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Zero-phonon Mn$^{2+}$ luminescence in natural grossular Ca$_3$Al$_2$(SiO$_4$)$_3$

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Abstract. A natural grossular garnet was found to have a luminescence spectrum with a narrow vibrational structure and short decay time that is unusual for minerals. We propose that such emission is generated by Mn$^{2+}$ accompanied by defect F-centers which both enhance the transition probability and give rise to sensitivity to optical bleaching and reconstitution via irradiation. The elevated Mn concentration in comparison with other potential luminescent impurities was confirmed by LIBS analysis. Such interpretation contradicts the traditional opinion that Mn$^{2+}$ centers in minerals are characterized only by broadband emission with very long decay times typical of d-d transitions.

Keywords: grossular, luminescence, fine structure, short decay, Mn$^{2+}$, F-centers

1 Introduction

Grossular, Ca$_3$Al$_2$(SiO$_4$)$_3$, is the Ca-Al species of the six common anhydrous minerals of the garnet group. The structure of the grossular is comprised of SiO$_4$ tetrahedra and AlO$_6$ octahedra joined to each other at their corners. Ca cations are in eight coordination surrounded by oxygen atoms in the form of a strongly distorted cube. Grossular presents a suitable matrix for the accommodation of different luminescence centers. The most common are Mn$^{2+}$, Mn$^{3+}$, replacing Ca; Mn$^{2+}$, Mn$^{4+}$, Cr$^{3+}$, and V$^{2+}$ replacing Al$^{3+}$; and Fe$^{3+}$ replacing Si$^{4+}$ [1].

Natural grossular luminescence was originally studied by continuous wave (CW) luminescence and was related to Cr$^{3+}$, which substitutes for the Al$^{3+}$ ions and occupies a distorted 6-coordinated site having trigonal symmetry C3i. Trivalent chromium in grossular has a relatively high crystal field, such that the vibronic $^4T_{2g}$ level is found at energies higher than the $^2E_g$ state. The luminescence spectra of Cr$^{3+}$ in grossular at room temperature contain a strong broad band peaking at 720 nm and three sharp lines centered at 697, 700, and 701 nm. The decay times of both R-lines were found to be
equal within the experimental error for a wide range of temperatures, as expected in the case of two thermalized levels. This indicates that the nonradiative transitions between them are much faster than any other radiative transitions in the system [2]. The luminescence of green grossular, the tsavorite variety, has also been studied [3], where vanadium content is usually substantially higher than Cr and whose physical color has been ascribed to $V^{3+}$ absorption [4]. The same luminescence of $Cr^{3+}$ in a strong crystal field position was found in these samples, accompanied by a broad IR band peaking at 1205 nm, which was ascribed to $V^{3+}$.

In other work, natural grossular samples from Franklin, NJ; Sierra de Cruces Range, Coahuila, Mexico; Asbestos, Canada; and Africa (Mali) have been studied by laser-induced time-resolved luminescence techniques. The combinations of luminescence and excitation spectra together with luminescence decay times enabled their interpretation as $Mn^{2+}$, $Mn^{3+}$, $Mn^{4+}$, $V^{2+}$, REE$^{3+}$ and possibly Ni$^{2+}$ emission centers [5].

Recently, natural grossular from Georgetown, California, was found to have very unusual narrow band luminescence emission with short decay time which differs from all luminescence centers previously studied. The type of luminescence features seen was unusual for mineral luminescence in general and could not be assigned. The aim of this paper is to interpret such luminescence using laser-induced time-resolved spectroscopy.

