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Infrared Spectra of the Solid Solution between Uvarovite and Spessartine

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Abstract

For infrared spectra of synthetic solid solutions between uvarovite and spessartine, the frequencies assigned to tetrahedral vibration decreased linearly as uvarovite content increased. For intermediate members of the series the ν_3 vibrations of SiO_4 tetrahedra tend to coalesce, suggesting random distribution of the dodecahedral and octahedral cations.

Introduction

The theoretical analysis of vibration spectra and the effect of neighboring cations on the spectra assigned to polyhedral sites have been more clearly described for garnet than for other double oxides, because of high symmetry and presence of isolated tetrahedra and octahedra in the garnet structure (Tarte, 1965; Hurrel *et al*, 1968; McDevitt, 1969; Moore and White, 1971a; Suwa and Naka, 1972, 1974).

In the present work, infrared (IR) spectra have been measured on synthetic garnet solid solutions between uvarovite and spessartine. Spectral change accompanied with the substitution of cations is discussed.

Experimental

Continuous solid solutions between uvarovite and spessartine were synthesized under 27.5 kbar and 1450°C as previously described by Naka, Suwa, and Kameyama (1975). Their IR spectra in the 4000 to 200 cm^{-1} range were measured from powders vacuum-pressed into KBr discs using a Nihon Bunko Model DS-402 grating spectrometer. Frequencies were calibrated against a polystyrene film.

Infrared Spectra

The IR spectra for spessartine-uvarovite solid solutions display bands (A-F in Fig. 1)—assigned to SiO_4 tetrahedra—whose frequencies decrease linearly as uvarovite content increases. In other words, this linear decrease of band frequency correlates with an increase in radii of the dodecahedral and octahedral cations, but seems independent of the electronegativity or the mass of these cations (Suwa and Naka, 1972, 1974). Since band A occasionally appears on the left side of band B as a shoulder peak, it may result from a combination of internal and/or external modes. Bands B, C, and D are assigned to the ν_3 vibration of SiO_4. Splitting this ν_3 vibration into three bands in the garnet structure is consistent with the results of site group and factor group analyses (Moore and White, 1971a; Suwa and Naka, 1972). However, the broadening and the degeneration of bands C and D into one band is remarkable in the intermediate members. Similar behavior was observed on the tetrahedral spectra of synthetic solid solutions between rare earth garnets and silicate garnet (Suwa and Naka, 1974). This indicates a random distribution of different cations interacting with the Si–O stretching mode in the intermediate members. Because all IR active modes of the garnet structure belong to the same irreducible representation, F_{1u}, they must be coupled to at least some extent.

The frequencies of bands E, F, and G assigned to the ν_4 vibration of SiO_4 appeared to be less coupled to the surrounding cations than in the case of the ν_3 vibration.

Bands H and I were assigned to octahedral vibration by Tarte (1965). These bands broaden and smear in the intermediate composition, but do not shift linearly with change of composition, indicating the substitution of Al^{3+} for Cr^{3+} in the octahedral site.

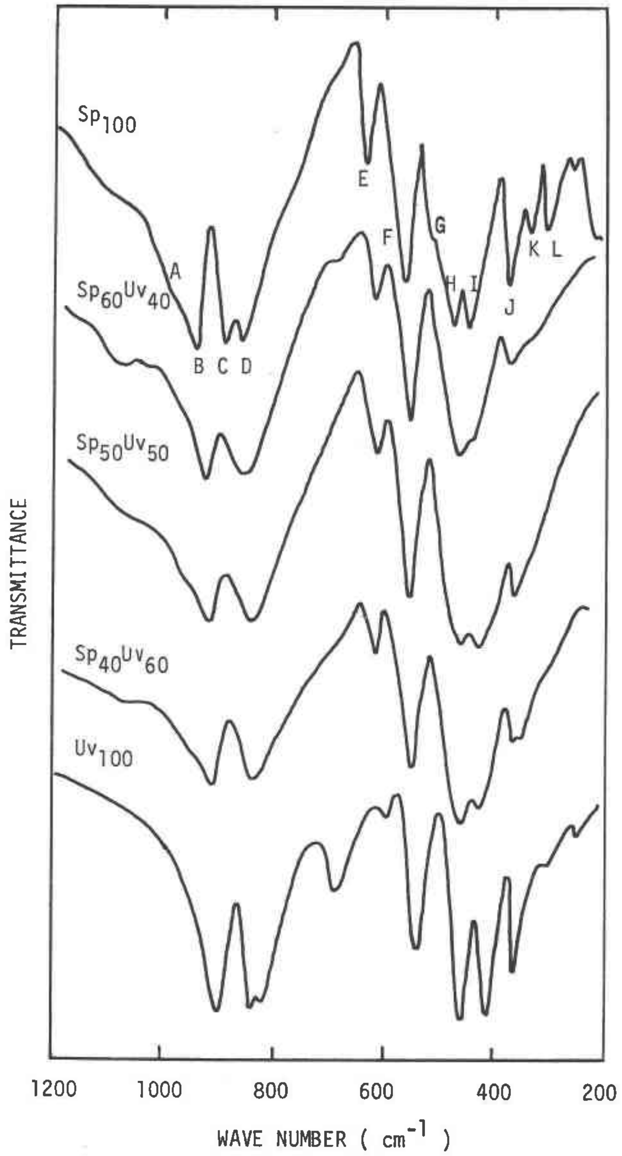

FIG. 1. IR spectra for uvarovite-spessartine solid solution. Bands marked by letters are the normal IR bands of the garnet structure. Compositions of the solid solution are represented by molar percent of end members. Sp: spessartine, Uv: uvarovite.

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