

ЭКСПЕРИМЕНТАЛЬНАЯ МИНЕРАЛОГИЯ

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© W. A. FRANKE,* P. LUGER,* M. WEBER,* T. I. IVANOVA**

LOW HYDROTHERMAL GROWTH OF SINCOSITE



В. А. ФРАНКЕ, П. ЛЮГЕР, М. ВЕБЕР, Т. И. ИВАНОВА. НИЗКОГИДРОТЕРМАЛЬНЫЙ РОСТ
 СИНКОЗИТА $\text{Ca}(\text{VO}/\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$

Синкозит $\text{Ca}(\text{VO}/\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ был синтезирован при 200 °С путем реакции монокристалла кальцита с раствором, содержащим VOCl_2 и H_3PO_4 . Описана кристаллическая структура.

The rare V^{4+} containing mineral sincosite from Sincos, Peru was first described by W. T. Schaller (1922). He assumed it to be isostructural to the uranium mica meta-autunite with VO^{2+} ions replacing the UO_2^{2+} units. Natural crystals are of poor quality due to turbostratic nature. Only M. E. Zolensky (1985) obtained a $hk0$ precession photograph of a crystal from South Dakota, Black Hills; he interpreted the structure to be tetragonal with $a = 8.895 \text{ \AA}$, $c = 12.727 \text{ \AA}$.

We obtained light green crystals by the slow reaction of a single crystal of calcite at 200 °C in an autoclave with a solution containing VOCl_2 and H_3PO_4 (0.01 mol). Rectangular platelets approximately of $200 \times 150 \mu\text{m}$ size grew perpendicular to the wall of the glass container. Sincosite was obtained also at 100 °C, but the crystal quality was very poor, the X-ray powder diffraction data of both grains fitted to JCPDS 39-318 sincosite.

Already M. E. Zolensky (1985) presumed the existence of isotypic compounds. Such isotypic compounds were synthesized substituting Mg for Ca, and As for P.

Single crystal analysis revealed for sincosite a structure indeed similiar to meta-autunite, but forming a triclinic cell (sp. gr. $P1$, $Z = 1$). The formula unit contains only four H_2O instead of five as presumed by M. E. Zolensky. It is seen from the following unit cell data, that only the Mg compound is tetragonal:

| Compound | a, Å | b, Å | c, Å | α, ° | β, ° | γ, ° | Pointgroup |
|---|-------|-------|--------|--------|-------|-------|------------|
| $\text{Ca}(\text{VO}/\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ | 6.354 | 6.329 | 6.598 | 106.72 | 94.10 | 90.06 | 1 |
| $\text{Ca}(\text{VO}/\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ | 6.502 | 6.484 | 6.719 | 106.43 | 85.49 | 90.36 | 1 |
| $\text{Mg}(\text{VO}/\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ | 6.251 | 6.251 | 13.448 | 90 | 90 | 90 | 4/m |

PO_4 and VO are forming dense packed layers in the plane (001), these layers are tied together by Ca fourfold coordinated by H_2O . The coordination number of Ca is seven:

* Freie Universität Berlin, Takustr. 6, D-14195 Berlin, Germany.

** St. Petersburg State University, Dept. of Crystallography, University Emb. 7/9, 199034, St. Petersburg, Russia.

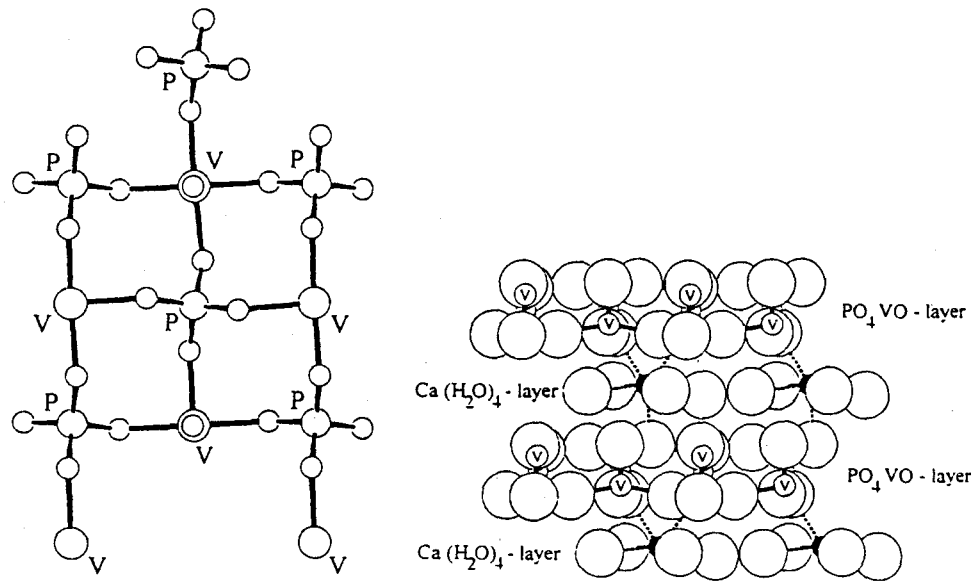


Fig. 1. Arrangement of the PO_4 tetrahedra and VO groups in the plane (001), Ca and H_2O are omitted.

Рис. 1. Распределение тетраэдров PO_4 и групп VO в плоскости (001), Ca и H_2O не показаны.

Fig. 2. Sincosite structure viewed in the direction [100]. Dense packing is demonstrated by showing four unit cells with oxygen size close to the real ionic radius (black circles: Ca).

Рис. 2. Вид структуры синкозита в направлении [100]. Плотность упаковки видна из показанных четырех элементарных ячеек с размерами кислорода, близкими к его реальному ионному радиусу; черные кружки — Ca.

4 oxygen from water, 2 oxygen from PO_4 tetrahedra from different layers and 1 oxygen from VO. No oxygen of H_2O is a next neighbour to V; thus V is fivefold coordinated.

The pseudotetragonal arrangement of PO_4 tetrahedra and VO groups is shown by fig. 1, whereas fig. 2 illustrates the dense packing of the whole structure.

The refractive indices measured $n\alpha' = 1.692$ and $n\beta' = 1.700$ are very similar to the values given by W. T. Schaller (1924), the direction of extinction for crossed nicols is [110].

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