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Optical spectroscopy study of type 1 natural and synthetic sapphires

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Abstract

Low iron, pale blue natural and synthetic sapphire samples were studied by low temperature absorption and luminescence spectroscopy. For comparison, a bicolour pink and blue corundum from Vietnam was also considered. From radioluminescence and photoluminescence excitation spectra of both Cr^{3+} and Ti^{3+} , experimental evidence was obtained for attributing an absorption band at $17\,500\text{ cm}^{-1}$, currently interpreted as $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$ intervalence charge transfer, to overlapping crystal field transitions of Cr^{3+} and Ti^{3+} . An important role was also proposed for Cr^{2+} ; indeed, it is possible to propose that the colour of pale blue sapphires is mainly determined by chromium in its two valence states while Ti^{3+} and Fe^{3+} have a minor role.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent decades a considerable amount of work on the causes of the colour of blue sapphire has been carried out, focusing on optical absorption studies of samples of various origins, both natural and synthetic, differently treated or grown.

Natural blue sapphires are commonly classified according to the absence (type 1) or to the presence (type 2) of an absorption band located at $11\,500\text{ cm}^{-1}$ and attributed to the ^5E spin-allowed transition of Fe^{2+} [1, 2]. Other impurity related features of the absorption spectra of both sapphire types are well interpreted in the frame of the crystal field theory. The bands observed at $22\,500\text{ cm}^{-1}$ and at $25\,500\text{--}26\,500\text{ cm}^{-1}$, in fact, are due to the $^4\text{A}_1$, ^4E , $^4\text{T}_2^{(b)}$ and ^4E spin-forbidden transitions of Fe^{3+} [3]. Moreover, Ti^{3+} reveals its presence [4, 5] through a double structured absorption with a prominent $20\,300\text{ cm}^{-1}$ peak and a smaller one at $18\,450\text{ cm}^{-1}$, attributed to the $^2\text{T}_2 \rightarrow ^2\text{E}$ transition, split by the loss of octahedral symmetry. These bands are easily detectable in samples doped with only Ti, while in blue sapphires they often overlap a stronger absorption at $17\,500\text{ cm}^{-1}$.

In the range from $13\,500$ to $21\,000\text{ cm}^{-1}$, the two absorption bands with maxima at $14\,500\text{ cm}^{-1}$ and at $17\,500\text{ cm}^{-1}$ are currently attributed to intervalence charge transfer (IVCT) transitions ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ and $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$, respectively), even if the role of Cr^{3+} was also taken into account [6]. However, it should be remarked that, although

the latter subject has been reviewed in the literature more than once [7, 8], the status of the discussion is still open.

With this in mind, the aim of this work is to update, by means of an analysis of the luminescence features of some selected samples, the interpretation of the blue sapphire optical absorption spectra. A similar approach was recently used by Platonov *et al* [9] for the interpretation of the kyanite absorption spectra.

2. Experimental details

The samples considered in this work are type 1 blue sapphires of various origins, including synthetic ones, as well as a bicolour, blue and pink corundum from Vietnam, useful for comparison purposes.

The samples were platelets $5 \times 5\text{ mm}$ wide and $0.5\text{--}3\text{ mm}$ thick, according to the range of absorption coefficient to be explored. The samples from Sri Lanka (Z2 and Z6) were homogeneous and clear, while the sample from Vietnam (Z9, currently named Mong Hsu) was not homogeneous, clear in the pink regions and cloudy blue in spots of different shape (stripes $\approx 1\text{ mm}$ wide; regular triangles $\approx 2\text{ mm}^2$ in size). Finally, the synthetic ones (Z10 and Z11) were clear, light blue and prepared by the Verneuil method. Details of the samples are reported in table 1.

