

CRYSTAL STRUCTURE OF γ - $\text{Cu}_2\text{V}_2\text{O}_7$ AND ITS COMPARISON TO BLOSSITE (α - $\text{Cu}_2\text{V}_2\text{O}_7$) AND ZIESITE (β - $\text{Cu}_2\text{V}_2\text{O}_7$)

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ABSTRACT

Single crystals of γ - $\text{Cu}_2\text{V}_2\text{O}_7$ were obtained by the method of chemical transport reactions. The crystal structure [triclinic, $P\bar{1}$, a 5.0873(10), b 5.8233(11), c 9.4020(18) Å, α 99.780(3), β 97.253(3), γ 97.202(3)°, V 269.20(9) Å³, $Z = 2$] has been solved by direct methods and refined to $R_1 = 0.021$ ($wR_2 = 0.049$) using 949 unique observed reflections with $|F_o| \geq 4\sigma_F$. The atomic arrangement contains two symmetrically independent Cu^{2+} cations. The Cu(1) site is coordinated by six O atoms to form a distorted Cu(1)O₆ octahedron, whereas the Cu(2) site is coordinated by five O atoms arranged at the vertices of an elongate Cu(2)O₅ square pyramid. Two symmetrically independent V^{5+} cations are tetrahedrally coordinated by four O atoms each. The O(5) atom bridges the V(1)O₄ and V(2)O₄ tetrahedra. The Cu(1)O₆ octahedra and Cu(2)O₅ square pyramids form two types of chains running parallel to the a axis. The chains are linked by V₂O₇ groups into a complex heteropolyhedral framework. The structure of γ - $\text{Cu}_2\text{V}_2\text{O}_7$ is closely related to the structures of α - $\text{Cu}_2\text{V}_2\text{O}_7$ (blossite) and β - $\text{Cu}_2\text{V}_2\text{O}_7$ (ziesite). The three structures are based upon chains of edge-sharing Cu^{2+} polyhedra linked by V₂O₇ groups. Similarity of the structure of γ - $\text{Cu}_2\text{V}_2\text{O}_7$ to the structures of blossite and ziesite indicates possible formation of this phase under natural conditions, such as those that occur in "dry" high-temperature fumaroles of the Izalco (El Salvador) and Tolbachik (Kamchatka, Russia) volcanoes. The structure of γ - $\text{Cu}_2\text{V}_2\text{O}_7$ can also be considered as a triclinically distorted derivative of the β - $\text{A}_2\text{P}_2\text{O}_7$ structure-type.

Keywords: γ - $\text{Cu}_2\text{V}_2\text{O}_7$, blossite, ziesite, fumarole, crystal structure.

SOMMAIRE

Nous avons synthétisé des monocristaux de γ - $\text{Cu}_2\text{V}_2\text{O}_7$ par la méthode de transfert chimique. La structure [triclinique, $P\bar{1}$, a 5.0873(10), b 5.8233(11), c 9.4020(18) Å, α 99.780(3), β 97.253(3), γ 97.202(3)°, V 269.20(9) Å³, $Z = 2$] a été résolue par méthodes directes, et affinée jusqu'à un résidu R_1 de 0.021 ($wR_2 = 0.049$) en utilisant 949 réflexions uniques observées ayant $|F_o| \geq 4\sigma_F$. L'arrangement des atomes contient deux cations Cu^{2+} symétriquement indépendants. L'atome Cu(1) est coordonné à six atomes d'oxygène pour former un octaèdre difforme, Cu(1)O₆, tandis que l'atome Cu(2) est coordonné à cinq atomes d'oxygène disposés aux coins d'une pyramide carrée Cu(2)O₅ élongée. Deux cations V^{5+} symétriquement indépendants sont en coordination tétraédrique à quatre atomes d'oxygène chacun. L'atome O(5) agit comme pont entre les tétraèdres V(1)O₄ et V(2)O₄. Les octaèdres Cu(1)O₆ et les pyramides carrées Cu(2)O₅ forment deux sortes de chaînes parallèles à l'axe a . Ces chaînes sont liées par les groupes V₂O₇ pour former une trame hétéropolyédrique complexe. La structure de γ - $\text{Cu}_2\text{V}_2\text{O}_7$ est étroitement liée à celles de α - $\text{Cu}_2\text{V}_2\text{O}_7$ (blossite) et de β - $\text{Cu}_2\text{V}_2\text{O}_7$ (ziesite). Les trois structures sont fondées sur des chaînes de polyèdres à Cu^{2+} à arêtes partagées, et liées par des groupes V₂O₇. La ressemblance de la structure de γ - $\text{Cu}_2\text{V}_2\text{O}_7$ aux structures de la blossite et de la ziesite indique la formation possible de cette phase dans la nature, par exemple dans le fumaroles "sèches" de haute température aux volcans d'Izalco (El Salvador) et Tolbachik (Kamchatka, Russie). On peut aussi considérer la structure de γ - $\text{Cu}_2\text{V}_2\text{O}_7$ comme dérivé difforme triclinique du type structural β - $\text{A}_2\text{P}_2\text{O}_7$.

