New data on the crystal-chemistry of fluoborite by means of SREF, SIMS, and EMP analysis

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ABSTRACT

The crystal structure of fluoborite \([\text{Mg}_3\text{F}_3(\text{BO}_3)]\) was refined by Dal Negro and Tadini (1974) who provided a complete structural model. Previously, Takeuchi (1950) had refined an OH-dominant fluoborite (OH ~70%), but the limited quantity of data (extracted from two Weissenberg-Buerger photographs) did not permit the location of H atoms. Dal Negro and Tadini (1974) also could not locate H atoms because they used a crystal with near end-member composition. We have located the H bond in an OH-dominant fluoborite from the Betic Cordilleras (SE Spain). Excellent quality X-ray data on two crystals of fluoborite allowed discovery and refinement of the H position in this mineral. Electron microprobe (EMP) and secondary-ion mass spectrometry (SIMS) analyses of the light elements H, B, and F have resulted in the formulation of special procedures to obtain accurate, high-quality quantitative data, which are presented in this paper. EMP, SIMS, and crystal structure refinement (SREF) data are in a good agreement. Linear equations are also presented to calculate the F content directly from cell parameters.

INTRODUCTION

Fluoborite is a rare mineral found in contact metamorphosed marble. It was first described by Geijer (1926) from Norberg (Sweden), where it was associated with norbergite. Following the proposal of Hawthorne (1983) for classification of borate-group minerals, which is based on the polymerization of high bond-valence polyhedra (in borates, the BO\(_3\) and BO\(_4\) polyhedra) or fundamental building blocks (FBB; Hawthorne et al. 1996), fluoborite is classified as the simplest borate and consists of homopolyhedral clusters of triangular-coordination BO\(_3\) polyhedra. It belongs to the 3 \(\bar{A}\) wallpaper structures group of Moore and Araki (1974) and contains pairs of edge-sharing infinite octahedral chains, forming ribbons along [001], cross-linked by BO\(_3\) triangles. These octahedral chains repeat every 3 \(\bar{A}\) along their length. The ribbons share vertices forming triangular and hexagonal tunnels. The triangular tunnels are filled with boron in triangular coordination with oxygen, and perpendicular to the \(c\) axis, whereas the hexagonal tunnels are empty.

The structure of fluoborite was determined by Takeuchi (1950), who described it as hexagonal with space group \(C6\bar{3}m\). The structure was confirmed by Dal Negro and Tadini (1974) who also confirmed the centrosymmetric character of this structure and proposed \(P6\bar{3}m\) as the space group. Natural fluoborite exhibits complete OH\(\rightarrow\)F substitution. In the past, the F-end-member was called “nocerite” (Brisi and Eitel 1957). The samples studied here represent a F-rich fluoborite in which the a unit-cell parameter (= 8.861 Å) falls between the values reported by Takeuchi (1950) and by Dal Negro and Tadini (1974) (= 9.06 and 8.827 Å, respectively), indicating a high F content and the presence of some OH.

EXPERIMENTAL PROCEDURES AND RESULTS

Sample description

Fluoborite crystals were hand-picked from a crushed sample of metamorphosed and metasomatized marble (HV-43) from Huerta del Vinagre, a small scheelite mine that crops out in the Guadaiza Unit of the Upper Alpujarride series, in the Betic Cordilleras, Spain. This sample is a magnesian skarn formed by interaction between dolomitic marbles and magmatic fluids from the surrounding granites. In particular, the sample represents an exoskarn almost entirely composed of monomineralic, metamorphic veins of calcite and humite-group minerals, with rare fluoborite and minor serpentine (from alteration of humite-group minerals). The humite-group minerals in these samples have very low Fe and Ti contents (Cámara 1997; Ottolini et al. 2000).

Single-crystal structure refinement

Data collection and refinement were carried out for crystals Fbor HV-43 n.2 and Fbor HV-43 n.3 with an automatic 4-circle Philips PW1100 diffractometer, using graphite-monochromatized MoK\(_\alpha\) radiation. The space group \(P6\bar{3}m\) has been confirmed. Unit-cell parameters \([a = 8.8612(12) \, \bar{A}, c = 3.1021(6) \, \bar{A}\) for Fbor HV-43 n.2; \(a = 8.8602(12) \, \bar{A}, c = 3.1021(6) \, \bar{A}\) for Fbor HV-43 n.3] were calculated from a least-squares refinement of 
\(d\) calculated for 56 rows of the reciprocal lattice by measuring the reflections in the range \(-35 < \theta < 35^\circ\). They are reported in Table 1 together with R-factors. Three equivalent hexagonal reflections \((hkl, hkl, and hkl)\) were collected in the \(\theta\) range 2–35\(^\circ\). The profiles were

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