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The Raman spectrum of $MgSiO_3$ ilmenite

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Abstract

The Raman spectrum of the high pressure polymorph of $MgSiO_3$ with an ilmenite-type structure has been obtained. The spectrum contains 7 definite bands and 3 other possible bands. Its overall form is similar to that of geikielite, $MgTiO_3$, which also has the ilmenite structure. The highest frequency modes occur near 800 cm^{-1}, and are probably at least partly associated with silicon-oxygen stretching motions. However, on the basis of vibrational calculations for corundum, it is unlikely that these may be simply related to vibrations of the $[SiO_6]$ groups in $MgSiO_3$-ilmenite.

Introduction

The hexagonal modification of $MgSiO_3$ was first synthesized at ultra high-pressure by Kawai et al. (1974) and identified as having an ilmenite-type structure by Ito and Matsui (1974). The ilmenite structure-type is stabilized in the pressure range from approximately 210–250 kbar at 1100°C (Ito and Yamada, 1981) suggesting this structure with octahedrally-coordinated Mg and Si could be an important constituent of the deep mantle. In the present work we have measured the Raman spectrum of this phase. Infrared and Raman spectra obtained for high-pressure phases are of particular interest since we can calculate their lattice vibrational thermodynamic properties using the model approach developed by Kieffer (1979). Vibrational calculations have been successful in constraining $\Delta S°$ for the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transitions in the Mg_2SiO_4 polymorphs (Akaogi et al., 1984). With Raman and infrared data, such calculations may provide constraints on entropies of ultra high-pressure phase transitions, e.g., the $MgSiO_3$ ilmenite → perovskite transition, when no other data can be obtained.

Experimental

The $MgSiO_3$ ilmenite used was kindly provided by Dr. E. Ito of Okayama University, Misasa, Japan. We were able to obtain the Raman spectrum by glancing angle reflection of the incident laser from a 0.7 mg pellet polycrystalline sample, using the 4880Å line of a Spectra-Physics 171 argon laser and a Spex 1402 double monochromator equipped with an RCA photomultiplier and photon-counting electronics. Laser power at the sample was approximately 50 mW, and slit widths were near 2 cm^{-1}. The Raman spectrum for $MgSiO_3$ ilmenite is shown in Figure 1.

Discussion

The high pressure $MgSiO_3$ ilmenite phase crystallizes in space group $R\bar{3}(C_{3}i^{2})$ and the primitive unit cell contains two formula units of $MgSiO_3$. Factor group analysis (e.g., Fateley et al., 1972) gives the number and symmetries of expected bands:

$$\Gamma_{MgSiO3\text{–}ilm} = 5\ Ag^{R} + 5\ Eg^{R} + 4\ Au^{IR} + 4\ Eu^{IR}.$$

The Raman spectrum of a mineral with the ilmenite structure should therefore contain 10 bands. We observe 7 definite bands for $MgSiO_3$ ilmenite (Fig. 1). This spectrum may be compared with the Raman spectrum of geikielite, $MgTiO_3$ (White, 1975), which also has the ilmenite structure. The overall forms of the spectra of both phases are similar, although the $MgTiO_3$ spectrum of White (1975) contains 13 identifiable bands, 3 more than expected from the factor group analysis, perhaps due to the presence of impurity phases. The major high frequency band of $MgTiO_3$ at 720 cm^{-1} has a shoulder at 780 cm^{-1}. We note a similar shoulder near 815 cm^{-1} on the major band at 789 cm^{-1} of $MgSiO_3$ ilmenite. Similarly, the 491 cm^{-1} band of $MgTiO_3$ has a shoulder (not noted by White, 1975) near 500 cm^{-1}. A similar high-frequency shoulder may be present on the 470 cm^{-1} band of $MgSiO_3$ (arrow on Fig. 1).

