being the thickness of a layer pair). For periodic structures $\vec{a} = \vec{a}_0$, $\vec{b} = \vec{b}_0$, $\vec{c} = (m/5)\vec{a}_0 + n\vec{c}_0$. In reciprocal space $\vec{a}^* = \vec{a}_0^* - (m/5n)\vec{c}_0^*$, $\vec{c}^* = \vec{c}_0^*/n$ defining the diffractive features. The m, n values are $\pm 1, 1; 0, 2; \pm 1, 3; 0, 4; 0, 6$ for P, L, HS, OP and T respectively. A single slip corresponds to an operation sequence $\dots 2.2.2.2m.2m.2.2.2\dots$, a single twinning- to $\dots 2.2.2m.2.2\dots$. Two planes bordering a N (11) layer or an H layer may serve as slip or twin planes respectively. Their choice is thus ambiguous, the corresponding mechanisms are not convincing and may have no direct relation to reality.

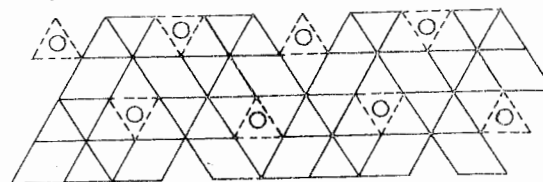


Fig. 1. Scheme of a BM quadruple NH11H. The octahedra are projecting into rhombi, circles indicate B-atoms.

PS-08.04.39 CRYSTALLOGRAPHIC STUDY ON A SERIES OF POLYMETALLATE OXYGEN CLUSTERS.

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Polyoxoanions are important for elucidating the biological and catalytic functions of metal chalcogenide clusters; a special type of chemistry seems to be related to reduced and mixed valence clusters.

If molybdate(VI) and tungstate(VI) are reduced in acidic solution under N_2 atmosphere, the resultant solution will be oxidized after exposition to air, and leads to the formation of novel and remarkable anions.

With that we call Red-Ox Reconstructing (ROR) method, we have successfully synthesized a series of different types of heteropolyanions including three new type of high-nuclearity of clusters. The types and characteristics of these structures are:

(1) Keggin-type anions: (1) $[\text{VMo}_{12}\text{O}_{40}]^{3-}$, space group $\text{Fm}\bar{3}\text{m}$, $a=22.334(2)$ Å, $V=11140$ Å³, $Z=8$, R factor is 0.055; (2) $[\text{VW}_{12}\text{O}_{40}]^{3-}$, space group $\text{P}\bar{4}3\text{m}$, $a=11.027(5)$ Å, $V=1340(11)$ Å³, $Z=1$, R factor is 0.054.