The content of Fe, Ti and Cr was qualitatively evaluated by an EDXRF Horiba apparatus. Ti is maximum in Z9 (0.1%

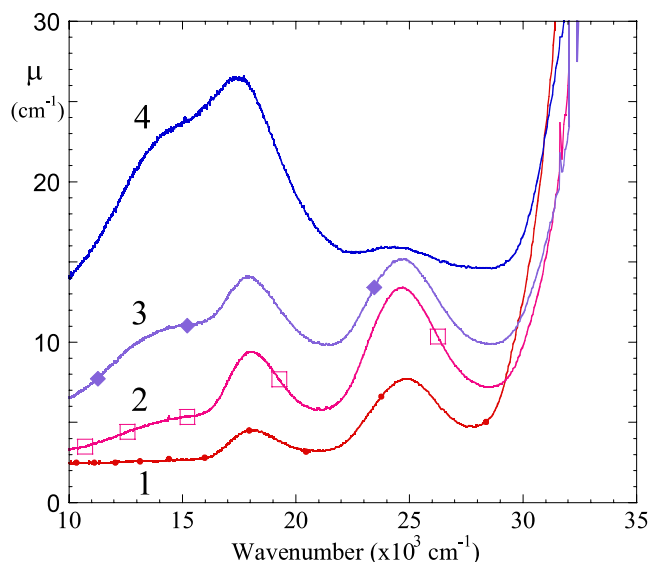


Figure 1. Room temperature absorption spectra of different spots of the Z9 sapphire: clear pink (1); light-violet (2) and dark-violet areas (3); blue spot (4).

Table 1. Details of the examined samples.

| Sample name | Provenance | Colour |
|-------------|----------------------|-------------------|
| Z2 | Sri Lanka | Pale blue |
| Z6 | Sri Lanka | Pale blue |
| Z9 | Vietnam (Mong Hsu) | From pink to blue |
| Z10 | Synthetic (Verneuil) | Blue |
| Z11 | Synthetic (Verneuil) | Blue |

in weight) and varies from 0.01 to 0.06% in weight in the other samples. Cr is maximum in Z9 (2.12% in weight) and varies from 0.01 to 0.03% in weight in the other samples. Fe is maximum in Z6 (0.35% in weight) and varies from 0.1 to 0.3% in weight in the other samples.

The absorption measurements were obtained by a Perkin-Elmer λ 950 spectrophotometer in the NIR–vis range. Absorption spectra were collected either at room temperature or at about 15 K, in the latter case the samples being clamped to the cold finger of a Galileo cryocooler (model K1).

Radioluminescence (RL) measurements were performed on a custom apparatus. The x-ray tube is a Philips 2274 operating at 20 kV and 5 mA. The average exposure time used to obtain a spectrum was about 30 s while the dose was approximately 1 Gy. The detector (CCD Spectrum One 3000 by Jobin Yvon) operates in the 9000–40 000 cm^{-1} spectral range. Incidentally, the absorption spectra recorded after the RL measurements did not reveal any substantial sample modification.

Photoluminescence (PL) and photoluminescence excitation (PLE) measurements were achieved by a Fluorolog 3.21 spectrometer provided by Jobin Yvon. The excitation source consists of a 450 W Xe lamp coupled with a 1200 grooves mm^{-1} double grating monochromator, whose slit width ranges from 7 mm to 10 μm and whose blaze wavelength is 330 nm. The signal detection equipment consists of a 1200 grooves mm^{-1} single grating monochromator (blaze at

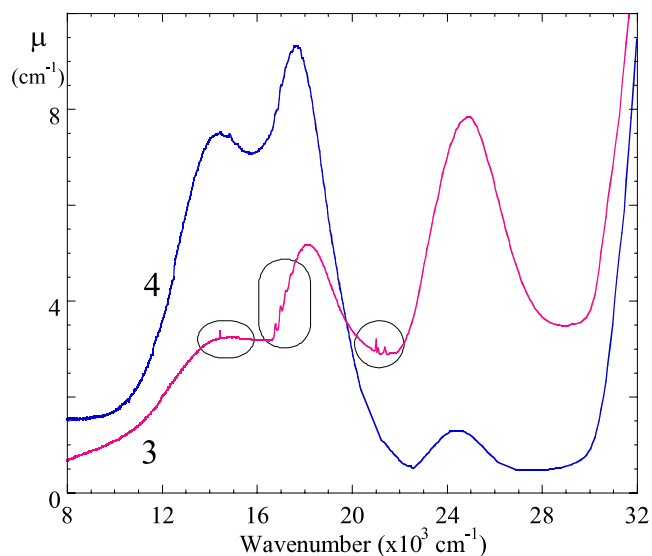


Figure 2. Absorption spectra of the Z9 pink and blue corundum at 17 K: (3) and (4) refer to the same areas of the sample shown in figure 1.

