

Luminescence and Radiation Defects in Irradiated Ruby

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Abstract. *The excitations of luminescence in irradiated and non-irradiated ruby crystals are investigated by means of highly polarized synchrotron radiation. In the VUV luminescence spectra the existence of quick and slow emission was observed in irradiated and non-irradiated crystals. The luminescence bands with maximum at 3.8 eV are produced by F^+ centers. A new type of quick luminescence was established for the band at 4.6 eV. It is called cross-luminescence and is connected with the recombination of valence band electrons with holes in low-lying core levels. It is shown that the band at 3.0 eV is not due to anionic centers (F^- centers), but is determined by a short lifetime emission center.*

Key words: irradiated ruby, emission spectrum, luminescence, excitation band.

I. INTRODUCTION

Spectroscopic investigations in the ultraviolet (UV) and vacuum ultraviolet (VUV) regions are one of the basic methods to obtain information about the electron structure of wide-band ionic crystals, e.g. corundum crystals (α - Al_2O_3) [1,2].

The wide-band ionic corundum (ruby) is of great interest because of its application as optical materials in UV-VUV regions as well as luminescence materials, such as scintillates for ion emission detectors, luminophors for memory cells, laser active media, materials for radiation defense. The development of radiation technologies needs materials that are stable with respect to high-energy particles (electrons, protons, neutrons, ions, γ -quanta, synchrotron radiation (SR)).

II. EXPERIMENTAL AND DISCUSSION

Low temperature (~ 9 K) emission (200...800 nm) and excitation (60...330 nm) spectra of Al_2O_3 single crystals doped with Cr^{3+} (0.1%), non-irradiated and irradiated by 50 MeV electrons with fluencies of $6 \cdot 10^{16}$ and $2 \cdot 10^{17}$ e/cm², have been measured at the SUPERLUMI station of HASYLAB at DESY (Hamburg) using synchrotron radiation from the DORIS storage ring.

The investigations have shown that in the fundamental absorption region of the luminescence excitation (LE) spectra one can see clearly pronounced relatively narrow bands in irradiated and non-irradiated corundum crystals (ruby). The investigated samples were grown by horizontally oriented crystallization.

Some bands in the LE spectra up to the fundamental absorption edge correlate well (to within the experimental error of 0.1 eV) with the absorption spectrum [3, 4].

Emission spectrum of non-irradiated ruby shows well-known narrow emission lines near 700 nm, which are due to radiative transitions from the lowest excited state 2E to the ground state 4A_2 of Cr^{3+} . The so-called R_1 , R_2 and N_2 narrow lines as well as a broader vibronic structure at the long-wavelength side of these lines can be well seen in the spectra [3]. Excitation spectrum of this emission shows relatively weak maximum at ~ 4.84 eV overlapped with a tail of the lower-energy (< 3.7 eV) band, a threshold of strong increase of intensity at ~ 6.0 eV, some broad structure in the range of 6.5...11.5 eV with a sharp but rather weak peak near 9.0 eV, the drop of intensity at $h\nu > 11.5$ eV, and relatively low-intense emission in the energy range above 13 eV. The weak excitation bands in the low-energy part of the spectrum correspond to parity-forbidden but spin-allowed transitions in Cr^{3+} ${}^4A_2 - {}^4T_1({}^4F)$ (< 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 the edge of parity-allowed charge-transfer transitions $\text{O}^{2-} - \text{Cr}^{3+}$. The photon energy ~ 9 eV corresponds to the edge of intrinsic absorption of the host, and the presence of some sharp structure in this region can be expected because of the combined effect of strong increase of absorption coefficient and near-surface non-radiative losses. The region between 9 and 11.5 eV contains zones of excitonic absorption of Al_2O_3 (8.8 eV $< h\nu < 9.4$ eV) and band-to-band transitions ($E_g = 9.4$ eV), but within the region of 9.4 eV $< h\nu < 11.5$ eV the electrons and holes created in a pair are closely spaced and recombine preferably at the same recombination center. The efficiency of excitation of Cr^{3+} emission is high in this region and decreases remarkably (but is still high enough) in the region of the creation of separated electron-hole pairs ($h\nu > 11.5$ eV). Emission and excitation spectra related to Cr^{3+} luminescence are very similar for non-irradiated and electron-irradiated crystals. Some increase of Cr^{3+} luminescence intensity observed for irradiated samples is most probably due to "geometrical" reasons. The only difference observed in the excitation spectra is the long-wavelength shift of the position of the sharp peak near 9 eV (by more than 0.05 eV for heavily irradiated sample compared to the non-irradiated one).

