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Luminescence and Dielectric Properties of Electron and Neutron Irradiated Corundum Single Crystals

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Abstract. The luminescence and electronic properties of electron and neutron irradiated α-Al_2O_3 single crystals are compared with those of non-irradiated sapphire crystals using photoluminescence spectroscopy and dielectric constant measurements. It is shown that high-energy particles create stable structural defects in the corundum single crystal lattice due to knocking-out of atoms from their standard positions in anion and cation sub-lattices. These defects are mainly associated with F and F+ centers as well as with other vacancies, interstitials and complex defects such as [Al + F] type aggregate centers.

Keywords: corundum, single crystal, "radiation memory", absorption, defects.

1. Introduction

Crystals of simple and complex oxides are among the most investigated objects. It is well known that in these materials oxygen vacancies exist in different charge states and significant concentrations. This suggests the change of defect concentration and crystal structure depending on the growth method, thermal annealing as well as irradiation, thus giving opportunity to change some physical properties of the crystals. The violation of stoichiometry in oxide materials, such as corundum, causes increased concentrations of structural defects with corresponding absorption and emission.

Due to its exceptional properties such as high radiation resistance, wide energy gap, transparency in a wide spectral range, and mechanical strength, aluminum oxide (Al_2O_3 – also called corundum or alumina) is widely used in many technological applications as various structural, electronic and optical materials. Some Al_2O_3-related compounds have also attracted much attention as low-cost dielectric materials due to their possible use as gate dielectrics in metal-oxide-semiconductor (MOS) systems, where they can substitute traditional SiO_2. Besides, Cr-doped Al_2O_3 is the host material of well-known Ruby lasers. For many years many experimental and theoretical investigations of pure and doped alumina samples have been conducted [1-5], however little is known about radiation damage occurring in these materials under heavy irradiation conditions. The key issue is degradation of their properties when applied in extreme conditions. Often such applications are accompanied with temperature changes. Therefore, temperature dependent studies are required. The defects, 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 and further treatment.

In this work, single crystals grown by two different methods are investigated with the aim to examine the effect of preparation methods on some crystal properties. Also, the defects created under electron and neutron irradiation are discussed and compared with the defects in the as-grown corundum samples. The effect of electron and neutron irradiation on the dielectric constant of single crystals is also evaluated.

2. Materials and technique

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 concentration of uncontrollable impurities in the used chemicals were below 10^{-3} wt. %.

As-grown pure single crystals were irradiated with electrons having 50 MeV energy using the "ARUS" linear electron accelerator (in Yerevan, Armenia) at a dose of 1.2×10^{17}-10^{18} e/cm^2 and 2 MeV neutrons using a neutron reactor (in Kiev, Ukraine) at a dose of 10^{18} n/cm^2. For comparison, non-irradiated crystals were investigated as well.

Time resolved luminescence investigations under UV/VUV (4-25 eV) synchrotron radiation (SR) excitation at 9-300 K were performed using the SUPERLUMI station (HASYLAB at DESY, Hamburg) [6], and under soft X-ray SR excitation using the S-60 electron synchrotron at Lebedev Physical Institute, Moscow [7].

Single crystals of typical size $15\times10\times1.7$ mm^3 were prepared for dielectric constant measurements. The electrodes for electrical measurements were sputtered in vacuum by evaporating Al on flat surfaces of the samples. The dielectric measurements were performed within 300 Hz – 1 MHz frequency range at 77 K and at room temperature. The measurement installation was designed by our group according to the Ac-bridge method and was calibrated with BM 400G Tesla capacitance meter. The samples were induced to sinusoidal measuring voltage with 100 mV amplitude, and the measurement precision was ± 0.05 pF.

3. Results and discussion

It is known that irradiation of α-Al_2O_3 with high-energy particles causes creation of point (F, F^+ etc.), complex [Al_iF] and aggregate defects. The latter ones, particularly Al^{3+}:[O^{2-}]$_6$, are created in corundum as a result of neutron and heavy ion (lead) irradiation. In crystals irradiated with 50 MeV electrons, these high-speed electrons lose significant part of their energy on ionization before the impact with atoms, therefore the concentration of vacancies and interstitial ions of O_i and Al_i is much less than in the case of neutron irradiation. In this case, the concentration of point defects is higher than that of aggregated clusters, complex centers or interstitial O_i and Al_i. In the case of neutron irradiation due to cascades of impacts, the concentration of knocked out atoms is more than in the case of electron irradiation, therefore the defect concentration depends on the type of irradiation.