(Traduit par la Rédaction)

Mots-clés: γ - $\text{Cu}_2\text{V}_2\text{O}_7$, blossite, ziesite, fumarole, structure cristalline.

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INTRODUCTION

Anhydrous copper vanadates are characteristic minerals of high-temperature volcanic fumaroles of Izalco volcano, El Salvador (Hughes & Stoiber 1985), and Tolbachik volcano, Kamchatka (Vergasova & Filatov 1993). The list of fumarolic mineral species that contain Cu and V as essential mineral-forming components includes: mcbirneyite, $\text{Cu}_3(\text{VO}_4)_2$ (Hughes *et al.* 1987a), blossomite, $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ (Robinson *et al.* 1987), ziesite, $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ (Hughes & Birnie 1980), fingerite, $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$ (Hughes & Hadidiacos 1985), stoiberite, $\text{Cu}_5\text{O}_2(\text{VO}_4)_2$ (Birnie & Hughes 1979), lyonsite, $\text{Cu}_3\text{Fe}_4(\text{VO}_4)_6$ (Hughes *et al.* 1987b), leningradite, $\text{PbCu}_3(\text{VO}_4)_2\text{Cl}_2$ (Vergasova *et al.* 1990), and coparsite $\text{Cu}_4\text{O}_2[(\text{As},\text{V})\text{O}_4]\text{Cl}$ (Vergasova *et al.* 1999). The purpose of the present work is to report the crystal structure of $\gamma\text{-Cu}_2\text{V}_2\text{O}_7$ which, along with blossomite and ziesite, is a trimorph of $\text{Cu}_2\text{V}_2\text{O}_7$.

The system $\text{CuO-V}_2\text{O}_5$ was investigated by several authors (Fleury 1966, 1969, among others). The presence of at least two distinct phases with composition $\text{Cu}_2\text{V}_2\text{O}_7$ was established, and structures of the α - (blossomite) and β - (ziesite) modifications were reported (Mercurio-Lavaud & Frit 1973a, b, Calvo & Faggiani 1975, Hughes & Brown 1989). Clark & Garlick (1978) and Rao & Palanna (1993) reported the existence of the other high-temperature phase, $\gamma\text{-Cu}_2\text{V}_2\text{O}_7$, that occurs at $\sim 705^\circ\text{C}$ and transforms to α - or $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ depending upon cooling rate. Clark & Garlick (1978) noted that it might be possible to obtain $\gamma\text{-Cu}_2\text{V}_2\text{O}_7$ at ambient temperatures by very rapid quenching techniques. We were able to obtain crystals of $\gamma\text{-Cu}_2\text{V}_2\text{O}_7$ by chemical transport reaction methods in the presence of alumina and to solve its crystal structure. We report our results herein.

EXPERIMENTAL

Synthesis

Crystals of $\gamma\text{-Cu}_2\text{V}_2\text{O}_7$ were obtained in the course of experiments of simulation of high-temperature fumarolic mineral associations by chemical transport reaction methods (Filatov *et al.* 1992). A 69 g mixture of CuO , V_2O_5 and Al_2O_3 with the $\text{Cu}:\text{Al}:\text{V}$ ratio of 1:1:1 was placed into a fused quartz ampoule and heated for 2 days with an imposed gradient from 560 to 410°C . The products of synthesis were black crystals of synthetic ziesite and $\gamma\text{-Cu}_2\text{V}_2\text{O}_7$, and white unreacted Al_2O_3 powder.