2. Experimental setup

2.1. Apparatus

The luminescence excitation sources were pulsed lasers, utilizing three harmonics of Nd-YAG (266, 355, 532 nm), and a tunable (210–2100 nm) Optical Parametric Oscillator (OPO, OPOLET) which delivers pulses of 5–10 ns duration. The luminescence was transmitted at the 90° direction to the excitation beam to a Shamrock SR 750-A spectrometer (gratings 300, 1200, and 2400 l/mm), equipped with a fast ICCD camera (Andor DH320-18U-03) through an optical fiber using a telescopic quartz lens system. The spectrometer + ICCD system’s best spectral and temporal resolutions were 0.02 nm and 1.5 ns, respectively. The laser and the ICCD were synchronized by a precise delay generator DG 645. The delay (D) and gate (G) times are specified in the figures.
The narrow bands intensities in the figures are presented in arbitrary units (a.u.); they may only be compared inside each figure, not between different figures. A kinetic series was used to measure the decay data, an approach well suited for recording the temporal evolution of a process. This was accomplished by measuring the intensity of emission as a function of the delay between the luminescence excitation and the opening of the temporal acquisition gate. The time-resolved luminescence measurements were performed over the 100-300 K temperature range. At 20 K, continuous-wavelength (CW) spectra were measured.

Laser-induced breakdown spectroscopy (LIBS) was employed using the first harmonic of Nd-YAG (1064 nm) and adding a focusing lens for plasma creation.

X-ray irradiation was accomplished by a Rigaku SmartLab SE X-ray powder diffractometer with Cu K-alpha X-ray wavelength of $\lambda=0.154$ nm. X-ray Cu long fine focus Ceramic tube was used with the following parameters: 2.2 kW, 0.4×12 mm focus, and long anode type. The voltage, current, energy and irradiation time were the following: 40 kV, 40 mA, 8,958 keV, and 24 h.

2.2. Samples

The grossular garnets were found near Georgetown, El Dorado Co., CA in a small occurrence of rodingite within serpentine. The samples consist mainly of small crystals of grossular (1-5 mm) assembled into aggregates constituting a grossularite rock, but looser aggregates with separable euhedral crystals were also found [6], some displaying a well-developed trapezohedral form. Some of the garnets exhibited strong pinkish-red luminescence under CW long-wave UV (365 nm), with the brightest response from those found near fissures in the deposit where fluid transport was assumed to be maximized. Powder XRD done at Lawrence Berkeley Laboratory showed near end-member grossularite cell dimensions, and micro-Raman analysis at Caltech verified that the species is grossular. No impurity phases were observed. Semi-quantitative XRF showed grossularite chemistry with small levels of Fe, Ti, and Mn impurities.
3. Experimental results

Three different luminescence centers are found in these grossular samples. Figure 1 presents the luminescence and excitation spectra of the first one. The emission at 300 K consists of a strong narrow band at 604.2 nm accompanied by several weaker ones at 582.7, 595.6, 617.2, 631.3, 644.9, and 660.8 nm (Fig. 1a). All narrow bands have the same decay time of 5.3 µs and the same excitation spectrum, which consists of two main bands at 375 and 530 nm (Fig. 1b). These bands coincide well with the second (532 nm) and third (355 nm) harmonics of the Nd-YAG laser.

![Figure 1](image_url)

**Figure 1.** Time-resolved luminescence (a) and excitation (b) spectra of the grossular sample at 300 K (D=20 ns, G=10 μs).

Figure 2 presents the time-resolved luminescence spectra at different temperatures (between 300 and 100 K) under excitation by 355 nm, where this emission is observed without influence from the other two luminescence centers. The decay time at 100 K is 7.2 µs, which is close to that at 300 K. At lower temperatures, the spectral positions of the bands remain mainly the same, but the emission intensity becomes substantially stronger, reaching saturation at approximately 100 K (Fig. 3a). The intensity ratio between the different bands changes with
temperature and vibrational structure appears on the band centered at 617.2 nm. The band half-width becomes narrower at low temperatures (Fig. 3b). The spectra at 20 K and 100 K are similar (Fig. 3). It is difficult to compare the intensities because the experimental setups for both temperatures were different.

