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# Updating of the interpretation of the optical absorption and emission of Verneuil synthetic and natural metamorphic blue sapphire: the role of $V^{2+}$, $V^{3+}$ and $Cr^{2+}$

**V Palanza, N Chiodini, A Galli, R Lorenzi, F Moretti, A Paleari and G Spinolo[1]**

Department of Materials Science, University of Milano-Bicocca, Via Cozzi 53, Milano 20125, Italy

[1]E-mail: giorgio.spinolo@mater.unimib.it

**Abstract**. In the blue colored sapphires of metamorphic origin and Verneuil synthetic studied here, the absorption-emission properties in the VIS-NIR range are largely determined by $Cr^{3+}$ and $Ti^{3+}$, as we have been able to demonstrate recently. In that work a sharp radio-luminescence band occurring at 870 nm in Verneuil blue sapphires was left unattributed: here we give evidence for the attribution of that band to the $^2E$ emission transition of $V^{2+}$, and for the existence of such an emission also in natural samples of metamorphic origin. After such a result, we accurately evaluated by EDXRF the V concentrations in various samples and found the ion more ubiquitous than foreseen. We then searched for and found, weak but diagnostic spin forbidden transitions and phonon sequences in the absorption spectra of samples sufficiently rich in V. The experimental results just mentioned allowed us to discuss the effects of the overlap of $V^{3+}$ and $Cr^{3+}$ spin-allowed absorption bands on the spectrum of the varieties of corundum under study. To complete the updating of the interpretation, we spent a further effort to strengthen the attribution of the absorption band at 14500 cm$^{-1}$ (currently interpreted as an IVCT ($Fe^{2+} \rightarrow Fe^{3+}$)) to the $^5E \rightarrow ^5T_2$ transitions of $Cr^{2+}$.

## 1. Introduction

The current interpretation of the absorption spectrum (particularly in the 14 to 21000 cm$^{-1}$ interval) of blue sapphire, but also of many other minerals, heavily relies on the mechanism of intervalence charge transfer transition, IVCT, between adjacent impurity ions, typical examples being $Fe^{2+} \rightarrow Fe^{3+}$ and $Fe^{2+} \rightarrow Ti^{4+}$.

The early proposal by Weyl [1] although supported by essentially visual observations, gained wide success among mineralogists, but 36 years later Mattson and Rossmann [2] observed that: "Many of the uncertainties regarding the characteristics of the IVCT transitions are due to an inadequate data base of unambiguous examples and the lack of a suitable theoretical framework". In the Summary of that paper the authors concluded that "Many of the characteristic ascribed to charge transfer transitions

have not proven accurate or unique". Quite strangely, in the necessity of a clearly defined description of the theoretical model and of the phenomenology related to IVCT, luminescence experiments have not been performed, just to complete the picture, to know what occurs to the electron after being promoted to the excited state and after the lattice rearranges around the new charge distribution: in the very wide and detailed "Subject Index" of the important manual Mineralogical applications of Crystal Field Theory by R. Burns [3], the subjects luminescence and/or fluorescence are absent.

We recently [4] tried to overcome such lack of information and performed radio- and photo-luminescence experiments on a few Type 1[2] light blue sapphire samples of metamorphic origin and Verneuil synthetic. Exciting in the IVCT ($Fe^{2+} \rightarrow Fe^{3+}$; $Fe^{2+} \rightarrow Ti^{4+}$) absorption bands we obtained the well known emissions of $Cr^{3+}$ and $Ti^{3+}$, behaving as isolated ions. The combined information of absorption and emission spectroscopy allowed us to propose quite a relevant change in the commonly accepted interpretation of a few bands present in the NIR and visible range of the absorption spectrum of those low iron ($\approx 10^3$ ppm) corundums naturally or artificially doped. In substance, we did not make use of the IVCT transition scheme so widely adopted [3,7] in discussing the causes of color of blue sapphire but obtained strong experimental evidence of the role of $Cr^{3+}$ and $Ti^{3+}$ in determining the absorption spectrum of such a gem. Through the comparison of Type 1 sapphire absorption spectra with those of aqueous solutions containing $Cr(OH)_6^{2+}$ complex ions [8], we also attributed the absorption band at 14500 cm$^{-1}$, currently interpreted as an IVCT, to the $^5E \rightarrow ^5T_2$ transitions of $Cr^{2+}$, a $d^4$ ion.