For the electron-irradiated 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. Three intense bands at 4.84, 5.39 and 5.96 eV observed in the excitation spectrum of 3.8 eV emission belong to the intra-center excitation of F^+ -centers. At higher energies a sharp peak at 8.96 eV is observed followed by a weak

emission in the region of fundamental absorption of Al_2O_3 crystal. In this energy range the contribution from the self-trapped exciton emission that overlaps with the F^+ center luminescence can modify the spectrum. The energy of the peak 8.96 eV exactly corresponds to the sharp minimum in the excitation spectra of Cr^{3+} emission observed just near the sharp peaks at ~ 9 eV. The decay time of F^+ center emission was found to be $\tau \sim 2.0$ ns. Our results on F^+ center emission in $\text{Al}_2\text{O}_3:\text{Cr}$ are in good agreement with those obtained earlier for pure Al_2O_3 .

In excitation spectra of 3.8 eV emissions of irradiated ruby crystals a relatively weak band is observed at 4.09 eV. At this energy the absorption band of interstitial aluminum ions (Al_i^+ centers) is observed for heavily (fluence $> 10^{18}$ e/cm 2) irradiated Al_2O_3 grown by Verneuil method [4]. These centers emit in the same region as F^+ -centers. The emission decay time under the excitation at 4.09 eV is approximately 1.0 ns. It is possible that the efficiency of Al_i^+ center creation under electron irradiation is higher in ruby than in pure Al_2O_3 and high enough concentration of these centers can be obtained in ruby at lower fluences [4,5].

Emission of F -centers at 3.0 eV is also observed from irradiated ruby crystals but its intensity is at least 20 times

lower than that of F^+ -centers. The much weaker intensity of F -center emission compared to the intensity of F^+ -center emission in irradiated ruby can be due to much lower concentration of F -centers in comparison with F^+ -centers created by electron irradiation in ruby, in contrast to the situation for pure Al_2O_3 (Fig.1).

The support of this explanation comes from the comparison of intra-center excitation of F^+ and F center emissions for ruby and pure Al_2O_3 . The band at 5.96 eV in excitation spectrum of F^+ emission overlaps with the main excitation band of F center emission at 6.05 eV. In pure irradiated Al_2O_3 the emission intensity of F centers is stronger than that of F^+ centers under excitation by photons with this energy, which corresponds to direct excitation of both F^+ and F centers, in contrast to irradiated ruby where accordingly the concentration of F centers should be much lower than that of F^+ centers. The low concentration of F centers in irradiated ruby can be explained by the presence of Cr^{3+} ions, which capture during irradiation the created electrons and holes that results in lower creation efficiency of F centers, which are formed by the capture of two electrons by oxygen vacancies [3-5].

III. CONCLUSIONS

The above results directly confirm that after irradiation a stoichiometric disturbance in the crystals occurs because of elastic interaction, and the observed change in luminescence intensity is a consequence of the increasing concentration of defects. The results of investigations can be used for understanding the mechanism of luminescence excitation, occurring in strongly anisotropic material.

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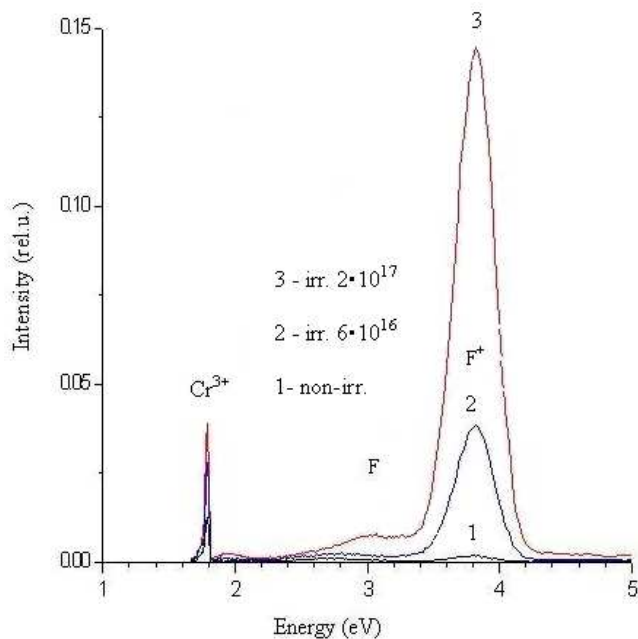


Fig. 1. Emission spectra of non-irradiated ruby and two ruby crystals irradiated by 50 MeV electrons with the fluences of $6 \cdot 10^{16}$ and $2 \cdot 10^{17}$ e/cm 2 , in the region of F^+ and F centers emission. Excitation energy is 5.96 eV. Temperature is 8.8 K.