550 nm), with the same features mentioned above in the case of the double grating one, and of a phototube detector (Hamamatsu R928P). Moreover, a cooling system composed of a set of rotary, diffusion and cryogenic pumps was used to perform PL measurements at low temperature (3.2 K). The cooling system is equipped with a resistance heater which enables PL spectra to be observed in the temperature range between 3.2 and 300 K.

3. Result and discussion

3.1. Optical absorption

In figure 1 room temperature absorption spectra of the inhomogeneous Z9 sample are shown, collected from different spots, coming from the pink to the blue zone. The spectrum (1) was collected from the pale pink region and it is typical of ruby, exhibiting the 4T_2 and 4T_1 spin-allowed transitions of Cr^{3+} , respectively at 18 100 and 24 500 cm^{-1} . The blue region (4) shows instead a spectrum similar to that of Sri Lanka type 1 sapphires (reported below in figure 4), while the light-violet (2) and the dark-violet ones (3) present intermediate absorption features.

Figure 2 shows instead the low temperature spectra collected from zones (3) and (4) of figure 1. In these spectra, the 4T_2 band of Cr^{3+} is strongly overlapped to a broad band peaked at 14 500 cm^{-1} (FWHM of about 4000 cm^{-1}). Due to the intensity of the strong overlapping band, the 4T_2 peak in (4) appears shifted at 17 500 cm^{-1} .

Moreover, these spectra show no evidence of peaks that can be either related to Fe^{2+} or Fe^{3+} ; in particular, the absence of the 5E spin-allowed transition band of Fe^{2+} at 11 500 cm^{-1} [1, 2] implies the absence of the Fe^{2+} ion in these samples. This experimental evidence raises some doubt regarding the origin of the band at 14 500 cm^{-1} , usually attributed to the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ IVCT transitions. By

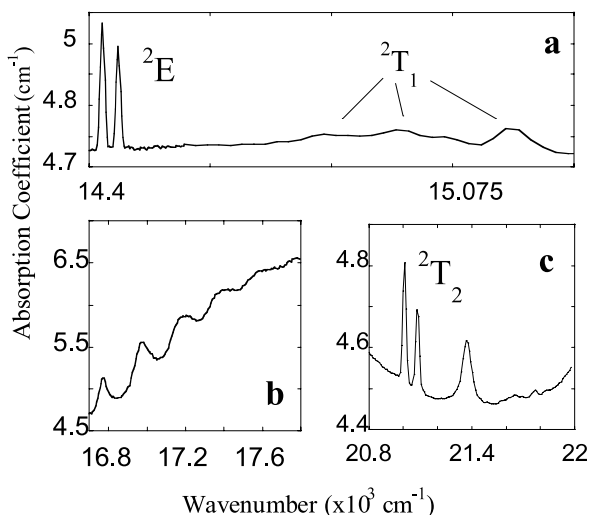


Figure 3. Expanded views of spectrum (3) of figure 2: (a) ²E and ²T₁ spin-forbidden bands; (b) vibronic structures related to the ⁴T₂ spin-allowed band and (c) ²T₂ spin-forbidden band.

comparison with the data reported in [10] for the Cr(H₂O)₆²⁺ complex ion in aqueous solutions and hydrated crystals, this absorption band could be attributed to the ⁵T₂ transition of the (d⁴) Cr²⁺ ion. However, this simple comparison cannot be considered as conclusive proof of the role of Cr²⁺ in the absorption at 14 500 cm⁻¹, although it seems more reliable than the Fe²⁺ → Fe³⁺ IVCT attribution, due to the absence of Fe²⁺ in type 1 sapphires. In order to confirm the role of Cr²⁺ in the absorption at 14 500 cm⁻¹, further investigations by EPR measurements will be carried out.

Some circled features of the spectrum (3) are conveniently expanded in figure 3. In figure 3(a), it is possible to identify the spin-forbidden ²E and ²T₁ of Cr³⁺. Figure 3(b) shows the low energy side of ⁴T₂ where six to eight equally spaced vibronic structures of about 200 cm⁻¹ are observable. In figure 3(c) the ²T₂ band, split by the spin-orbit interaction and by the small trigonal deformation of the oxygen octahedron, is shown. The same splitting is present for ²T₁, although less evident, in figure 3(a).

