

## Are Oxygen vacancies at the origin of orange luminescence of corundum?

MAXENCE VIGIER<sup>1</sup> AND EMMANUEL FRITSCH<sup>2</sup>

<sup>1</sup>Institut des Matériaux Jean Rouxel - Arc International

<sup>2</sup>Institut des Matériaux Jean Rouxel UMR6502

Presenting Author: maxence.vigier@cnrns-immn.fr

There are three main colors of luminescence in corundum ( $\text{Al}_2\text{O}_3$ ). First, the well-known red luminescence of  $\text{Cr}^{3+}$ , second, the blue luminescence related to titanium and, third, the orange one which is the subject of this work. There are few discussions of the origin of this orange emission in corundum, except that it is believed to be related to a hole center. We characterized about 50 samples of mostly natural corundum from five different localities, synthetics and Be-diffused gems, using classical gemology, LA-ICP-MS, EPR and luminescence spectroscopies.

Chemical analysis revealed relatively pure corundum, with a low concentration of iron and high concentration of divalent cation (mostly  $\text{Mg}^{2+}$ ) compared to other, non-luminescent corundum. The Fe vs Ga/Mg ratio indicates always a metamorphic origin.

The orange luminescence is associated with a broad emission band (about 200 nm FWHM) centered between 610 and 630 nm. The luminescence decay time is about 1-10  $\mu\text{s}$ . Heating at about 1273 K does not influence the emission or excitation. The excitation spectrum associated with this luminescence revealed always the same absorptions, in different relative proportions, located at about 253, 315, 353, 415, 485 and 563 nm. Physics literature associates these absorption/excitation bands with a family of defects called the F-centers (i.e. oxygen vacancies for corundum). These defects are known to be common in many oxides. These centers may accommodate the charge imbalance due to the presence of divalent cations, as detected in LA-ICP-MS. Unfortunately, in ESR, due to the everpresent signal of  $\text{Cr}^{3+}$ , F-centers cannot be visible. Nevertheless, all our results point consistently to attribute orange emission to  $F_2$ -centers related to divalent cations that is two oxygen vacancies coupled most likely to two  $\text{Mg}^{2+}$ . Most of the excitation is caused by F-centers as well, but occasionally excitation energy is transmitted through  $\text{Cr}^{3+}$ ,  $\text{V}^{3+}$  and even rarely  $\text{Mn}^{4+}$ .