Raman spectra of $\beta$-$\text{Mg}_2\text{SiO}_4$ (modified spinel) and $\gamma$-$\text{Mg}_2\text{SiO}_4$ (spinel)

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ABSTRACT

We have obtained new Raman spectra for the polymorphs $\beta$-$\text{Mg}_2\text{SiO}_4$ (modified spinel) and $\gamma$-$\text{Mg}_2\text{SiO}_4$ (spinel). The spectrum for $\beta$-$\text{Mg}_2\text{SiO}_4$ is completely different from that reported earlier, whereas that for $\gamma$-$\text{Mg}_2\text{SiO}_4$ is better defined and shows the five peaks expected for the spinel structure. Despite the differences between these and our earlier Raman spectra, the heat capacities and entropies calculated for these phases using Kieffer’s model remain unchanged.

INTRODUCTION

Recently we presented infrared and Raman spectra for the polymorphs $\beta$-$\text{Mg}_2\text{SiO}_4$ (modified spinel) and $\gamma$-$\text{Mg}_2\text{SiO}_4$ (spinel) and used Kieffer’s (1979a, 1979b, 1979c, 1980) vibrational model to calculate heat capacities and entropies for these phases (Akaogi et al., 1984). In that study, we did not observe all of the expected peaks for $\gamma$-$\text{Mg}_2\text{SiO}_4$, and the spectrum obtained for $\beta$-$\text{Mg}_2\text{SiO}_4$ bore an uneasy resemblance to that of forsterite. For these reasons, we have re-examined the Raman spectra of $\beta$- and $\gamma$-$\text{Mg}_2\text{SiO}_4$.

The new Raman spectra for $\beta$- and $\gamma$-$\text{Mg}_2\text{SiO}_4$ obtained in the present study are shown in Figure 1. Both samples were part of the same batch studied previously (Akaogi et al., 1984). Raman spectra were obtained from individual 10–20-µm grains using an Instruments S.A. U-1000 micro-Raman instrument with a Coherent Innova 90-4 Ar* laser for sample excitation. Laser power at the sample ranged from 10 to 50 mW for a 1-µm spot size, and spectral bandpass was near 3 cm⁻¹.

$\gamma$-$\text{Mg}_2\text{SiO}_4$

The spectrum for $\gamma$-$\text{Mg}_2\text{SiO}_4$ shows two strong bands at 795 and 837 cm⁻¹ and weaker peaks at 600, 370, and 302 cm⁻¹ (Fig. 1, Table 1). These correspond to the five Raman modes ($A_{1g} + E_g + 3F_{2g}$) expected for the spinel structure (White and DeAngelis, 1967; Fraas et al., 1973; O’Horo et al., 1973). The weak features at 918 cm⁻¹ and near 720 cm⁻¹ could be due to a trace of $\beta$-$\text{Mg}_2\text{SiO}_4$ in the sample (see below). The three lower-frequency peaks of $\gamma$-$\text{Mg}_2\text{SiO}_4$ are very weak, which accounts for their not being observed in our earlier study. There was no evidence for the bands suggested near 455 and 550 cm⁻¹ by Akaogi et al. (1984). Guyot et al. (1986) have recently presented a high-frequency Raman spectrum for a natural spinel ($\text{Mg}_{0.34}\text{Fe}_{0.66}$)$_2\text{SiO}_4$ and observed three bands at 796, 844, and 880 cm⁻¹. The bands at 796 and 844 cm⁻¹ probably correspond to the 795 and 837 cm⁻¹ peaks observed in the present study. The additional band at 880 cm⁻¹ could be due to some impurity phase or could reflect a lowering of symmetry in the spinel due to Fe-Mg ordering (White and DeAngelis, 1967).