In figure 4 the spectra in the 8000–36 000 cm⁻¹ range of two type 1 sapphires, Z2 and Z6, are shown. These spectra are similar, but more complex, than the Z9 one. It is possible to distinguish several bands due to different chromophoric ions: the ⁴T₂ and ⁴T₁ bands of Cr³⁺ at 17 500 cm⁻¹ and at 24 500 cm⁻¹, respectively (attributions confirmed by the PLE and PL measurements reported below); the ⁴A₁, ⁴E at 22 500 cm⁻¹, the ⁴T₂(a), ⁴E at 25 500–26 500 cm⁻¹ and the ⁴T₁(b) at 30 000 cm⁻¹ of Fe³⁺. The band at 17 500 cm⁻¹ is composite and its overall intensity should be due to the overlapping of different transitions occurring in this energy range: the ⁴T₂ of Cr³⁺, the high energy side of ⁵T₂ of Cr²⁺ and the low energy side of the ²E of Ti³⁺. In particular, the role of Ti³⁺ absorption has been proposed on the basis of the RL and PL results described in the next paragraph.

In figure 5 the optical absorption spectra of synthetic samples Z10 and Z11 are shown. They reveal the presence of the two spin-allowed transitions (⁴T₂ and ⁴T₁) of Cr³⁺, at

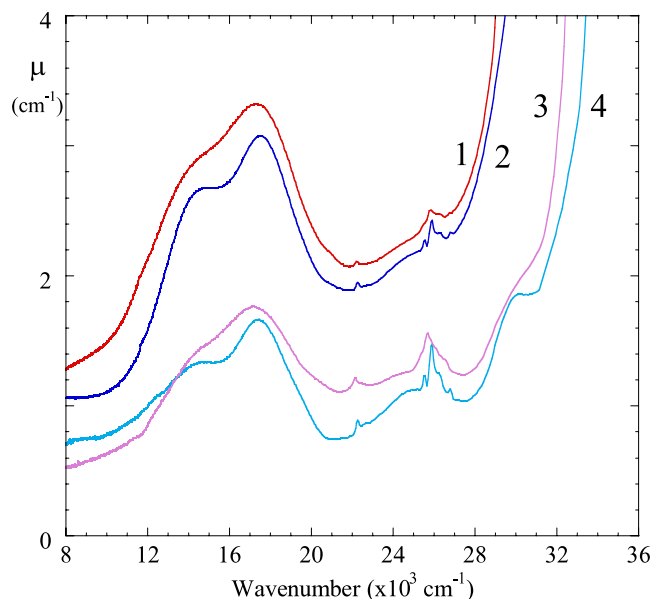


Figure 4. Absorption spectra of Sri Lanka sapphires: (1) room temperature spectrum of Z2, (2) low temperature spectrum of Z2 (18 K), (3) room temperature spectrum of Z6, (4) low temperature spectrum of Z6 (18 K). A 1 cm⁻¹ constant was added to the spectra of sample Z2.

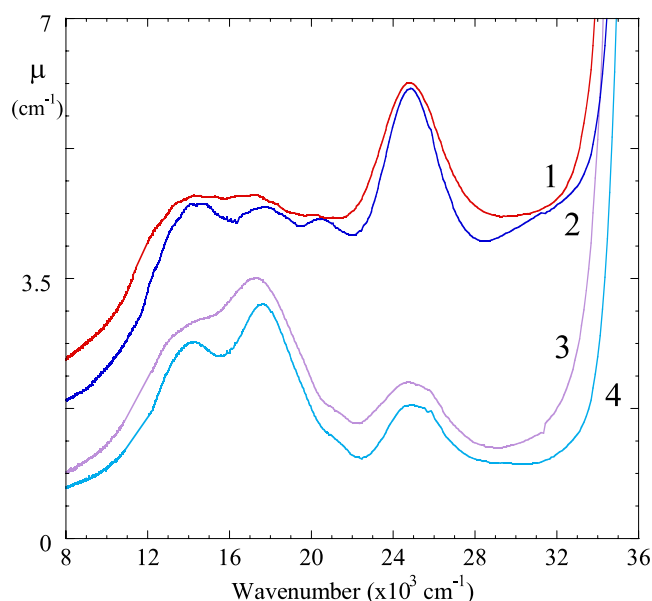


Figure 5. Absorption spectra of synthetic sapphires: (1) room temperature spectrum of Z10, (2) low temperature spectrum of Z10 (19 K), (3) room temperature spectrum of Z11, (4) low temperature spectrum of Z11 (19 K). A 1.5 cm⁻¹ constant was added to the spectra of sample Z10.