Apart from the re-interpretation of the absorption spectra of the type of corundums under study, it obviously emerged a consideration of broader impact, in accordance with the remarks of the authors of ref. [2], on the validity of the IVCT mechanism. We then performed luminescence measurements on other minerals, specifically magmatic Type 2 blue sapphires and cordierite, exciting them in the IVCT region: the interpretation that we proposed in two papers now submitted for publication, has only to do with the presence of non interacting impurity ions of transition elements.

Let us now return to Type 1 sapphires. In that paper [4], a sharp peak (which later turned out to be a doublet) occurring at $\approx 11700$ cm$^{-1}$ in the radio-luminescence spectrum of a Verneuil sample was left without attribution.

We will show in the following that such emission is undoubtedly due to the $^2E \rightarrow ^4A_2$ transition of $V^{2+}$, a $d^3$ ion. We solved the problem after performing with great attention the Energy Disperse X-Ray Fluorescence (EDXRF) analysis on the set of samples just studied. Vanadium, as appears in Table 1 shown below, is rather ubiquitous also in natural samples, in concentrations low, but with measurable optical effects.

As a matter of fact, EPR and optical behavior of vanadium in artificially doped $Al_2O_3$ were well described in the physico-chemical literature [9,10,11]. After realizing that, we thought it reasonable to re-examine with greater attention the data on the set of samples just studied [4] and, for sake of comparison, on an intentionally vanadium doped Verneuil corundum. Luminescence of V is not very efficient, in comparison to that of $Cr^{3+}$, but clearly interpreted. The contribution of V to the absorption spectrum is not easy to evaluate quantitatively, as pointed out in the mineralogical literature [12,13], since the absorption of $V^{3+}$ and $Cr^{3+}$ strongly overlap. For reasons of completeness, we also re-considered the attribution of the band at 14500 cm$^{-1}$, proposed in ref. [4]: we here confirm the early suggestion after analyzing the evolution that undergoes, upon oxidation, the absorption spectrum of an aqueous solution containing $Cr(H_2O)^{2+}$ aquo-ions.

The new interpretation of Type 1 blue sapphire absorption spectra proposed in ref. [4] and completed here gives account of the presence of the various transition elements found in the EDXRF analysis, although in a semi-quantitative way, paying a tribute to the dishomogeneities of the available samples. A result that goes beyond the specific attribution, is that all the ions present in the crystals behave as "non interacting"; this is the simple, although substantial contribution of the present work.

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[2] Natural blue sapphires are classified according to the absence (Type 1) or to the presence (Type 2) of an absorption band located at 11500 cm$^{-1}$ and attributed to the $^5E$ spin-allowed transition of $Fe^{2+}$ [5,6].

## 2. Experimental

The sapphire samples studied here were cut from raw crystals, polished to optical grade and reduced in size obtaining to platelets 5x5 mm wide and 0.5 to 3 mm thick, according to the range of absorption coefficient to be explored. All samples were blue sapphires with exception of Z9 where two distinct colored regions were present: one pink and the other blue. Synthetic samples were prepared by flame fusion (Verneuil) process. The crystalline phase and homogeneity of both natural and synthetic samples was confirmed by Raman spectroscopic analysis. Their content of Ti, V, Cr, Fe, Ga was evaluated by quantitative EDXRF analysis, taking into account the matrix autoabsorption effects and the secondary excitation effects [14]: the results are shown in Table 1 together with the analogous data on few of the metamorphic and synthetic samples studied recently [4].

Samples of magmatic origin, although with a similar content of V were not considered since in those corundums the emission of V is undetectable, due to the overlap with the strong, characteristic $^5E$ absorption of $Fe^{2+}$.

**Table 1.** Quantitative EDXRF analysis, the values are given in ppm in weight.

| Sample | | Type | Provenance | Ti | V | Cr | Fe |
|---|---|---|---|---|---|---|---|
| **Z9** | **(rose)** | Mong-Hsu metamorphic | Vietnam | 940±28 | <15 | 1200±14 | 686±16 |
| | **(blue)** | | | 1852±35 | 13±4 | 746±17 | 518±17 |
| **Z2** | | Metamorphic | Sri-Lanka | 850±80 | 25±2 | 25±2 | 1230±12 |
| **Z6** | | Metamorphic | Sri-Lanka | 280±30 | 25±3 | 20±2 | 1475±150 |
| **Z10** | | Synthetic | Verneuil | 271±19 | 109±5 | <15 | 755±12 |
| **Z11** | | Synthetic | Verneuil | 898±24 | 124±4 | 44±10 | 1050±14 |
| **Z30** | | Synthetic | Verneuil | 2300±20 | 60±5 | 45±5 | 1800±20 |
| **ZV** | | Synthetic | Verneuil | <45 | 3090±16 | 147±16 | 80±17 |