Figure 1 shows the emission spectra of pure corundum crystals irradiated with electrons and neutrons. The luminescence is recorded under X-ray SR excitation at 77 K. Three broad emission bands

peaked at 165, 325 and 420 nm are observed in the investigated range. In previous works the emissions at 325 and 420 nm was observed in non-irradiated samples and supposed to be related to oxygen vacancies in different charge states [2, 8, 9, 13, 14]. These are the main and unavoidable defects in Al_2O_3. In this work, it can also be suggested that the 325 nm band is related to the luminescence of F^+ centers (with a lifetime of 2.05 ns, Fig.1) and the 420 nm band originates from F centers with much longer life-time. Time resolved spectroscopy showed ~2 ns decay time for the 325 nm emission (under 230 nm excitation). These results, as well as the excitation spectra (see below) confirm our interpretation of the origin of the defects.

However, as it can be seen from Fig. 1, the relative intensities of F and F^+ related luminescence bands in the samples are different. Corundum crystal irradiated with neutrons shows the strongest intensity of the F^+ related luminescence, which is ~4 times higher than that of the F center luminescence. In the case of neutron irradiation, the role of impact (knockout) mechanism in defect formation is suggested to be higher than in the case of electron irradiation. Hence, the probability of F^+ center creation by impact mechanism is higher than that of F centers. In contrast to irradiation with neutrons, protons or heavy ions, in the case of electron irradiation, the ionization damage supersedes the displacement, therefore just irradiation with electrons is the best suited to evaluate the effects of ionizing radiation on materials.

In the irradiated by electron crystals the intensities of F and F^+ centers luminescence are almost the same. Besides, the intensity of luminescence in HOC crystal irradiated at a dose of 1.2×10^{17} e/cm^2 is lower approximately by an order of magnitude than that in Verneuil crystal, irradiated at a dose of 10^{18} e/cm^2. The reason of the 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 methods on radiation resistance needs further investigation.

The VUV emission at ~165 nm with ~8.5 ns lifetime of the shortest component was observed at low temperatures in all samples and is ascribed to radiative recombination of self-shrunk excitons [3]. It is characteristic that several decay components are observed starting from ns-range, relative contribution of which varies depending on the excitation mechanisms involved.

Figure 2 shows excitation spectra of the F^+ center luminescence 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 that for the Verneuil crystal. As it was shown earlier [2] and is presented in Fig. 2, the excitation efficiency is practically negligible because of the excitonic absorption near 10 eV. The same applies to the band-to-band transitions region, testifying that the energy transfer to the color centers (intrinsic absorption) is not efficient. However, above ~20 eV, where multiplication of electronic excitations (MEE) starts, the efficiency of excitation in both crystals becomes noticeable. The decrease of relative efficiency of F^+ center excitation in the Verneuil crystal in the MEE range can be due to non-radiative losses related to other types of defects existing in this crystal.

As for the defect luminescence, one could expect that the impact excitation of defect centers by hot photoelectrons can be observed at the energies below ~20 eV, namely above $E_g + E_{def} \sim 15$ eV. According to the experimental data, such processes are not very probable for 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 that needed for reaching defect centers (see [10,13,14] 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; it is determined by absorption coefficients that exceed their values in the transparency range by several orders of magnitude. Therefore, a significant mismatch is possible between the defect concentration profiles (μm and mm range for electrons and neutrons, respectively) created by particles in the sample and the absorption depth of VUV photons in nm range. This physically prohibits the excitation of defect centers, which has to be taken into account in the applications where materials are modified by particle beams.

Next, frequency dependences of dielectric constant, ε`(f), were measured for electron and neutron irradiated crystals in order to find out relations between structural peculiarities of the material and its dielectric parameters. Figure 3 presents the experimental results. It is known that the dielectric constant of the material ε` strongly depends on the material structure, dipole moments, and external conditions, the measurement frequency and temperature.

The results of dielectric constant measurements for non-irradiated and electron and neutron irradiated corundum crystals show that though the shapes of curves for irradiated samples are similar to those for non-irradiated crystals, the absolute value of ε` is significantly different.