![Figure 2](image_url)

**Figure 2.** Time-resolved luminescence spectra recorded at the room and lower temperatures under the excitation by 355 nm (D=20 ns, G=10 μs).

![Figure 3](image_url)

**Figure 3.** Luminescence intensity (a) and half-width (b) as a function of temperature.
This emission is thermally very stable. However, the narrow bands become noticeably less intense with exposure to green laser irradiation (532 nm) (Figs. 4 a-c) and are easily bleached by such laser exposure. This process is reversible, and the luminescence is restored under the X-ray irradiation (Fig. 4d). When the narrow band emission becomes weaker, the second luminescence center dominates the spectrum. It is a broad band peaking at 650-660 nm with a relatively short decay time of 5.8 µs, which is very similar to the decay of the narrow band emission. At lower temperatures, this emission becomes weaker and does not exhibit new spectroscopic features.

![Figure 4](image-url)

**Figure 4.** Emission bleaching under laser irradiation (a-c) and its restoration after X-ray irradiation (d). The broader second luminescence center becomes visible after bleaching.

Using a long delay time of 50 µs, the first two emission centers are quenched, and the third luminescence center is detected. At 300 K, it consists of a broad luminescence band peaking at 590 nm with a very long decay time of 15 ms (Fig. 5a). At 100 K, the band becomes narrower (Fig. 5b), but the peak position and decay time are nearly the same. At 20 K, the band is even narrower, and additional narrow bands appear (Fig. 5c).
Figure 5. The third long-lived luminescence center at different temperatures: a and b – time-resolved with a delay of 50 µs and the gate of 1 ms; the 20 K spectrum (c) was obtained by CW spectroscopy.

3. Interpretation

As mentioned above, the most probable luminescence centers which have been found in the grossular structure, are Mn$^{2+}$, Mn$^{3+}$, REE$^{2+}$, and REE$^{3+}$ replacing Ca; Mn$^{2+}$, Mn$^{4+}$, Cr$^{3+}$, V$^{2+}$ replacing Al$^{3+}$; and Fe$^{3+}$ replacing Si$^{4+}$ [1-5]. Transition metals in minerals, such as Mn, Cr, and V, may be detected by LIBS with sensitivity sufficient for luminescence activation [1]. Figure 6 presents the breakdown spectrum of the grossular under the study in the spectral ranges relevant for Mn, Cr, and V identification [7]. Only the diagnostic lines of Mn were detected (Fig. 6a), while the lines of Cr (425.43 and 427.48 nm) and of V (437.5 and 437.9 nm) were absent (Figs. 6b-c).
Figure 6. Breakdown spectra of the grossular with diagnostic lines of Mn and the absence of the lines of Cr and V. Mn and Fe had been detected previously via XRF.

4.1 Narrow band at 603 nm at 300 K – zero-phonon line of Mn$^{2+}$

When you see narrow luminescence lines in Ca-bearing minerals, the first suspicion is trivalent Rare Earth Elements (REE$^{3+}$). Nevertheless, the lifetime of several microseconds is rather short for forbidden f-f transitions and the strong enhancement of luminescence intensity at low temperature is not typical for REE$^{3+}$. The luminescence of multiple REE$^{3+}$ had previously been found in natural grossular with sharp lines and long decay times that are strongly different from our case (Fig. 7d) [5]. Additionally, the study of artificial grossular activated by REE, particularly by Eu, did not detect such emissions [8]. Sharp line emission may be due to Cr$^{3+}$ commonly substituting in the octahedral sites, but it takes place at longer red wavelengths in the region of 680-700 nm, and the so-called R-lines are strongly forbidden and usually have much longer decay times. The same considerations are true for Mn$^{4+}$ or V$^{2+}$, which are isoelectronic with Cr$^{3+}$.