Absorption spectra have been obtained by the aid of a Perkin-Elmer 950 Spectrophotometer in the NIR-Vis-UV range. Absorption spectra were taken down to about 20 K, the samples being clamped to the cold finger of a cryocooler Galileo, mod. K1. Radio-luminescence measurements were performed on a homemade apparatus: the X Ray generator was operated at 20 KV and 5 mA. The average time of exposition for obtaining a spectrum was of ≈30 sec and the dose ≈1 Gy. The detector (CCD Spectrum One 3000 by Jobin-Yvon) was effective in the 40000 to 9000 cm$^{-1}$ spectral range.

The comparison between absorption spectra recorded before and after the RL measurement did not reveal any detectable modification caused by X-ray irradiation. $CrCl_2$ used to prepare aqueous solutions were anhydrous powders (purity 99,99 %) by Sigma Aldrich and the oxidation was obtained by controlled addition of $H_2O_2$.

## 3. Results and discussion

### 3.1. Radio–luminescence and the role of $V^{2+}$

We show first in figure 1 the results on radio–luminescence of representative samples of natural metamorphic (Z2 and Z9), a blue synthetic Verneuil sapphire (Z11) and a heavily V doped synthetic corundum. $Ti^{3+}$ emission ($^2E \rightarrow ^2T_2$) is always present in relation to a rather relevant Ti concentration (with the exception of ZV, practically Ti-free). $Cr^{3+}$ emission ($^2E \rightarrow ^4A_2$) is present in Z9 and ZV and at the limit of detection in Z2 and Z11 (few dozens of ppm). $V^{2+}$ emission is at the limit of detection in Z2 and Z9 (10-20 ppm of V), clearly observable in Z11 and Z30 (not shown in the figure 1) and rather evident together with its phonon sidebands, in ZV. In the latter sample, there was enough intensity to allow narrowing of the slit width, and, at low temperature, with an improved resolution, the detection

of the doublet nature of the emission due to the downwards transition $^2E \rightarrow ^4A_2$ of $V^{2+}$. In the same conditions (low temperature), also the $Cr^{3+}$ emission in Z9 and Z11 and $V^{2+}$ emission in Z2 and Z9 are clearly observed.

Sturge [11] has given sound evidence that the absorption of Vanadium corundum is entirely due to $V^{3+}$ and the system does not show fluorescence. After heavy (100 MRad) irradiation sharp luminescence lines were observed and attributed to $V^{2+}$ ions, created by the ionizing radiation. The concentration of these ions was so weak, that an absorption spectrum could not be measured. In place of that, the excitation spectrum of the luminescence lines was obtained and interpreted in terms of the $d^3$ Tanabe-Sugano diagram.
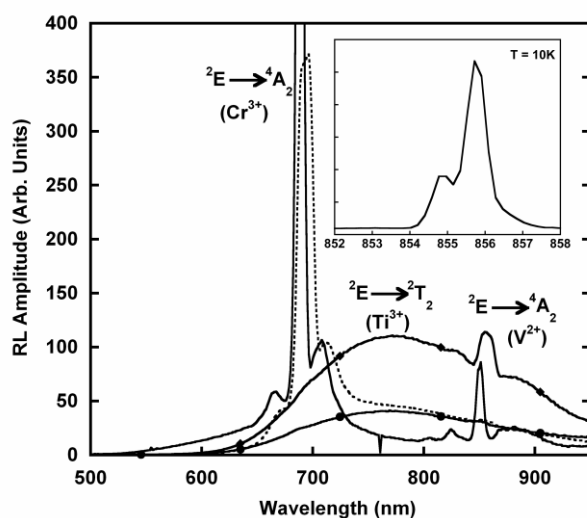


**Figure 1.** Radio-luminescence spectra at 300 K of: Z9 (dotted line), Z11 (black diamonds), Z2 (black circles), and ZV (full line). In the inset is shown, for sample ZV, the doublet nature of the emission of $V^{2+}$.

