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Absorption and emission spectroscopy in natural and synthetic corundum

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In the frame of an extensive project on the optical characterization of the many varieties of corundum (see:www.gemdata.mater.unimib.it) we reconsidered the current interpretation of the absorption spectra with particular attention to the bands attributed to the IVCT mechanism
$Fe^{2+} \rightarrow Fe^{3+}$ and $Fe^{2+} \rightarrow Ti^{4+}$.
A detailed study was devoted to natural metamorphic and Verneuil synthetic pale blue sapphires .
In that paper (I.Fontana et al 2008) we gave experimental evidence that the band at 17500 cm-1 often attributed to $Fe^{2+} \rightarrow Ti^{4+}$ IVCT transitions is in reality due to the 4T2 crystal field transition of Cr^{3+} partially overlapped by the 2E of Ti^{3+}. The results of radio and photoluminescence excitation experiments obtained there, led us to propose that the color of these sapphires is mainly due to Cr in its two valence states ; Ti 3+ and Fe^{3+} have a minor role.
After those encouraging results, we decided to apply the same approach to the study of deep blue and yellow sapphires of magmatic origin. Evaluation of impurity ion concentration by EDXRF revealed that in all these samples the concentration of Fe is quite high (around 1%) while Cr and Ti are barely detectable.
Characteristic of the absorption spectra of deep blue samples is the dominant presence of the 5E spin allowed transition of Fe^{2+}; Fe^{3+} has a minor role due to the fact that all d5 transitions are spin forbidden and ,consequently, very weak. In yellow sapphires Fe is totally in its 3+ valence state.
In these cases, the color from yellow to blue, sometimes even within the same sample, depends. on oxidizing or reducing growth conditions.
Even if the concentrations of Cr and Ti are very low, their characteristic emissions are the only ones observable down to 10000 cm-1 in radio and photoluminescence spectra. This piece of evidence suggested us to propose for the absorption bands present in the 14000 to 21000 cm-1 range, often attributed to IVCT, the same attribution given to the analogous bands in metamorphic sapphires absorption spectra.
In conclusion, both for metamorphic, synthetic and magmatic sapphires we reached a quite complete interpretation of the spectroscopic data in terms of “non interacting impurity ions”.
Orange, purple and green sapphires absorption spectra may also be discussed in terms of such interpretative approach.

References

Fontana I, LeDonne A, Palanza V, Binetti S and Spinolo G (2008) Optical spectroscopy study of type 1 natural and synthetic sapphires. J. Phys:Condens.Matter 20:125228-125232