Luminescence and Radiation Defects in Electron-Irradiated Al$_2$O$_3$ and Al$_2$O$_3$:Cr

A. Lushchik, V.N. Makhov$^1$, E. Aleksanyan$^2$, V.V. Harutunyan$^2$, M. Kirm, A. Kotlov, V. Nagirnyi, and S. Vielhauer

Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia

$^1$P.N. Lebedev Physical Institute, Leninskii Prospect 53, 119991 Moscow, Russia

$^2$Yerevan Physics Institute, Alikhanian Brothers Str. 2, 375036 Yerevan, Armenia

In the present work, the low-temperature (~9 K) emission (1.6-9.0 eV) and excitation (3.75-20 eV) spectra of Al$_2$O$_3$ single crystals doped with Cr$^{3+}$ (~500 ppm) (ruby), non-irradiated and irradiated by 50-MeV electrons (up to fluences of $2\times10^{17}$ e/cm$^2$), have been studied and compared with the luminescence properties of 50 MeV-electron-irradiated undoped Al$_2$O$_3$. Special attention was paid to the idea of luminescent protection against non-impact mechanisms of radiation defect creation in wide-gap materials, which has recently been considered [1]. At 300 K, the 50-MeV electrons create F and F$^+$ centers in Al$_2$O$_3$ both by impact (knock-out) and non-impact (via decay of electronic excitations) mechanisms. It is supposed that direct energy transfer by hot electrons or hot holes to luminescent impurity centers in wide-gap materials can drastically decrease the efficiency of hot recombinations of electrons with holes, thus, serving as “luminescent protection” against the non-impact mechanisms. The present study continues the analysis of the prospects of increasing the radiation resistance of $\alpha$-Al$_2$O$_3$ crystals.

The measurements have been performed at the SUPERLUMI set-up. The emission and excitation spectra were recorded with a 0.3 m Czerny-Turner-type monochromator-spectrograph SpectraPro-308i equipped with a R6358P (Hamamatsu) PMT. Discrimination between the fast and slow emissions was achieved by measuring signals within the “short” and “long” time windows ($\Delta t$) delayed (by $\delta t$) with respect to excitation pulses of synchrotron radiation.

The emission spectra of both non-irradiated and electron-irradiated ruby crystals in the red spectral region show well-known narrow emission lines (so-called R-lines) around 1.79 eV, which are due to transitions from the lowest excited state $^2E$ to the ground state $^4A_2$ of Cr$^{3+}$. In the excitation spectra of Cr$^{3+}$ red emission (Fig.1) the weak bands in the low-energy part correspond to the transitions in Cr$^{3+}$ $^4A_2$ – $^4T_{1,2}(^4F)$ (<3.7 eV) and $^4A_2$ – $^4T_1(^4P)$ (4.84 eV), whereas the strong increase of emission intensity at $h\nu$ > 6 eV is related to charge-transfer transitions O$^{2-}$ - Cr$^{3+}$.

The self-shrunk exciton emission at 7.6 eV, which is observed in undoped Al$_2$O$_3$ under photoexcitation [2], was not detected in the studied ruby crystals. The probable reason for its strong suppression in ruby is an efficient energy transfer to Cr$^{3+}$ ions since the emission at 7.6 eV overlaps with strong absorption of Cr$^{3+}$ (due to charge-transfer transitions).

For the electron-irradiated ruby crystals, the band at 3.8 eV, which is due to radiative decay of F$^+$ centers, dominates in the emission spectrum in the blue/UV spectral range (Fig.2). Three intense bands at 4.84, 5.39 and 5.96 eV in the excitation spectrum of the 3.8 eV emission (Fig.1) belong to the intra-center excitation of F$^-$-centers. The decay time of F$^-$ center emission was found to be $\tau = 2.0\pm0.1$ ns, independent of the fluence value. Generally, our results on F$^-$ center emission in Al$_2$O$_3$:Cr are in good agreement with those obtained earlier for pure Al$_2$O$_3$ [3].

The emission of F centers peaking at 3.0 eV is also observed from irradiated Al$_2$O$_3$ crystals but its intensity is at least 20 times lower than that of F$^-$ centers. The weak emission of F$^-$ and F centers (with a comparable intensity) can be seen also in the spectrum of non-irradiated ruby crystal, but the intensity of these emissions is about two orders of magnitude lower than that of F$^-$ center emission from the crystal irradiated with the fluence of $2\times10^{17}$ e/cm$^2$. The much weaker intensity of F center emission compared to the intensity of F$^-$ center emission in irradiated ruby can be explained by a much lower concentration of F centers compared to that of F$^+$ centers created in 50-MeV-electron-irradiated ruby.
The band at 5.96 eV in the excitation spectrum of F\(^+\) emission overlaps with the main absorption band of F centers at 6.05 eV, i.e. excitation at 5.96 eV results in intracenter excitation of both F\(^+\) and F centers. In pure irradiated Al\(_2\)O\(_3\), the emission intensity of F centers is much stronger than that of F\(^+\) centers under excitation by 5.96 eV photons, in contrast to irradiated ruby where the ratio of emission intensities for F and F\(^+\) centers is opposite. However, the integrated intensity of emission in both bands is of the same order for these two kinds of crystals. Anyway, we can conclude that a part of the energy absorbed by Al\(_2\)O\(_3\):Cr during irradiation is not spent for F-center formation, but is transferred to impurity centers.

Hence, doping of Al\(_2\)O\(_3\) with Cr\(^{3+}\) can be considered as some kind of luminescent protection against defect creation. Generally, it is supposed that defect creation in oxides, such as Al\(_2\)O\(_3\), which are resistant against low-density irradiation, can be strongly suppressed by doping because of direct impact excitation of impurity ions by hot photocarriers that decreases the efficiency of defect creation due to the recombination of hot electrons and holes [1]. Nevertheless, there is not enough data obtained so far for a detailed analysis of the doping influence on non-impact mechanisms of defect creation in Al\(_2\)O\(_3\). Thus, additional studies are needed in order to find out the exact mechanisms of lowering the efficiency of F-center creation in ruby compared to undoped Al\(_2\)O\(_3\). In particular, another possible processes of decreasing the efficiency of F centers creation should also be considered, e.g. the lower efficiency of electrons capture by the as-grown oxygen vacancies always available in oxygen deficient Al\(_2\)O\(_3\) because of a competing capture of carriers by Cr\(^{3+}\) ions, or transformation of F centers into F\(^+\) centers with a participation of Cr\(^{3+}\) ions.

This work was supported by Estonian Science Foundation (Grant No. 6652) and the European Community Research Infrastructure Action within the FP6 Program through the Contract RI3-CT-2004-506008 (IA-SFS).

References