Laser-induced time-resolved luminescence spectroscopy of minerals: a powerful tool for studying the nature of emission centres

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Most of emission spectra of minerals present overlapping features of several types of luminescence centres. However, luminescence lifetime, which is a measure of the transition probability from the emitting level, is a characteristic and unique property. The best way for a combination of the spectral and temporal nature of the emission can be determined by laser-induced time-resolved spectroscopy. The method involves recording of the emission only during a specific time "window" that begins either with the end of the pulse or at a certain point of time afterwards (Gaft et al. 2005).

The following spectroscopic parameters have to be defined for the identification of emission centres nature: time-resolved luminescence and excitation spectra, optical absorption spectrum, and decay time. Those parameters and their behaviour with temperature enable to propose potential luminescence centres provided their spectroscopic behaviour corresponds to what has been observed experimentally. In the next step, one has to consider the crystallochemical probability of those centres presence in specific mineral as intrinsic element or impurity which substitutes the intrinsic cations (Gorobets and Rorojine 2001). Additional confirmation can be obtained by studying the artificial analogue of the respective mineral either using the nominally pure compound or analysing specifically doped crystals. The correlation of the observation of the specific luminescence with particular impurity concentration may indicate the source of the emission but it is not proof of the origin, and can sometimes be misleading. Nevertheless, it may be useful and laser-induced breakdown spectroscopy (LIBS) could be used to found it. The main objective of the paper is to summarize the new luminescence spectroscopy data for minerals. Besides well-established luminescence centres, several others are proposed, such as Mn^{3+}, Mn^{4+}, V^{2+}, Ni^{2+}, Pb^{+}, Mn^{3+}, Sb^{3+}, and Tl^{+}. Detailed information on the underlying interpretations may be found in the corresponding original papers quoted.

Figure a presents luminescence spectra of green sillimanite Al_2SiO_5 obtained at 100 K. A broad red band was ascribed to Cr^{3+} luminescence in a weak crystal field and confirmed in a study of synthetic sillimanite activated by Cr (Gaft et al. 2012). Figure b presents luminescence spectra of orange Mn-bearing kyanite Al_2SiO_5 where the narrow lines at 679.3, 694.7, and 697.0 nm were ascribed to Mn^{4+} (Gaft et al. 2011). Several narrow lines in time-resolved luminescence spectra of grossular and sillimanite were also ascribed to Mn^{4+} (Gaft et al. 2013; Gaft et al. 2012). The broad asymmetric band peaking at 719 nm (Fig. c) with two broad excitation maxima at 455 and 615 nm in grossular was ascribed to V^{2+} (Gaft et al. 2013), the same as the lines peaking at 702.2, 707.5, and 716.1 nm in sillimanite (Gaft et al. 2012). Emissions related to Mn^{3+} were found in the Mexico grossular (Fig. d) (Gaft et al. 2013) and in orange Mn-kyanite (Gaft et al., 2011). Emission related to Ni^{2+} was found in grossular, peaking at 685 nm and having a short decay time of 6.6 µs (Fig. e) (Gaft et al. 2013). Infrared emission related to Pb^{+} was detected in potassium feldspar with elevated Pb concentration (Kusnetsov and Tarashchan 1988; Erfurt 2003). The decay times determined in our study confirm the assignment to Pb^{+} (Fig. f).

One variety of calcite is characterized by intense blue emission under short-wave UV lamp excitation with an extremely long decay time, accompanied by pink-orange luminescence under long-wave UV excitation with very short decay time. This calcite contains negligible quantities of impurities, which may be connected to such luminescence, and it was concluded that both luminescence bands are radiation-induced (Gaft et al. 2008).

It was confirmed that the broad yellow luminescence band in zircon is radiation induced (Nasdala et al. 2011). Similar results were presented recently for the yellowish green defect luminescence of He-irradiated and subsequently heated diamond (Nasdala et al. 2013).

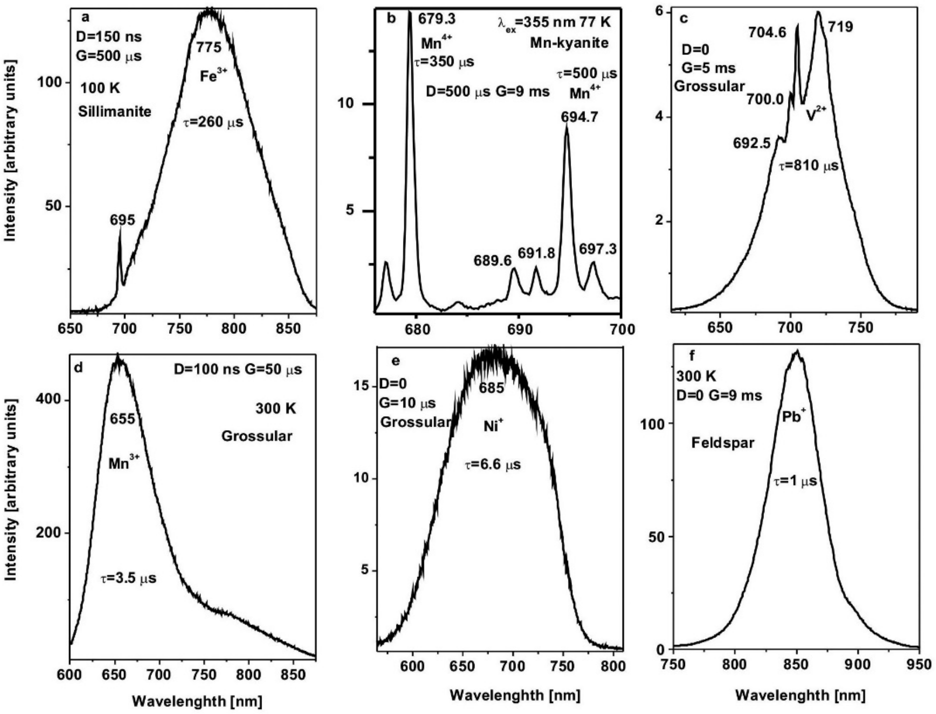

Fig. 1. *Time resolved luminescence spectra of sillimanite (**a**), kyanite (**b**), grossular garnet (**c–e**), and K-feldspar (**f**).*

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