Thermally Modulated Absorption of Fe\(^{2+}\), Fe\(^{3+}\), and Mn\(^{2+}\) in Spessartine and Almandine Garnets

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Abstract

The thermally modulated absorption (TMA) of two spessartine and two almandine garnets show absorption peaks with positive temperature coefficient in the region between 10,000 cm\(^{-1}\) and 25,000 cm\(^{-1}\) at room temperature. The TMA peaks in the 16,000-25,000 cm\(^{-1}\) region are 3d \(\rightarrow\) 3d forbidden transitions of Fe\(^{3+}\), Fe\(^{2+}\), and Mn\(^{2+}\) ions and agree generally with the presently accepted assignment.

In the 10,000-16,000 cm\(^{-1}\) region, the TMA spectra show an unexpected strong band near 12,000 cm\(^{-1}\). This new 12,000 cm\(^{-1}\) band and the known 14,000 cm\(^{-1}\) band are interpreted as intervalence charge transfer (IVCT) from 8-coordinate Fe\(^{3+}\) (VIII) to Fe\(^{2+}\) at octahedral (VI) and tetrahedral (IV) site, respectively. We speculate that the temperature coefficient of IVCT absorption, da/dT, can be positive or negative depending on whether the initial and final site of IVCT being different, (e.g., garnets) or equivalent (e.g., micas and vivianite) type(s), respectively.

We propose a minor modification on the 3d \(\rightarrow\) 3d forbidden assignment of Fe\(^{3+}\) (VIII).

Introduction

The complicated absorption spectra of silicate garnets in the visible region have been extensively measured and are attributed to the absorption of 3d \(\rightarrow\) 3d forbidden transitions of Fe\(^{2+}\), Fe\(^{3+}\), Mn\(^{2+}\) etc (e.g., Manning, 1967, 1972). The most recent assignment is based on the linear dependence of the band intensity on the ion-concentration and the overall fit of the spectra by computer-generated energy level diagrams (Moore and White, 1972).

The measurement of thermally modulated absorption spectra (TMA), which records directly the spectra of the temperature-derivative of the absorption coefficient, da/dT, has been demonstrated (Loh, 1972) to be a useful technique in supplementing the conventional absorption spectra.

This paper reports the TMA spectra of two spessartine and two almandine natural garnets between 10,000 cm\(^{-1}\) and 25,000 cm\(^{-1}\) at room temperature.

Results and Discussion

The experimental setup and the sample requirements of TMA have been reportedly previously (Loh, 1972). P. G. Manning of Ottawa has generously contributed all samples and W. Richmond of Great Malvern has kindly performed the TMA measurements.

In Figure 1 the TMA spectra are given for spessartine from Ceara, Brazil (curve A) and from Broken Hill, New South Wales (curve B), as well as for almandine from Gore Mountain, New York (curve C) and from Zillerthal, Austria (curve D). The peaks for the Ceara spessartine and the Zillerthal almandine (see Table 1 for assignments) are designated by the same lower-case letters and numbers used by Moore and White (1972) for pyralspite and ugrandite garnets. These spectra may be interpreted to represent:

(a) intervalence charge transfer Fe\(^{2+}\) \(\rightarrow\) Fe\(^{3+}\) in the low-energy region, from 10,000 cm\(^{-1}\) to \(\sim\) 15,000 cm\(^{-1}\).

(b) 3d \(\rightarrow\) 3d forbidden transitions of 8-coordinate Fe\(^{2+}\) between 16,000 cm\(^{-1}\) and 25,000 cm\(^{-1}\).
(c) $3d \rightarrow 3d$ forbidden transition of octahedral Fe$^{3+}$ at 23,300 cm$^{-1}$.

(d) $3d \rightarrow 3d$ forbidden transitions of 8-coordinate Mn$^{2+}$ at 21,000 cm$^{-1}$, 23,700 cm$^{-1}$ and 24,500 cm$^{-1}$ in spessartine.