It is necessary to mention that for the non-irradiated sample the dependency curve within the whole range of measurement frequencies is flat, and for 1 kHz ε`=12.59 at room temperature and ε`=11.82 at T=78 K. As can be seen from Fig. 3, the electron and neutron irradiation of corundum cause a significant decrease of ε`. The electron irradiation causes the decrease of dielectric constant at 1 kHz by $\Delta\varepsilon_e$`=2.62 at 300 K and by $\Delta\varepsilon_e$`=1.91 at 77 K, while in case of neutron irradiation $\Delta\varepsilon_n$`=2.44 at 300 K and $\Delta\varepsilon_n$`=2.72 at 77 K. The results demonstrate that for neutron irradiated samples the change in ε` is significantly stronger at low temperatures) than for electron irradiated samples. The observed changes of ε_n` in neutron irradiated crystals are obviously related to the radiation-induced structural defects (point defects, clusters etc.), concentration of which is especially high in these samples. The difference in absolute values of dielectric parameter ε` is due to the space charge polarization caused by enhanced degree of structural disorder [11]. Thus, the radiation-induced defects and structural peculiarities are of critical importance for the dielectric constant of corundum single crystals. Particularly, a decrease of dielectric constant depends on irradiation type. In [12] the γ-irradiation of YAG crystals doped with different ions caused a decrease of ε`, and the authors explained it by the increase in concentration of oxygen vacancies.

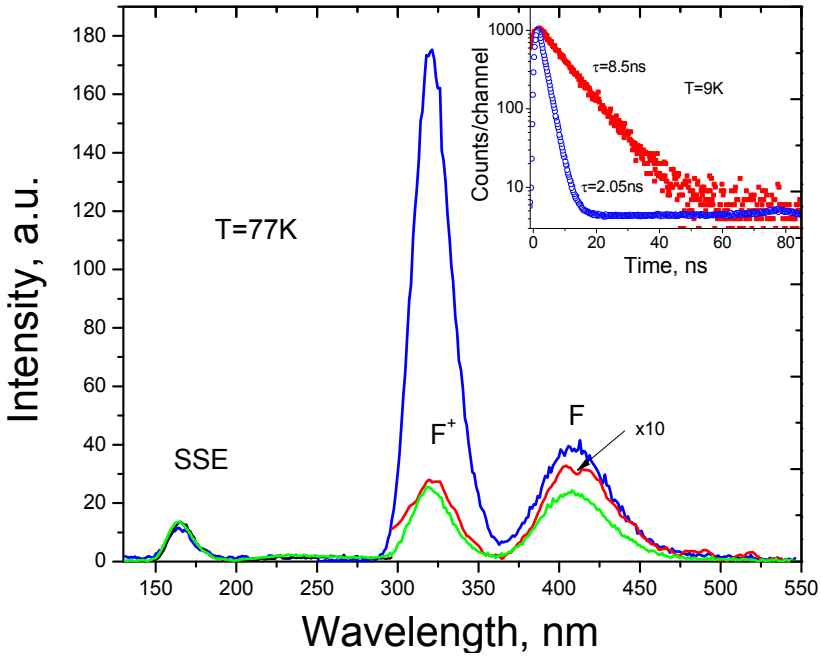

Fig.1. Emission spectra of α-Al_2O_3 single crystals under soft X-ray excitation peaking at ~1 KeV. Spectra are scaled to intrinsic emission at 165 nm. Blue: α-Al_2O_3 - HOC, n-irradiated 10^{18} n/cm^2, E=2 MeV; Red: α-Al_2O_3 - HOC, e-irradiated 1.2×10^{17} e/cm^2, E=50 MeV, Green: α-Al_2O_3 - Verneuil, e-irradiated 10^{18} e/cm^2, E=50 MeV. The inset shows the decay kinetics of self-shrunk exciton (SSE) (red squares: emission at 163 nm, excitation at 138 nm) and F^+ emission (blue circles: emission at 328 nm, excitation at 230 nm) at 9 K for HOC crystal.