17 500 cm⁻¹ and 25 000 cm⁻¹, respectively, the ²T₂ → ²E transition of Ti³⁺ at 20 500 cm⁻¹ and the ⁵T₂ transition of Cr²⁺ at 14 500 cm⁻¹.

From a comparison with the results obtained on the other samples, we can conclude that sample Z9 is substantially a ruby in which chromium is more (Cr³⁺) or less oxidized (Cr²⁺). This particular type of ruby, unlike the ‘regular’ ruby

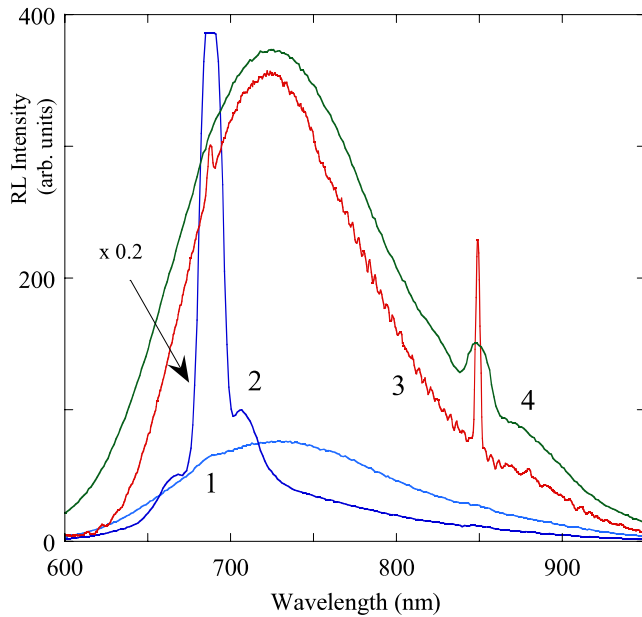


Figure 6. Radioluminescence spectra of: (1) Z2 at room temperature (RT), (2) Z9 at RT, (3) Z10 at 10 K and (4) Z10 at RT. Spectrum (2) was multiplied by a factor of 0.2 to improve clarity.

which grows in permanently oxidizing conditions, becomes blue in those areas where the chromium ion faces reducing conditions: as a result, the transparent window between the low energy side of 4T_2 of Cr^{3+} and the limit of the visible range ($16\,000\text{--}13\,500\text{ cm}^{-1}$) is suppressed by the growth of the absorption due to 5T_2 of Cr^{2+} . As a consequence, the red light is absorbed and transmission is allowed only in the blue window between 4T_2 and 4T_1 bands of Cr^{3+} .

The interpretation of the causes of colour in Sri Lankan and synthetic sapphires follows the same scheme, considering the lower chromium concentration. Therefore, no IVCT processes between Fe^{2+} and Ti^{3+} or between Fe^{2+} and Fe^{3+} are involved in determining the colour of these blue sapphires.

In conclusion, it should be remarked that, when the substitutional impurity is an aliovalent ion (i.e. Fe^{2+} , Mn^{2+} , Cr^{2+} for Al^{3+}), the problem of charge compensation must always be considered. While it is known that in beryl the charge compensation is due to the alkali ions in the structural channels, in corundum we are not yet able to specify the defect (or the trace impurity) responsible for the charge compensation.

3.2. Radio- and photoluminescence

As mentioned above, some of the attributions made in the previous paragraph have been proposed on the basis of the radio- and photoluminescence results obtained on the same samples.