Data collection

A crystal selected for the X-ray data collection was mounted on a Bruker three-circle X-ray diffractometer operated at 50 kV and 40 mA and equipped with a

SMART 1K CCD area detector. More than a hemisphere of data was collected using monochromatic $\text{MoK}\alpha$ X-radiation, with frame widths of 0.3° in ω , and with a 60 s count for each frame. The unit-cell parameters (Table 1) were refined from 559 reflections using least-squares techniques. The intensity data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical absorption-correction was based upon 544 intense reflections. The crystal was modeled as an ellipsoid, which lowered R_{int} from 0.050 to 0.021.

Structure solution and refinement

The Bruker SHELXTL Version 5 system of programs was used for determination and refinement of the crystal structure. The structure was solved by direct methods in the centrosymmetric triclinic group $P\bar{1}$ and refined to an R_1 value of 0.021, calculated for the 949 unique observed ($|F_o| \geq 4\sigma_F$) reflections. Final atom coordinates and anisotropic displacement parameters are given in Table 2, selected interatomic distances are listed in Table 3. Table 4 provides a bond-valence analysis calculated using bond-valence parameters taken from Brown (2002). Calculated and observed structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

X-ray powder-diffraction study

X-ray powder-diffraction pattern of $\gamma\text{-Cu}_2\text{V}_2\text{O}_7$ was measured using a DRON-2 powder diffractometer ($\text{CuK}\alpha$ radiation, λ 1.5406 Å) (Table 5). The powder pattern is in good agreement with the results of crystal-structure analysis. The unit-cell parameters calculated using least-squares method on the basis of 21 reflections with 2θ in the range 15 to 57° , are: a 5.087(3), b 5.827(3), c 9.364(5) Å, α 99.90(3), β 97.10(4), γ 97.35(5) $^\circ$, V 268.1(2) Å³.

TABLE 1. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS FOR $\gamma\text{-Cu}_2\text{V}_2\text{O}_7$.

| | | | |
|---------------------------|------------|--|--------------------|
| a (Å) | 5.0873(10) | D_{calc} (g/cm ³) | 4.21 |
| b (Å) | 5.8233(11) | Crystal size (mm) | 0.08 × 0.06 × 0.04 |
| c (Å) | 9.4020(18) | Radiation | $\text{MoK}\alpha$ |
| α (°) | 99.780(3) | R_{m} | 0.021 |
| β (°) | 97.253(3) | Total reflections | 1509 |
| γ (°) | 97.202(3) | Unique reflections | 1119 |
| V (Å ³) | 269.20(9) | Unique $ F_o \geq 4\sigma_F$ | 949 |
| Space group | $P\bar{1}$ | R_1 | 0.021 |
| F_{000} | 320 | wR_2 | 0.049 |
| μ (cm ⁻¹) | 111.35 | S | 0.949 |
| Z | 2 | | |

Note: $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2) / 3$; $s = \{ \sum [w(F_o^2 - F_c^2)] / (n - p) \}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

