

Elasticity of franklinite and trends for transition-metal oxide spinels

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ABSTRACT

The pressure dependence of single-crystal elastic moduli of a natural Mn-rich franklinite, $(\text{Mn}_{0.40}\text{Fe}_{0.16}^{2+}\text{Zn}_{0.37}\text{Mg}_{0.03})(\text{Fe}_{1.94}^{3+}\text{Al}_{0.08})\text{O}_4$, has been determined by GHz-ultrasonic interferometry in a diamond-anvil cell to 9.8 GPa. The room-pressure elastic constants of franklinite are $C_{11} = 244(3)$ GPa, $C_{12} = 142(4)$ GPa, and $C_{44} = 77(2)$ GPa. Linear pressure derivatives of C_{11} and C_{12} are 4.3(3) and 3.8(3), respectively, whereas the C_{44} modulus exhibits softening, fitted in the $P \leq 10$ GPa pressure range to $C_{44} = 77(2) + 0.29(2)P - 0.018(2)P^2$ GPa. The average of Hashin-Shtrikman bounds on the adiabatic bulk modulus (K_{S0}) of franklinite is 175(3) GPa, with pressure derivative $K'_S = 4.3(3)$, and the shear modulus $G_0 = 66(2)$ GPa with $G' = 0.09(3)$. The isothermal compressibility of franklinite was determined from a separate high-pressure, single-crystal X-ray diffraction experiment to 7.8 GPa, yielding $K_{T0} = 173.5(7)$ GPa fitted with a fixed pressure derivative of $K'_T = 4$. When K' is fixed to the ultrasonic value of 4.3, we obtain $K_{T0} = 172.2(7)$ GPa. In contrast to iron-free gahnite (ZnAl_2O_4), franklinite exhibits pressure-induced mode softening of C_{44} similar to magnetite (Fe_3O_4). Between end-member compositions ZnFe_2O_4 (franklinite) and MnFe_2O_4 (jacobsite), the bulk modulus decreases linearly with increasing %Mn, however we observe non-linear behavior in other elastic moduli, especially C_{44} , which displays a pronounced negative anomaly for the mid-range Mn composition. Applying Birch's law to $AB_2\text{O}_4$ -type spinels reveals that oxide spinels containing transition metals on both A and B sites follow a distinct trend from other spinels.

Keywords: Spinel, elasticity, transition metals, equation of state