In situ Raman spectroscopy measurements of MgAl_2O_4 spinel up to 1400 °C

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ABSTRACT

In-situ Raman measurements using a gated spectroscopy system revealed irreversible changes at 800–1000 °C in a natural red spinel (with 2 cation mol% Cr and 1 cation mol% Zn) and at 1100–1200 °C in a natural clear spinel (without Cr or Zn). Our observations of rapid broadening of a mode at 409 cm^{-1} and the appearance of two weak modes at 210 and 520 cm^{-1} at the transition temperature confirm the association of these features with cation disordering proposed by previous quench studies. Furthermore, we found that the frequencies of modes at 313 and 666 cm^{-1} change at the transition temperature. The discontinuous frequency decrease of the mode at 313 cm^{-1} and the increase in the frequency of the mode at 666 cm^{-1} can be explained by the entrance of heavier Al atoms into the tetrahedral sites and the entrance of lighter Mg atoms into the octahedral sites, respectively. Our study demonstrates that in-situ Raman spectroscopy is a powerful tool for studying cation disordering in spinel-structured minerals at high temperature.

Keywords: Spinel, Raman spectroscopy, order-disorder transition, high temperature

INTRODUCTION

Spinel-structured minerals, such as magnetite and ringwoodite, are important for understanding many geological and geophysical problems, such as paleomagnetism and mantle discontinuities. In ordered spinel (MgAl_2O_4), Mg and Al atoms are in the tetrahedral and the octahedral sites, respectively. Some Al atoms enter into the tetrahedral sites through an order-disorder transition at high temperature (Wood et al. 1986; Yamanaka and Takéuchi 1983; Peterson et al. 1991):

\[ \text{IV} \text{Mg}^{2+}\text{VI} \text{Al}^{3+}_x \text{O}_4 \leftrightarrow \text{IV} \text{Mg}^{2+}_{1-x} \text{Al}^{3+}_x \text{O}_4 \]

(1)

where the superscripts represent the coordination numbers of the cations and x is the fraction of Al atoms in the tetrahedral sites, known as the inversion parameter. Spinels with x = 0 and x = 1 are called “normal” and “inverse,” respectively.

Due to the similarities in the X-ray scattering cross sections between Mg^{2+} and Al^{3+}, it has been challenging to directly determine the fraction of Al atoms in the octahedral and tetrahedral sites using X-ray diffraction (Yamanaka and Takéuchi 1983). In neutron diffraction, because Mg and Al atoms show much more contrast, direct characterization of cation disorder is possible (Peterson et al. 1991). However, neutron diffraction is not readily accessible as other techniques.

Raman spectroscopy has been used to study cation disorder in spinel. In some MgAl_2O_4 spinels, more Raman modes have been observed than predicted by group theory (Fraas et al. 1973; O’Horo et al. 1973; Cynn et al. 1992). It has been suggested that most of these extra features are related to cation disorder (Cynn et al. 1992; Van Minh and Yang 2004; Chopelas and Hofmeister 1991). For example, an extra mode has been observed at 727 cm^{-1} in synthetic and heat-treated natural spinels that are thought to be partially inverted (Cynn et al. 1992; Chopelas and Hofmeister 1991). In addition, asymmetric broadening of the most intense mode at 410 cm^{-1}, \( E_g \), has been related to cation disorder as it is observed only in synthetic or heat-treated natural spinel (Cynn et al. 1992; Chopelas and Hofmeister 1991).

However, most Raman measurements for spinel to date have been conducted on temperature-quenched samples, although some in situ high-temperature Raman spectra were presented by Cynn et al. (1992). It has been thought that fast cooling after synthesis or heat treatment may help preserve cation disorder after quench (Cynn et al. 1992). However, previous diffraction (Yamanaka and Takéuchi 1983) and NMR (Wood et al. 1986) studies have suggested that cation disorder at high temperature is not fully preserved through the quench process.

One of the most important problems of using a conventional dispersive Raman technique for in situ high-temperature measurements has been the detection of intense thermal radiation from samples. This can be partially resolved by using short wavelength laser beams, such as 457.9 nm of an Ar-ion laser (e.g., Yashima et al. 1997). However, thermal radiation above 800 °C is too intense even at the near UV range for this technique to yield sufficient signal-to-background ratio. Pulsed lasers have been synchronized with gated detectors to study materials at extreme high temperature (Bernardez et al. 1992; Exarhos and Schaal 1991; Fayette et al. 1994; Herchen and Cappelli 1991; McCarty 1990). The principle can be easily understood from the fact that photon counting statistics are determined by the Poisson distribution (Mulac et al. 1978), and acquisition time has an inverse relation with signal/background. Thus, by decreasing data acquisition time and accumulating many spectra, signal-to-background ratio can be enhanced.

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