Two modes of $A_{1g}$ and $F_{2g}$ symmetry respectively are expected from symmetric ($r_1$) and asymmetric ($r_3$) stretching of the tetrahedral SiO₄ units. By analogy with previous work on silicate olivines (Piriou and McMillan, 1983), these two may be assigned to the strong peaks at 795 and 837 cm⁻¹. It is further reasonable to assign the stronger 795 cm⁻¹ peak to the $r_1$-derived $A_{1g}$ mode, since this motion is fully symmetric within both the site and the factor group (Piriou and McMillan, 1983). Yamanaka and Ishii (1986) have recently obtained the Raman spec-
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| Table 1. Raman peak positions for \( \beta\) and \( \gamma\)-Mg\(_2\)SiO\(_4\) |
|-----------------|-----------------|-----------------|
| 230             | 268             | 298             |
| 302             | 328             | 340             |
| 368             | 370             | 369             |
| 400             | 425             | 443             |
| 489             | 511             | 551             |
| 584             | 600             | 675             |
| 723             | 778             | 794             |
| 849             | 842             | 836             |
| 918             | 1100            |

* Data for \( \gamma\)-Ni\(_2\)SiO\(_4\) from Yamanaka and Ishii (1986).

trum of Ni\(_2\)SiO\(_4\) spinel. In this case, the \( \nu_1\)-derived \( A_{2g}\) mode was found at 849 cm\(^{-1}\), at higher frequency than the \( \nu_1\)-derived \( F_{2g}\) mode at 810 cm\(^{-1}\) (Table 1). Yamanaka and Ishii (1986) identified a second \( F_{2g}\) mode of Ni\(_2\)SiO\(_4\) spinel at 675 cm\(^{-1}\). This allows the assignment of the 600-cm\(^{-1}\) peak of \( \gamma\)-Mg\(_2\)SiO\(_4\) to \( F_{2g}\) symmetry (Fig. 1; Table 1). The remaining two modes in the spectrum of \( \gamma\)-Mg\(_2\)SiO\(_4\) occur at 370 and 302 cm\(^{-1}\). The \( E_g\) mode of MgAl\(_2\)O\(_4\) spinel has been unambiguously identified at 410 cm\(^{-1}\) (O'Horo et al., 1973; Fraas et al., 1973; Ishii et al., 1982), whereas Yamanaka and Ishii (1986) found the \( E_g\) mode of Ni\(_2\)SiO\(_4\) spinel at 369 cm\(^{-1}\). This strongly suggests the assignment of the 370-cm\(^{-1}\) peak of \( \gamma\)-Mg\(_2\)SiO\(_4\) to the \( E_g\) mode (Table 1). Finally, Yamanaka and Ishii (1986) calculated their \( F_{2g}\) mode at 190 cm\(^{-1}\) to represent libration of rigid SiO\(_4\) groups relative to the metal sublattice. If this model is accepted for \( \gamma\)-Mg\(_2\)SiO\(_4\), two extreme cases may be considered to account for the mass difference between Ni and Mg, assuming the net force fields in the two spinels to be similar. The first case assumes that the SiO\(_4\) groups and the metal atoms participate equally in the libration: this gives a reduced mass for the Ni system of 35.947 and for Mg spinel of 19.034. Applying this mass ratio to the 190-cm\(^{-1}\) peak of Ni\(_2\)SiO\(_4\) gives a predicted frequency of 261 cm\(^{-1}\) for the same motion in Mg\(_2\)SiO\(_4\) spinel. In the other extreme, it might be assumed that the SiO\(_4\) groups remain stationary and only the metal cations are displaced: this case gives a mass ratio of \( m_{\text{Ni}}/m_{\text{Mg}} = 1.568\), or a predicted frequency of 298 cm\(^{-1}\) for Mg\(_2\)SiO\(_4\) spinel. This is remarkably close to the observed peak at 302 cm\(^{-1}\), which we consider may be assigned as the remaining \( F_{2g}\) mode (Table 1). If our reasoning is correct, this would indicate that this lowest-frequency \( F_{2g}\) mode is predominantly associated with motion of the octahedral cations in the spinel structure. This is consistent with the observation of the analogous \( F_{2g}\) mode of MgAl\(_2\)O\(_4\) spinel near 310 cm\(^{-1}\) (O'Horo et al., 1973; Fraas et al., 1973; Ishii et al., 1982). Since the mass of Al is close to that of Mg, it is reasonable to expect similar octahedral-cation libration frequencies for MgAl\(_2\)O\(_4\) and \( \gamma\)-Mg\(_2\)SiO\(_4\).

