

The crystal structure of sulfoborite, $Mg_3SO_4(B(OH)_4)_2(OH)F$

R. F. GIESE, JR.

*Center for Crystallographic Research
Roswell Park Memorial Institute
Buffalo, New York*

*and Department of Geological Sciences
State University of New York at Buffalo
Amherst, New York 14226*

AND G. PENNA

*Hooker Chemical Corporation
Research Center
Grand Island, New York*

Abstract

Sulfoborite, $Mg_3SO_4(B(OH)_4)_2(OH)F$, is orthorhombic, space group *Pnma* with $a = 10.132$, $b = 12.537$ and $c = 7.775\text{\AA}$ (all $\pm 0.001\text{\AA}$). There are four formula units in the unit cell. The crystal structure has been solved using Sayre's equation. All atoms including hydrogens have been located and refined by least squares to an *R*-value of 0.044. The magnesium ions are of two types; $MgO_2F(OH)_3$ and $MgOF(OH)_4$. The two types of octahedra share an edge and/or corners among themselves. The sulphate tetrahedron shares corners with both types of octahedra and these three units form crude sheets centered about the mirror planes. The sheets are jointed by the boron tetrahedra into a three-dimensional structure. Three hydrogen atoms do not participate in hydrogen bonding, the remaining two form normal hydrogen bonds.

Introduction

The original descriptions of sulfoborite indicated a chemical formula of $Mg_6H_4(BO_3)_4SO_4 \cdot 7H_2O$ (Naupert and Wense, 1893) and orthorhombic symmetry with point group *mm2* (Bücking, 1893). The mineral has been studied several times since 1893 and no agreement as to the chemical composition was evident. Lobanova (1968) proposed the formula $Mg_6B_4O_{10}(SO_4)_2 \cdot 9H_2O$ even though his published analysis indicated 4.7% fluorine and 0.34% chlorine. Braitsch (1961) suggested $Mg_6SO_4(BO_2OH)_4 \cdot 8H_2O$ as the formula and confirmed by single crystal X-ray diffraction the orthorhombic symmetry. He could not distinguish between the space groups *Pcmn* and *Pc2₁n*. Kondrat'eva (1964) analyzed several samples and confirmed the Lobanova formula. More recently, Ostrovskaya (1967) used infrared spectroscopy to demonstrate the presence of hydroxyl and the absence of water indicating that previous analyses had incorrectly equated OH to H_2O . In addition, it was

concluded that the boron was tetrahedrally and not trigonally coordinated.

The major differences between these proposed formulae lie in the amounts of water of hydration, hydroxyl and hydrogen. At the time this work was begun, we were not aware of Ostrovskaya's paper and we felt that a crystal structure determination was the only way to resolve these questions. Since the mineral contains only light elements, it was hoped that the hydrogen atoms could be located and refined. The resulting structure would, in addition to resolving the question of the chemistry of sulfoborite, provide some interesting information about hydrogen bonding and the role of fluorine and hydroxyls in this structure. A preliminary report of the structure analysis was presented by Giese and Penna (1968). Ioryish *et al.* (1976) have published an independent structure determination which differs from that of Giese and Penna in being less accurate, in apparently misidentifying one of the anions and in not locating the hydrogen atoms. For these very important reasons, the structure is reported here.