TABLE 2. ATOM COORDINATES AND DISPLACEMENT PARAMETERS FOR γ -Cu₂V₂O₇

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} | <i>U</i> ₁₁ | <i>U</i> ₂₂ | <i>U</i> ₃₃ | <i>U</i> ₂₃ | <i>U</i> ₁₃ | <i>U</i> ₁₂ |
|-------|-------------|--------------|------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Cu(1) | 0.26344(9) | 0.15492(8) | 0.51698(5) | 0.0128(1) | 0.0094(2) | 0.0164(3) | 0.0128(3) | 0.00625(19) | -0.0005(2) | -0.00025(19) |
| Cu(2) | 0.28090(9) | 0.14584(8) | 0.00655(5) | 0.0126(1) | 0.0121(2) | 0.0123(2) | 0.0122(3) | -0.00089(18) | -0.0014(2) | 0.00474(19) |
| V(1) | 0.16373(12) | -0.32508(11) | 0.21877(7) | 0.0095(2) | 0.0095(3) | 0.0095(3) | 0.0092(3) | 0.0013(2) | 0.0006(2) | 0.0015(2) |
| V(2) | 0.28516(12) | -0.26957(10) | 0.69728(6) | 0.0091(2) | 0.0094(3) | 0.0090(3) | 0.0085(3) | 0.0014(2) | 0.0006(2) | 0.0010(2) |
| O(1) | 0.0885(5) | -0.1078(4) | 0.6023(3) | 0.0118(5) | 0.010(1) | 0.012(1) | 0.014(1) | 0.0054(10) | 0.0003(10) | 0.0018(11) |
| O(2) | 0.4145(5) | -0.1774(4) | 0.3498(3) | 0.0141(6) | 0.012(1) | 0.014(1) | 0.015(1) | 0.0028(11) | -0.0028(11) | 0.0008(11) |
| O(3) | 0.0486(5) | -0.1293(4) | 0.1195(3) | 0.0133(6) | 0.012(1) | 0.014(1) | 0.014(1) | 0.0044(11) | -0.0007(11) | 0.0029(11) |
| O(4) | 0.3846(5) | -0.1248(4) | 0.8774(3) | 0.0123(5) | 0.012(1) | 0.013(1) | 0.011(1) | -0.0008(10) | -0.0016(10) | 0.0048(11) |
| O(5) | 0.1051(5) | -0.5550(4) | 0.6891(3) | 0.0145(6) | 0.015(1) | 0.013(1) | 0.015(1) | 0.0033(11) | 0.0035(11) | 0.0002(11) |
| O(6) | 0.5498(5) | -0.3136(4) | 0.6176(3) | 0.0123(5) | 0.012(1) | 0.012(1) | 0.014(1) | 0.0043(10) | 0.0021(10) | 0.0021(11) |
| O(7) | 0.2637(6) | -0.5429(5) | 0.1096(3) | 0.0195(6) | 0.022(2) | 0.018(1) | 0.018(2) | -0.0019(11) | 0.0008(12) | 0.0093(12) |

TABLE 3. SELECTED BOND-LENGTHS (Å) IN THE STRUCTURE OF γ -Cu₂V₂O₇

| | | | |
|------------|----------|-----------|----------|
| Cu(1)-O(2) | 1.909(3) | V(1)-O(7) | 1.665(3) |
| Cu(1)-O(1) | 1.950(3) | V(1)-O(2) | 1.689(3) |
| Cu(1)-O(6) | 1.959(2) | V(1)-O(3) | 1.705(3) |
| Cu(1)-O(1) | 2.008(2) | V(1)-O(5) | 1.837(3) |
| Cu(1)-O(5) | 2.422(3) | <V(1)-O> | 1.72 |
| Cu(1)-O(2) | 2.540(3) | | |
| <Cu(1)-O> | 2.13 | V(2)-O(6) | 1.648(3) |
| | | V(2)-O(1) | 1.727(3) |
| Cu(2)-O(3) | 1.909(3) | V(2)-O(4) | 1.740(3) |
| Cu(2)-O(7) | 1.923(3) | V(2)-O(5) | 1.779(3) |
| Cu(2)-O(4) | 1.931(3) | <V(2)-O> | 1.72 |
| Cu(2)-O(4) | 1.989(2) | | |
| Cu(2)-O(3) | 2.348(3) | | |
| <Cu(2)-O> | 2.02 | | |

TABLE 4. BOND-VALENCE ANALYSIS FOR γ -Cu₂V₂O₇

| Atom | O(1) | O(2) | O(3) | O(4) | O(5) | O(6) | O(7) | Σ |
|----------|-----------|-----------|-----------|-----------|------|------|------|----------|
| Cu(1) | 0.48,0.41 | 0.54,0.10 | | | 0.13 | 0.47 | | 2.13 |
| Cu(2) | | | 0.54,0.16 | 0.51,0.43 | | | 0.52 | 2.16 |
| V(1) | | 1.36 | 1.30 | | 0.91 | | 1.45 | 5.03 |
| V(2) | 1.23 | | | 1.19 | 1.07 | 1.52 | | 5.00 |
| Σ | 2.12 | 2.00 | 2.00 | 2.13 | 2.11 | 1.99 | 1.97 | |

Summations are reported in valence units (v.u.).

