THE CRYSTAL STRUCTURE OF CALCIRTITE: A NEW DERIVATIVE STRUCTURE OF CaF_2-CeO_2 TYPE

Yu. A. Pyatenko and Z. V. Pudovkina

Institute of Mineralogy, Geochemistry, and Rare-Element Chemical Crystallography

Translated from Kristallografiya, Vol. 6, No. 2, pp. 196-199,
March-April, 1961
Original article submitted September 16, 1960

An x-ray study has been made on the mineral calcirtite $Ca(Zr, Ca)_2 Zr_4 (Ti, Fe)_2 O_{16}$, which is tetragonal and whose lattice parameters are a = 15.30, c = 10.20 A; space group $I4_1/acd$. The structure is derived from the cubic fluorite-cerianite structure.

The new mineral calcirtite [1] is an oxide mineral containing Ca, Zr, and T. Its composition (analyst A. V. Bykova) gives the formula $Ca_{1.015} Zr_{2.894} Ti_{1.105} Fe_{0.104} Nb_{0.004} O_9$, which in ideal form is $CaO \cdot 3ZrO_2 \cdot TiO_2$ $CaZr_3TiO_9$. It has been observed [1] that the powder pattern resembles that given by pyrochlore, all the strong lines being the same. Pyrochlore itself has a structure derived from that of fluorite [2]; this structure is uncommon, and occurs only in CaF_2, CeO_2, ThO_2, UO_2, and certain other compounds. This shows that we may assume that the structure is of the CaF_2-CeO_2 type.

T. B. Zdorik kindly provided the specimens for this work; they included no crystal with proper faces, so all diffraction patterns were recorded from transparent isometric pieces of size 0.3-0.4 mm.

X-ray goniometry [3] demonstrated that the mineral is tetragonal (Laue class 4/mmm), which is in agreement with the uniaxial optical pattern. The Bravais lattice and the lattice parameters were found from oscillation patterns; the latter were refined from the pinacoidal reflections on the layer lines. The lattice is body-centered (I), with c exactly 2/3a: a = 15.30 ± 0.06, c = 10.20 ± 0.04 A. The affinity with CaF_2-CeO_2 is sufficient explanation of the cause of the multiples of 5.1 A.

We deduced the number of atoms in the unit cell on the basis of the above empirical formula; the specific gravity is 4.99, and the molecular weight of a formula unit is 503.50, so N = 14.26. The cation numbers are not integers, so N should not be rounded off; the number of atoms in the cell is to be found by multiplying the cation numbers by 14.26. The individual values are

$$\left.\begin{array}{ll}\mathrm{Ca} — 14.47 & \\ \mathrm{Zr} — 41.27 & \\ \left.\begin{array}{l}\mathrm{Ti} — 14.47\\ \mathrm{Fe} — 1.48\\ \mathrm{Nb} — 0.06\end{array}\right\} & 16.01\end{array}\right\} 71.75$$

$$\mathrm{O} — 128.34 \sim 128$$

Isomorphous substitution is clearly very important, so the cations may be grouped; only the number of oxygen atoms has been rounded off to 128.

We used a KFOR camera to record the layer lines [0 trace (second on c) and the zeroth on a]. The systematic absences are in agreement with an I lattice; reflections with h + k + l = 2n are present. All hk0 with h =2n are present; so are all h0l with l = 2n, but only hh$l$ with 2h + l = 4n occur. These define the group uniquely as D_{4h}^{20} - $I4_1/acd$. Strong and weak reflections alternate in a very characteristic fashion in the above layer lines, the strong ones being those allowed for an F lattice whose parameters are $a' = {}^1/_3 a = {}^1/_2 c = 5.1$ A.

The weak reflections occur as a result of an 18-fold expansion of the unit cell (3 × 3 × 2 = 18) relative to CeO_2; the causes of this are that the cations form an ordered array and that the atoms deviate slightly from the ideal positions.

