The substitution Fe$^{3+}$-Al and the isosymmetric displacive phase transition in synthetic zoisite: A powder X-ray and infrared spectroscopy study

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ABSTRACT

The Fe$^{3+}$-Al substitution in synthetic zoisite was studied in the system CFASH at 2.0 GPa and 750 °C (compositional range: 0.0–0.14 $X_{ps}$). The samples were characterized by powder X-ray diffraction, FTIR, and electron microprobe. Discontinuities in refined lattice parameters at ~0.05 $X_{ps}$ are attributed to two distinct and hitherto unknown modifications, zoisite I ($<0.05 X_{ps}$) and zoisite II ($>0.05 X_{ps}$). The following lattice parameters were derived:

(zoisite I)

a (Å) = –3.72 × 10$^{-2}$ × $X_{ps}$ + 16.1913
b (Å) = 6.43 × 10$^{-2}$ × $X_{ps}$ + 5.5488
c (Å) = 3.43 × 10$^{-2}$ × $X_{ps}$ + 10.0320
V (Å$^3$) = 11.4 × $X_{ps}$ + 901.3

(zoisite II)

a (Å) = –8.26 × 10$^{-2}$ × $X_{ps}$ + 16.2061
b (Å) = 8.14 × 10$^{-2}$ × $X_{ps}$ + 5.5486
c (Å) = 1.18 × 10$^{-1}$ × $X_{ps}$ + 10.0263
V (Å$^3$) = 19.3 × $X_{ps}$ + 901.6

In both modifications, substitution of Fe$^{3+}$ expands the M3 octahedron, resulting in opposed rotations of the corner-linked T1 and T2 tetrahedra of the Si2O7 group. The extent of rotation is limited and controls the maximum Fe$^{3+}$ content in zoisite I and II. With increasing Fe$^{3+}$ content, zoisite I transforms to zoisite II and zoisite II to clinozoisite. The transformation from zoisite I to II can be classified as a substitutionally induced isosymmetric displacive phase transition.

Four significant IR bands were observed at ~3250, ~3195, ~3155, and ~2170 cm$^{-1}$. The first three bands are attributed to the configurations Al$_2^{[M1,2]}$O10-H◊◊◊O2-Al$_2^{[M1,2]}$(Al,Fe$^{3+}$)$^{[M3]}$, Al$_2^{[M1,2]}$O10-H◊◊◊O4-Al$_2^{[M1,2]}$Fe$^{3+}$[M3], and Al$_2^{[M1,2]}$O10-H◊◊◊O4-Al$_2^{[M1,2]}$Al[M3]. O10-H◊◊◊O2 is bifurcated between the two symmetrically arranged O2 and O2’ atoms. The band at ~2170 cm$^{-1}$ is interpreted as the first overtone of the bending vibration of O10-H◊◊◊O2. In analogy with the results from powder XRD the IR bands show discontinuities at ~0.05 $X_{ps}$, confirming the two modifications of zoisite.

INTRODUCTION

Systematic changes in the structures of minerals, such as changes in bond lengths and bond angles, which determine the degree of distortion of coordination polyhedra, are common in solid solutions. These changes may significantly influence the ability of a structure to incorporate trace elements, which can accompany the substitution in major elements. A detailed knowledge of how a structure reacts to an isomorphous substitution is necessary to explain for example its geochemical behavior as a host for trace elements. Furthermore, the substitution of cations of different size might induce phase transformations and can mimic structural changes in solid solutions induced by pressure or temperature (e.g., Heaney 2000).

Zoisite, the orthorhombic variety of the epidote mineral group with the idealized formula Ca$_2$Al$_2$[SiO$_4$/Si$_2$O$_7$(O/OH)] contains up to 20 mol% of the hypothetical end-member Ca$_2$Al$_2$Fe$^{3+}$[SiO$_4$/Si$_2$O$_7$(O/OH)] (pistacite) and its composition can be expressed as $X_{ps}$ = Fe$^{3+}$(Fe$^{3+}$ + Al−2). It can be a modally important rock-forming mineral in metabasites and metamars, especially at high pressure in the blueschist, epidote-amphibolite, and eclogite facies. Because of its stability at high pressure, it is considered to be an important carrier of H$_2$O to depth in subduction zones (Schmidt and Poli 1994; Poli and Schmidt 1998) and might control the budget of Sr, Pb, Mn, Cr, and LREE in high-pressure and ultra-high-pressure metasites (Nagasaki and Enami 1998; Brunsmann et al. 2000). Despite its petrological importance, little is known about Fe$^{3+}$-zoisite and the response of its structure to increasing iron content. It is not clear how the maximum amount of Fe$^{3+}$ in zoisite is controlled by the structure and how this relates to the lattice parameters. Nothing is known about possible modifications of zoisite and the ideal or non-ideal behavior of its solid solution.

The structure of zoisite (Fig. 1) was determined by Fesenko et al. (1955, 1956), and was later refined by Dollase (1968). It contains one type of endless octahedral chain parallel to b with two distinct octahedral sites M1,2 and M3, which are occupied