Sound velocities and elastic constants of ZnAl₂O₄ spinel and implications for spinel-elasticity systematics

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ABSTRACT

The pressure dependence of the sound velocities, single-crystal elastic constants, and shear and adiabatic bulk moduli of a natural gahnite (ZnAl₂O₄) spinel have been determined to ~9 GPa by gigahertz ultrasonic interferometry in a diamond anvil cell. The elastic constants of gahnite are (in GPa): C₁₁ = 290(3), C₁₂ = 196(4), and C₄₄ = 146(2). The elastic constants C₁₁ and C₄₄ have similar pressure derivatives of 4.48(10) and 5.06(8), while the pressure derivative of C₄₄ is 1.47(3). In contrast to magnetite, gahnite does not exhibit C₄₄ mode softening over the experimental pressure range. The adiabatic bulk modulus Kₐ is 209(5) GPa, with pressure derivative Kₐ' = 4.8(3), and the shear modulus Gₐ = 104(3) GPa, with G' = 0.5(2). Gahnite, along with chromite (FeCr₂O₄) and hercynite (FeAl₂O₄) type is also of practical importance to industrial applications; the ferrites are composed of Fe₂O₃ mixed with various Mn, Zn, Ni, and Mg oxides and are strong magnets utilized in many electronic, communications, and power-switching devices.

INTRODUCTION

Minerals with the spinel structure and general formula AB₂O₄ are among the most common non-silicate oxides in the Earth’s crust and upper mantle. Spinels have cubic symmetry (space group Fd3m, 8 formula units per unit cell), and have an essentially cubic close-packed array of oxygen. A characteristic feature of this structure is the ability to host a wide range of divalent, trivalent, and tetravalent cations; over 100 natural and synthetic phases adopt this structure. In the normal spinel structure, the A cations occupy the tetrahedral site and B cations occupy the octahedral site ([A⁰B⁶]O₄). Inverse spinels contain four-coordinated B cations, while the six-coordinated site contains a mixture of A and B cations ([B⁰⁶(A,B)O₄]). In addition to magnesiomagnete-magnetite (MgFe₂O₄−Fe₃O₄) and spinel−hercynite (MgAl₂O₄−FeAl₂O₄), the zinc-spinels franklinite−gahnite (ZnFe₂O₄−ZnAl₂O₄) form a limited solid solution at high temperature and are important accessory phases in various rock types, but most notably in the Franklin marble and skarn deposits (Carvalho and Sclar 1988; Frondel and Baum 1974). Moreover, the silicate spinel, ringwoodite γ-(MgFe)₂SiO₄, is expected to be the dominant phase in the lower part of Earth’s transition zone between about 520 and 660 km depth. Because spinels exhibit pressure-induced phase changes (Fei et al. 1999; Funamori et al. 1998; Irfune et al. 2002; Levy et al. 2000), they are often used as model minerals for deep-Earth mineralogy. The spinel structure type is also of practical importance to industrial applications; the ferrites are composed of Fe₂O₃ mixed with various Mn, Zn, Ni, and Mg oxides and are strong magnets utilized in many electronic, communications, and power-switching devices.

Most previous studies of spinel elasticity have relied on static compression (X-ray diffraction) to determine the isothermal bulk modulus Kᵢ and Kᵢ' = dKᵢ/dP from pressure-volume data (Chang and Barsch 1973; Haavik et al. 2000; Hazen 1993; Irfune et al. 2002; Levy et al. 2000, 2001; Mao et al. 1974; Yutani et al. 1997). Pressure dependence of the single-crystal elastic constants (Cᵢ) for natural spinels have only been reported for spinel (Yoneda 1990) and magnetite (Reichmann and Jacobsen 2004), thus, single-crystal-elasticity systematics are only now emerging. Due to the relative structural simplicity of close-packed spinels, single-crystal-elasticity data will provide a better understanding of the different effects of pressure on structure and bonding because they can be modeled to a first approximation as ionic compounds with bond strengths according to Coulombic forces (e.g., Hazen 1993). However, simple theory is not always effective when close-packed structures contain transition metals as nearest-neighbor.

It was shown recently (Reichmann and Jacobsen 2004) by means of gigahertz-interferometry measurements on the inverse spinel magnetite [Fe⁴⁺(Fe³⁺Fe⁴⁺)] that the 3d transition-metal element Fe has a dramatic effect on the elastic high-pressure behavior, especially on C₄₄. This modulus has a negative pressure derivative and was interpreted to be a soft mode preceding the structure transition at ~20 GPa (Reichmann and Jacobsen 2004). It is now of special interest to investigate how the single crystal and bulk elastic properties