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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)	(zoisite II)
a (Å) = $-3.72 \times 10^{-2} \times X_{ps} + 16.1913$	a (Å) = $-8.26 \times 10^{-2} \times X_{ps} + 16.2061$
b (Å) = $6.43 \times 10^{-2} \times X_{ps} + 5.5488$	b (Å) = $8.14 \times 10^{-2} \times X_{ps} + 5.5486$
c (Å) = $3.43 \times 10^{-2} \times X_{ps} + 10.0320$	c (Å) = $1.18 \times 10^{-1} \times X_{ps} + 10.0263$
V (Å^3) = $11.4 \times X_{ps} + 901.3$	V (Å^3) = $19.3 \times X_{ps} + 901.6$

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 Si_2O_7 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$\cdots$O2-$Al_2^{[M1,2]}$(Al,Fe^{3+})$^{[M3]}$, $Al_2^{[M1,2]}$-O10-H$\cdots$O4-$Al_2^{[M1,2]}Fe^{3+[M3]}$, and $Al_2^{[M1,2]}$-O10-H$\cdots$O4-$Al_2^{[M1,2]}Al^{[M3]}$. O10-H$\cdots$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$\cdots$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.