The $V^{2+}$ emission behavior appears very similar to that of the other two $d^3$ ions i.e. $Cr^{3+}$ and $Mn^{4+}$, phonon sidebands included, and so the experimental observations were explained with a high level of confidence. The energy position of our doublet coincides with that studied in ref. [11] and so we do not hesitate to give the same interpretation. In our case, during X-ray irradiation free electron and holes are created, $V^{3+}$ ions capture electrons, become temporarily excited $V^{2+}$, and then the electrons in the excited state of $V^{2+}$ decay with emission of a photon. However, we confirm the results of ref. [11] since the 488 nm line of the Argon ion laser did not excite the $V^{2+}$ emission in our samples.

*3.2. Optical absorption and the role of $V^{3+}$*

The absorption spectrum of vanadium (entirely $V^{3+}$) doped corundum is well known, including the vibrational structure and the polarization of the various bands [10,11]. Our synthetic ZV sample, in which vanadium is the dominant impurity, confirm literature data. In natural, Type 1 samples, V is present (see Table 1) in a concentration two orders of magnitude lower and, again, is entirely $V^{3+}$ ($d^4$): its absorption bands overlap the bands due to $Cr^{2+}$, $Cr^{3+}$ and $Ti^{3+}$ and, as a consequence, the analysis of the spectrum is not simple.

In order to have an insight in the complex absorption pattern, we chose the synthetic sample Z11 which has an absorption spectrum and composition similar to the natural samples Z2 and Z6 [4] but a concentration of vanadium quite higher and compare it with the spectrum of a natural bicolor blue-pink sample from Vietnam, Z9, richer in chromium, in figure 2a.

We chose to make this comparison because $Cr^{3+}$ and $V^{3+}$ having a spectrum similar in general shape and in energy position of the principal spin-allowed transitions the $^3T_2$ (17400 cm$^{-1}$) and $^3T_1$ (25000 cm$^{-1}$) of $V^{3+}$ and the $^4T_2$ (18100 cm$^{-1}$) and $^4T_1$ (24500 cm$^{-1}$) of $Cr^{3+}$ may generate some confusion in the specific attributions. However, in figure 2b we appreciate that in Z11 there is, from 15800 to 16800 cm$^{-1}$, the vibronic series typical of $^3T_2$ of $V^{3+}$ and in Z9 there is, from 16800 to 18000 cm$^{-1}$ the vibronic

series typical of the $^4T_2$ of $Cr^{3+}$; further, obviously, the broad bands on which these structures are superposed have different peaks, as pointed out just above. Another broad band is presenting the absorption spectrum, peaking at $\approx 14600$ cm$^{-1}$: this one will be discussed in the next sub-section.

The attributions given in [4] on Z2 and Z6 spectra shown in figure 4 of that paper, at this point, must be updated, also in consideration of the fact that chromium and vanadium are present in similar amounts: in Z2 and Z6 the band peaking at $\approx 17500$ cm$^{-1}$ is quite likely due to the superposition of $^3T_2$ of $V^{3+}$ and the $^4T_2$ of $Cr^{3+}$; the band peaking at $\approx 24500$ cm$^{-1}$ is quite likely due to the superposition of $^3T_1$ of $V^{3+}$ and the $^4T_1$ of $Cr^{3+}$. This analysis has already been proposed, although qualitatively, in ref. [12,13].
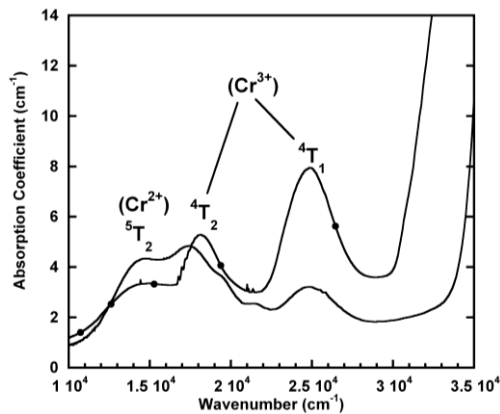


**Figure 2a.** Absorption spectra at 10 K of Z11 (full line), and Z9 (black circles) in a dark violet region of the sample.
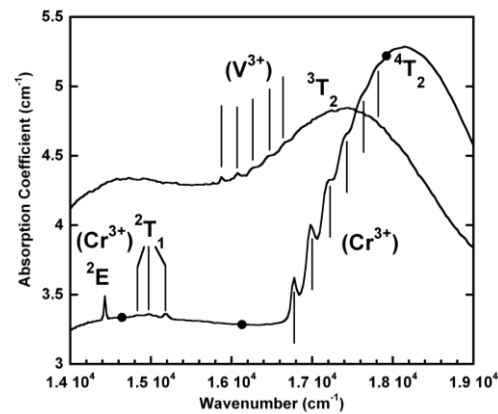
**Figure 2b.** Vibronic sequences characteristic of $V^{3+}$ and $Cr^{3+}$, in sample Z11 (full line), and Z9 (black circles).