Thus, we must look for other less traditional explanations. The main difficulty is the almost complete absence of luminescence spectra of minerals studied at very low
temperatures (lower than 77 K), where fine structure might be observed. Further discussion requires a brief theoretical introduction. At such low temperatures, some emission bands, which are broad and featureless at room temperature, begin to narrow and to show sharp lines on the short wavelength edge. These features are due to the resolution at low temperatures of transitions, in which one, two, or more phonons of a particular vibrational mode are created. The strongest and sharpest line, however, at the shortest wavelength in emission is usually the transition in which no phonons are created at all. This zero-phonon line (ZPL) is therefore a purely electronic transition, and its spectral position gives us the precise separation of the emitting state and the final state (usually the ground state). A parameter that describes the degree to which a luminescent center exhibits a ZPL is called the Huang-Rhys factor (S). This parameter can be defined as the number of phonons of a particular mode that are created in emission or absorption and is a measure of the interaction of the emitting electronic states and the final state of the luminescence center with the vibrating lattice in which it finds itself. If S > 6 or 7, then the interaction with the lattice is so strong that a ZPL cannot usually be detected even at 4.2 K. If on the other hand S < 1, then the spectrum is dominated by ZPL, although a weak single-photon sideband may also be present at longer wavelengths. This sideband is merely a spectrum of the various vibrational or phonon modes associated with the luminescent ion and its immediate environment [9].

Figure 7 presents this process schematically [10]. At low temperature, the maximum peak intensity occurs at the location of ZPL, and the vibrational sidebands only occur at the longer wavelength side of the ZPL, which is in accordance with the case of materials with weak electron-phonon coupling (Fig. 7a). However, the emission intensities of vibrational sidebands from the short wavelength side increase and they are unseparated at high temperature (Fig. 7(b)), which causes the broadening of emission bands with increasing temperature. The shapes of emission spectra can be explained by the coupling of electronic transitions with the vibrational levels. When the luminescent ions with surrounding ligands are located at the equilibrium position, the system is at the lowest electronic energy. The equilibrium position could be displaced as the transition occurs from the ground state to the excited state. The displacement ΔR depends on the strength of the electron-phonon coupling, which is characterized by S. The quantum mechanical description of the energy potential results in the occurrence of the discrete vibrational state. The energy difference between the adjacent vibrational levels is so-called phonon energy hω. When the transition occurs from the ground state to higher vibrational levels of the excited state, it decays quickly to the lowest vibrational level of the excited state by multi-photon relaxation. Subsequently, it
returns to the vibrational level of the ground state by radiative decay. The radiative decay from $v' = 0$ to $v = 0$ is the ZPL. The radiative decay from $v' = 0$ to other higher vibrational levels results in the vibrational sidebands. The intensity of the vibrational sidebands is relatively weak compared to the ZPL due to the low phonon energy at low temperatures. As temperature increases, the increase in phonon density of states induces the increase in vibrational sidebands and simultaneously the decrease in the ZPL intensity. In addition, radiative decays from higher vibrational levels of the excited state occur, which lead to the vibrational sidebands at shorter wavelength side of the ZPL. The decay time in such cases is very long, namely several ms.

Figure 7. Configuration coordinate diagrams with emission spectra at 10 (a) and 300 K (b) [10].

