

Spectroscopy of a birefringent grossular from Asbestos, Quebec, Canada

GEORGE R. ROSSMAN, ROGER D. AINES¹

Division of Geological and Planetary Sciences,² California Institute of Technology,
Pasadena, California 91125

ABSTRACT

The infrared spectra of birefringent garnets from Asbestos, Quebec, Canada, show strong anisotropy in the OH stretching region, but are devoid of anisotropy in the Fe²⁺ electronic bands and in the SiO₄ overtone region. These results suggest that the birefringence arises from a noncubic orientation of the OH groups that are from a minor hydrogrossular component.

INTRODUCTION

Garnets from a variety of occurrences often show birefringence that violates the cubic symmetry of the mineral (Foord and Mills, 1978). The birefringence has been previously attributed to cation ordering that results in a lowered symmetry (Takeuchi and Haga, 1976; Hirai and Nakazawa, 1982). Strain induced by compositional zonation was likewise offered as the origin of birefringence in synthetic Y-Al garnets (Kitamura and Komatsu, 1978). Kalinin (1967) concluded from synthesis experiments that birefringence occurs in garnets of intermediate, rather than endmember, compositions. He also concluded that it was not due to the presence of water in the garnet structure because he synthesized birefringent garnets above 600°C, a temperature he considered too high for water to be incorporated.

Because our recent studies have indicated that minor amounts of a hydrogarnet component can be found in garnets, even those from high-temperature conditions of formation (Aines and Rossman, 1984), we have conducted a spectroscopic study of a birefringent garnet to determine whether all components of the garnet share a noncubic environment and whether, indeed, "water" could be a factor in the birefringence. Previously, it had been shown that in the spectrum of biaxial examples of the hexagonal mineral osumilite, the portions of the vibrational spectrum arising from the framework and traces of incorporated water have hexagonal anisotropy, whereas the portion of the spectrum arising from Fe²⁺ has lower symmetry (Goldman and Rossman, 1978). Presumably, the biaxiality was arising from the Fe²⁺. A parallel study of the garnet could examine the silicate portions, spectroscopically active cations, and the hydrogarnet component.

Experimental details

The garnet was from the Jeffrey mine, Asbestos, Quebec, Can-

ada, Caltech collection no. 15005. Electron-microprobe analysis indicated it to be nearly endmember grossular with 0.71 wt% MnO and 1.46% FeO with little zonation. Infrared and thermal analysis indicated a H₂O content of 0.035 wt% (Aines and Rossman, 1984). Instrumental details are similar to those already described in Aines and Rossman.

The garnet is light orange, gem quality, and free of obvious layering, intergrowths, and schiller. A cross section in polarized light revealed alternating layers of different birefringence, each parallel to existing dodecahedral faces. These layers are 0.1 to 0.5 mm thick. The birefringence is variable, but always less than 0.001. Spectroscopic measurements were made in those individual layers that had the greatest and most homogeneous birefringence.

RESULTS AND DISCUSSION

The spectra in the 25 000 to 4000 cm⁻¹ (400 to 2500 nm) region show no anisotropy. The spectra were obtained with linearly polarized light vibrating along the two extinction directions with samples at least 1 mm thick. The three major absorption bands in this region arise from electronic transitions of Fe²⁺ and are similar to published spectra (White and Moore, 1972). Because they show no difference between the two orientations, they indicate that the local environment of the Fe²⁺ is cubic. Spectra in the 2000–1500 cm⁻¹ region likewise show no anisotropy. Absorptions in this region are due to the first overtone of the fundamental silicate vibrations. The overtone region was used because the fundamental absorptions themselves near 1000 cm⁻¹ are too intense to obtain on scale with a thin slice of garnet. The lack of anisotropy in the SiO₄ vibrations indicates that the bulk of the SiO₄ units are in an environment of cubic symmetry.

The absorptions in Figure 1 result from OH incorporated in the garnet structure. They occur at energies similar to the OH absorptions found in a number of grossulars (Aines and Rossman, 1984). They show a remarkable degree of anisotropy. Anisotropic absorptions have not been observed in the spectra of garnets that are not optically birefringent. These results suggest that the cause of birefringence in these garnets is a low-symmetry distribution of the OH groups, but do not indicate whether the

¹ Present address: Department of Earth Sciences, Lawrence Livermore National Laboratory, University of California, Livermore, California 94550.

² Contribution number 4238.

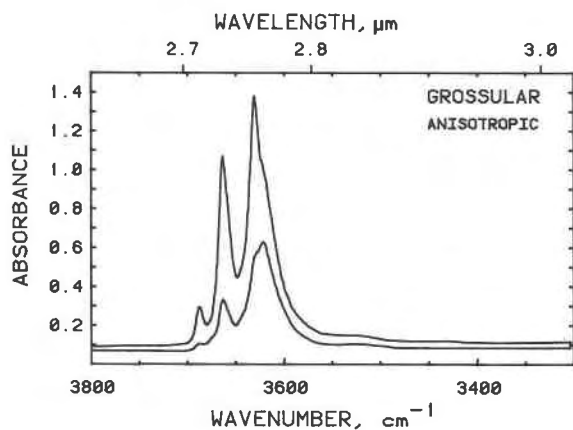


Fig. 1. Infrared absorption spectra of a grossular from Asbestos, Quebec. The two spectra represent the maximum and minimum absorption in this wavenumber region through a birefringent zone of the crystal. They have been slightly displaced vertically for clarity. Sample thickness: 150 μm .

OH orientation is a primary feature or whether the OH groups respond in turn to another component that is subject to preferential orientation during growth. The closeness of the composition of this garnet to the endmember composition and the lack of anisotropy in the Fe^{2+} spectra suggest that Fe-Al ordering is not the cause of the anisotropy in these particular garnets.

Water-related birefringence is uncommon in garnets. During the course of our survey of the water content of natural garnets (Aines and Rossman, 1984), a large number of birefringent garnets were observed including some rhythmically zoned andradites with birefringence up to

0.01. Most of these samples also contained a hydrogarnet component, but the IR spectrum in the O-H stretching region was not anisotropic. Only one other sample was observed with characteristics similar to those reported here. It was from Belvidere Mountain, Vermont, an altered ultramafic body similar to the occurrence at Asbestos. It had a polarization ratio of 4.9:1 for the band at 3680 cm^{-1} .

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