In ref. [4], we had not yet perceived the role of vanadium and evaluated its concentration, and so we thought it safe to use the excitation spectrum of the chromium emission to give an attribution to the absorption peaks some of which were until then attributed to IVCT transitions. Another observation speaks in favor of a role for $V^{3+}$: in $Cr^{3+}$ the $^4T_1$ has an intensity greater than $^4T_2$ in both E⊥c and E‖c polarized light spectra; in $V^{3+}$ the $^3T_1$ has an intensity lower than $^3T_2$ in E⊥c polarized light spectra, the opposite occurring for E‖c spectra. The difference in intensity that we observe for the two $V^{3+}$-$Cr^{3+}$ mixed bands for Z11 in figure 2 (and Z2 and Z6 in figure 4 of [4]) may only be interpreted considering the effect of the presence of $V^{3+}$. In order to strengthen the argument, we chose a sample, Z30, with a V concentration similar to Z2 and Z6, rather low, so to make impossible the detection of the diagnostic vibronic sequence of narrow lines but with the optic axis in the plane of the slab, so to allow the measurement of E⊥c and E‖c spectra, shown in figure 3. Again, we see that the stronger intensity of the E⊥c band at $\approx 17600$ cm$^{-1}$ (respect to that at $\approx 24000$ cm$^{-1}$) may be interpreted as being due to a relevant contribution of the $^3T_2$ of $V^{3+}$. On the opposite, in figures 2a and 2b, the spectrum of sample Z9, shows what occurs when $Cr^{3+}$ is dominant: the $^2E$ and $^2T_1$, although weak, are observable; the vibronic series superposed to the $^4T_2$ is observable as well and the $^4T_2$ has an intensity lower than the $^4T_1$.
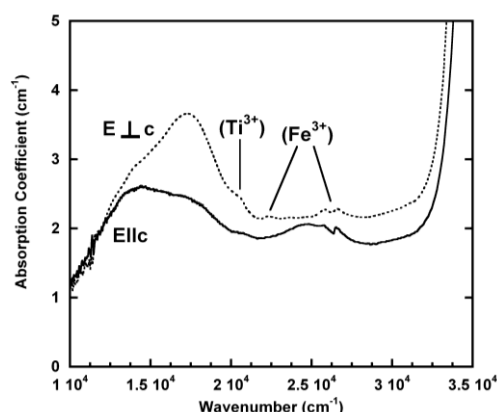
**Figure 3.** Absorption spectra of Z30: E‖c (dotted line), and E⊥c (full line).

### 3.3. Optical absorption and the role of $Cr^{2+}$

As just pointed out, in Fig 2a, in both Z9 and Z11 spectra, we observe a broad band peaking at ≈14600 cm$^{-1}$ that deserves a separate comment. In mineralogical literature such band is usually attributed to $Fe^{2+} \rightarrow Fe^{3+}$ IVCT. However other interpretations should be considered in these systems, since the attribution to $Fe^{2+} \rightarrow Fe^{3+}$ IVCT processes appears quite less grounded for these two samples. In fact, the absence of bands peaked at 11500 cm$^{-1}$ ($^5$E spin-allowed transition of $Fe^{2+}$) is a strong spectroscopic evidence that iron is present predominantly as $Fe^{3+}$ rather than $Fe^{2+}$. So, the probability of find couples of $Fe^{2+}/ Fe^{3+}$ ions able to give IVCT should be significantly lower than in the other samples. Thus, we considered other reasonable sources of color focusing our attention on the transition metal species detected by EDXRF (Table 1) and examining the different valence states of their cations. The spectral region of interest (13000-15000 cm$^{-1}$) is inconsistent with the absorption spectra of $Ti^{3+}$, the two valence states of iron $Fe^{2+}$ and $Fe^{3+}$, vanadium $V^{2+}$ and $V^{3+}$ and $Cr^{3+}$. On the other hand, $Cr^{2+}$ ions might give a contribution in this spectral region. Although this valence state is not the most stable for chromium, $Cr^{2+}$ can not be classified as an exotic ion. In fact $Cr^{2+}$ is responsible for the coloration of many minerals such as some forsterites [15,16], diopsides [17-19], spinels [20,21], gillespites [22] and chromites [23] and this configuration has been already studied in aqueous solutions [8]. This study is indeed able to give a clear preliminary indication of the main CF effects expected for divalent and trivalent chromium in octahedral coordination, even though it neglects the distortion effects occurring in the solid state, as far as the main terms of the CF intensity depends only on the type of ligand and its distance from the metal. As a matter of fact the 10 Dq separation for a fixed cation and ligand field symmetry varies according to the spectrochemical series in which, $O^{2-}$ and $H_2O$ ligands are contiguous [3], thus leading to a crystal field of similar intensity. Consequently the absorption spectra differences expected for $Cr^{2+}$ and $Cr^{3+}$ in corundum may be qualitatively analyzed on the basis of aqueous solution data. Since $Cr^{2+}$ aqueous solutions may be readily prepared and their nature and stability are confirmed by optical absorption, one may gradually oxidize $Cr^{2+}$ to $Cr^{3+}$ by adding the proper molar quantity of an oxidizing agent. In our case the results of this experiment are summarized in figure 4 where oxidation has been performed using $CrCl_2$ as starting salt and $H_2O_2$ as oxidizing agent and following the oxidation process from a solution containing chromium predominantly as $Cr^{2+}$ to a solution containing exclusively $Cr^{3+}$. It is worth to note that the initial and final solution absorption spectra are consistent with those reported in literature [8].

