

pyrargyrite, the band positions in stephanite spectra are shifted to higher vibrational regions than those in pyrargyrite. This may be attributed to the complex structure of the stephanite and the effect of the surrounding elements.

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MS41 P06

C and/or C₂ in Reduced Rare Earth Carbide Halides
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Keywords: Rare Earth, Cluster, Endohedrals

The variety of compounds of Rare Earth metal carbide halides REX_nX_z ($X=Cl, Br, I$) is unexpectedly large. As known from the structural chemistry of the metal-rich compounds of 4d and 5d elements frequently discrete or condensed metal clusters occur [1]. For many cluster topologies the M_6X_{12} with an octahedral core is dominating. For the electron-poor Rare Earth metals the clusters are nearly always stabilised by interstitial atoms [2]. In the case of carbon as endohedral (i) single C atoms, (ii) C₂ dimers are known as well as both C and C₂ entities simultaneously (iii). According to X-ray analysis the C atoms and the C₂ dumbbells are statistically disordered in the center of the RE octahedra for (iii). The C/C₂ disorder is accompanied by an elongation/contraction of the Rare Earth metal clusters. The occurrence of isolated C atoms or C₂ units is determined firstly by the size of the surrounding RE cage and secondly by the electron count for the compound. A simple ionic treatment in the Zintl-Klemm concept in connection with the qualitative molecular orbital scheme for a C₂ dimer can reasonably predict the expected length of the C-C-distance. In all known examples the maximum formal charge assigned to the C₂ units is -6 corresponding to an ethanide ion C₂⁶⁻. When the formal charge exceeds 6- the dimers are no longer stable with respect to dissociation into two C⁴⁻ ions. On the other hand, when the surplus of electrons is consumed in metal metal bonds also C₂ dimers are possible. When the formal charge on C₂ becomes less than 6-, shorter C-C distances result as in the ethenide ions C₂⁴⁻. Our investigations on REX_nX_z compounds confirm these expectations.

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MS41 P07

Structural disorder in natural pearceite-T2ac: A combined TEM and SCXREF study

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Keywords: structural disorder, crystal structure, polytypism

Pearceite-T2ac is a member of the pearceite-polybasite group of minerals. These minerals - general formula $[Ag,CuS_4][Ag,Cu]_6M_2S_7$ with $M = Sb, As$ - have been recently structurally characterized [1,2,3]. On the whole, the structure of the polytype pearceite-T2ac can be described as a regular succession of two module layers stacked along the *c* axis: a first module layer (labeled *A*), with general composition $[(Ag,Cu)_6(As,Sb)_2S_7]^{2-}$, and a second module layer (labeled *B*), with general composition $[Ag_9CuS_4]^{2+}$. In the structure, (As,Sb) forms isolated (As,Sb)S₃ pyramids typically occurring in sulfosalts, copper links two sulfur atoms in a linear coordination, and silver occupies sites with coordination ranging from quasi linear to almost tetrahedral. In the *B* layer the silver cations are found in various sites corresponding to the most pronounced probability density function locations of diffusion-like paths. The structure was solved and refined on a twinned crystal up to $R = 4.34\%$ in the space group *P321*. It was anticipated that correlated local ordering of the relative positioning of the heavily disordered Ag cations within the *B* module layers might give rise to structured diffuse scattering. An electron diffraction study searching for this was therefore carried out on the same natural sample used for the structural investigation (sample AB6829, Naturhistorisches Museum of Vienna). The discovery of a highly structured, essentially continuous diffuse intensity distribution (particularly in the vicinity of the $[1\bar{1}1]$ and $[441]$ zone axis orientations) shows that the diffusion of neighbouring Ag ions must be highly correlated both within the *a-b* planes as well as from one such plane to the next. More detailed electron diffraction studies are underway to attempt to determine the detailed shape of the observed diffuse distribution and to model the real space Ag ion ordering presumed to be responsible.

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MS41 P08

Hybrid twinning in staurolite M. Nespolo^a, G. Ferraris^b
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Keywords: Effective twin index; Hybrid twinning; Staurolite

Staurolite gives two penetration twins, known as 90° or "Greek cross" twin 60° or "Saint Andrew" cross, with twin elements $4_{[100]}$ or $2_{[013]}$ for the former, and $3_{[102]}$ or $2_{[313]}$ for the latter [1,2]. The Greek cross twin has twin index 6, at the upper limit of Friedel's empirical limit for the occurrence of twinning, while the Saint Andrews twin has twin index 12, far too high to be more than an exceptional case. Despite this unusually high twin index, the Saint Andrews twin is the most frequent twin in staurolite and its occurrence frequency cannot be explained on the basis of the classical reticular theory of twinning.

