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The crystal chemistry of shcherbinaite, naturally occurring V_2O_5

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Abstract

Shcherbinaite, naturally occurring V_2O_5, has been discovered in the high-temperature fumaroles of Izalco volcano, El Salvador, and Bezymyanny volcano, Kamchatka, U.S.S.R. The Izalco mineral occurs as euhedral golden-yellow needles and laths up to 1 cm in length. The crystals, which formed as sublimates from volcanic gases, are found coating basaltic breccia fragments in the summit crater fumaroles. The mineral is associated with bannermanite.

An electron microprobe study of shcherbinaite demonstrated that the mineral is pure V_2O_5 and contains no detectable impurities or alkali metals such as occur in solid solution in oxide bronze compounds. A comparison of the lattice parameters and crystal structures of shcherbinaite and synthetic V_2O_5 showed that the compounds are essentially identical. All lattice parameters are within 1 standard deviation and all atomic positional and thermal parameters are within 2.3 standard deviations of those found in the synthetic compound.

Introduction

Stoiber and Duerr (1963) reported the first natural occurrence of crystalline V_2O_5. The compound, which was the first high-temperature vanadium mineral known, was discovered as fine-grained euhedral crystals coating basaltic breccia fragments in the summit crater fumaroles of Izalco volcano, El Salvador. Subsequent to its discovery at Izalco volcano the mineral was found in the fumaroles of the andesitic Novvy dome at Bezymyanny volcano, Kamchatka, U.S.S.R. On the basis of this discovery, the mineral was named shcherbinaite (Borisenko *et al.*, 1970). The description of the Bezymyanny phase was, however, only qualitative in many respects. Because of the poor quality of the crystals, single-crystal X-ray photographs were unobtainable. Furthermore, owing to incrustations coating the crystals and limitations of wet chemical analytical methods, a single chemical analysis totaling less than 40 wt.% V_2O_5 was obtained.

In view of the complete lack of detailed data on the phase and the discovery of bannermanite, a coexisting mineral in the natural alkali metal vanadium oxide bronze system (Hughes and Finger, 1983), a detailed study of the shcherbinaite from Izalco volcano was undertaken.

Locality and occurrence

Izalco volcano is a basaltic composite cone that has been intermittently active since its birth in 1770. The volcano rises to an altitude of 1965 m, with 650 m relief. It has an approximate volume of 2 km^3. The geology of the volcano is described by Meyer-Abich (1958), Rose and Stoiber (1969), and Stoiber *et al.* (1975).

Since 1963 the fumarolic gases and minerals of the summit crater have received extensive study (Stoiber and Duerr, 1963; Stoiber and Rose, 1970, 1974; Stoiber *et al.*, 1975; Birnie and Hughes, 1979; Hughes and Birnie, 1980; Hughes and Finger, 1983). Vanadium was found to be one of the distinctive elements in the fumarole mineral suite. The suite includes stoiberite ($Cu_5V_2O_{10}$), ziesite (β-$Cu_2V_2O_7$), bannermanite [$(Na,K)_xV_x^{4+}V_{6-x}^{5+}O_{15}$], $Cu_3V_2O_8$, and $Cu_4V_2O_9$.

Shcherbinaite is found in the "MR" and "L" fumaroles at Izalco (Stoiber *et al.*, 1975, Fig. 1). The mineral occurs as a sublimate from the fumarolic gases, and is found as golden-yellow laths up to 1 cm long. The euhedral crystals are found coating basaltic breccia fragments in the oxide zone of the fumaroles, approximately 1 m below the surface. Shcherbinaite is often intimately intergrown with bannermanite.

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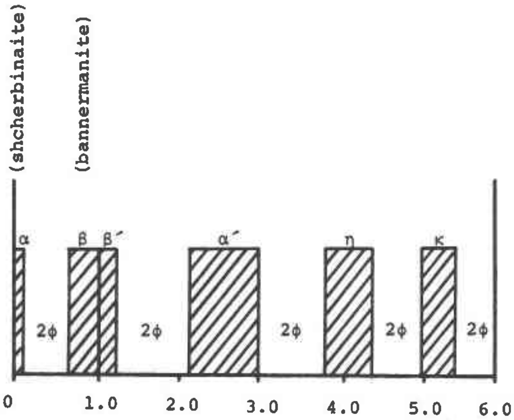

Fig. 1. Range of solid solutions in the oxide bronze system $Na_xV_2O_5$. Striped areas represent one-phase regions, with phase designation above region. Phase regions determined at 600°C (after Hagenmuller, 1973).

Chemistry

Pure V_2O_5 occurs as an end-member oxide in the alkali metal vanadium oxide bronze system (Fig. 1). In this system, solid solution occurs with the addition of monovalent ions to the structure (Hughes and Finger, 1983). The electrons donated by the monovalent electropositive ions (Na,K) are contributed to the covalent V–O array, and charge balance is maintained by reduction of one V^{5+} to V^{4+} for each monovalent ion present in the structure. The monovalent ions are located in crystallographic sites that are created by tunnels in the V_2O_5 structure. The α-phase vanadium oxide bronze, which is isostructural with pure V_2O_5, can accommodate minor amounts of Na, up to $Na_{0.02}V_2O_5$ at 600°C (Hagenmuller, 1973). Because the Izalco shcherbinaite invariably coexists with bannermanite, the β-phase vanadium oxide bronze (Hughes and Finger, 1983), it is suggested that the two minerals (bannermanite and shcherbinaite) actually crystallized in the two-phase region of coexisting α- and β-phase vanadium oxide bronzes (Fig. 1). In order to determine the extent of solid solution in shcherbinaite, a complete electron microprobe study was undertaken.

