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Spectra of Shock-Affected Rhodonite: A Discussion[1]

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Introduction

Recently, Gibbons, Ahrens, and Rossman (1974) proposed that the irreversible reduction of Mn^{3+} to Mn^{2+} is responsible for the spectral changes induced by the shock-loading of rhodonite at pressures up to 496 kbar.

However, as the present report shows, this hypothesis is probably erroneous because the important spectral changes can be explained more readily by pressure-induced intensification or broadening of the $O^{2-} \rightarrow (Mn^{2+}, Fe^{2+})$ charge-transfer absorption centered in the ultraviolet.

Discussion

Spectra A and B in Figure 1 (after Gibbons *et al*) are respectively those of an unshocked specimen of rhodonite and a specimen of rhodonite that was shock-loaded to 496 kbar. On the basis of a visual examination, Gibbons *et al* concluded that the bands at 540 and 1530 nm of spectrum A are not present in spectrum B. They argued that the two bands are due to Jahn-Teller-split components of the ^5E ground state of Mn^{3+}, and that high pressure reduces Mn^{3+} to Mn^{2+} with the concomitant disappearance of the absorption bands. Figures 2a and 2b are respectively resolutions of spectra A and B of Figure 1. They have been replotted on a linear energy scale after subtraction of the ultraviolet absorption edge and have been resolved approximately into Gaussian components with a Dupont curve resolver. Although these processes distort the original spectra somewhat, the spectra in Figure 2 are considered to be essentially representative of rhodonite before and after shock-loading to 496 kbar.

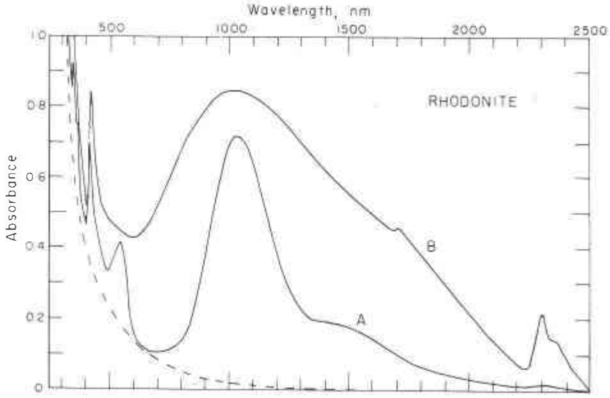

FIG. 1. Absorption spectra of unshocked rhodonite (A) and rhodonite shocked to 496 kbar (B) (after Gibbons, Ahrens, and Rossman, 1974). Visually estimated uv-background absorbance shown by dashed curve.

Although the low-energy features in particular of spectra 2(b) are appreciably broader than their counterparts in spectrum 2(a), the number and intensity of the components are similar in both. It is evident that the features at approximately 540 and 1500 nm (18,500 and 6,600 cm^{-1}), which Gibbons *et al* assigned to Mn^{3+}, are also present in the spectrum of shock-loaded rhodonite. This observation strongly argues against the case of pressure-induced reduction of Mn^{3+} to Mn^{2+}.

Fe^{2+} Absorption

It is well established that, in the near infrared, six-coordinated Fe^{2+} in many silicate minerals exhibits two crystal-field bands separated by 1500 to 6000 cm^{-1} (Faye, 1972). In certain cases the low-energy band is the less intense of the two. Moreover, there is often a good correlation between the average energy of the two bands and the average Fe^{2+}–O bond distance for a particular material (Faye, 1972).

The average energy of the resolved bands at ~10,000 and ~6,500 cm^{-1} in the rhodonite spectra (Fig. 2) is 8,300 cm^{-1}, a value that is appropriate for an average Fe^{2+}–O bond distance of 2.22Å (Faye, 1972) and which compares favorably with the average bond distance of 2.25Å for the cations in the M_1, M_2, M_3, and M_4 six-coordinated positions of rhodonite (Peacor and Niizeki, 1963). If the band at 10,000 cm^{-1} is the only *d–d* feature ascribed to Fe^{2+} in rhodonite, then an average Fe^{2+}–O bond distance of 2.13Å would seem to pertain; however, this value is inappropriately low for rhodonite.

