Excitonic and Electron-Hole Excitation Mechanisms of Impurity Centres in MgO:Cr\textsuperscript{3+} and MgO:Ca\textsuperscript{2+} Crystals

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Close-packed fcc MgO crystals have found various applications. In the bulk of highly pure MgO crystals with a wide energy gap and valence band ($E_g = 7.783$ eV, $E_v = 7–8$ eV), electrons (e), holes (h) and excitons ($e_0$) possess high mobility and do not undergo transformation into the self-trapped state. However, even MgO crystals, grown by the arc-fusion method (~3100 K) from 5N purity salt, contain some amount of impurities (0.02–2 ppm), which can be detected by sensitive luminescent methods. Thus Cr\textsuperscript{3+} serve as impurity luminescence centres, while Ca\textsuperscript{2+} manifest themselves in radiative and non-radiative decay of near-impurity-localized electronic excitations.

The excitation spectra of Cr\textsuperscript{3+}-emission in the region of direct excitation of impurity centres were studied long ago [1]. Figure 1 shows a well-known spectrum of the imaginary part of dielectric constant $\varepsilon_2$ [2]. The formation of hydrogen-like excitons with $n = 1, 2, 3$ occurs in the energy region below $E_g$. The edge emission of free excitons revealed in the cathodoluminescence spectrum by Feldbach and Kuusmann is shown as well. According to EPR measurements, the concentration of Cr\textsuperscript{3+} ions in our MgO samples does not exceed 5 ppm. The emission spectra of Cr\textsuperscript{3+} centres have been measured by a nitrogen cooled CCD detector at the excitation of MgO by synchrotron radiation (the SUPERLUMI station of HASYLAB) selectively forming $e_0$ in different states (some of these spectra are shown in Fig. 2). The shape of all spectra practically coincides with that measured at the excitation by photons of $h\nu = 7.69$ eV, which form the lowest singlet excitonic state. At 9 K, excitons migrate over a vast distance, meet with Cr\textsuperscript{3+} centres in cubic and tetragonal configurations and transfer the energy to these centres. The luminescence of Cr\textsuperscript{3+} is also detected at the formation of separated e and h by photons of 8 eV (Fig. 2), 10.5 and 16.7 eV. A part of highly mobile holes reaches the surface and becomes localized there.

The low-temperature irradiation of the MgO single crystals containing purposely introduced impurity hole traps with photons of $h\nu > E_g$, X-rays or an electron beam causes the formation of e-h pairs. Highly mobile valence holes undergo rapid localization near dominant hole trapping centres, while conduction electrons lose their energy excess down to the bottom of the band via fast vibronic relaxation. Thereupon totally relaxed e mainly recombined with the trapped holes. Using the EPR method it was shown that Be\textsuperscript{2+} impurity ions substitute for Mg\textsuperscript{2+} cations and serve as efficient hole traps in MgO:Be\textsuperscript{2+} [3]. After hole trapping, the [hBe]\textsuperscript{+} centre with an effective positive charge is
formed. These \([h\text{Be}]^+\) centres are stable up to 195 K [4]. At low temperature, the luminescence at \(~6.2\text{ eV}\) arises at the recombination of free \(e\) with \([h\text{Be}]^+\) trapped-hole centres (see, e.g., [4]).

The broadband emission with the maximum at \(~6.9\text{ eV}\) was detected long ago in nominally pure MgO crystals and assigned presumably by several authors to the luminescence of self-trapped excitons. However, it was shown later that the intensity of this emission sharply increases in MgO:Ca\(^{2+}\) crystals parallel to the rise of Ca\(^{2+}\) concentration up to 200 ppm [5]. In addition, a quasiline emission at \(~7.65\text{ eV}\) was revealed, while the emission of free excitons (7.68–7.70 eV) was suppressed. So, it was suggested that the \(~6.9\text{ V}\) emission is caused by the recombination of conduction electrons with the holes, localized nearby Ca\(^{2+}\) impurity ions substituted for Mg\(^{2+}\) (\([h\text{Ca}]^+\) trapped-hole centres). The thermal stability of \([h\text{Ca}]^+\) remained unclear. Figure 3 shows the temperature dependences of the luminescence intensity measured for the quasiline emission at 7.65 eV and broadband emission at \(~6.8\text{ eV}\) (bandwidth of \(~0.8\text{ eV}\), measurement was performed at 7.1 eV) at the steady excitation of MgO:Ca\(^{2+}\) by 25 eV photons, which selectively forms separated \(e\) and \(h\). The thermal quenching of the emissions starts above \(~40\text{ K}\) and the intensities are decreased by half at about 50 K. The thermal release of the holes from \([h\text{Ca}]^+\) centres leads to the appearance of mobile \(h\), their partial retrapping by deeper traps or the recombination with the electrons still localized at some traps (tentatively at bivacancies). The latter process leads to a broadband recombination luminescence with the maximum at \(~2.9\text{ eV}\), which was also detected at the delocalization of \(h\) from \([h\text{Be}]^+\) trapped-hole centres in MgO:Be\(^{2+}\) (see, e.g., [4]). The 48 K peak of thermally stimulated luminescence (TSL) is dominant just for 2.9 eV emission in MgO:Ca\(^{2+}\) irradiated by X-rays at 6 K (see Fig. 3).

It is worth noting that \([h\text{Be}]^+\) and \([h\text{Ca}]^+\) centres possess a dipole momentum and a Coulomb charge and can efficiently participate at non-radiative recombination with either totally relaxed or hot conduction electrons. "Hot" recombinations are especially important under the irradiation forming extremely high density of \(e-h\) pairs. The energy released via this hot recombination is sufficient for the creation of Frenkel defects in the vicinity of impurity hole centres.

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References