The peak of $^5T_2$ of $Cr^{2+}$ occurs at ≈14000 cm$^{-1}$. The intensity of the $^5T_2$ of $Cr^{2+}$ is about one third of that of the $^4T_2$ of $Cr^{3+}$; as a consequence, in the spectrum relative to the third oxidation step (taken as an example), although the concentration of the two ions, $Cr^{2+}$ and $Cr^3$, is rather balanced, the $^4T_2$ and $^4T_1$ of $Cr^{3+}$ give the most relevant contribution. Once more we remark that we do not pretend to give quantitative relevance to the aquo-ion model, but the observations we just made represent an important information useful to interpret the spectral features and the relative intensity contributions of the

different valence states in which chromium may be present inside an octahedron of oxygens, an obvious example being the spectrum of the bicolor blue-pink sample from Vietnam of figure 2a.
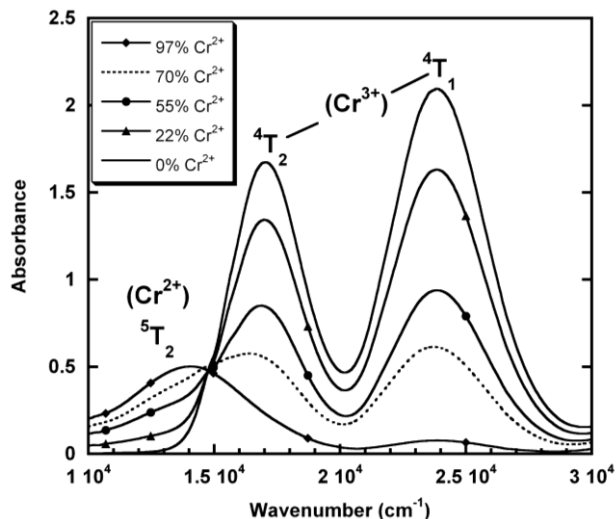


**Figure 4.** Absorption spectra of the oxidation steps sequence of an initially $Cr^{2+}$ aqueous solution. In the inset is indicated the correspondence spectrum $Cr^{2+}$ concentration.

## 4. Conclusions

Since twenty years, also inside the mineralogists community, the IVCT model was criticized [2] because there was an "inadequate data base of unambiguous examples and of theoretical framework". The situation has not changed, and still the model is the currently used frame to interpret the optical absorption spectra of many minerals, beginning from sapphire.

The luminescence studies carried on recently [4] and in the present work, coupled with accurate EDXRF analysis and low temperature absorption spectra allow a rather detailed the re-interpretation of the absorption spectra of a class of sapphires, that involves the role of impurity ions not considered up to now and behaving as non-interacting-ions, as the standard crystal field theory provides. Apart from the details of the re-interpretation, that we consider rather convincing, it obviously emerges a consideration of broader impact, in accordance with the remarks of the authors of ref. [2], on the reliability of the IVCT mechanism.

Last but not least, we want to underline the methodological contribution, the importance of matching data coming from different techniques, in order to reach a reasonably complete description of the impurity related properties of a crystal.

## Acknowledgments

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