American Mineralogist, Volume 90, pages 1062–1072, 2005

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

KANA SENDA,[1] KIYOTAKA ISHIDA,[1,*] AND DAVID M. JENKINS[2]

[1]Department of Environmental Changes, Graduate School of Social and Cultural Studies, Kyushu University, 4-2-1 Ropponmatsu, Chuo-ku,
Fukuoka 810-8560, Japan
[2]Department 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 ^{IV}Si and ^{IV}Ge 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-^{A}Na(K) and (MgMgMg)-OH/OD-$^{A}\square$ ($\square$ = 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.