Orientation dependence of REE\textsuperscript{3+} photoluminescence spectra and a possible artefact

Reissner, C., Lenz, C.*, Nasdala, L.

Institut für Mineralogie und Kristallographie, Universität Wien, Althanstraße 14, 1090 Wien, Austria
*e-mail: christoph.lenz@univie.ac.at

Quantifications of rare earth elements (REEs) from emission intensities have been proposed for several minerals (Barbarand & Pagel 2001; Habermann 2002; MacRea et al. 2012). A potential semi-quantitative estimation of trace elements via luminescence intensity requires to consider and maintain a broad range of carefully calibrated conditions, including reliable standard materials, system stability, and system response (Cesbron et al. 1995, Barbarand and Pagel 2001). Even though being a well-known luminescence phenomenon (Owen et al. 1998; Barbarand and Pagel 2001; Finch et al. 2003), the orientation-dependence of REE\textsuperscript{3+} emissions is often neglected, which may result in biased conclusions.

As an example, we have studied the orientation-dependence of the photoluminescence (PL) emission of trace Nd\textsuperscript{3+} (\(4F_{3/2} \rightarrow 4I_{9/2}\) electronic transition) in synthetic xenotime–(Y). Our results reconfirm that the emission intensity depends strongly on the direction of the emitted light being analysed. Especially in PL, the intensities observed are further affected by the polarisation of the incident laser beam. Figure 1 demonstrates effects of the orientation of electric field vector (\(E\)) relative to crystallographic directions. First, changing the polarisation direction of the laser beam causes the intensity of the luminescence bands to vary appreciably (Fig. 1a). Second, by placing a polarisation filter in the emission pathway it can be demonstrated that the luminescence emission itself is polarised (Fig. 1b). To avoid potentially biased interpretations, such effects need to be considered in discussing PL intensities.

![Figure 1](image)

Fig. 1. Orientation-dependence of the laser-induced PL (532 nm excitation) of Nd\textsuperscript{3+} (\(4F_{3/2} \rightarrow 4I_{9/2}\)) in synthetic Nd\textsuperscript{3+}-doped YPO\textsubscript{4} (xenotime; I\textsubscript{4}1/amd). Two examples are presented for how the polarization of the incident laser beam (a) and the polarization of the emitted light analysed (b) affect intensities. Experimental geometries are reported using the so-called Porto notation (Damen et al. 1966).
Fig. 2. Photoluminescence emissions of Nd$^{3+}$ ($^{4}F_{3/2} \rightarrow ^{4}I_{9/2}$) in synthetic Nd-doped, xenotime-structured YPO$_4$ (532 nm excitation). Spectra were obtained without polarisation filter and 1800 lines/mm grid.

In addition to the orientation dependence described above, we noticed a hitherto unrecognised possible artefact that is caused by the grating in the optical pathway. The intensity ratios of Nd$^{3+}$ luminescence emission bands near 880 nm wavelength vary appreciably, depending on the grating used. The pairs of spectra shown in Figs. 1a and 2 were obtained under identical geometries and conditions (same Horiba LabRAM–HR800 spectrometer, objective, laser power, accumulation time, measurement point, etc.), however with different gratings. The spectra pair shown in Fig. 1a was recorded with a grating with 600 lines/mm whereas a grating with 1800 lines/mm was used for the spectra pair shown in Fig. 2. Most remarkably, spectra obtained with the 600 lines/mm grid and an analyser in the optical pathway (Fig. 1b) are very similar to spectra observed with the 1800 lines/mm grid but without any analyser. This observation may indicate that the 1800 lines/mm grating acts similar to a polariser, perhaps due to high refracting angles in the near-infrared spectral range.

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References: