The crystal structure of kelyanite, (Hg$_2$)$_6$(SbO$_6$)BrCl$_2$

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ABSTRACT

The crystal structure of kelyanite, a rare mercury mineral that was found in oxidized mercury-antimony ores in the Kelyana deposit (Buryatia, Russia), has been determined. The preliminary formula of kelyanite was $\text{Hg}_2\text{Sb}_3\text{Cl}_3\text{Br}_2\text{O}_4$ (assuming the presence of both the Hg$^{2+}$ and Hg$^{4+}$). In contrast to this assumption, kelyanite appears to contain only monovalent Hg and its revised formula is $(\text{Hg}_2\text{Sb}_3\text{O}_6)$ BrCl$_2$. Kelyanite is trigonal, space group $P3$, $a = 13.560(4)$ Å, $c = 10.004(6)$ Å, $V = 1593(1) \text{ Å}^3$, and $Z = 3$. In the structure, Hg atoms form six crystallographically independent pairs [dumbbells of composition (Hg$_2$)$_2^+$] with Hg-Hg distances of 2.482(3)–2.519(2) Å. The Hg and O atoms form O-Hg-O systems with Hg-O bond lengths of 1.98(3)–2.33(3) Å and HgHgO angles of 140.3(7)–168.3(9)$^\circ$. Mercury atoms in the (Hg$_2$)$_2^+$ dumbbells have additional coordination to O, Cl, and Br atoms [Hg-O 2.62(2) Å, Hg-Cl 2.68(1)–2.97(1) Å, and Hg-Br 3.00(1)–3.55(1) Å]. Three crystallographically independent Sb atoms are octahedrally coordinated by O atoms with Sb-O distances of 1.96–2.14 Å. The (Hg$_2$)$_2^+$ dumbbells link the (SbO$_6$) octahedra in a 3D structure.

Keywords: Kelyana mercury deposit, Hg mineral, mercury-antimony oxide-halide, (Hg$_2$)$_2^+$ dumbbell, crystal structure, X-ray diffraction

INTRODUCTION

As a part of the general study of the crystal chemistry of minerals containing low-valence Hg, we have studied the crystal structure of kelyanite. Kelyanite is an Hg-Sb-O mineral containing chlorine and bromine from the Kelyana mercury deposit (Buryatia, Russia) described by Vasil’ev et al. (1982). This rare supergene mineral is probably the result of decomposition of primary Sb and Hg sulfides such as cinnabar and stibnite. Kelyanite occurs as irregular grains. Its brown-red or cherry-red aggregates are closely associated with calomel, eglestonite, shakhovite, and antimony oxides.

At present, there are about 30 known minerals of low-valence Hg such as calomel, Hg$_2$Cl$_2$ (Calos et al. 1989), eglestonite, (Hg$_2$)$_2$O$_4$Cl$_2$H (Mereiter et al. 1991), edgarbaileyite, Hg$_3$Si$_2$O$_7$ (Angel et al. 1990), vasilievite, (Hg$_2$)$_2$O$_4$Br$_2$(BrCl)$_2$(CO$_3$) (Cooper and Hawthorne 2003), etc., but only one of them, namely, shakhovite, Hg$_2$Sb(OH)$_3$O$_2$ (Tillmanns et al. 1982), contains Hg and Sb. The main features of the structures of these minerals and related synthetic compounds is the presence of cluster groups: (Hg$_2$)$_2^+$ dumbbells and more rarely (Hg$_2$)$_4^{2+}$ triangles (Pervukhina et al. 1999a, 1999b).

Mercury minerals are particularly difficult to characterize with regard to their correct chemical formula because of the high atomic weight of Hg in comparison to lighter elements. Crystal-structure analysis plays an important role in the determination of the valence states of Hg and in detecting light elements.

Physical and optical properties, composition, and X-ray characteristics of kelyanite were originally studied using a natural specimen, but the structure of this mineral could not be solved at that time. Preliminary structural work showed the possible space groups $C2/m$, $C2$, $Cm$, and $C2/c$ with the unit-cell parameters: $a = 23.50 \pm 0.12$ Å, $b = 13.62 \pm 0.06$ Å, $c = 10.31 \pm 0.05$ Å, $\beta = 97.01 \pm 0.12^\circ$ (Vasil’ev et al. 1982). Using data obtained by elemental analysis (JXA-5A and JSM-35 electron microprobe), the composition of kelyanite was determined as: Hg = 85.6, Sb = 4.7, Cl = 3.31, Br = 0.91, and O = 5.35 wt% (Vasil’ev et al. 1982), which leads to the formula Hg$_{10}$Sb$_{0.375}$Cl$_{0.84}$Br$_{0.106}$O$_{1.06}$O$_{12}$. With regard to the experimental density (8.51–8.69 $\text{g/cm}^3$), the preliminary formula of kelyanite, according to experimental data, could be written as Hg$_{34}$Sb$_3$Cl$_6$Br$_2$O$_{28}$ with $Z = 2$ (assuming the presence of both the Hg$^{2+}$ and Hg$^{4+}$).

SINGLE-CRYSTAL X-RAY DIFFRACTION

A single crystal of dimensions 0.10 × 0.05 × 0.03 mm was selected for X-ray diffraction measurement. The unit-cell parameters and diffraction intensity data were measured at room temperature, using a single-crystal Bruker X8 Apex diffractometer equipped with a 4K CCD detector. The crystallographic data, data collection parameters, and refinement parameters are summarized in Table 1. Kelyanite crystallizes in the trigonal space group $P3$ and exhibits the following unit-cell parameters (from 2815 reflections): $a = 13.560(4)$ Å, $c = 10.004(6)$ Å, and $V = 1593(1) \text{ Å}^3$. The calculated density, assuming a cell content of...