\( \beta\)-Mg\(_2\)SiO\(_4\)

The new spectrum of \( \beta\)-Mg\(_2\)SiO\(_4\) is also shown in Figure 1, and peak positions are listed in Table 1. In our previous study we obtained a spectrum for this phase which bore a strong resemblance to forsterite, but with considerable band broadening and large frequency shifts in some bands (see Akaogi et al., 1984, Fig. 4). The present spectrum is very different from that of forsterite (Servoin and Piriou, 1973; Ishii, 1978). We suggest that in our earlier study, the sample of \( \beta\)-Mg\(_2\)SiO\(_4\) transformed under the laser beam during the Raman scattering experiment to give a phase with some structural resemblance to forsterite. Such a transformation could be photo-induced (Brawer and White, 1978) or could simply involve local heating of the sample. Since the transformation was highly localized, probably within a 30–50-\(\mu\)m region at the point of laser contact with the sample, it went undetected in our post-Raman characterization of the sample. In the present study, we carried out micro-Raman experiments on individual grains and could observe the behavior of the sample as the laser beam was applied. In previous studies where high-pressure phases have transformed under the beam, we observed instabilities in the optical diffraction pattern of the scattered beam on the microscope screen, and the appearance of the sample changed in the region of the laser spot on optical examination (Ross et al., 1986). Neither of these phenomena were observed in the present study of \( \beta\)-Mg\(_2\)SiO\(_4\) for a wide range of laser power, and we are confident that the present spectrum in fact represents \( \beta\)-Mg\(_2\)SiO\(_4\).

The crystal structure of \( \beta\)-Mg\(_2\)SiO\(_4\) was studied by Moore and Smith (1970) and refined by Horiuchi and Sawamoto (1981). A number of authors have discussed the structure of this “\( \beta\)-phase” in relation to the olivine and spinel structures (Horiuchi et al., 1980, 1982; Hazen and Finger, 1981; Hyde et al., 1982; Price, 1983). The \( \beta\)-phase structure forms one member of a continuous range of spinelloid structures. Davies and Akaogi (1983) have found via transmission-electron microscopy that spinelloids in the NiAl\(_2\)O\(_4\)-Ni\(_2\)SiO\(_4\) system are commonly intergrowths of several spinelloid structural units, even for samples that appear single-phase to X-ray diffraction. Such stacking disorder usually leads to some band broadening in vibrational spectra of crystalline phases (e.g., White, 1974; Rossman, 1979). The Raman peaks for \( \beta\)-Mg\(_2\)SiO\(_4\) obtained in this study are just as sharp as those for olivine (Piriou and McMullan, 1983) or spinel (Fig. 1). This suggests that \( \beta\)-Mg\(_2\)SiO\(_4\) represents a pure endmember structure with no microstructural disorder due to intergrowth of other possible spinelloid stackings. This is consistent with transmission-electron microscopy on the same sample (P. Davies, pers. comm., 1986), which found no evidence for spinelloid intergrowths in the \( \beta\)-Mg\(_2\)SiO\(_4\) sample.
From symmetry analysis, 39 Raman active modes are expected for $\beta$-Mg$_2$SiO$_4$ (Akaogi et al., 1984). In the present study, 20-25 peaks are unambiguously observed (Fig. 1; Table 1). Without a detailed single-crystal study, no symmetry assignments can be made, although it is likely that the two strong peaks at 723 and 918 cm$^{-1}$ are of $A_g$ symmetry. These bands are qualitatively similar to the major peaks of the pyrosilicate akermanite at 661 and 904 cm$^{-1}$ (Scheetz, 1972; Sharma and Yoder, 1979). The akermanite structure contains Si$_2$O$_7$ groups. The 661-cm$^{-1}$ peak is usually assigned to a symmetric vibration associated with the SiOSi linkage, and the 904 cm$^{-1}$ peak is attributed to symmetric stretching of terminal -SiO$_2$ groups (Lazarev, 1972; Sharma and Yoder, 1979; McMullan, 1984). The structure of $\beta$-Mg$_2$SiO$_4$, also contains Si$_2$O$_7$ units (Horiuchi and Sawamoto, 1981). We attributed to symmetric stretching of terminal -SiO$_2$, associated with the SiOSi linkage, and the 904 cm$^{-1}$ peak is usually assigned to a symmetric vibration associated with the SiOSi linkage (Izarev, 1972; Sharma and Yoder, 1979). The major peaks of the pyrosilicate akermanite at 661 and 918 cm$^{-1}$; these are probably due to rotational modes of H$_2$O adsorbed on the sample or in the sample chamber (A. M. Hofmeister, pers. comm., 1986; Ross et al., 1986).

