

LETTERS

Crystal-field and charge-transfer spectra of (Mg,Fe)SiO₃ perovskite

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ABSTRACT

The optical and near-infrared absorption spectrum of a synthetic silicate perovskite (Mg_{0.94}Fe_{0.06}SiO₃) was obtained in the range from 1000 to 25000 cm⁻¹. The spectrum shows three main features. (1) A system of crystal-field bands is centered at 7000 cm⁻¹, which is caused by the transition ⁵E_g → ⁵T_{2g} of Fe²⁺ in the dodecahedral site of the structure. (2) A broad band due to Fe²⁺ → Fe³⁺ intervalence charge transfer occurs at 14900 cm⁻¹. (3) A sharp increase in absorption above 20000 cm⁻¹ probably results from O-Fe³⁺ charge transfer. From these data, the crystal-field parameters of Fe²⁺ in the dodecahedral site of the perovskite structure can be extracted. This yields a crystal-field splitting (Δ) = 6835 cm⁻¹ and a crystal-field stabilization energy (CFSE) = 4350 cm⁻¹. If the splitting of the ground state (estimated as 500 cm⁻¹) is neglected, one obtains Δ = 7085 cm⁻¹ and CFSE = 4251 cm⁻¹. This means that the CFSE of Fe²⁺ in perovskite approximately equals the CFSE in magnesiowüstite (4320 cm⁻¹). Therefore, the preferential partitioning of Fe²⁺ into the wüstite phase cannot be explained by a simple crystal-field model. The existence of strong absorption bands over the entire range from mid-IR to UV indicates that perovskite is a very poor thermal conductor at high temperatures where radiative heat transfer dominates.

INTRODUCTION

Silicate perovskite (Mg,Fe)SiO₃ is generally assumed to be the major constituent of the lower mantle (e.g., Ito et al., 1984), where it coexists with magnesiowüstite (Mg,Fe)O. The presence of Fe in the perovskite phase strongly alters its physical properties, in particular the electrical and thermal conductivity. If both Fe²⁺ and Fe³⁺ are present, electrical conductivity can increase by orders of magnitude because of electron hopping between Fe atoms with different valence states. Absorption of infrared and visible radiation due to crystal-field and charge-transfer transitions of Fe²⁺ and Fe³⁺ in the perovskite lattice would reduce the thermal conductivity of the lower mantle. Therefore, as Sherman (1991) pointed out "understanding the crystal chemistry of iron in perovskite may be fundamental to understanding the thermal evolution of the earth." A deeper knowledge of the crystal chemistry of Fe in the perovskite structure would also help to understand the partitioning of Fe between the wüstite and perovskite phase, as well as between the metallic core and the lower mantle.

Both X-ray diffraction (Kudoh et al., 1990) and Mössbauer data (McCammon et al., 1992) show that Fe²⁺ enters the dodecahedral site in the perovskite structure, whereas Fe³⁺ substitutes for Si⁴⁺ in the octahedral site (McCammon et al., 1994). The single previous study of the optical and

near-infrared spectrum of silicate perovskite (Shen et al., 1994) suggested the existence of a crystal-field band of Fe²⁺ around 7000 cm⁻¹. However, the fine structure of this band could not be resolved, and charge transfer bands were not detectable. This paper presents new spectroscopic measurements that show the splitting of the crystal-field bands as well as the location of charge-transfer bands in (Mg,Fe)SiO₃ perovskite. From these data, the crystal-field splitting and the crystal-field stabilization energy of Fe²⁺ in perovskite can be obtained.

EXPERIMENTAL METHODS

(Mg,Fe)SiO₃ perovskite was synthesized in a multianvil apparatus at 1650 °C and 240 kbar with an experiment duration of 13 min. As a starting material, we used synthetic clinopyroxene with a composition identical to that of perovskite, mixed with a small amount of excess SiO₂ and sealed in a Re capsule. The resulting product, perovskite with a small amount of stishovite, was crushed at liquid-N₂ temperature in a WC pellet press. The color of the sample was dark brown. The sizes of individual perovskite grains were around 10 μm. Microprobe analyses yielded a bulk composition of Fe_{0.06}Mg_{0.94}SiO₃ for the perovskite. Using stishovite as an internal standard, the lattice constants of the perovskite were determined from powder X-ray diffraction data as *a* = 4.7844, *b* = 4.9312,

