Luminescence Spectroscopy of Electron and Neutron Irradiated α-Al_2O_3 Single Crystals

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Abstract. *Electronic properties of electron and neutron irradiated α-Al_2O_3 single crystals were investigated using photoluminescence spectroscopy.*

Key words: Corundum, electron and neutron irradiation, F and F^+ centers, luminescence spectroscopy.

I. Introduction

Due to its exceptional properties such as high radiation resistance, wide energy gap, transparency in wide spectral range and mechanical strength aluminum oxide (Al_2O_3 - corundum) is widely used in many technological applications, with its use in various structural, electronic and optical materials. Besides Cr-doped Al_2O_3 is well-known Ruby-laser host material. For many years experimental and theoretical investigations of pure and doped alumina samples have been conducted [1, 2, 3], however less attention has been paid to the radiation damage occurring in these materials under heavy irradiation conditions. The oxygen vacancies in different charge states (F and F^+ centers) are the main luminescence centers in pure corundum and their content in the material is determined by the preparation method. Therefore single crystals, grown by two different methods were investigated in this work. Also electron and neutron irradiation effect from the point of view of defect creation is discussed and compared with the as-grown corundum samples.

II. Experimental

The subjects of study were nominally pure (undoped) corundum (α-Al_2O_3) single crystals grown by horizontally oriented crystallization (HOC) and Verneuil methods. The concentrations of uncontrollable impurities in the chemicals used were below 10^{-3} wt. %.

As-grown single crystals were irradiated using 50 MeV electrons at the "ARUS" linear electron accelerator (in Yerevan, Armenia) with the irradiation dose of $1.2\cdot10^{17}$-10^{18} e/cm^2 and 2 MeV neutrons at a neutron reactor (in Kiev, Ukraine) with the irradiation dose of 10^{18} n/cm^2.

Time resolved luminescence investigations under VUV-visible (4-25 eV) synchrotron radiation (SR) excitation at 9-300 K were performed at the SUPERLUMI station (HASYLAB at DESY, Hamburg) [4] and under soft X-ray SR excitation at the S-60 electron synchrotron at Lebedev Physical Institute, Moscow [5].

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III. Results and Discussion

Emission spectra of pure corundum crystals irradiated with electrons and neutrons are shown in Fig. 1. The luminescence is recorded under X-ray SR excitation at 77 K. Three emission bands located at 165 nm, 325 nm and 420 nm regions are observed in the investigated range. The emission at 325 and 420 nm has been observed before in non-irradiated samples in previous works and supposed to be related with oxygen vacancies in different charge states [2, 6, 7]. In this work it can also be suggested, that the first fast component is related with luminescence of F^+ centers (with a lifetime of 2.05 ns) and the latter one originates from F centers with much longer life-time. Time resolved spectroscopy as well as the excitation spectra confirm our interpretation.

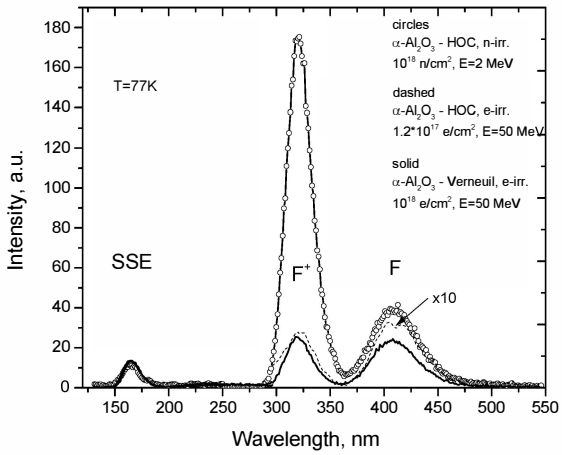

Fig. 1. Emission spectra of α-Al_2O_3 single crystals under soft X-ray excitation peaking at ~1keV. Spectra are normalized to intrinsic emission at 165 nm.

However as it can be seen from Fig. 1 the relative intensity of F and F^+ related luminescence bands in samples are different. Neutron irradiated corundum crystal shows the strongest intensity of F^+ related luminescence, which is ~4 times higher than F center luminescence. Under neutron irradiation the role of defect creation with impact (knock-out) mechanism is suggested to be higher than under electron irradiation. Therefore the possibility of F^+ center creation with impact mechanism is higher than for F centers.