(e) a possible $3d \rightarrow 3d$ transition of tetrahedral Fe$^{3+}$ at $\sim 22,300$ cm$^{-1}$.

a. Intercalence Charge Transfer from Fe$^{2+}$ to Fe$^{3+}$ at $\sim 12,000$ cm$^{-1}$ and $\sim 14,000$ cm$^{-1}$

The most surprising result of the TMA spectra of Figure 1 is the presence of a strong peak at $\sim 12,500$ cm$^{-1}$ for spessartines and at $\sim 12,200$ cm$^{-1}$ for almandines. In Manning's spectra (Manning, 1967, Figs. 1-4), this peak seems hidden in the background absorption which is contributed, on the low-energy side, by the high-energy tail of the strong Fe$^{2+}$ absorption at $\sim 8,000$ cm$^{-1}$ and, on the high-energy side, by the onset of visible absorptions from $\sim 14,000$ cm$^{-1}$ on. We emphasize that TMA spectra, like other types of derivative spectra, will "pull" out the broad and weak absorption band from absorption tails of neighboring bands. The strength of a TMA band is not necessarily proportional to the absorption strength of the band but is proportional to the derivative of the absorption with respect to temperature.

To demonstrate that the TMA spectra in Figure 1 are real and not due to instrumental artifacts, we intentionally included in curve D the false signal at its left end, $\leq 9,500$ cm$^{-1}$. This portion of curve D—which starts from the low value of the $d\alpha/dT \approx 0$ at frequency $\sim 9,000$ cm$^{-1}$, reaches a maximum negative $d\alpha/dT$ at $\sim 9,500$ cm$^{-1}$, and thence starts to yield "real" signal at higher photon energies—that illustrates that the AC output of the photomultiplier is not a true signal if $d\alpha/dT$ starts from a small (positive or negative) value since the signal-to-noise ratio there is low. On the other hand, the left ends of curves A, B, and C (Fig. 1) represent true signals since the curves start from large (negative) values of $d\alpha/dT$, instead of small (negative) values of $d\alpha/dT$. It is understandable that samples A, B, and C have larger AC signal-to-noise ratios than that of sample D, because the former are thinner and hence more transparent than the latter, as indicated in the caption of Figure 1. Previous TMA spectra below $\sim 10,000$ cm$^{-1}$ compare satisfactorily with known DC spectra (Loh, 1972).

We assign the closely related bands, $d'(\sim 12,500$ cm$^{-1}$) and $d(\sim 14,000$ cm$^{-1}$), as intervalence charge-transfer bands which correspond to the transfer of an electron from Fe$^{2+}$ on the dodecahedral site to Fe$^{3+}$ on the octahedral site, and to Fe$^{3+}$ on the tetrahedral site, respectively. Reasons for these assignments are:

1. The strength, the bandwidth of $\sim 3,000$ cm$^{-1}$ at half-height, and the location at $\sim 12,000$ cm$^{-1}$ to $\sim 15,000$ cm$^{-1}$ of both $d'$ and $d$ bands are all comparable to the Fe$^{2+} \rightarrow$ Fe$^{3+}$ charge-transfer band in micas and vivianite (Loh, 1972).
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2. The d' and d bands are stronger and broader than the rest of high-energy peaks, which are known to be 3d → 3d forbidden transitions of Fe**, Fe*, and Mn** (e.g., Moore and White, 1972; Manning, 1972). This is best illustrated by curve A in Figure 1.

3. The energy levels of Fe**(VIII) in the Tanabe-Sugano diagram of Moore and White (1972) can not include this ~12,000 cm⁻¹ new band d' as a split component of ³T₁ level, since peaks d, e, and f have already been used as the three components of ³T₁ level in D₂ site symmetry. Furthermore, the energy of band d' at ~12,000 cm⁻¹ is either too low for ³T₁ level or too high for the allowed transition to ⁵E level, as can be seen from the Tanabe-Sugano diagram of Moore and White (1972, Fig. 7).

4. We assign the d' band at ~12,500 cm⁻¹ as Fe**(VIII) + Fe***(VI) → Fe***(VIII) + Fe**(VI) and d band at ~14,000 cm⁻¹ as Fe**(VIII) + Fe***(IV) → Fe***(VIII) + Fe**(IV) because:
   a. The octahedral site (VI) with Al - 0 = 1.89 Å is larger than the tetrahedral site (IV) with Si-O = 1.63 Å (Gibbs and Smith, 1965). The large Fe** ion will, therefore, have lower energy at the VI-site than at the IV site.
   b. The octahedron around Fe***(VI) shares an edge with a neighboring dodecahedron around Fe**(VIII), while the tetrahedron around Fe**(IV) has only a corner common with a neighboring dodecahedron (Gilleo and Geller, 1958). This may again suggest that the charge transfer between the VI and VIII sites occurs at lower energy than that between the IV and VIII sites.