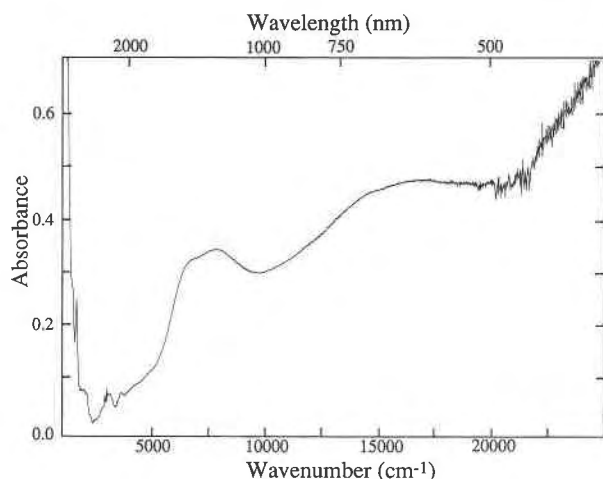


Fig. 1. Unpolarized absorption spectrum of polycrystalline $\text{Mg}_{0.94}\text{Fe}_{0.06}\text{SiO}_3$ perovskite, thickness 50 μm .

and $c = 6.9037 \text{ \AA}$ (all cell parameters $\pm 0.0005 \text{ \AA}$). According to the results of Mössbauer experiments (to be published elsewhere), 10% of the total Fe in the perovskite is Fe^{3+} , and 5% is present in the intermediate valence state $\text{Fe}^{2.5+}$ because of electron delocalization.

Optical and infrared absorption spectra were measured in the range from 1000 to 25000 cm^{-1} using a Bruker IFS 120 HR high-resolution FTIR spectrometer equipped with a Bruker IR microscope. An irregular chip of polycrystalline perovskite with a thickness of about 50 μm was measured with a 30- μm diameter beam. Different spots of the sample yielded virtually identical spectra. No attempt was made to polish the surfaces of the sample, since that could cause perovskite to become amorphous. Three hundred scans with a resolution of 4 cm^{-1} were accumulated in the spectral ranges from 1000 to 10000 cm^{-1} (CaF_2 beamsplitter, W source, MCT detector), 9000 to 15000 cm^{-1} (quartz beamsplitter, W source, Si diode detector) and 12500 to 25000 cm^{-1} (quartz beamsplitter, Xe arc source, Si diode detector) and merged to produce the final spectrum.

RESULTS

Figure 1 shows the uncorrected, unpolarized optical and near infrared absorption spectrum of perovskite. The following features can be observed: (1) A sharp increase in absorption occurs below about 1500 cm^{-1} because of the fundamental lattice vibrations of perovskite. (2) A narrow peak occurs at 1597 cm^{-1} . This peak can be assigned to the first overtone of the fundamental lattice vibration of perovskite at 797 cm^{-1} (Williams et al., 1987, and Lu et al., 1994, report a slightly lower frequency for this band). (3) Some weak bands between 2500 and 4000 cm^{-1} are due to stretching vibrations of OH, which is present in trace amounts. A detailed inspection of the spectra shows three sharp features at 2855, 2921, and 3391 cm^{-1} . These frequencies are close to OH-stretching frequencies in pe-

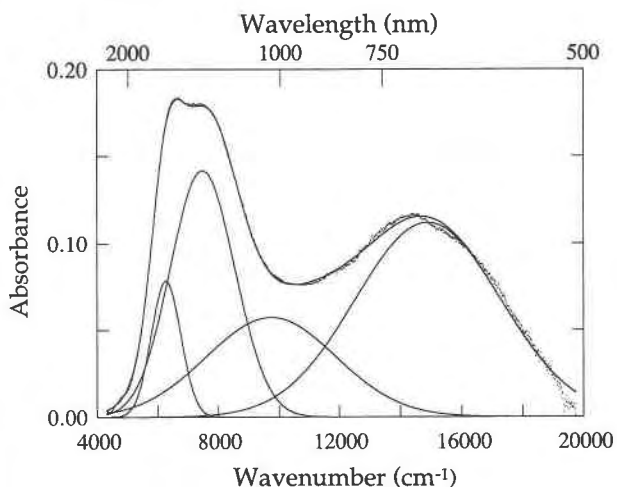


Fig. 2. Spectrum of polycrystalline $\text{Mg}_{0.94}\text{Fe}_{0.06}\text{SiO}_3$ perovskite after background correction and deconvolution into Gaussian components. Measured data are shown as dots.

