Site occupancies in synthetic monoclinic amphiboles: Rietveld structure refinement and infrared spectroscopy of (nickel, magnesium, cobalt)-richterite

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ABSTRACT

Amphiboles were synthesized at 750 °C, 1 kbar (H2O) on the binary joins (nickel, magnesium)-richterite and (magnesium, cobalt)-richterite. Structural variations and site occupancies were characterized by Rietveld structure refinement, with final R_Bragg indices in the range 4–9%, and by powder infrared spectroscopy in the principal OH-stretching region. Site-occupancy refinement of Ni-Mg and Mg-Co distributions give the partition coefficients over M1,3 and M2 where

\[ K_{M2} = \frac{(M_2/Ni)_{M1,3}}{(Ni/Mg)_{M2}} \]

and

\[ M_2 = Ni \text{ or } Co \]

where \( K_{M2} > 1.0 \). Ni-Co does not affect the ordering of Ni-Mg and Mg-Co over the octahedral sites. The infrared spectra of intermediate binary compositions show fine structure caused by ordering of Ni-Mg or Mg-Co over the M1,3 sites and by ordering of Na and vacancy at the A site; thus intermediate compositions show an eight-band spectrum in the principal OH-stretching region. Precise band intensities were derived by nonlinear least-squares fitting of Gaussian band shapes to the observed spectra. The relative observed intensities of the combinations of bands \( 3f_i + 2f_e + f_c \) and \( f_i + 2f_e + 3f_c \) are in accord with the equations of Burns and Strens (1966), indicating that there is no significant variation in molar absorptivity with frequency (energy) for individual bands within a single sample (spectrum). Combined with the results of Skogby and Rossman (1991) on polarized single-crystal infrared spectra of amphiboles, this result suggests that different local configurations of M1,3 cations in amphiboles couple such that the transition probabilities of the associated OH groups are equal.

INTRODUCTION

The experimental techniques by which synthetic amphiboles are characterized have considerably increased in number during the last decade (Hawthorne 1983a; Graham et al. 1989; Raudsepp et al. 1991; Della Ventura 1992). The standard methods of powder X-ray diffraction and optical microscopy have been augmented by single-crystal X-ray diffraction (e.g., Boschmann et al. 1994; Oberti et al. 1995), infrared (Robert et al. 1989; Della Ventura 1992; Della Ventura and Robert 1990), Raman (Della Ventura et al. 1991) and MAS NMR spectroscopies (Raudsepp et al. 1987a; Welch et al. 1994), EXAFS and XANES (Mottana et al. 1990; Paris et al. 1993), and HRTEM (Maresch and Czank 1983, 1988; Maresch et al. 1994; Ahn et al. 1991). The Rietveld method (Rietveld 1969; Young et al. 1977) is proving to be very useful for the characterization of cation site occupancies and bulk compositions in synthetic amphiboles (Raudsepp et al. 1987a, 1987b; Della Ventura et al. 1993a, 1993b; Robert et al. 1993; Jenkins and Hawthorne 1995). With reference to the present study, Della Ventura et al. (1993b) characterized the ordering behavior in synthetic (nickel, magnesium, cobalt)-potassium-richterite and showed that Ni-Mg and Mg-Co show ideal distributions over the M1,3 and M2 sites, with \( K_v \) values of 4.26 and 1.92, respectively. Here, we present analogous results for the solid-solution series (nickel, magnesium) and (magnesium, cobalt)-richterites with end-member compositions richterite [Na(NaMg)SiO2(OH)], Ni-rich richterite [Na(NaNi)SiO2(OH)], and Co-rich richterite [Na(NaCo)SiO2(OH)] and compare the results with data for the analogous potassium-richterite series.

EXPERIMENTAL DETAILS

Details of synthesis procedures are given by Della Ventura et al. (1993b). Compositions were prepared along the binary joins (nickel, magnesium)-richterite and (magnesium, cobalt)-richterite.