Numerous single crystals were prepared for electron microprobe analysis by mounting the laths with the short dimension perpendicular to the microscope stage, with the largest surface area for analysis. Because of the thin dimension perpendicular to the beam (often less than 5 μm) the samples were not polished; many crystals had, however, an exceptionally smooth natural surface, suitable for microprobe analysis.

The best of the samples were initially analyzed on a JEOL SEM/Microprobe with energy-dispersive techniques. No elements other than V were noted; however, the small concentration of Na_2O present in the α-phase vanadium oxide bronze (0.34 wt.% in $Na_{0.02}V_2O_5$) would be near or below the level detectable by energy-dispersive methods. This analysis did suggest that heavier ions were not present in the V_2O_5 from Izalco.

Quantitative analyses for V, Na, and K were performed on a single-channel wavelength dispersive JEOL 35 SEM/Microprobe (15 kV accelerating voltage and 191 picoamps beam reference current). Vanadium metal, diopside–jadeite (DIJD35), and orthoclase were used as standards for V, Na, and K, respectively.

Analyses of 15 crystals showed that only V was present; analyses totaling as high as 97.55 wt.% V_2O_5 (O_2 by stoichiometry) were obtained. The difference from 100% is assumed to be due to unpolished surfaces and finitely thick grains. To verify further the purity of the compound, multichannel wavelength scans were made using LiF, PET, and TAP analyzing crystals. These scans covered the entire range of elements detectable ($Z \geq 9$). Stripchart recordings showed that no elements other than V were present.

The first quantitative chemical analyses of shcherbinaite thus demonstrate that it is the pure pentavalent oxide of vanadium. The absence of any detectable amounts of cations other than V is probably a result of crystallization through the natural sublimation process. The results of the electron microprobe study suggest that the solid solution field of the vanadium oxide bronze is nonexistent in the natural system, and the composition of shcherbinaite is limited to the pure V_2O_5 end member.

X-ray crystallography

Borisenko *et al.* (1970) were unable to obtain single-crystal X-ray photographs from the Bezymyanny shcherbinaite because of the poor quality of the crystals. For this reason, a precession study was undertaken with MoK_α radiation (0.70930Å, Zr filter). The high-quality single crystals from Izalco provided excellent material for single-crystal film studies.

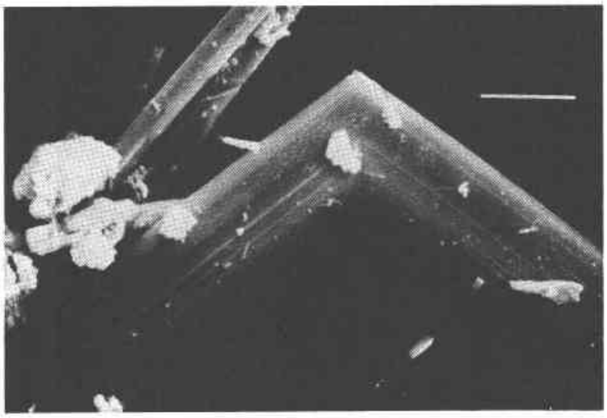

Fig. 2. SEM micrograph of a twinned crystal of shcherbinaite (photo courtesy of M. L. Malinconico). Scale bar represents 10 μm.

The single-crystal precession photos taken precessing about the *a* and *b* axes showed the diffraction geometry to be consistent with the orthorhombic space group *Pnmm* (No. 59). This result agrees with the work of Bachmann *et al.* (1961) on synthetic single crystals. The axes of shcherbinaite are related to those of the Bachmann study by the transformation matrix [010/100/001].

The unit cell parameters of the Izalco shcherbinaite were determined by a least-squares method with 12 reflections measured on a four-circle diffractometer. The parameters are a = 4.364(8), b = 11.50(2), and c = 3.561(4); all values differ by $<1\sigma$ from the values determined by Bachmann *et al.* (1961) for synthetic V_2O_5.

A detailed crystal structure study of synthetic V_2O_5 (R = 0.04) was performed by Bachmann *et al.* (1961). The present study also included a structure refinement on the natural material which showed all atomic positions within 2.3σ of the Bachmann *et al.* study. Because of the small size and large aspect ratio of the Izalco material, refinement below wR = 0.061 was not obtained. Thus, the reader is referred to the Bachmann *et al.* study for details on the crystal structure of V_2O_5.

Physical properties

Shcherbinaite occurs as euhedral golden-yellow needles and laths up to 1 cm long. The lath-like habit is most common, with crystals elongated on [001] and flattened on [100].

Shcherbinaite displays two perfect cleavages, {010} and {001}. As noted by Bachmann *et al.* (1961), previous workers have found only a poor {001} cleavage at best in synthetic material; however, in shcherbinaite, the cleavage is well developed. Bachmann *et al.* also note a {100} cleavage (their {010}) that results from cleaving the 2.774Å VO(1) bond, but this cleavage is unobservable in the natural material because of the crystal habit.

The density of shcherbinaite is 3.38 g/cm^3, as calculated from the X-ray cell volume with two formula units of V_2O_5 per unit cell. The mineral displays a brittle tenacity. Shcherbinaite does not fluoresce in short- or long-wave ultraviolet radiation.

With {100} parallel to the microscope stage, shcherbinaite is straw-yellow and non-pleochroic in plane polarized light. Under crossed polars, shcherbinaite is length fast; thus c must coincide with X or Y. The mean index of refraction, calculated by the rule of Gladstone and Dale, is 2.25.

Shcherbinaite commonly forms contact twins (Fig. 2). Examination of the twin members shows that they are separated by a 94° rotation angle about [100], as confirmed by precession photographs. This rotation suggests a {031} twin composition plane.

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