TABLE 5. X-RAY POWDER-DIFFRACTION PATTERN OF γ -Cu₂V₂O₇

| <i>I</i> _{obs} | <i>d</i> _{obs} , Å | <i>hkl</i> | <i>I</i> _{calc} | <i>d</i> _{calc} , Å |
|-------------------------|-----------------------------|-----------------------|--------------------------|------------------------------|
| 8 | 5.654 | 0 1 0 | 16 | 5.673 |
| 8 | 3.940 | 0 $\bar{1}$ 2 | 20 | 3.941 |
| 16 | 3.532 | $\bar{1}$ $\bar{1}$ 1 | 18 | 3.533 |
| 25 | 3.142 | 1 0 2 | 28 | 3.141 |
| 96 | 3.128 | $\bar{1}$ $\bar{1}$ 2 | 100 | 3.127 |
| 100 | 3.063 | 1 1 2 | 73 | 3.058 |
| 39 | 3.016 | $\bar{1}$ 1 2 | 81 | 3.012 |
| 53 | 2.8351 | 0 2 0 | 23 | 2.8366 |
| 31 | 2.6429 | 1 $\bar{2}$ 0 | 38 | 2.6453 |
| 7 | 2.5184 | 1 1 2 | 20 | 2.5161 |
| 16 | 2.4947 | 2 0 0 | 38 | 2.4943 |
| 8 | 2.4168 | $\bar{1}$ 1 3 | 5 | 2.4174 |
| 28 | 2.3053 | 0 $\bar{2}$ 3 | 7 | 2.3050 |
| 16 | 2.2850 | 1 2 2 | 30 | 2.2851 |
| 11 | 2.1979 | $\bar{1}$ 2 2 | 19 | 2.1959 |
| 8 | 2.0611 | 2 0 2 | 18 | 2.0628 |
| 28 | 1.8469 | $\bar{1}$ $\bar{2}$ 4 | 20 | 1.8469 |
| 17 | 1.7403 | 1 1 4 | 15 | 1.7407 |
| 7 | 1.6472 | $\bar{1}$ 2 4 | 25 | 1.6484 |
| 5 | 1.6405 | 0 3 2 | 25 | 1.6397 |
| 28 | 1.6107 | 2 $\bar{1}$ 4 | 31 | 1.6107 |

RESULTS

The structure of γ -Cu₂V₂O₇ contains two symmetrically independent Cu²⁺ cations (Fig. 1). The Cu(1) site is coordinated by six oxygen atoms to form a distorted Cu(1)O₆ octahedron. It consists of four short equatorial Cu²⁺-O bonds (1.909–2.008 Å) and two long apical Cu²⁺-O bonds (2.422, 2.540 Å). The Cu(2) site is coordinated by five oxygen atoms arranged at the vertices of an elongate Cu(2)O₅ square pyramid. Both coordinations are typical for Cu²⁺ oxysalts, and their distortions correspond to the first-order Jahn–Teller effect (Burns & Hawthorne 1995).

The two symmetrically independent V⁵⁺ cations are tetrahedrally coordinated by four atoms of oxygen. The <V⁵⁺-O> bond lengths in the VO₄ tetrahedra are 1.72 Å, which is in agreement with the grand value of 1.72(1) Å reported for tetrahedrally coordinated V⁵⁺ cations in vanadates by Shannon & Calvo (1973) (see also Schindler *et al.* 2000a, b). The O(5) atom provides the bridge between the V(1)O₄ and V(2)O₄ tetrahedra; the V–O(5)–V bond angle is equal to 134.9(2)°. The VO₄ groups are distorted, with the V–O(5) bonds being the longest bonds in both tetrahedra.

