

Raman spectra of β -Mg₂SiO₄ (modified spinel) and γ -Mg₂SiO₄ (spinel)

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ABSTRACT

We have obtained new Raman spectra for the polymorphs β -Mg₂SiO₄ (modified spinel) and γ -Mg₂SiO₄ (spinel). The spectrum for β -Mg₂SiO₄ is completely different from that reported earlier, whereas that for γ -Mg₂SiO₄ 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 β -Mg₂SiO₄ (modified spinel) and γ -Mg₂SiO₄ (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 γ -Mg₂SiO₄, and the spectrum obtained for β -Mg₂SiO₄ bore an uneasy resemblance to that of forsterite. For these reasons, we have re-examined the Raman spectra of β - and γ -Mg₂SiO₄.

The new Raman spectra for β - and γ -Mg₂SiO₄ 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- μ m 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- μ m spot size, and spectral bandpass was near 3 cm⁻¹.

γ -Mg₂SiO₄

The spectrum for γ -Mg₂SiO₄ 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 β -Mg₂SiO₄ in the sample (see below). The three lower-frequency peaks of γ -Mg₂SiO₄ 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 (Mg_{0.74}Fe_{0.26})₂SiO₄ 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 ob-

served 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 (ν_1) and asymmetric (ν_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 ν_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-

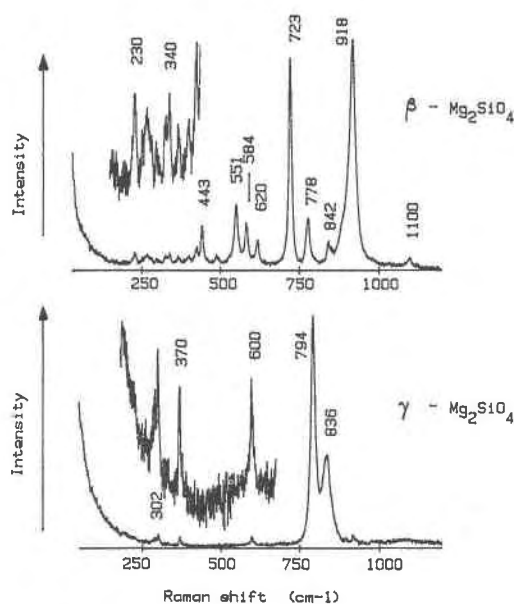


Fig. 1. Raman spectra of β - and γ -Mg₂SiO₄.

TABLE 1. Raman peak positions for β - and γ -Mg₂SiO₄

β -Mg ₂ SiO ₄	γ -Mg ₂ SiO ₄	γ -Ni ₂ SiO ₄ *	
230			
268			
298	302	190	F_{2g}
328			
340			
368	370	369	E_g
400			
425			
443			
489			
551			
584	600	675	F_{2g}
620			
723			
778	794	849	A_{1g}
842	836	810	F_{2g}
918			
1100			

* Data for γ -Ni₂SiO₄ from Yamanaka and Ishii (1986).

trum of Ni₂SiO₄ spinel. In this case, the ν_1 -derived A_{1g} mode was found at 849 cm⁻¹, at higher frequency than the ν_3 -derived F_{2g} mode at 810 cm⁻¹ (Table 1). Yamanaka and Ishii (1986) identified a second F_{2g} mode of Ni₂SiO₄ spinel at 675 cm⁻¹. This allows the assignment of the 600-cm⁻¹ peak of γ -Mg₂SiO₄ to F_{2g} symmetry (Fig. 1; Table 1). The remaining two modes in the spectrum of γ -Mg₂SiO₄ occur at 370 and 302 cm⁻¹. The E_g mode of MgAl₂O₄ 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 Ni₂SiO₄ spinel at 369 cm⁻¹. This strongly suggests the assignment of the 370-cm⁻¹ peak of γ -Mg₂SiO₄ 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 SiO₄ groups relative to the metal sublattice. If this model is accepted for γ -Mg₂SiO₄, 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 SiO₄ 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 Ni₂SiO₄ gives a predicted frequency of 261 cm⁻¹ for the same motion in Mg₂SiO₄ spinel. In the other extreme, it might be assumed that the SiO₄ groups remain stationary and only the metal cations are displaced: this case gives a mass ratio of $m_{Ni}/m_{Mg} = 1.568$, or a predicted frequency of 298 cm⁻¹ for Mg₂SiO₄ 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 MgAl₂O₄ 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 MgAl₂O₄ and γ -Mg₂SiO₄.

β -Mg₂SiO₄

The new spectrum of β -Mg₂SiO₄ 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 β -Mg₂SiO₄ 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- μ 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 β -Mg₂SiO₄ for a wide range of laser power, and we are confident that the present spectrum in fact represents β -Mg₂SiO₄.

The crystal structure of β -Mg₂SiO₄ was studied by Moore and Smith (1970) and refined by Horiuchi and Sawamoto (1981). A number of authors have discussed the structure of this " β -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 β -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 NiAl₂O₄-Ni₂SiO₄ 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 β -Mg₂SiO₄ obtained in this study are just as sharp as those for olivine (Piriou and McMillan, 1983) or spinel (Fig. 1). This suggests that β -Mg₂SiO₄ 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 β -Mg₂SiO₄ sample.

From symmetry analysis, 39 Raman active modes are expected for β -Mg₂SiO₄ (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 Si₂O₇ 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 -SiO₃ groups (Lazarev, 1972; Sharma and Yoder, 1979; McMillan, 1984). The structure of β -Mg₂SiO₄ also contains Si₂O₇ units (Horiuchi and Sawamoto, 1981). We suggest similar interpretations for the strong 723- and 918-cm⁻¹ Raman peaks of β -Mg₂SiO₄, as symmetric stretching vibrations associated with the SiOSi linkage and the terminal -SiO₃ groups, respectively. The weak Raman peak near 1100 cm⁻¹ could be due to an asymmetric stretching mode of the SiOSi linkage (Lazarev, 1972) and associated with the strong infrared bands in this region (Akaogi et al., 1984), although Jeanloz (1980) observed no analogous high-frequency bands in his infrared spectrum of β -Co₂SiO₄. The lowest-frequency Raman mode of β -Mg₂SiO₄ occurs at 230 cm⁻¹ (Table 1). Akaogi et al. (1984) suggested infrared modes at 208, 188, and 130 cm⁻¹ [the 226-cm⁻¹ frequency reported in Akaogi et al. (1984) was a misprint: the frequency was 266 cm⁻¹]; these are probably due to rotational modes of H₂O adsorbed on the sample or in the sample chamber (A. M. Hofmeister, pers. comm., 1986; Ross et al., 1986).

VIBRATIONAL 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 α -, β - and γ -Mg₂SiO₄ 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 Mg-Al₂O₄ 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 β - or γ -Mg₂SiO₄ 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 Mg₂SiO₄ phase transformations calculated by Akaogi et al. (1984) were in excellent agreement with values obtained from phase-equilibrium and calorimetric experiments.

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