Spectra of Mn$^{2+}$ emission at very low temperatures sometimes demonstrate a ZPL. For example, in Zn$_4$B$_6$O$_{13}$:Mn$^{2+}$ the luminescence spectrum at 300 K consists of one relatively narrow emission band at 540 nm with a long decay time of 12 ms, while at 10 K the spectrum is totally different and exhibits the strong very narrow line at 534 nm accompanied by several weaker lines. The sharp line at 534 nm was assigned to the ZPL of the $^4T_1 \rightarrow ^6A_1$ transition. The ZPL accompanies vibrational sidebands at 538, 548, and 560 nm. The emission intensity of the ZPL decreases while the intensities of the vibrational sidebands increase with increasing temperature. The band shape changes gradually and becomes broad and asymmetric up to room temperature. The strong zero-phonon line was explained by relatively large phonon energy and a small S factor [10].
Narrow line Mn\(^{2+}\) luminescence has been found in ZnGd\(_2\)O\(_4\):Mn\(^{2+}\) where in both excitation and luminescence spectra fine structure was observed. The emission spectrum due to the transition \(^4\)T\(_1\)–\(^6\)A\(_1\), was ascribed to a zero-phonon line at 499.8 nm and vibronic sidebands [11]. The vibronic sideband frequencies of the luminescence and excitation transitions \(^4\)T\(_1\)–\(^6\)A\(_1\), \(^6\)A\(_1\)–\(^4\)T\(_2\), and \(^6\)A\(_1\)–\(^4\)A\(_1\) compared with frequencies from IR and Raman spectra. From the high intensity of the zero-phonon line and the equality of the vibronic frequencies in the emission and excitation spectra, it can be concluded that the Huang-Rhys factor is small.

The spectra described above relate to Mn\(^{2+}\) in tetrahedral coordination, where, because of the relatively weak crystal field, the luminescence is green. But zero-phonon lines are also known for Mn2+ in octahedral coordination, where, because of the relatively large crystal field, the luminescence is orange-red. For example, in KMnF\(_3\) and KZnF\(_3\) activated by Mn\(^{2+}\), those lines are situated at 580.6 and 571.1 nm, respectively. The nature of these ZPLs must be magnetic dipole (MD) transitions because the electric dipole (ED) mechanism is forbidden for Mn\(^{2+}\) in O\(_h\) symmetry [12].

The closest situation to our case is the photoluminescence spectra at a relatively high temperature of 77 K in yttrium aluminum garnet (YAG) activated by Mn. Here, a broad orange luminescence band in the range 580-620 nm appears at 300 K, while the luminescence spectrum measured at 77 K contains a sharp line at 587 nm and a series of weaker lines on the longwave side of the sharp line [13]. It may be seen that the spectral behavior of Mn\(^{2+}\) described above appears similar to what we observe with the grossular. We also have intense narrow lines at low temperatures with weak accompanying broader bands, while, at higher temperatures, the narrow line becomes weaker and the sidebands more intensive. Figure 8 shows the high-resolution spectrum at 100 K with vibronic sidebands frequencies. Because all the lines have the same excitation spectrum, we suppose that they all must be associated with one luminescence center. Figure 9 depicts IR and Raman spectra of our grossular together with Raman of transparent grossular from Canada. Because of strong orange emission, the Raman lines in our case are relatively weak against the background of the luminescence. Nevertheless, the strongest Raman lines at 370-380 cm\(^{-1}\) and 800-900 cm\(^{-1}\) are clearly seen. Table 1 presents the comparison of phonons detected by luminescence with the frequencies of IR and Raman modes. The similarity of those frequencies with those received from Raman and IR spectra (Fig. 9) is reasonable. The super-fine structure may be connected to spin-orbital splitting or to a Jahn-Teller effect. Another interpretation is also possible. All
luminescence lines, besides the very weak one at 628.3 nm, may be approximated by ZPL interaction with phonons having energies of ~ 300 and 400 cm\(^{-1}\), which correspond to several Raman and IR active modes.

**Figure 8.** High-resolution luminescence spectra in different spectral ranges in nm and cm\(^{-1}\) at 100 K with vibronic sidebands frequencies.