The structure of γ -Cu₂V₂O₇ can be described as based upon coordination polyhedra of cations. The Cu(1)O₆ octahedra and Cu(2)O₅ square pyramids form two types of chains running along the *a* axis (Figs. 2c,

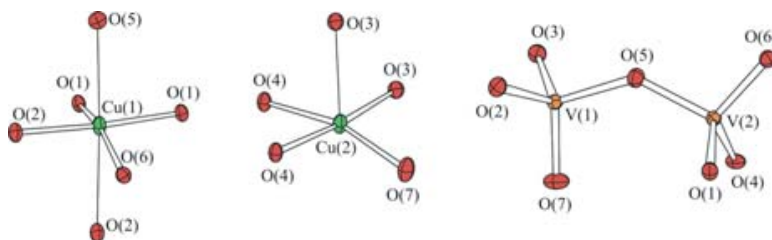


FIG. 1. Cu coordination polyhedra and configuration of the $V_2O_7^{4-}$ group in the structure of $\gamma\text{-Cu}_2V_2O_7$. Ellipsoids are drawn at 50% probability level.

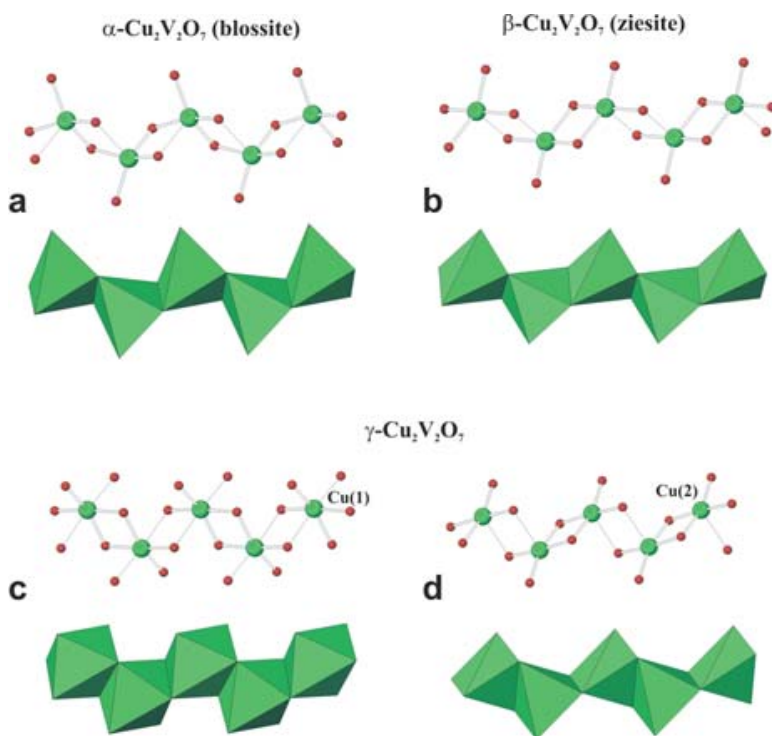


FIG. 2. Chains of Cu coordination polyhedra in the structures of blossite (a), ziesite (b) and $\gamma\text{-Cu}_2V_2O_7$ (c, d). Legend: Cu^{2+} cations: green, O^{2-} anions: red, Cu^{2+} coordination polyhedra: green.

d). One chain is composed solely of edge-sharing $\text{Cu}(1)\text{O}_6$ octahedra, whereas the other is composed solely of edge-sharing $\text{Cu}(2)\text{O}_5$ square pyramids. The chains are linked by V_2O_7 groups into a complex heteropolyhedral framework (Fig. 3f).

DISCUSSION

Relationships to blossite and ziesite

The structure of $\gamma\text{-Cu}_2V_2O_7$ is closely related to the structures of $\alpha\text{-Cu}_2V_2O_7$ (blossite; Mercurio-Lavaud & Frit 1973b, Calvo & Faggiani 1975) and $\beta\text{-Cu}_2V_2O_7$