The unit cell of CeO_2 contains four cations and eight oxygen atoms (the same applies to ThO_2, UO_2, etc), and an 18-fold expansion would imply 72 cations and 144 oxygen atoms. The cell actually contains that number of cations ($71.75 \approx 72$), but there are only 128 oxygen atoms. The expansion is accompanied by the loss of 16 (= 144-128) oxygen atoms, which as a percentage (11.1%) is slightly less than that found for pyrochlore (12.5%) [2].

Analysis of group D_{4h}^{20} shows that the ideal structure of CeO_2 can be reproduced in only two cases, namely, when the first cations are placed (I) at the special positions $\bar{4}$ and (II) between them at (222). If we put the origin at $\bar{4}$, these two arrays become (I) 8(a)+ 32(g)+32(g); (II) 8 (b)+ 16 (f) + 16 (f) + 32 (g) [4]. The O atoms take up the same positions in both cases; their sites are uniquely determined by the cation array.

The Patterson projection P (uv) derived from 95 independent hk0 reflections showed that the basic pattern is that of CaF_2 and that the deviations from the ideal positions are extremely small. A completely random array is improbable, but we lacked evidence for any

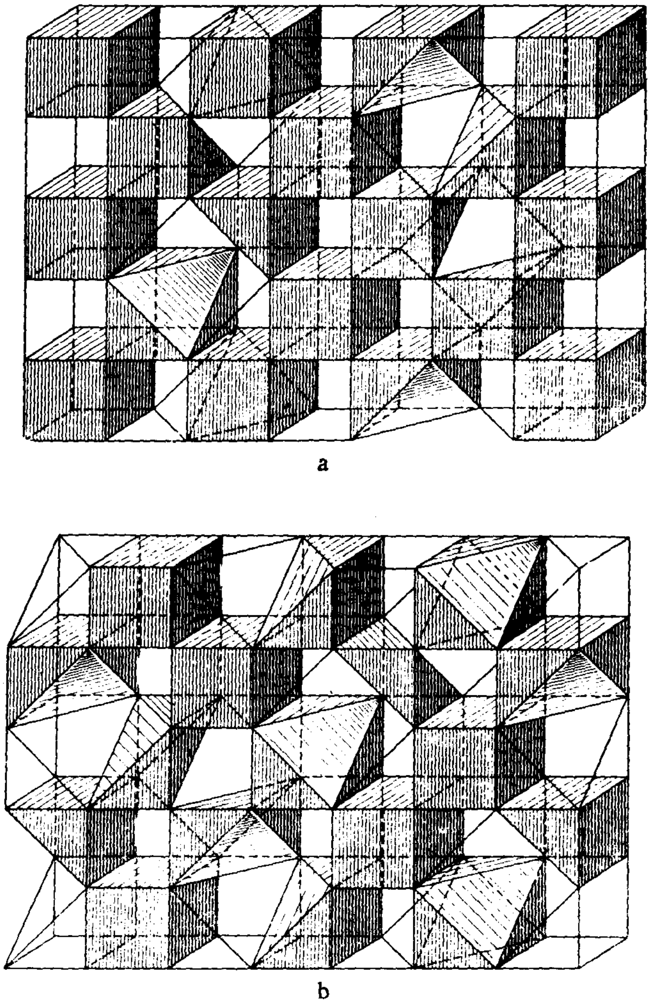

Fig. 1. Two layers in the structure of calcirtite.