**VIBRATION MODELS OF HEAT CAPACITY AND ENTROPY**

In our earlier work (Akaogi et al., 1984), we used Kieffer's (1979a, 1979b, 1979c, 1980) vibrational model to calculate the heat capacities and entropies of $\alpha$-, $\beta$- and $\gamma$-Mg$_2$SiO$_4$ and hence estimate the entropy changes for these high-pressure phase transitions. Akaogi et al. (1984) noted that the vibrational calculations were relatively unconstrained owing to lack of data on the elastic and vibrational properties of these phases. In particular, the spinel structure has seven vibrational modes (15 degrees of freedom) at the Brillouin zone center that are spectroscopically inactive (Fraas et al., 1973; O'Horo et al., 1973). In a preliminary lattice dynamical calculation for MgAl$_2$O$_4$ spinel using a rigid ion model, Thompson and Grimes (1978) have suggested at least one mode occurring 100-150 cm$^{-1}$ below the lowest observed Raman or infrared bands. Such low-lying modes would be expected to have a significant effect on the heat capacity of the phase (Kieffer, 1979a, 1979b, 1979c, 1980; Akaogi et al., 1984; Ross et al., 1986).

We have carried out a number of heat-capacity calculations to explore the effect of the new Raman data on the calculations reported in Akaogi et al. (1984). It was not possible to obtain reasonable heat capacities for either $\beta$- or $\gamma$-Mg$_2$SiO$_4$ on the basis of the vibrational spectra alone, probably owing to the large number of spectroscopically inactive modes in both phases and to the lack of information on vibrational mode dispersion for either phase. Those models which did give heat capacities and entropies comparable to the current limited published data (see Akaogi et al., 1984) were in fact similar to the range of model vibrational spectra proposed by Akaogi et al. (1984), and the calculated values were in essential agreement with that earlier work. This result is reassuring, since the entropy changes for the Mg$_2$SiO$_4$ phase transformations calculated by Akaogi et al. (1984) were in excellent agreement with values obtained from phase-equilibrium and calorimetric experiments.

**ACKNOWLEDGMENTS**

The Raman spectroscopy was supported by NSF Grant EAR-8407105 to P. McMullan. We thank E. Ito for kindly providing the sample of $\gamma$-Mg$_2$SiO$_4$ and S. Akimoto for his assistance and facilities in preparation of the $\beta$-Mg$_2$SiO$_4$ phase. We also thank A. Navrotsky and N. Ross for their comments on this manuscript and A. M. Hofmeister for a helpful review.

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MANUSCRIPT RECEIVED JULY 30, 1986
MANUSCRIPT ACCEPTED NOVEMBER 20, 1986