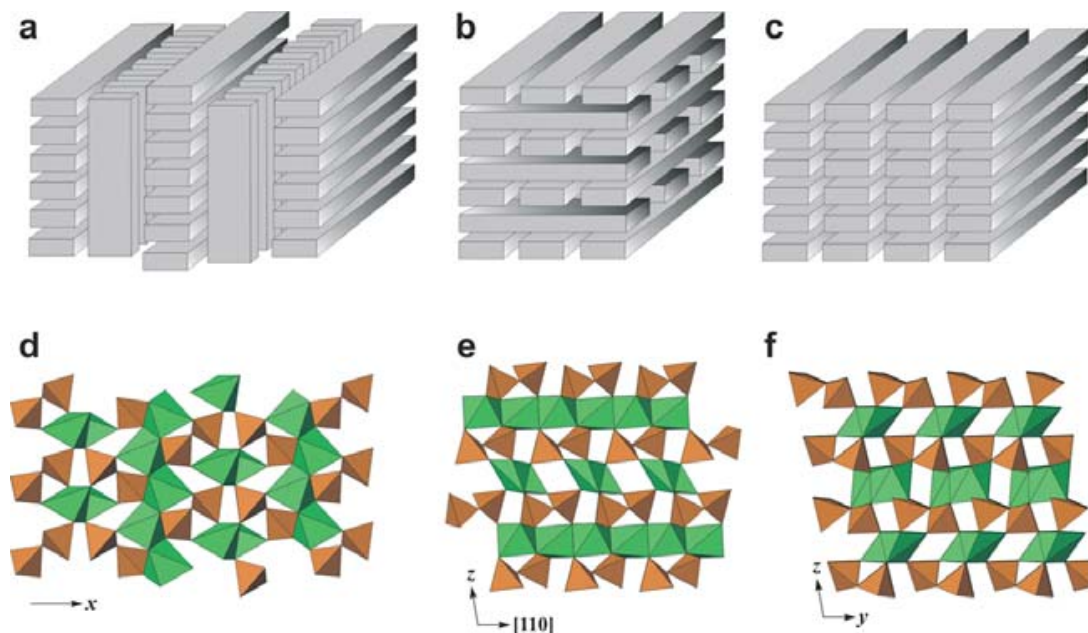


FIG. 3. Schemes illustrating orientation of chains of Cu^{2+} coordination polyhedra in the structures of blossomite (a), ziesite (b), and γ - $\text{Cu}_2\text{V}_2\text{O}_7$ (c). Projections of the structures of blossomite (d), ziesite (e) and γ - $\text{Cu}_2\text{V}_2\text{O}_7$ (f). Legend: Cu^{2+} coordination polyhedra: green, VO_4^{3-} tetrahedra: light brown.

(ziesite; Mercurio-Lavaud & Frit 1973a, Hughes & Brown 1989). In the structures of blossomite and ziesite, there is only one symmetrically independent Cu^{2+} cation coordinated by five O atoms. The geometry of the CuO_5 polyhedra in blossomite and ziesite corresponds to an apically elongate square pyramid and is very similar to the coordination at the $\text{Cu}(2)$ site in γ - $\text{Cu}_2\text{V}_2\text{O}_7$. The CuO_5 pyramids share edges to form chains that are parallel to $[011]$ and $[0\bar{1}\bar{1}]$ in blossomite (Fig. 2a) and to $[110]$ and $[\bar{1}\bar{1}0]$ in ziesite (Fig. 2b). Thus, in contrast to the chains of Cu polyhedra in γ - $\text{Cu}_2\text{V}_2\text{O}_7$, similar chains in the structures of blossomite and ziesite are not parallel to the same direction, but extend in two approximately perpendicular directions. The orientation of chains of edge-sharing CuO_n polyhedra in three polymorphs of $\text{Cu}_2\text{V}_2\text{O}_7$ may be schematically represented by diagrams shown in Figures 3a, b, c. There the chains are shown as parallelepipedal slabs. In the scheme of the blossomite structure (Fig. 3a), there are two series of slabs with perpendicular orientations. The planes of the slabs are also perpendicular. In ziesite, there are again two orientations of slabs, but their planes are parallel. In γ - $\text{Cu}_2\text{V}_2\text{O}_7$, all chains are parallel, and their planes also are parallel.