White (1975) compared the spectra of geikielite and corundum. The ilmenite-type structure is closely related to that of corundum in that arrangement of oxygen atoms in both structure-types is based on a distorted hexagonal closest packing with two-thirds of the octahedral sites filled. In $MgSiO_3$ ilmenite, Mg and Si are completely ordered in alternating layers in the octahedral sites (Horiuchi et al., 1982). The space group symmetry is thus reduced from $R\bar{3}c(D_{3d}^{6})$ for corundum to $R\bar{3}(C_{3i}^{2})$ in ilmenite. The resulting loss of the *c*-glide transforms the Raman

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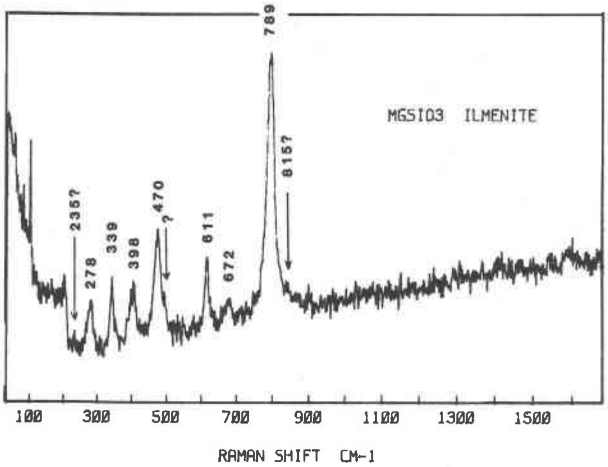

Figure 1. Raman spectrum of $MgSiO_3$ ilmenite. The asymmetric "band" near 200 cm^{-1} is due to a spectrometer ghost and the sharp peaks below 100 cm^{-1} are laser plasma lines and rotational lines of N_2 and O_2 in the air.

inactive A_{2g} and A_{1u} modes of the corundum structure into active Ag and A_u modes for ilmenite. The Raman spectra of corundum (α-Al_2O_3) show the expected 7 bands (Porto and Krishnan, 1967; White, 1975). The high frequency bands in $MgTiO_3$ and $MgSiO_3$ ilmenite have higher relative intensities than those of α-Al_2O_3, while the bands observed for $MgTiO_3$ and $MgSiO_3$ extend to lower frequencies than for α-Al_2O_3. These differences partly reflect the change of symmetry.

There has been considerable discussion in the literature regarding the assignment of characteristic bands or regions in the infrared and Raman spectra of silicate and related minerals to specific structural groups such as $[SiO_4]$ tetrahedra and $[SiO_6]$ octahedra (e.g., Tarte, 1962, 1963; Lazarev, 1972). Such assignments have generally relied on the internal mode approximation, where crystal modes are related to vibrations of the particular molecular group. For example, in the present context, Tarte and Ringwood (1963) obtained infrared spectra for the pyroxene and ilmenite (high-pressure) forms of $MgGeO_3$. They noted that the highest frequency bands of $MgGeO_3$ ilmenite fell below 700 cm^{-1}, while the high-frequency band group for the pyroxene form appeared between 900 and 700 cm^{-1}. These authors discussed this frequency shift in terms of characteristic Ge–O stretching frequencies of $[GeO_4]$ (pyroxene) and $[GeO_6]$ (ilmenite) structural units. This type of analysis for $MgSiO_3$ ilmenite would tend to assign the strong Raman band at 789 cm^{-1} (Fig. 1) as characteristic of Si–O stretching of $[SiO_6]$ units. However, Iishi (1978) has carried out a lattice dynamical calculation for corundum, related to the ilmenite structure. None of the calculated normal modes may be simply correlated with internal vibrations of the $[AlO_6]$ groups, but are all true lattice modes often involving motion of one sublattice block against another. The corundum bands between 600 and 750 cm^{-1} tend to involve mainly displacement of oxygen against relatively stationary aluminum, while those between 300 and 500 cm^{-1} involve mainly aluminum displacements. It is likely that the lattice modes of $MgSiO_3$ ilmenite are similar, with bands above 600 cm^{-1} probably associated with oxygen motion against *both* Mg and Si, and are thus probably not characteristic of octahedral $[SiO_6]$ groups. In general, it is suggested that the internal mode approximation to characterize metal coordination be used with same caution, especially in such condensed structures.

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