**Figure 9.** IR (a) and Raman (b) spectra of our grossular and Raman of Canada grossular (c).
Table 1. The comparison of phonons (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Luminescence</th>
<th>Raman</th>
<th>Infrared</th>
<th>Energy difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>301</td>
<td>380</td>
<td>300-380</td>
<td>301</td>
</tr>
<tr>
<td>694</td>
<td>542</td>
<td>540</td>
<td>393</td>
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<tr>
<td>894</td>
<td>829, 886</td>
<td>828, 905</td>
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<tr>
<td>997</td>
<td>1005</td>
<td></td>
<td>303</td>
</tr>
<tr>
<td>1387</td>
<td></td>
<td></td>
<td>390</td>
</tr>
</tbody>
</table>

Nevertheless, several features in our case contradict the typical model for a ZPL in Mn\(^{2+}\): very short decay time for this forbidden transition, extremely high-temperature stability, when it dominates the spectrum even at 300 K, and strong optical bleaching with subsequent intensity gain under X-ray irradiation. A possible explanation might be found by analogy with the strongly forbidden d-d transitions of Cr\(^{3+}\) luminescence in MgAl\(_2\)O\(_4\) observed after neutron irradiation. The decay time of the Cr\(^{3+}\) transitions prior to irradiation was approximately 8 ms, while after irradiation it was reduced to about 14 \(\mu\)s, indicating a much more allowed transition. The large decrease in the fluorescence lifetime of the neutron-irradiated sample was explained by the enhancement of the oscillator strengths of Cr\(^{3+}\) impurities perturbed by the presence of F centers, which are negative-ion vacancies with a trapped electron present for charge compensation. The nearby F center increases the oscillator strength of Cr\(^{3+}\) by three orders of magnitude by introducing odd components to the crystal field or by exchange coupling between the F center and the Cr\(^{3+}\) impurity [14].

Thus, it is possible to assume that the short decay time and the high luminescence intensity relate to Mn\(^{2+}\) luminescence center modified by an F center. The oxygen missing in the lattice may be the source for F-centers formation, while Na\(^+\) substitution in Ca\(^{2+}\) position enables its stabilization. Sodium presence was confirmed by our LIBS data. The structural defect participation potentially explains the luminescence optical bleaching and its regeneration by X-ray irradiation. Bleaching involves the removal of the trapped electrons in the F centers, while irradiation may replenish these electrons from deeper traps.

The question remains: what is the structural position of this unusual Mn\(^{2+}\) luminescence center in grossular? The most logical is the substitution for Ca\(^{2+}\) which has the
same valence and similar ionic radius (1.26 and 0.97 Å, respectively, in 8-coordination). Nevertheless, the substitution for the Al$^{3+}$ site is also possible (0.67 Å in 8-coordination) and is well documented in several minerals [16]. Additionally, it has been shown previously that Mn$^{2+}$ in yttrium aluminum garnet can enter any of the three kinds of garnet sites, namely the distorted cubic (8-coordinated), octahedral and tetrahedral sites [17]. Based on ZPL theory, the reason for the lack of prominent phonon structure at low temperatures is related to the degree of interaction between the electronic states of the Mn$^{2+}$ ion and the vibrating lattice in which it resides. In the case of the strong or moderately strong interaction, phonon structure will not be evident. Hence, in our case, the interaction must be weak, and correspondingly the Hyang-Rhys factor is small [18]. This appears unusual for d-d transitions but has also been detected in the ZPL luminescence of Fe$^{3+}$ in synthetic forsterite [19].

4.2 Broad band at 660 nm – Ni$^{2+}$

At first sight, based on the emission band maximum and decay time, this luminescence band is like a previously ascribed Mn$^{3+}$ center [5]. But more detailed analysis contradicts such a conclusion (Fig. 10). Unlike Mn$^{2+}$, luminescence from Mn$^{3+}$ is not well known in minerals. Besides natural grossular, Mn$^{3+}$ emission was previously reported in orange Mn-containing kyanite [20]. Recently, it was detected in natural beryl and vesuvianite [21]. Red-colored beryl exhibits at 300 K an intense emission band due to the $^5T_2 \rightarrow ^5E''$ transition at 630 nm with $\tau_{630} = 0.6$ μs. At 77 K, the double-structured emission band has maxima at 617 and 674 nm with $\tau_{617} = 15$ μs and $\tau_{674} = 183$ μs. The emission bands were ascribed to $^1T_2 \rightarrow ^5E$ transition. It is evident that such behavior is like found in Mexico grossular but does not correspond to the grossular we are examining.