rovskite reported by Meade and Ito (1993) and Meade et al. (1994). However, since our measurements were carried out on a polycrystalline aggregate, we cannot rule out that the bands are due to OH on grain boundaries or trace impurities. (4) Multiple bands are centered around 7000 cm^{-1} because of the crystal-field transitions of Fe^{2+} . The position of these bands is close to those of Fe^{2+} in the dodecahedral site of garnets (White and Moore, 1972; Rossman, 1988; Burns, 1993). (5) A very broad band has a maximum around 15000 cm^{-1} . The position and width of this band indicate a likely assignment to Fe^{2+} - Fe^{3+} intervalence charge transfer (Burns, 1993; Mattson and Rossman, 1987). (6) A steep increase of absorption occurs at frequencies above 20000 cm^{-1} , probably because of charge transfer between O and Fe^{3+} , although scattering at grain boundaries and imperfections of the crystals might contribute to this effect.

Crystal-field bands of Fe^{3+} are not detectable in the spectrum because of the low intensity of these spin-forbidden bands and because of overlap with the much stronger charge-transfer bands.

In order to investigate the fine structure of the crystal-field and intervalence charge-transfer bands, a background correction was carried out by a spline fit, and the corrected spectrum was deconvoluted into Gaussian components. The result is shown in Figure 2 for the range between 4000 and 20000 cm^{-1} . A minimum of four Gaussian components was required to obtain a reasonable fit of the spectrum. Positions, widths, and intensities of the band components obtained by deconvolution are given in Table 1.

In an undistorted dodecahedral environment, only one spin-allowed crystal-field band of Fe^{2+} from the transition ${}^5E_g \rightarrow {}^5T_{2g}$ would be observed. Because the magnitude of the crystal-field splitting in a dodecahedral site is only half that in an octahedral site under otherwise equal

conditions (Burns, 1993), this band should occur at significantly lower frequency than the bands of ⁶Fe²⁺ in silicate minerals. Octahedral Fe²⁺ usually absorbs around 10000 cm⁻¹; therefore, only the two Gaussian components at 6283 and 7486 cm⁻¹ could be caused by the crystal-field transition of Fe²⁺ in perovskite. Because of the monoclinic site symmetry (m) of the dodecahedral site in perovskite (Kudoh et al., 1990), the ⁵T_{2g} state should be split into three components, giving rise to three discrete absorption bands. Only two bands were obtained by deconvolution. However, the width and intensity of the band at 7486 cm⁻¹ are much larger than those for the 6283-cm⁻¹ band, suggesting that the band at 7486 cm⁻¹ consists of two Gaussian components separated by a frequency smaller than the half width of the individual bands. If one assumes this separation to be on the order 800 cm⁻¹, which is consistent with the observed half widths, the individual components of the ⁵E_g → ⁵T_{2g} transition are at 6283, 7086, and 7886 cm⁻¹, indicating that all three components of the T_{2g} term are separated by about 800 cm⁻¹. Note that the magnitude of the assumed separation between the two components at 7086 and 7886 cm⁻¹ has no effect on the calculation of the crystal-field stabilization energy carried out below. The splitting of the E_g term cannot be measured directly; however, an estimate can be obtained by comparison with the energies of the crystal-field states of Fe²⁺ in the dodecahedral site of garnet. The magnitude of the splitting of the ⁵T_{2g} state in garnet is about twice that observed in perovskite. The splitting of ⁵E_g in garnet was estimated from Mössbauer spectroscopy to be about 1100 cm⁻¹ (Burns, 1993), and, since the magnitude of the splitting of ⁵E_g should correlate with the splitting of ⁵T_{2g}, a plausible value for the splitting of the ⁵E_g ground state (δ) of Fe²⁺ in perovskite is 500 cm⁻¹.