It should be noted that in addition to the orientations of chains of CuO_n polyhedra, the structures are different in terms of orientations of the V–V vectors of the V_2O_7 groups. In ziesite and γ - $\text{Cu}_2\text{V}_2\text{O}_7$, all V–V vec-

tors are parallel, whereas in blossomite, the V_2O_7 groups have two different non-parallel orientations of the V–V vectors. From this viewpoint, we can conclude that the structure of γ - $\text{Cu}_2\text{V}_2\text{O}_7$ is more closely related to the structure of β - $\text{Cu}_2\text{V}_2\text{O}_7$ (ziesite). The $\gamma \Rightarrow \beta$ phase transition does not include rotation of divanadate groups and, from a structural point of view, seems more favorable than the $\gamma \Rightarrow \alpha$ and $\beta \Rightarrow \alpha$ transitions. This is in general agreement with the data of Clark & Garlick (1978) that, on cooling, γ - $\text{Cu}_2\text{V}_2\text{O}_7$ slowly undergoes the reversible transformation to the α -phase, but transforms rapidly to β - $\text{Cu}_2\text{V}_2\text{O}_7$ at 600°C . However, it should be noted that, at ambient conditions, blossomite (α - $\text{Cu}_2\text{V}_2\text{O}_7$) is the only stable phase, whereas both ziesite and γ - $\text{Cu}_2\text{V}_2\text{O}_7$ are metastable. This fact allowed Hughes & Birnie (1980) to suggest that the presence of ziesite is an indicator of fumarole temperature between 760° and 770°C .

Clark & Garlick (1978) pointed out that γ - $\text{Cu}_2\text{V}_2\text{O}_7$ can be synthesized at temperatures of $>680^\circ\text{C}$. However, in our experiments, this phase formed at much lower temperatures, between 410 and 560°C . We ascribe this contradiction to the conditions of synthesis, namely vacuum conditions and presence of alumina, which probably affected physicochemical equilibria of the system CuO – V_2O_5 . The similarity of the γ - $\text{Cu}_2\text{V}_2\text{O}_7$ structure to the structures of blossomite and ziesite indicates the possible formation of this phase in natural

conditions, such as those that occur in “dry” high-temperature fumaroles of the Izalco and Tolbachik volcanoes.

Relationships to the $A_2B_2X_7$ compounds

It should be noted that the $A_2B_2O_7$ compounds with $B = P$ and V are highly prone to polymorphism, owing to the flexibility of the B_2O_7 groups (Parada *et al.* 2003). The B_2O_7 groups rotate and distort in order to adapt to the size and electronic structure of the A cation, as was shown by Schindler & Hawthorne (1999) for the β - $Cu_2V_2O_7$ – α - $Zn_2V_2O_7$ solid solution. There are several structure-types in which the $A_2B_2O_7$ compounds crystallize. The structure of γ - $Cu_2V_2O_7$ is most closely related to the structure of triclinic β - $Fe_2P_2O_7$ (Stefanidis & Nord 1982, Hoggins *et al.* 1983). The unit-cell dimensions of β - $Fe_2P_2O_7$ (a 5.517, b 5.255, c 4.488 Å, α 98.73, β 98.33, γ 103.81°) are related to those of γ - $Cu_2V_2O_7$ (Table 1), except that the c parameter of γ - $Cu_2V_2O_7$ is doubled owing to the higher degree of distortion of the V_2O_7 groups in comparison to the P_2O_7 groups. In turn, the triclinic structure of β - $Fe_2P_2O_7$ is a distorted version of the β - $A_2P_2O_7$ structure-type [$A = Cu, Co, Mn, Ni, Zn$; see Parada *et al.* (2003) for references] that crystallize in space group $C2/m$. It should be noted that the β - $A_2P_2O_7$ structure-type is also characteristic of some divanadates such as β' - $Zn_2V_2O_7$ (Krasnenko *et al.* 2003), β - $Mn_2V_2O_7$ (Dorm & Marinder 1967, Liao *et al.* 1996), and $Cd_2V_2O_7$ (Au & Calvo 1967, Sokolova *et al.* 1986). Thus, the structure of γ - $Cu_2V_2O_7$ can be considered as a triclinically distorted derivative of the β - $A_2P_2O_7$ structure-type. However, no directly isostructural compound exists for γ - $Cu_2V_2O_7$.

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