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SPINELS RENAISSANCE—PAST, PRESENT, AND FUTURE

The elasticity of $MgAl_2O_4$–$MnAl_2O_4$ spinels by Brillouin scattering and an empirical approach for bulk modulus prediction†

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Abstract

The elastic constants C_{ij} of a set of synthetic single crystals belonging to the join $MgAl_2O_4$–$MnAl_2O_4$ (spinel sensu stricto–galaxite) were determined by Brillouin spectroscopy at ambient conditions. The C_{11} component tends to remain constant for Mg-rich compositions ($X_{Mn} < 0.5$) and decreases in Mn-rich compositions, whereas C_{12} increases and C_{44} decreases almost linearly from $MgAl_2O_4$ to $MnAl_2O_4$. The bulk modulus K_S is weakly dependent upon Mg-Mn substitution within experimental uncertainties, whereas the shear modulus G decreases with increasing Mn^{2+} content. For $MnAl_2O_4$, C_{11} = 271.3(1.3) GPa, C_{12} = 164.8(1.3) GPa, C_{44} = 124.9(5) GPa, K_S = 200(1) GPa, and G = 88.7(5) GPa.

Based on the "polyhedral approach," we developed a model that describes the crystal bulk moduli of the $MgAl_2O_4$–$MnAl_2O_4$ spinels in terms of their cation distribution and the polyhedral bulk moduli of the different cations. We refined a set of values for the effective polyhedral bulk modulus of Mg, Mn^{2+}, and Al in tetrahedral (T) and octahedral (M) sites, which span from 153 to 270 GPa ranking as follows: $K^M_{Mn} < K^M_{Mg} < K^T_{Mg} \approx K^T_{Mn} < K^M_{Al} << K^T_{Al}$.

Crystal bulk modulus was perfectly reproduced within 0.1% for all Mn^{2+}-bearing samples. We also found a high linear correlation between the effective polyhedral bulk modulus and the ionic potential, IP, of the coordinating cations: K_i^j (GPa) = 20(2) IP + 108(10) (where i indicates the cation and j the polyhedral site). We tested this simple correlation by calculating the specific effective polyhedral bulk modulus of several cations in T and M coordination and then predicting the crystal bulk modulus for several spinel compositions. The success of our simple correlation in modeling the bulk modulus of spinels outside the $MgAl_2O_4$–$MnAl_2O_4$ system is encouraging, and suggests that the relationships between chemical composition, cation distribution and elastic properties in spinel-structured minerals and materials can indeed be expressed by relatively simple models.

Keywords: Spinels, galaxite, elasticity, Brillouin scattering, cation distribution, crystal chemistry