Comparative compressibility and structural behavior of spinel MgAl$_2$O$_4$ at high pressures: The independency on the degree of cation order

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ABSTRACT

The equation of state and the crystal structure evolution with pressure were determined for two single crystals of pure natural MgAl$_2$O$_4$ spinels with different degrees of order. The two samples studied were cut from a larger single crystal and one of them was experimentally disordered at high temperature. The two crystals, showing an inversion parameter $x$ of 0.27 and 0.15 at ambient conditions, were loaded together in a diamond anvil cell and their unit-cell edge was measured up to about 7.5 GPa at 14 different pressures. The unit-cell volume, $V_0$, the bulk modulus, $K_0$, and its first pressure derivative, $K'_0$, were simultaneously refined using a third-order Birch-Murnaghan equation of state, giving the following coefficients: $V_0 = 529.32(2)$ Å$^3$, $K_0 = 193(1)$ GPa, $K'_0 = 5.6(3)$ for the ordered sample and $V_0 = 528.39(2)$ Å$^3$, $K_0 = 192(1)$ GPa, $K'_0 = 5.4(3)$ for the disordered one. Complete intensity data were collected at 0, 0.44, 2.92, 7.34, and 8.03 GPa in a separate experiment. For the ordered and disordered samples the oxygen atomic coordinate $u$ remains practically unchanged inside the investigated pressure range with an average value of 0.2633(5) and 0.2614(2), respectively. As a consequence, the polyhedral compressibilities are similar and are not influenced by the Mg/Al distribution over the two crystallographic sites. This also suggests that pressure has little or no influence on the degree of order in the MgAl$_2$O$_4$ spinel.

Keywords: X-ray single-crystal diffraction, spinel, cation ordering, high pressure

INTRODUCTION

Spinels, with general chemical formula AB$_2$O$_4$ (in common 2-3 spinels A is a divalent cation and B a trivalent), are among the most studied oxide phases in the Earth sciences, because they can be used as petrogenetic indicators (Princivalle et al. 1989, 1999; Sack 1982; Sack and Ghiorso 1991) as well as a structural model for minerals stable at pressure/temperature conditions of the Earth’s mantle (e.g., ringwoodite, Sasaky et al. 1982; Hazen 1993). Spinels show a simple crystal structure (space group Fd$ar{3}$m) characterized by two symmetrically distinct polyhedra: an octahedron, M, and a tetrahedron, T, occupied by divalent and trivalent cations. The number of occupied octahedral sites is twice that of the tetrahedral ones. The tetrahedral cation is located at 1/8,1/8,1/8, while the octahedral cation at 1/2,1/2,1/2. The oxygen has coordinates located at 1/8,1/8,1/8, while the octahedral cation at 1/2,1/2,1/2.

The number of occupied octahedral sites is always twice that of the tetrahedral sites. Spinels sensu stricto, MgAl$_2$O$_4$ ss, is one of the most common spinels, and both its high-temperature and high-pressure behavior have been extensively investigated (Finger et al. 1986; Redfern et al. 1999; Hazen and Yang 1999; Pavese et al. 1999; Carbonin et al. 2002; Levy et al. 2003; Martignago et al. 2003). Andreozzi et al. (2000) suggested a linear relationship between $x$ and $u$ according to the expression:

$$ u = 0.2651 - 0.0123x $$  

Several works have shown that cation disordering increases with temperature, in contrast the influence of pressure is still a matter of controversy. Finger et al. (1986) investigated a single-crystal of natural spinel up to about 4 GPa at room temperature, and concluded that $u$ decreases slightly with pressure. Pavese et al. (1999) in a neutron powder diffraction study at high pressure