Although the above arguments suggest that both the ~10,000 cm^{-1} (~1000 nm) and ~6,500 cm^{-1}

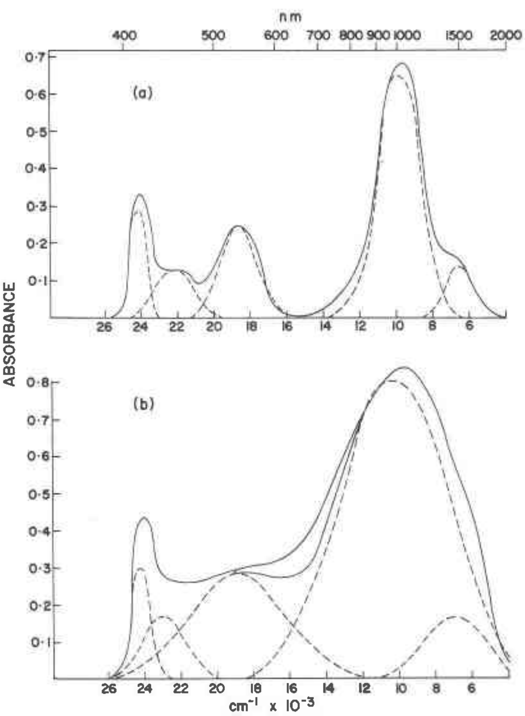

FIG. 2. (a) and (b) are respectively resolutions, on a linear energy scale, of spectra A and B of Figure 1.

(~1500 nm) bands belong to Fe^{2+}, Gibbons *et al* concluded that the latter band, as well as the 540 nm band, is due to Mn^{3+}. Figure 3 shows the spectrum (measured by the author) of a specimen of New Jersey rhodonite containing substantially less Fe (~0.2%) than the specimen (~1.4%) of Gibbons *et al.*

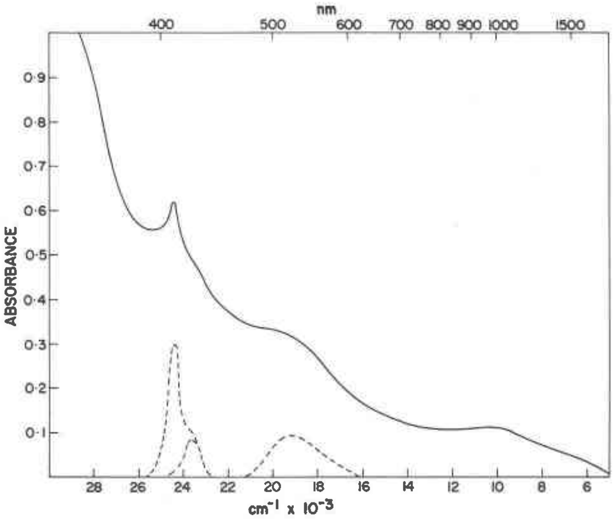

FIG. 3. Absorption spectrum of specimen of New Jersey rhodonite containing 0.2 percent Fe (thickness ~0.012 cm). Dashed envelopes are resolved *d–d* bands of Mn^{2+}.

In this spectrum there is only very weak absorption at ~1500 nm and this does not correlate well with the Mn-band centered at 520-540 nm; however, it is consistent with the iron content of the specimen.

It is worthy of mention that the half-width (breadth at half-height) of the 1500-nm band in the spectrum of unshocked rhodonite (Fig. 2a) is ~2000 cm^{-1}, a value that is typical of *d–d* bands of Fe^{2+}. If the band arises from the transition between components of the Jahn-Teller-split ^5E_g ground state of Mn^{3+}, as is claimed by Gibbons *et al*, then it should be exceptionally broad, *i.e.* $\geq\sim 5{,}000\ cm^{-1}$ (Davis, Fackler, and Weeks, 1968).