RL is a simple but only qualitative tool for obtaining information about the presence of activator ions in a matrix. In fact, there is no trivial correlation between the emission intensity and the activator concentration, since the former depends on the capture cross section of excited electrons at the emitting centres. Furthermore, capture from deep electronic

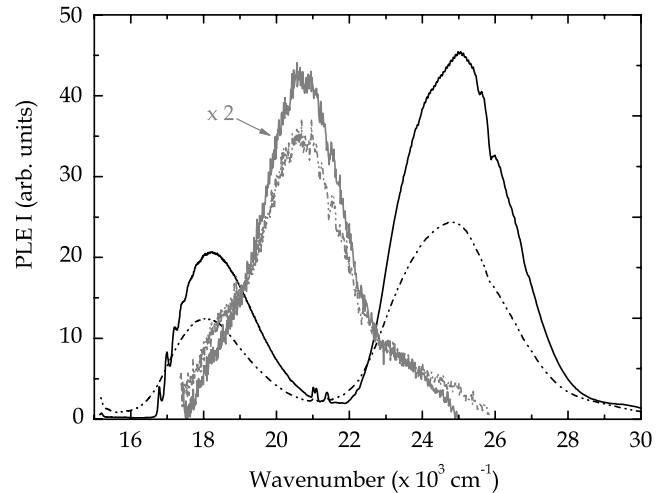


Figure 7. PLE spectra carried out on sample Z2 with a spectral resolution of 1 nm. The Cr^{3+} PLE spectra are reported as black lines (-3.2 K , $-\text{---}-300\text{ K}$), while the Ti^{3+} PLE spectra are shown by grey lines (-3.2 K , $-\text{---}-300\text{ K}$).

traps represents a competitive non-radiative process. In spite of these apparent drawbacks, RL studies are particularly useful in the case of samples like those considered in this work, since the signals related to Cr^{3+} and Ti^{3+} are detectable even at room temperature, due to the good luminescence yield of both these ions when present as impurities in corundum.

Last but not least, photoluminescence excitation spectra enable a helpful completion of the absorption data.

Typical RL spectra are reported in figure 6. The samples show, with different intensity, a RL emission spectrum in which the characteristic luminescence bands of Cr^{3+} (at $14\,300\text{ cm}^{-1}$) and of Ti^{3+} (at $13\,500\text{ cm}^{-1}$) [11] appear superimposed, but are easily distinguishable since the former is sharp and the latter broad.

The usual $14\,300\text{ cm}^{-1}$ emission of Cr^{3+} was not observed in the room temperature RL spectra of the synthetic samples, while at 10 K, the Ti^{3+} emission becomes narrower and the Cr^{3+} emission detectable. Incidentally, an emission peak is present at $11\,700\text{ cm}^{-1}$ (850 nm), the possible relation of which with Fe^{3+} is under careful consideration, particularly in yellow corundum.

Furthermore, it could be observed that in Z9 (curve 2 in figure 6) Cr^{3+} emission is predominant, while in synthetic sample (curves 3, 4 in figure 6) the Ti^{3+} emission is the most intense. Considering that the Cr^{3+} absorption peaks are well detectable for all samples while the ${}^2T_2 \rightarrow {}^2E$ transition of Ti^{3+} is barely observable, becoming evident only in the synthetic sapphires, it could be concluded that the capture cross section of the Ti^{3+} excited state is considerably greater than that of the Cr^{3+} one. In summary, in all the considered samples, both Cr^{3+} and Ti^{3+} are present as substitutional impurities and their emission bands are typical of isolated ions.

PL excitation spectra of the Cr^{3+} and Ti^{3+} emissions observed by RL are reported in figure 7. As can be observed, the excitation spectra of the Cr^{3+} and Ti^{3+} emissions are clearly distinct and quite similar to the absorption spectra of

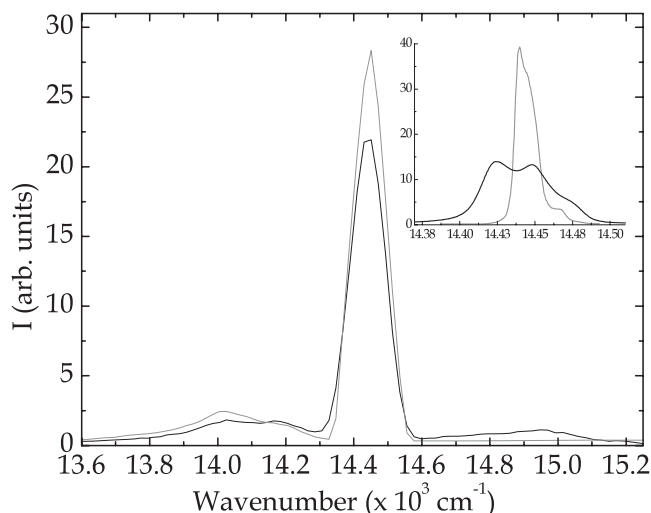


Figure 8. PL spectra for an excitation energy of $25\,000\text{ cm}^{-1}$ and a spectral resolution of 5 nm (-3.2 K , -300 K). In the inset the same spectra with a spectral resolution of 0.04 nm are shown.