For the d' and d bands in Figure 1, da/dT is positive whereas it is negative for Fe**(VI) → Fe**(IV) absorption in micas and vivianite (Loh, 1972). We attribute this change in sign to the change of site-type involved in the charge transfer of Fe**(VI) → Fe**(IV).

Following Moore and White (1972) the peaks e, f, g, h, k, and c in Figure 1 are 3d → 3d forbidden transitions of Fe**(VIII). Since we assign peak d, which has been interpreted by Moore and White as 3d → 3d forbidden absorption of Fe**(VIII),

### Table 1. Absorption Peaks and Level Assignments of Fe**, Fe*, and Mn** in Spessartine and Almandine Garnets

<table>
<thead>
<tr>
<th>Label</th>
<th>Almandine from Zillerthal</th>
<th>Spessartine from Sillerthal</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>d'</td>
<td>12,200</td>
<td>12,500</td>
<td>Fe**(VIII) + Fe**(VI) → Fe**(VIII) + Fe**(VI)</td>
</tr>
<tr>
<td>d</td>
<td>14,000</td>
<td>14,700</td>
<td>Fe**(VIII) + Fe***(VI) → Fe**(VIII) + Fe***(VI)</td>
</tr>
<tr>
<td>e</td>
<td>16,200</td>
<td>16,600</td>
<td>Fe**(VIII) + Fe**(VI)</td>
</tr>
<tr>
<td>f</td>
<td>17,600</td>
<td>17,900</td>
<td>Fe**(VIII) + Fe**(VI)</td>
</tr>
<tr>
<td>g</td>
<td>19,200</td>
<td>19,300</td>
<td>Fe**(VIII) + Fe**(VI)</td>
</tr>
<tr>
<td>h</td>
<td>20,300</td>
<td>20,200</td>
<td>Fe**(VIII) + Fe**(VI)</td>
</tr>
<tr>
<td>i</td>
<td>21,000</td>
<td>21,300</td>
<td>Fe**(VIII) + Fe**(VI)</td>
</tr>
<tr>
<td>j</td>
<td>23,300</td>
<td>23,200</td>
<td>Fe**(VIII) + Fe**(VI)</td>
</tr>
<tr>
<td>k</td>
<td>25,000</td>
<td>25,000</td>
<td>Fe**(VIII) + Fe**(VI)</td>
</tr>
<tr>
<td>l</td>
<td>22,300</td>
<td>22,300</td>
<td>Fe**(VIII) + Fe**(VI)</td>
</tr>
<tr>
<td>m</td>
<td>16,700</td>
<td>16,500</td>
<td>Fe**(VIII) + Fe**(VI)</td>
</tr>
<tr>
<td>n</td>
<td>12,800</td>
<td>12,800</td>
<td>Fe**(VIII) + Fe**(VI)</td>
</tr>
</tbody>
</table>

b. 3d → 3d Forbidden Transitions of 8-Coordinated Fe**

Following Moore and White (1972) the peaks e, f, g, h, k, and c in Figure 1 are 3d → 3d forbidden transitions of Fe**(VIII). Since we assign peak d, which has been interpreted by Moore and White as 3d → 3d forbidden absorption of Fe**(VIII),
with \( d' \) as charge transfer bands, we suggest also a minor modification on the energy level of \( \text{Fe}^{3+} \) (VIII) assigned by Moore and White. We assign the absorption in the regions of peaks ef, gh, and k as the levels of \( ^3T_1, ^3E \), and \( ^3T_2 \) respectively, of \( \text{Fe}^{2+} \) (VIII) in spessartine and almandine. The effect of \( D_2 \) splitting of these levels is likely hidden in the complicated structure, which may be resolved in a low temperature TMA spectra.

c. \( 3d \rightarrow 3d \) Forbidden Transitions of Octahedral \( \text{Fe}^{3+} \)

