Eur. J. Mineral.
2008, **20**, 1019–1026
Published online July 2008

The $P2_1/m$- $C2/m$ phase transition in synthetic amphiboles in the system Li_2O–Na_2O–MgO–SiO_2–H_2O: a high-T FTIR study

GIANCARLO DELLA VENTURA[1,4,*], FABIO BELLATRECCIA[1], GIANLUCA IEZZI[2,3,5], ROBERTA OBERTI[4] and FERNANDO CÁMARA[4]

[1] Dipartimento di Scienze Geologiche, Università Roma Tre, Largo S. Leonardo Murialdo 1, 00146, Roma, Italy
*Corresponding author, e-mail: dellaven@uniroma3.it
[2] Dipartimento di Scienze della Terra, Università "G. D'Annunzio", 66013 Chieti Scalo, Italy
[3] Department of Seismology and Tectonophysics, Istituto Nazionale di Geofisica e Vulcanologia, Roma, 00100 Italy
[4] CNR-Istituto di Geoscienze e Georisorse, unità di Pavia, via Ferrata 1, 27100 Pavia, Italy
[5] Presently at: Dipartimento di Geotecnologie per l'Ambiente ed il Territorio, Università G. D'Annunzio, 66013 Chieti, Italy

Abstract: The $P2_1/m \leftrightarrow C2/m$ phase-transition has been studied by high-T FTIR analysis on a series of synthetic amphiboles in the Li_2O–Na_2O–MgO–SiO_2–H_2O (LNMSH) system. Spectra were collected in the T range 25–450 °C on KBr disks. All examined amphiboles have $P2_1/m$ symmetry at room T. Their OH-stretching FTIR spectrum consists of two main bands at ~ 3740 and 3715 cm^{-1}. At the transition temperature (T_c), these bands merge into one single absorption centred at ~ 3720 cm^{-1}, and no further change is observed beyond this T. Significant modifications consisting in peak shifting and band broadening are also observed in the MIR (medium infrared) 1300–640 cm^{-1} region. T_c values for the different compositions were estimated based on various methods; the most reliable procedure is considered to be the fit of Landau 2-4-6 potentials using band shifts observed in the MIR region. The T_c values obtained for all samples are consistent with previous results obtained on two members of the series examined here by single-crystal or synchrotron powder HT-XRD (high-T X-ray diffraction). They correlate linearly with the aggregate cation radius at $M(4)$ [T_c (°C) = 803–533 $\langle r_{M(4)} \rangle$; $R^2 = 0.97$]. This work thus provides a measure of the role played by the size of the $M(4)$ polyhedron in determining the T_c in simple chemical systems where the B-site occupancy (and geometry) is the only variable. The slope of the equation is far less steep in the LNMSH system than in cummingtonite; crystal-chemical reasons for this behaviour are discussed, and the local order between A and monovalent B cations is suggested to be the major constraint. In more complex systems, inspection of the available data shows that other factors such as the aggregate size of the strip of octahedra must be taken into account.

Key-words: synthetic amphiboles, LNMSH system, HT-FTIR spectroscopy, phase transition, lithium.

Introduction

Monoclinic amphiboles with small B cations (Mg, Fe^{2+}) undergo a displacive $P2_1/m \leftrightarrow C2/m$ phase-transition as a function of temperature (T) and/or pressure (P), and the T_c and P_c values depend on composition and/or cation order, which may be followed by the aggregate cation radius at the $M(4)$ site, $\langle r_{M(4)} \rangle$ (Yang & Hirschmann, 1995; Yang & Prewitt, 2000; Boffa Ballaran *et al*., 2000, 2001, 2004). More recently, the same transition behaviour was detected in synthetic amphiboles with 1:1 monovalent and small divalent B cations (*e.g*., ^{B}(NaMg) and ^{B}(LiMg)), and evidences were found that T_c depends on the aggregate cationic radius at both the $M(4)$ and $M(1,2,3)$ sites (Cámara *et al*., 2003a, 2008; Iezzi *et al*., 2004, 2005; Welch *et al*., 2007). Notwithstanding these efforts, a comprehensive P-T-X model for the phase transition in amphiboles still needs to be developed.

Oberti *et al*. (2000) used single-crystal X-ray refinement (SREF), Secondary Ion Mass Spectrometry (SIMS), and Fourier Transform Infrared spectroscopy (FTIR) to show that some synthetic amphiboles obtained by Gibbs *et al*. (1962) and Maresch & Langer (1976) in the Li_2O-Na_2O-MgO-SiO_2-H_2O (LNMSH) system have a very peculiar mixture of B cations ($Mg_{0.97}Li_{0.27}H_{0.12}Na_{0.64}$) and $P2_1/m$ symmetry. This finding prompted a series of experimental studies aimed at characterizing the actual composition and structural features of LNMSH amphiboles under different T, P and X conditions.

Cámara *et al*. (2003a) and Iezzi *et al*. (2004) showed by single-crystal XRD analysis that the Li-free $^{A}Na_{0.81}\,^{B}(Na_{0.81}Mg_{1.19})\,^{C}Mg_5\,^{T}Si_8O_{22}\,^{W}(OH)_2$ composition (sample 334) has $P2_1/m$ symmetry at room T, and undergoes a second-order $P2_1/m \leftrightarrow C2/m$ phase transition at T_c = 257 °C. Iezzi *et al*. (2005) found by synchrotron-

DOI: 10.1127/0935-1221/2008/0020-1836
0935-1221/08/0020-1836 $ 3.60