Effects of Heating

In addition to considering the effects of pressure on the rhodonite spectrum, Gibbons *et al* performed heating experiments on unshocked rhodonite in a hydrogen-argon atomosphere and observed essentially no change during heating from room temperature to 1250°C (just below the melting point). Because the intensity of the 540 nm band was similar for both the heated and unheated specimens, it was concluded that the hydrogen heat-treatment did not reduce Mn^{3+}, the ion thought to be responsible for the 540 nm band. A more likely explanation for the lack of change is that all the manganese in rhodonite is Mn^{2+} and therefore is not amenable to further reduction. It also follows that the 540 nm band is part of the Mn^{2+} spectrum.

The spectra of pyroxmangite, bustamite, and serandite all contain a feature in the 520-550 nm range which, as in rhodonite, has been assigned to the $^6A_{1g} \rightarrow {}^4T_{1g}$ transition of Mn^{2+} (Manning, 1968). If the 540 nm band of rhodonite is due to Mn^{3+} then, by analogy, the above-listed silicates would also be expected to contain a measurable amount of Mn^{3+}—an unlikely prospect considering their structural differences and the wide variety of geological environments in which they occur.

Gibbons *et al* also heated an unshocked specimen of rhodonite in hydrogen at 1360°C (just above the melting point) and recorded its spectrum after quenching. They noted that the 540 nm band was replaced by one at 514 nm and concluded that Mn^{3+} had been reduced to Mn^{2+} and that the latter band was due to the $^6A_{1g} \rightarrow {}^4T_{1g}$ transition of Mn^{2+}. As Gibbons and co-workers aptly stated, it is probable that after melting the manganese ions will not have the same environment as in rhodonite and therefore spectral changes are to be expected. It is this author's opinion that, on melting, the environment around the

Mn^{2+} ion expands and consequently the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transition occurs at higher energy as the crystal-field strength decreases in accord with the energy-level diagram for a d^5 ion. Thus it is reasonable to assume that the 514 and 540 nm features represent the same transition in Mn^{2+}. A similar trend is to be expected for the band due to the ${}^6A_{1g} \rightarrow {}^4T_{2g}$ transition, which appears as a shoulder between 400 and 450 nm in both the spectra of melted and unmelted specimens, but the spectra are too poorly resolved for this to be easily confirmed. That the sharp band at 415 nm does not shift after melting of the rhodonite is consistent with its being due to the field-independent transition ${}^6A_1 \rightarrow ({}^4A_1, {}^4E)$.

Conclusion

In view of the arguments presented above, it is considered that only Mn^{2+} is spectrally detectable in rhodonite, and that pressure does not affect the valence state of manganese. It is probable that the combined effects of pressure and temperature sufficiently disrupt the rhodonite lattice that a multitude of electronic configurations or crystal field-states arise for the metal ions and consequently there is a broadening of all absorption bands with the possible exception of field-independent *d–d* bands of Mn^{2+}. Also, it is to be expected that the intensity of charge transfer (in the uv) would increase under pressure with decreasing *M*-O bond length and hence give apparent broadening.

Because of its effect of 'swamping' the 540-nm band (Fig. 1), the broadening of the uv-absorption edge is the most important spectral effect of shock-loading rhodonite. Because Mn^{2+} and Fe^{2+} are the only transition metal ions detectable in rhodonite, it is likely that the uv-absorption is primarily due to $O^{2-} \rightarrow (Mn^{2+}, Fe^{2+})$ charge-transfer. Such charge-transfer processes are of great importance in determining the optical properties of tourmaline, for example (Faye, Manning, Gosselin, and Tremblay, 1974).

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