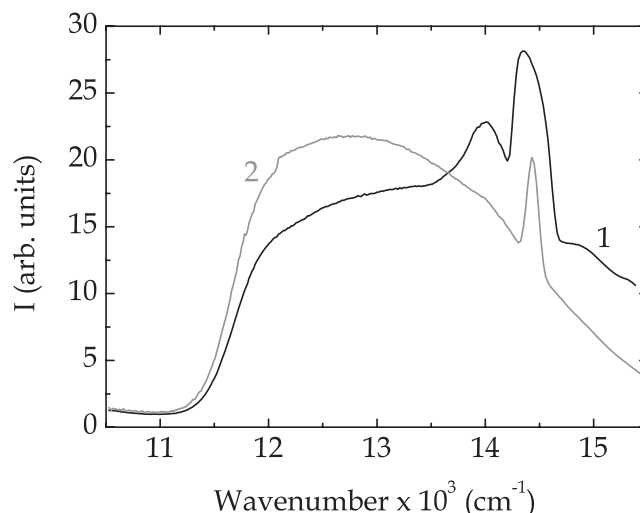


Figure 9. PL spectra at room temperature of samples Z2 (dark line labelled as 1) and Z11 (grey line labelled as 2) carried out with an excitation energy of $20\,000\text{ cm}^{-1}$ and a spectral resolution of 14 nm .

these ions (including the vibronic peaks, the 2T_2 narrow bands of the Cr^{3+} absorption spectrum and the splitting of the 2E of Ti^{3+}). This experimental evidence strongly supports the interpretation of the absorption spectra proposed above. Very similar PLE spectra were obtained for all the samples, the different intensities being due to the different concentration of the ions involved.

Figure 8 shows the PL spectra of Cr^{3+} , excited in a selective way. At room temperature, the usual $14\,300\text{ cm}^{-1}$ emission of Cr^{3+} , accompanied by phonon absorption and emission sidebands, was observed. At low temperatures, the phonon absorption sidebands disappear and, at higher resolution (see the inset in figure 8), the narrow peak reveals a complex and temperature-dependent structure.

As shown in figure 9, it is very difficult to obtain a completely selective excitation of Ti^{3+} , due to the strong overlap with 4T_2 of Cr^{3+} .

4. Conclusions

Type 1 blue sapphires of different origin were studied. Through the comparison of absorption, luminescence excitation and luminescence spectra we proposed an interpretation of the absorption bands present in the NIR and visible ranges which doesn't involve IVCT processes, frequently considered in the analysis of the important features of the blue sapphire absorption spectra. In particular, we confidently attributed the absorption band at $17\,500\text{ cm}^{-1}$ to the 4T_2 transition of Cr^{3+} and the absorption band at $24\,500\text{ cm}^{-1}$ to the 4T_1 of Cr^{3+} . Therefore, in spite of the interpretation currently given in most gemmology manuals, we concluded that chromium in its two valence states is the dominant chromophoric impurity in type 1 sapphires, while iron and titanium play a marginal role in the causes of sapphire colour.

We observed also that the Ti^{3+} emission at $13\,500\text{ cm}^{-1}$ correlates with peaks in the PLE spectra due to the Ti^{3+} absorption at $18\,000\text{--}21\,000\text{ cm}^{-1}$, overlapping the high energy tail of the $17\,500\text{ cm}^{-1}$ band.

Finally, we proposed the attribution of the $14\,500\text{ cm}^{-1}$ peak to the 5T_2 transitions of Cr^{2+} , (d^4) atomic configuration, by comparison with the absorption spectra of the $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ complex ion present in aqueous solutions and hydrated crystals.

Acknowledgments

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