In electron irradiated crystals the intensities of F and F^+ centers luminescence are about the same. Besides, the intensity of luminescence in HOC crystal irradiated with a dose of $1.2\cdot10^{17}$ e/cm^2 is about an order of magnitude lower than for Verneuil crystal, irradiated with 10^{18} e/cm^2. The reason of reduced intensity can be the lower dose of irradiation, however it is important to note that corundum

crystals, grown by the HOC method have a smaller amount of as-grown defects, than the Verneuil grown crystal. Therefore the role of growth method on radiation resistance needs further investigation.

The VUV emission at ~165 nm with ~8 ns lifetime of the shortest component was observed at low temperatures in all samples and it is ascribed to radiative recombination of self-shrunk excitons [3]. It is typical that there are several decay components starting from ns-range observed, which exact values vary due to contribution of non-radiative processes.

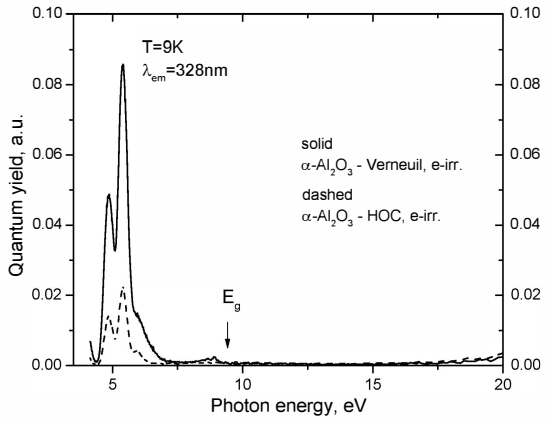

Fig. 2. Excitation spectra of F^+ center emission in α-Al_2O_3 single crystals at 9 K. Multiplication of intrinsic electronic excitations starts above $2E_g$.

The excitation spectra of the F^+ center luminescence are shown in fig. 2 for two electron irradiated crystals. Two peaks at 4.8 eV and 5.4 eV are due to the characteristic absorption bands (E_{def}) of F^+ centers. The absolute intensity of F^+ emission in the host transparency excitation range in the case of the HOC crystal is ~4 times lower than for the Verneuil crystal. As it is shown earlier [2] and shown in Fig. 2 the excitation efficiency is practically negligible through the excitonic absorption below 10 eV. The same applies for band-to-band transitions region, testifying that energy transfer is not efficient to the color centers in the intrinsic absorption. However above ~20 eV, where multiplication of electronic excitations (MEE) starts, the efficiency of excitation in both crystals is comparable. The decrease of relative efficiency of F^+ center excitation in the Verneuil crystal in the MEE range can be due to non-radiative losses on other type of defects, existing in this crystal.

For defect luminescence one could expect that the impact excitation of defect centers by hot photoelectrons can be expected at lower energies, above $E_g + E_{def} \sim 15$ eV. According to the experimental data such processes are not very probable at the defect concentrations induced by electron irradiation in the samples studied. It means that free mean path of low energy secondary electrons is less than needed for reaching defect centers (see [8] and references therein). On the other hand in the region of intrinsic absorption the penetration depth of photons (and consequently of hot photoelectrons) is very small, controlled by absorption coefficients exceeding the values in the transparency range by several times. Therefore, there is possibly a significant mismatch between the defect concentration profiles (μm and mm range for electrons and neutrons, respectively) in the sample created by particles and the absorption depth of VUV photons in nm ranges. This prohibits physically excitation of defect centers, which has to be taken into account in the applications, where materials were modified by particle beams.

IV. Conclusions

α-Al_2O_3 single crystals irradiated with the 50 MeV electrons and 2 MeV neutrons were investigated using luminescence methods with SR as an excitation source. The irradiation by 2 MeV neutrons causes efficient formation of F^+ centers in the corundum crystal, resulting in the strongest luminescence intensity of the 325 nm band. The crystals grown by Verneuil and HOC methods show different defect luminescence intensities, which are due to the initial defect concentration and also to their changes induced by irradiation with different doses by 50 MeV electrons. The luminescence of defects in α-Al_2O_3 is efficiently excited in the defect related absorption bands in the transparency range of the crystal host and practically not in the MEE region, where inelastic scattering of hot photoelectrons could be responsible for excitation of defect luminescence in corundum. Such type of excitation is not realized because of the profile of defects in the irradiated samples.

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