The sharpness of the peak m at 23,300 cm\(^{-1}\) in curve A (Fig. 1) supports its assignment by Manning (1972) and by Moore and White (1972) as the field-independent level \( ^4A_1^e(G) \) of \( \text{Fe}^{3+} \) (VI). Lower levels of \( \text{Fe}^{2+} \) (VI) probably appear as minor structures in curve A, e.g., \( ^4T_2(G) \) as a rest, No. 4, at \(-16,800 \) cm\(^{-1}\) and \( ^4T_1(G) \) as a shoulder, No. 3, at \(-12,800 \) cm\(^{-1}\).

d. \( 3d \rightarrow 3d \) Forbidden Transitions of 8-Coordinated \( \text{Mn}^{3+} \) in Spessartine

Following Manning and Moore and White, the sharp peak p at 24,600 cm\(^{-1}\) should be the field-independent level \( ^4A_1^e(G) \) of \( \text{Mn}^{3+} \) (VIII). The shoulder n at 23,700 cm\(^{-1}\) and peak j at 21,000 cm\(^{-1}\) are \( ^4T_2(G) \) and \( ^4T_1(G) \), respectively, of \( \text{Mn}^{3+} \) (VIII) in spessartine, curves A and B.

e. A Possible \( 3d \rightarrow 3d \) Forbidden Transition of Tetrahedral \( \text{Fe}^{3+} \)

There is some controversy over the observation of \( \text{Fe}^{3+} \) (IV) absorption in almandine and spessartine. Manning (1972) assigned some \( 3d \rightarrow 3d \) forbidden peaks of \( \text{Fe}^{3+} \) (IV) in almandine \( ^4A_1^e(E(G) \text{ at } 24,200 \text{ cm}^{-1} \) and \( 24,800 \text{ cm}^{-1} \) \) and in spessartine. He determined the peaks of \( \text{Fe}^{3+} \) (IV) by curve-resolution of the optical spectra combined with a comparison with the \( \text{Fe}^{3+} \) (IV) spectra of yttrium garnets. Moore and White (1972) reported the \( \text{Fe}^{3+} \) (IV) absorption in ugrandite garnets, which have \( \text{Ca}^{2+} \) on the dodecahedral site and are otherwise very closely related to almandine and spessartine. They did not observe the \( \text{Fe}^{3+} \) (IV) absorption in almandine and spessartine.

We suggest that the field-independent level \( ^4A_1^e(G) \) of \( \text{Fe}^{3+} \) (IV) in spessartine and almandine appears as a minor peak (No. 7, Fig. 1) at \(-22,300 \) cm\(^{-1}\), the same location as that in ugrandite garnets assigned by Moore and White. A field independent peak should be sharp, but our best TMA spectrum (curve A, Fig. 1) shows only two sharp peaks m and p, which have been previously assigned as field-independent levels of \( \text{Fe}^{3+} \) (VI) and \( \text{Mn}^{3+} \) (VIII). Curve A does not show a third sharp peak which could be assigned to \( \text{Fe}^{3+} \) (IV). However, such a third sharp peak could appear as a minor structure, No. 7, hidden in the long steep slope at \(-22,300 \) cm\(^{-1}\) on the high-energy side of the peak k in both curves A and B for spessartines. Furthermore, the TMA spectra of almandine in curves C and D, which exhibit a broad, peak m even for the well-accepted field-independent level of octahedral \( \text{Fe}^{3+} \) (Manning, 1972; Moore and White, 1972), shows a moderate peak No. 7 at \(-22,300 \) cm\(^{-1}\). Our observation that the No. 7 peak is relatively more distinct in the TMA spectra of almandine than that of spessartine is consistent with the finding of Manning (1972) that the concentration ratio \( \text{Fe}^{3+} \) (IV) to \( \text{Fe}^{3+} \) (VI) in almandine is greater than that in spessartine.

Conclusion

The thermally modulated absorption spectra of spessartine and almandine reveal a new band at \(-12,000 \) cm\(^{-1}\) which has been hidden in the background absorption in the conventional optical spectra. This new band and the known band at \(-14,000 \) cm\(^{-1}\) may be interpreted as intervalence charge transfer from \( \text{Fe}^{2+} \) (VIII) to \( \text{Fe}^{3+} \) (VI) and \( \text{Fe}^{3+} \) (IV), respectively.

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