From the spectroscopic data given above, the crystal-field splitting (Δ) and the crystal-field stabilization energy (CFSE) of Fe²⁺ in perovskite can be calculated. If the frequencies of the three observed transitions are labeled ν₁ = 6283 cm⁻¹, ν₂ = 7086 cm⁻¹, ν₃ = 7886 cm⁻¹, the crystal-field splitting is given by (White and Moore, 1972):

$$\Delta = \frac{1}{3}(\nu_1 + \nu_2 + \nu_3) - \frac{1}{2}\delta.$$

This yields Δ = 6835 cm⁻¹. If δ were assumed to be 0, one would obtain Δ = 7085 cm⁻¹. The crystal-field stabilization energy is given by (White and Moore, 1972)

$$\text{CFSE} = \frac{3}{5}\Delta + \frac{1}{2}\delta.$$

This yields CFSE = 4350 cm⁻¹ for δ = 500 cm⁻¹ and Δ = 4251 cm⁻¹ for δ = 0.

The broad band at 14902 cm⁻¹ has a half width that is characteristic for Fe²⁺-Fe³⁺ intervalence charge-transfer transitions (Mattson and Rossman, 1987) and occurs in the frequency range where this transition is expected (Burns, 1993). The band at 9745 cm⁻¹ is only poorly constrained, and the physical significance of this component, which is necessary for deconvoluting the spectra, is questionable. Both the intensity and the precise position of the band are somewhat dependent on the type of

TABLE 1. Deconvolution of crystal field and intervalence charge-transfer bands into Gaussian components

Peak position (cm ⁻¹)	Width (cm ⁻¹)	Linear extinction coefficient (cm ⁻¹)	Integral extinction coefficient (× 10 ³ cm ⁻²)
6283	1147	15.7	19.1
7486	2498	28.3	75.4
9745	5034	11.5	61.4
14902	5585	22.4	133.3

Note: width = full width at half height. Extinction coefficients are defined by $\epsilon = A/d$, where ϵ is the extinction coefficient, A is the linear or integrated absorbance, and d is the thickness. Because of the uncertainties in the thickness of the sample, the errors of the extinction coefficients may be 10–20%.

base-line correction carried out. It is possible, however, that this band is also due to intervalence charge transfer, but at a rather low energy. This would be consistent with the half widths of this band and with the dispersion of Fe²⁺-Fe³⁺ distances in the orthorhombic perovskite structure. Although there is only one distance between the octahedral and the dodecahedral cation in the cubic perovskite structure, four distances occur in the distorted orthorhombic structure. According to the structure refinement of Horiuchi et al. (1987), these distances are 2.79, 2.90, 3.01, and 3.24 Å. Therefore, the two absorption bands at 14902 and 9745 cm⁻¹ could correspond to two vectors between the dodecahedral Fe²⁺ and the ⁶Fe³⁺. Since the dodecahedra and the octahedra in the perovskite structure share faces, charge transfer could occur at unusually low energies, below 10000 cm⁻¹ (Burns, 1993).

DISCUSSION

Because of the combination of crystal-field and charge-transfer bands, (Mg,Fe)SiO₃ perovskite shows strong absorption over the entire IR and visible range, implying that at high temperatures where radiative transport dominates, perovskite is an extremely poor thermal conductor. Since perovskite contains substantial amounts of Fe³⁺ even in equilibrium with metallic Fe (McCammon et al., 1992), charge-transfer bands contribute to optical absorption throughout the mantle.

Whereas the intervalence charge transfer observed in our spectra reduces the thermal conductivity, it provides a possible mechanism for a strong increase in electrical conductivity by electron hopping (polaron conductivity). This phenomenon could be a possible explanation for electrical semiconductivity of the lower mantle.

The crystal-field stabilization energy of Fe²⁺ in perovskite (CFSE = 4350 cm⁻¹) almost equals that in magnesiowüstite (CFSE = 4320 cm⁻¹; Burns, 1993). Therefore, the preferential partitioning of Fe into magnesiowüstite in equilibrium with perovskite cannot be explained by differences in CFSE, as suggested by Shen et al. (1994). Probably the electron delocalization between Fe²⁺ and Fe³⁺ in the two phases has to be considered in order to understand the partitioning of Fe. The CFSE of Fe²⁺ in perovskite of 3332 cm⁻¹ obtained by Shen et al. (1994)

is in error because they measured the spectrum of perovskite only above 4600 cm⁻¹; they observed a band around 7000 cm⁻¹ and assumed on the basis of electrostatic calculations that two additional crystal-field bands occur at 4432 cm⁻¹ and 4198 cm⁻¹, outside of the measured range. Our measurements clearly show that there are no bands at these frequencies (see Fig. 1).

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