The occurrence frequency of the Saint Andrews twin becomes less intriguing once it is explained as hybrid twin [3]. Hybrid twins are twins in which more than one concurrent sublattice exists, contributing to the overall lattice restoration, which is higher than what the classical twin index states. These concurrent sublattices occur when

more than one (direct) lattice element exists which is quasi-perpendicular to the twin element, where "quasi" mean within the accepted limit on the obliquity. In a hybrid twin, each sublattice is responsible for a partial restoration of the lattice nodes; the degree of approximation of this restoration differs for each sublattice and is directly related to the obliquity of each sublattice. The overall restoration is measured by the *effective twin index*, which is the ratio of the multiplicity of the cell of the sublattice with higher index and the number of lattice nodes quasi-restored by all the concurrent sublattices [3]. In the case of the Saint Andrews twin, there are two lattice planes quasi-perpendicular to the [313] twin axis.

- (231), corresponding to an index of 12 and an obliquity of 0.90° ;
- (352), corresponding to an index of 10 and an obliquity of 6.21° .

When these sublattices, which are both monoclinic, are taken into account, two nodes out of the 12 in the cell defined by [313] and (231) are quasi-restored, although with different obliquity, and the effective twin index is 6. The degree of lattice restoration is therefore comparable to that of the Greek cross twin.

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MS41 P09

MXL – a program for analysis of mix-layered structures Max Nickolsky^a, Victoriya Krupskaya,^a
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Keywords: mixed-layer structures, X-ray diffraction, modular crystallography

A method of identification and evaluation of the main probability parameters characteristic of mixed-layer structures, with no need for more than a good tracing of the basal reflections were suggested by Djakonov [1].

The method is based on the analysis of so-called Z-function. Physically Z-function is the self-convolution of electron density. Thus Z-function is proportional to 1-dimensional Patterson function such that its value at each point z is proportional to the product of the electron densities in planes separated by the distance z . Z-function presents principle and secondary maxima. For mixed-layer structures Z-function contain principle peaks if z is equal to the distance between identical layers. Positions and the heights of the secondary peaks depend to the internal structure of the layers. Analysis of the Z-function for mixed-layer structures is complicated by the secondary peaks which can overlap with principal peaks.

Accurate interpretation of Z-function provides information about type of layers, their relative concentration and way of alteration in the mixed-layer mineral.

MXL software package which calculate and interpret Z-function has been developed. The only required data is the set of integral intensities and positions of the reflections on the X-ray profile. Experimental data is corrected by Lorentz factor. Output data contain Z-function values for given thickness, positions of the principle and secondary maxima, probability parameters characteristic of mixed-layer structure.

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MS41 P10

Crystal chemistry of disordered layer-like oxonitridosilicates Oliver Oeckler, Juliane A. Kechele, Florian Stadler, Tobias Rosenthal, Hans Koss, Wolfgang Schnick, *Department of Chemistry and Biochemistry, LMU Munich, Germany.* E-mail: oliver.oeckler@gmx.de

Keywords: disordered solids, oxide and silicate crystallography, electron microscopy of crystals

Oxonitridosilicates have received remarkable attention owing to their suitability as host lattices for rare-earth doped phosphors in light-emitting diodes [1]. The luminescence properties of the compounds $\text{MSi}_2\text{O}_2\text{N}_2$ ($M = \text{Ca, Sr, Ba}$) are particularly promising [2-4]. For the profound understanding of these properties, detailed knowledge of the associated crystal chemistry is essential; however, numerous real structure effects complicate its investigation.

Unlike oxosilicates, layered structures such as those of $\text{MSi}_2\text{O}_2\text{N}_2$ [5, 6] exhibit highly condensed SiO_3 tetrahedra interconnected by N^{3-} atoms. These layers are interconnected via cations coordinating terminal O atoms of the tetrahedra. Both the cation arrangement and the silicate layers are highly pseudosymmetric. This fact gives rise to numerous real structure effects, which have been investigated in detail by means of high-resolution electron microscopy (HRTEM) complemented by the analysis of X-ray data including diffuse scattering and powder methods.

Comparable to the role of SiO_2 in silicate chemistry, the defect wurtzite structure of sinoite ($\text{Si}_2\text{N}_2\text{O}$) provides a basis for many oxonitridosilicates structures, and parts of it are frequently retained in complex structures. In addition, silicate layers may be interconnected by AlN_4 tetrahedra, for example in the compound $\text{SrAlSi}_4\text{N}_7$ [7]. Only a few basic structural motifs build up a number of compounds with compositions in the range $\text{SrAl}_{\leq 1}\text{Si}_{4.5}\text{N}_{6-8}\text{O}_{0-1}$ where silicate layers are partially interconnected by additional tetrahedra as well as larger cations. Owing to pronounced pseudosymmetry and versatile modes of interconnection, all of these compounds are highly disordered. However, they possess long-range ordered average structures that are evident from sharp Bragg reflections. The disorder involves the interchange of structure parts that accept different, but similar surroundings, ultimately leading to phasoids in some cases. As evidenced by HRTEM, complex diffraction patterns can be understood assuming domain structures, polytypism, and low-dimensional defects.

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