The elasticity of $\text{MgAl}_2\text{O}_4$–$\text{MnAl}_2\text{O}_4$ spinels by Brillouin scattering and an empirical approach for bulk modulus prediction

**ENRICO BRUSCHINI**1,*, SERGIO SPEZIALE2, GIOVANNI B. ANDREOZZI1, FERDINANDO BOSI1,3 and ULF HÅLENIUS3

1Department of Earth Sciences, Sapienza University of Rome, Piazzale Aldo Moro, 5, I-00185 Rome, Italy
2Helmholtz Centre Potsdam–GFZ German Research Center for Geosciences GFZ, Telegrafenberg, 14473 Potsdam, Germany
3Department of Geosciences, Swedish Museum of Natural History, Box 50007, SE-10405 Stockholm, Sweden

**ABSTRACT**

The elastic constants $C_{ij}$ of a set of synthetic single crystals belonging to the join $\text{MgAl}_2\text{O}_4$–$\text{MnAl}_2\text{O}_4$ (spinel sensu stricto–galaxite) were determined by Brillouin spectroscopy at ambient conditions. The $C_{11}$ component tends to remain constant for Mg-rich compositions ($\chi_{\text{Mg}} < 0.5$) and decreases in Mn-rich compositions, whereas $C_{12}$ increases and $C_{44}$ decreases almost linearly from $\text{MgAl}_2\text{O}_4$ to $\text{MnAl}_2\text{O}_4$. The bulk modulus $K_b$ is weakly dependent upon Mg-Mn substitution within experimental uncertainties, whereas the shear modulus $G$ decreases with increasing Mn$^{2+}$ content. For $\text{MnAl}_2\text{O}_4$, $C_{11} = 271.3(1.3)$ GPa, $C_{12} = 164.8(1.3)$ GPa, $C_{44} = 124.9(5)$ GPa, $K_b = 200(1)$ GPa, and $G = 88.7(5)$ GPa.

Based on the “polyhedral approach,” we developed a model that describes the crystal bulk moduli of the $\text{MgAl}_2\text{O}_4$–$\text{MnAl}_2\text{O}_4$ 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: $K_{\text{Al}}^{\text{T}} < K_{\text{Mn}}^{\text{T}} < K_{\text{Mg}}^{\text{T}} \approx K_{\text{Al}}^{\text{M}} < K_{\text{Mn}}^{\text{M}} << K_{\text{Mg}}^{\text{M}}$.

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: $K_i$ (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 $\text{MgAl}_2\text{O}_4$–$\text{MnAl}_2\text{O}_4$ 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

**INTRODUCTION**

Many relevant minerals and materials, which are intensively studied in many fields of Earth and materials sciences, adopt the spinel structure. Oxide spinels are important accessory minerals in many crustal and mantle rocks and Fe-bearing ringwoodite, the spinel-structured polymorph of (Mg,Fe)$_2$SiO$_4$, is probably the dominant phase in mantle transition zone (Barnes and Roeder 2001; Frost 2008; Pearson 2014). Materials with spinel structure quite often show remarkable and useful physical properties, such as colossal magnetoresistance, mechanical strength coupled with thermal stability, optical transparency, catalytic activity, etc. (e.g., Grimes 1975; Fabian et al. 2001; Song and Zhang 2004; Fierro et al. 2005; Jörg and Krischanitz 2006; Gehmann et al. 2013).

Spinel-structured compounds have an almost ideal cubic close-packed arrangement of anions (e.g., Hill et al. 1979; Sicafu s and al. 1999). Considering only one unit cell, the 32 anions produce 64 tetrahedral interstices and 32 octahedral ones. However, only 8 tetrahedral interstices (T) and 16 octahedral interstices (M) are occupied by cations. The general formula of spinel compounds is $(A_1)_i(B_2)_jX_i$ where $A$ and $B$ are cations, $X$ are anions, and $i$ is the inversion degree. In the majority of spinels divalent (A) and trivalent (B) cations can occupy both the tetrahedrally and the octahedrally coordinated T and M sites. When all the trivalent cations are in the octahedra (and hence all the divalent cations are in the tetrahedra) the spinel has an inversion equal to zero. The opposite situation occurs when one half of the trivalent cations are in the tetrahedra (and hence all the divalent cations are in the octahedra) and the spinel has an inversion equal to one. Both these configurations can be regarded as ordered. However, most of the natural and synthetic spinels are disordered, with an inversion degree between zero and one. The spinel structure can accommodate a large variety of cations by shifting the anion position along the <111> directions, described by the anion fractional coordinate $(u \ u \ u)$. Knowing $u$ and the unit-cell parameter $a$, it is possible to obtain any geometrical feature (such as bond lengths and bond angles) of the spinel structure.

To date, much effort has been devoted to the experimental and