The spectral similarity is substantially higher with Ni$^{2+}$ luminescence spectrum previously proposed in transparent grossular from Canada [5]. When Ni$^{2+}$ ions with 3d$^8$ electronic configuration are inserted in an insulating host, their energy levels are strongly affected by the electrostatic potential generated by neighboring ions. The d$^8$ free ion ground energy term $^3F$ is transformed to a lower $^3A_{2g}$ energy level and to two excited levels $^3T_{2g}$ and $^3T_{1g}$. The next excited energy level $^1D$ is split in $^1E_g$ and $^1T_{2g}$. The third level in increasing order is the $^3P$, which is transformed into a $^3T_{1g}$ level. For systems with weak crystalline field, the $^3T_{2g}$ ($^3F$) is the first excited level, while for Ni$^{2+}$ ions in a stronger crystalline field the first excited state is the $^1E$ ($^1D$) energy level. Three luminescence bands in the near IR,
red and green parts of the spectrum characterize Ni\(^{2+}\) luminescence correspondingly and relate to electron transitions from the lowest excited state \(^{3}T_{2g}\) or \(^{1}E\), with \(^{1}T_{2g}(D)\rightarrow^{3}T_{2g}(F)\) and \(^{1}T_{2g}(D)\rightarrow^{3}A_{2g}(F)\) electron transitions [22]. The connection with Ni\(^{2+}\) was confirmed by the luminescence spectrum of artificial GGG activated by Ni\(^{2+}\), which is very similar to those in our grossular [5] with a short decay time of 0.5 \(\mu\)s. The relatively short decay time of such emission connected to this spin-forbidden radiative transition may be tentatively explained as being caused by the mixing of singlet and triplet states.

![Graphs showing luminescence spectra](image1.png)

**Figure 10.** The comparison of short-lived orange luminescence in the grossular under the study (a, b) and the previously studied from Mexico orange (c, d) and Canada transparent (e, f) [5].

### 4.3 Broad band at 590 nm – Mn\(^{2+}\)

Such emission was previously studied and attributed to Mn\(^{2+}\). This was done based on luminescence and excitation spectra together with the long decay time typical to the forbidden \(^{4}T_{1g}\rightarrow^{6}A_{1g}\) transition of Mn\(^{2+}\) ions in octahedral sites [5]. Similar luminescence was found also in yttrium aluminum garnet (Y\(_{3}\)Al\(_{5}\)O\(_{12}\), YAG) activated by Mn and ascribed to Mn\(^{2+}\) in octahedral sites [7]. The narrow emission line at 565.1 nm found at 20 K is evidently connected to this Mn\(^{2+}\) luminescence. This feature corresponds well with the zero-
phonon line at 17700 cm\(^{-1}\) (565.0 nm) detected in the luminescence spectra of Mn\(^{2+}\) in the 6-coordinated site in natural calcite at 7 K [18]. Evidently, we see here the usual Mn\(^{2+}\) luminescence center in the Ca\(^{2+}\) position in the grossular structure.

5 Summary

A natural grossular garnet having a near end-member composition was found to have an unusual Mn\(^{2+}\) emission with fine structure and a shorter excited state lifetime than usually expected. The shorter lifetime appears to be consistent with the proximity of defect F-centers which both enhance the transition probability and give rise to sensitivity to optical bleaching and reconstitution via irradiation. A Ni\(^{2+}\) center is also observed, along with an Mn\(^{2+}\) center characteristic of other natural garnets, substituting for Ca in the 8-coordinated site.

6 Acknowledgements

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Highlights

➢ We studied narrow band time-resolved luminescence of natural grossular
➢ We found zero-phonon luminescence of Mn\textsuperscript{2+} with short decay time
➢ We found additional band of evidently Ni\textsuperscript{2+}
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.