

High-pressure behavior of zoisite

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ABSTRACT

A high-pressure single-crystal X-ray diffraction (XRD) study has been carried out on two natural zoisite samples $\text{Ca}_2\text{Al}_{3-x}\text{Fe}_x\text{Si}_3\text{O}_{12}\text{OH}$, one Fe-free ($x = 0$) and one Fe-rich ($x = 0.12$). The unit-cell parameters were determined for the Fe-free sample at 18 different pressures up to 7.76 GPa and for the Fe-rich sample at 13 different pressures up to 7.63 GPa. The $P(V)$ data for both of the samples were fitted by a third-order Birch-Murnaghan equation of state (BM3 EoS). The equation of state coefficients are: $V_0 = 903.39(5) \text{ \AA}^3$, $K_{T0} = 122.1(7) \text{ GPa}$, and $K'_0 = 6.8(2)$ for the Fe-free sample and $V_0 = 906.95(5) \text{ \AA}^3$, $K_{T0} = 119.1(7) \text{ GPa}$, and $K'_0 = 7.3(2)$ for the Fe-rich sample. This shows that the addition of Fe in to the crystal structure of zoisite leads to a slight softening of the structure.

Both compositions exhibit axial compressibilities $\beta_c > \beta_a \gg \beta_b$, with the compressibilities of the a and b axes of the two samples being indistinguishable. The softening of the bulk modulus of zoisite with Fe content follows from softening of the c -axis of the structure. A high-pressure structural study of the Fe-free sample showed that the main compression mechanisms in the structure are the compression of soft inter-octahedral distance along [001] and soft intra-octahedral distances along [010] directions, while along [100] the main compression occurs because of the compression of stiff intra-octahedral distances. The substitution of Fe on to the M3 octahedral site of the structure leads to an increase of the intra-octahedral distance of the M3 that triggers the rotation of M12 and therefore leads to the softening of the M12 inter-octahedral distances that accounts for the softening of the c -axis of the structure.

Keywords: Zoisite, high pressure, X-ray diffraction, compressibility, OH, water, hydrous minerals