X-ray Rietveld refinement and FTIR spectra of synthetic (Si,Ge)-richterites

KANA SENDA,1 KIYOTAKA ISHIDA,1,∗ AND DAVID M. JENKINS2

1Department of Environmental Changes, Graduate School of Social and Cultural Studies, Kyushu University, 4-2-1 Ropponmatsu, Chuo-ku, Fukuoka 810-8560, Japan
2Department of Geological Sciences and Environmental Studies, Binghamton University, Binghamton, New York 13902-6000, U.S.A.

ABSTRACT

Richteritic amphiboles in which tetrahedral Si was substituted for Ge were synthesized using internally heated gas vessels at 795–905 °C and 720–756 MPa. There is complete solid-solution between 4Si and 4Ge richterite. The materials were characterized by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), analytical transmission electron microscopy (AN-TEM), electron microprobe analysis (EMPA), X-ray diffraction (XRD) Rietveld structure refinement, and Fourier-transform infrared spectroscopy (FTIR). X-ray diffraction data for the richterites indicate that, with increasing Ge replacement for Si, all cell parameters (= a, b, c, and β) increase linearly and the rotation angle of the double chains increases. Refinement of the Ge and Si contents at the tetrahedral sites indicate that the Ge content at the T2 site is greater than at the T1 site for amphiboles of intermediate composition. Deuteration experiments were also made for the purpose of FTIR analysis. Infrared OH/OD-stretching bands attributed to the configurations (MgMgMg)-OH/OD=Na(K) and (MgMgMg)-OH/OD=□(□ = vacancy) were observed. The frequency of the former bands decreases linearly with increasing Ge content, while the frequency and the intensity of the latter band decreases with increasing Ge content. Both sets of OH/OD-stretching bands show a continuous or one-mode change along the compositional join without any identifiable fine structure, indicating a lack of any short-range ordering within the tetrahedral double chain. The Si-O (at 1200–800 cm–1) and Ge-O (at 950–700 cm–1) stretching bands show similar continuous down-frequency shifts, and interactions of their modes are very small. The chain deformation bands of Si•Si-O, Si•Ge-O, and Ge•Ge-O are observed at 770–650, 660–590, and 590–510 cm–1, respectively, with the frequency range of their absorption bands becoming narrower with increasing Ge content. A weak and broad OH librational band appears at 600 cm–1 in Si-richterite. With increasing Ge for Si substitution this band shifts upward in frequency, becoming centered at 650 cm–1 in Ge-richterite, which is the opposite behavior to the downward frequency shift of the OH/OD-stretching vibrations. The most notable aspect of this study is the continuous changes that are observed in the structure (cell dimensions, bond distances) and infrared spectra of richterite with replacement of Si by Ge. The only long-range ordering effect that was clearly observed was the preference of Ge over Si at the tetrahedral T2 site for intermediate compositions. Evidence for short-range ordering that can be observed in the OH-stretching region of the Ge-analogue of talc was not observed in Ge-richterite.

INTRODUCTION

Although many crystal-chemical studies have been made of synthetic richterites with various ionic substitutions (Charles 1975; Robert et al. 1989, 1993; Pawley et al. 1993; Della Ventura et al. 1993a, 1993b, 1995a, 1996b, 1997, 1999; Hawthorne et al. 1997; Melzer et al. 2000), studies of Ge replacing Si in amphiboles of richterite (or any) composition have not been previously reported. As silicon (atomic number = 14, 29Si = 0.26 Å; Shannon 1976) and germanium (atomic number = 32, 68Ge = 0.40 Å) have similar chemical characteristics but different physical properties, numerous germanates have been investigated as silicate analogues of mantle minerals for obtaining crystal-chemical and pressure-temperature (P-T) stability information. Large differences in the physical properties of Ge and Si are useful for obtaining crystal chemical information for synthetic amphiboles through the X-ray powder diffraction Rietveld method and by FTIR spectroscopy. The X-ray scattering power for Ge is 2.29 (= 32/14) times larger than Si and a large chemical shift is expected for infrared spectra arising from the mass effect (Ge is 2.58 times heavier than Si). Some assignments of the bands in the mid-infrared spectra of amphiboles were made by Lazarev (1972), Gillet et al. (1989), Ishida (1990), and Andrut et al. (2000); however, there are many features of these spectra still needing investigation.

We have performed hydrothermal syntheses of Ge-substituted Si-richterites for the purpose of determining (1) the effects that cation substitutions into the tetrahedral chain will have on the structure (cell dimensions and bond distances), (2) the presence of any long-range Si-Ge ordering at the tetrahedral sites (by XRD), (3) the presence of any short-range Si-Ge ordering (by FTIR), and (4) the effects of Ge substitution for Si on the lattice-vibration region of the FTIR spectra. In addition, deuteration experiments were performed to help identify any fine structure in the hydroxyl-stretching region (3800–3600/2800–2600 cm–1) and to identify OH oscillations (librations) that occur in the lattice vibration range (1300–400 cm–1) of the FTIR spectra.