Ideal Coordinates for the Structure of Calcirtite

Atom	x	y	z
8 Ca	0	0	1/4
6.5 Ca + 9.3 Zr	1/6	1/6	1/4
16 Ti (Fe, Nb)	1/3	1/3	1/4
32 Zr	1/6	0	1/2
16 O_I	1/4	1/4	1/8
16 O_{II}	1/4	1/12	1/8
32 O_{III}	1/4	1/12	3/8
32 O_{IV}	1/12	1/12	1/8
32 O_V	1/12	1/12	5.8

other kind of array, so we were forced to assume that all atoms had the same scattering power in order to establish the signs of the structure factors. Two ρ (xy) projections of the electron density were constructed, the first only from the strong reflections and the second from all. The latter showed substantial differences between the heights of the various peaks, which was evidence for some degree of order in the structure. Moreover, the deviations from the ideal positions were found to be not more than 0.10-0.15 A in the xy projection. Unfortunately, Fourier methods could not be applied to examine the structure further; the F^2 series gave no promise of improvement on account of the high symmetry and special features of the structure, since individual interatomic vectors could not be isolated. An attempt to refine the coordinates from the electron-density patterns was unsuccessful, because the cell is large and the signs of the weak superlattice reflections could not be established with certainty.

Sixteen O atoms are lost when the cell of calcirtite is derived from 18 cells of CeO_2; deletion of one (of the three) 16-fold sets (namely those O atoms that lie on fourfold screw axes) results in an improbably structure having channels along $\underline{z}$ (all oxygen atoms on one line are removed). The anion patterns resulting from the removal of either of the other two 16-fold sets (on horizontal twofold axes) are almost identical; the pattern can be used to construct a likely model for calcirtite, in which some of the cubes in the parent structure become polyhedra of two different kinds (one kind a cube lacking one corner, the other a cube lacking two opposite corners). Pyrochlore has only cubes and octahedra, because there are only two types of cation (Ca and Nb); calcirtite has three types of polyhedra, because the cations are Ca, Zr, and Ti. Our final model for the structure gave good agreement with the heights of the electron-density peaks. The cation array is as follows. Eight Ca atoms fill cubes, which alternate along $\bar{4}$ axes parallel to z with empty polyhedra of the same kind (Fig. 1a). A layer parallel to (100) contains two rows of alternating empty and full figures with seven corners, the layer being adjacent to a row of Ca figures; the former figures contain 32 Zr atoms in general positions. A layer of another type lies along [100] near the above layer (Fig. 1 b); It consists of the above Zr figures and of rows containing filled octahedra and cubes, which are supplemented also by empty figures with seven corners. The octahedra contain 16 Ti (Fe, Nb) atoms; the cubes, 6.5 Ca + 9.3 Zr, which are randomly distributed over the 16-fold positions. The table gives the coordinates

This structure gives the Ti atoms their natural octahedral environment; 32 of the 41.3 Zr atoms also have their natural coordination number of seven [5]. One set of eight cubes contains only Ca atoms; the other 16 cubes contain Ca and Zr arranged at random. In these the large Ca atoms form the appropriate complement to the small Zr atoms. The valencies of the O atoms are found to deviate from two by not more than 11%, which is much less than the permitted amount (25%).

Formulas that distinguish between atoms that occupy crystallographically distinct positions are $Ca_8(Ca_{6.5}, Zr_{9.3}) Zr_{32}(Ti, Fe)_{16}O_{128}$ and $Ca(Ca_{0.8}, Zr_{1.2}) Zr_4 (Ti, Fe)_2O_{16}$.

The atoms are displaced slightly from the ideal positions, but the deviations cannot be large, as the experimental results indicate and as would be required by the high symmetry and special structure. The last feature also indicates that there can be no change in the coordination numbers as a result of the transition from the ideal structure to the real one.

LITERATURE CITED

1. T. B. Zdorik, G. A. Sidorenko, and A. V. Bykova, Doklady Akad. Nauk SSSR (in press).
2. N. V. Belov, Min. Sborn. L'vov. Geol. Obshch. 4, 21 (1950).
3. M. M. Umanskii and S. S. Kvitka, Izvest. Akad. Nauk SSSR, ser. fiz. 15, 147 (1951).
4. International Tables for X-ray Crystallography 1 (1952).
5. N. V. Belov, Kristallografiya 5, No. 3, 460 (1960). [Soviet Physics-Crystallography, Vol. 5, p. 436].