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Structural properties and compressibility of spinels: More questions than answers

Paweł Piszora[1], Jolanta Darul[1], Waldemar Nowicki[1], Christian Lathe[2], Stefan Carlson[3], Yngve Cerenius[3]

1. *Adam Mickiewicz University, Faculty of Chemistry, Grunwaldzka 6, Poznań 60-780, Poland* **2.** *GeoForschungsZentrum Potsdam, (GFZ), Telegrafenberg A17, Potsdam D-14473, Germany* **3.** *Lund University, MAX-lab, Lund SE-221 00, Sweden*

e-mail: pawel@amu.edu.pl

Materials with the spinel structure have been extensively used in many electronic and magnetic applications. Spinel oxides are extremely versatile compounds with general formula AB_2O_4, where A and B are divalent and trivalent cations, respectively. Various models have been proposed regarding the dominant factors that contribute to the variations of elastic properties with chemical composition and cation distribution in the spinel structure. The similarity of the bulk modulus value for spinel oxides is known to be a consequence of the volumetric dominance of oxide ions with a cubic close-packed structure. The bulk modulus of an oxide ion in these compounds is about 200 GPa [1], and this value is roughly similar to bulk moduli of many spinel oxides, as it has been found empirically and theoretically [1,2]. A local distortion of the coordination polyhedra, due to the Jahn-Teller effect, can lead frequently to deviation from the rule and turn out structures to be controlled by the size and compressibility of cations, as shown in the lithium manganese oxide [3].

There has been a limited number of papers on the crystallite size dependence of the bulk modulus for the spinel structure oxides, and no clear trend has been observed for various materials. From the reported papers, some materials exhibit a decrease of bulk modulus with decreasing particle size, while some nanomaterials show compressibility similar to their bulk counterparts [4]. Materials with opposite tendency are also known. The mineral maghemite, γ-Fe_2O_3 has a cubic spinel type structure. Nanocrystalline maghemite, have been reported as much less compressible than bulk material (K_0=305 ± 15 GPa and K_0=203 ± 10 GPa for nanocrystalline and bulk material, respectively) [5]. Another sample with a structural formula $Fe_8[Fe_{13.33}\square_{2.67}]O_{32}$, (where □ denotes vacancy) had an exceptionally low bulk modulus of bulk and nanocrystalline form of K_0=124±11 GPa with K'_0=30±7 and K_0=143±14 GPa with K'_0=43±9 respectively. Here the first derivative values K'_0 are exceptionally high and both deviations have been ascribed to the presence of vacancies on octahedral sites [6].

Another factor affecting the bulk modulus is the distribution of cations, characterized by inversion parameter. This parameter is defined as the fraction of divalent metal cations that moves to octahedral sites from tetrahedral sites. Theoretical calculations, using the DFT formalism, have indicated sensitivity of the bulk modulus to the inversion parameter in $AlCo_2O_4$ of K_0=235.7 GPa and K_0=221.8 GPa in the normal and fully inversed spinel, respectively [7]. A small change in chemical composition of spinel can lead to significant changes in its compression behavior. The bulk modulus of $Mg_{0.4}Al_{0.6}[Al_{1.8}\square_{0.2}]O_4$ ('defect sample') is only 171(2) GPa while for stoichiometric disordered spinel $MgAl_2O_4$ is of 193 GPa [8]. However, in another paper, concerning the equation of state, Nestola et al. [9] have indicated that there are no differences in the bulk modulus for the ordered and disordered spinel samples.

In addition to the above factors, also the measurement conditions affect the results, especially, the pressure hydrostaticity level (dependent on the applied pressure transmitting medium) seems to be crucial for proper interpretation of compression results for oxides with the spinel structure [10,11]. Synchrotron radiation measurements revealed that $LiMn_2O_4$ displays an extremely sensitive structural response to deviatoric stress [3], however, nanostructured materials can accommodate more stress compared to their bulk counterparts [12].
Our presentation does not only show the new experimental results, but also provides clues to understanding empirical facts concerning structural properties and compression behavior of spinels.

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