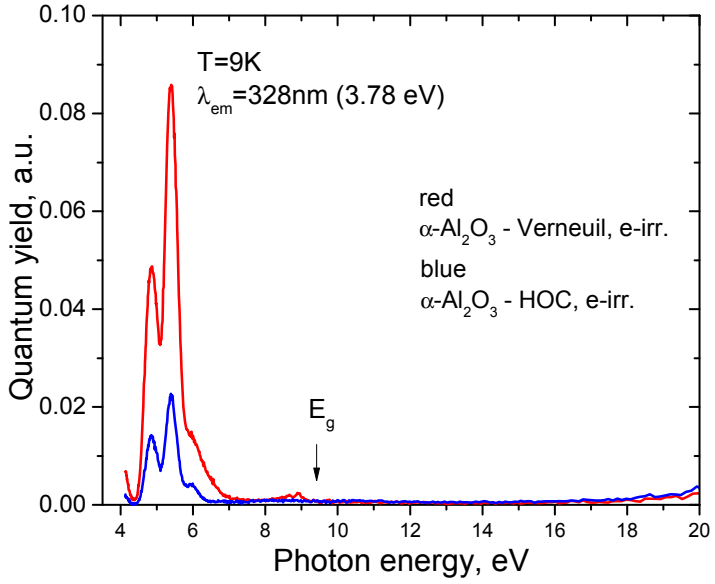

Fig. 2. Excitation spectra of the F^+ center emission in α-Al_2O_3 single crystals at 9 K. Multiplication of intrinsic electronic excitations starts above $2E_g$.

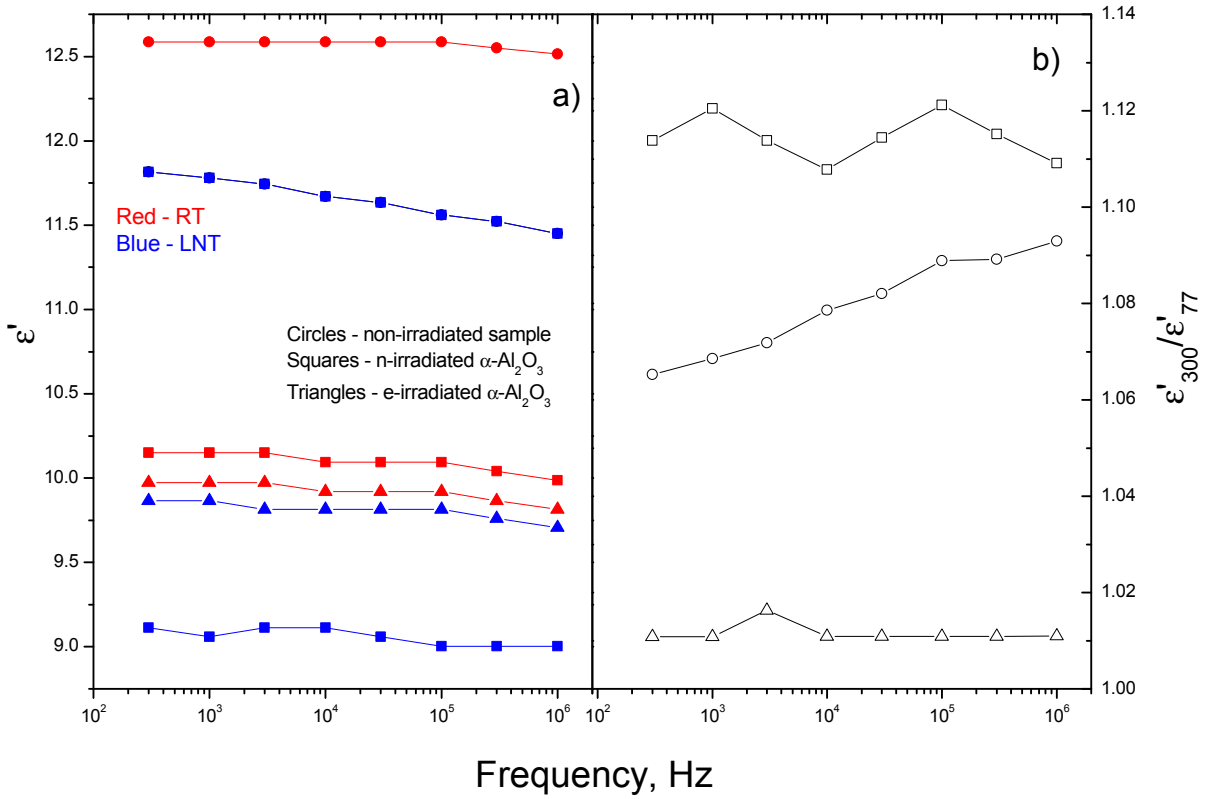

Fig. 3. a) Frequency dependences of dielectric constant ε`(f) for non irradiated and both electron- (E = 50 MeV, D=6×10^{17} el/cm^2) and neutron (E = 2 MeV, D=10^{18} n/cm^2) irradiated samples measured at room and liquid nitrogen temperatures.

4. Conclusions

A comparative study of optical and dielectric properties of α-Al_2O_3 single crystals irradiated with 50 MeV electrons and 2 MeV neutrons is performed using luminescence methods with SR as an excitation source and dielectric constant measurements. The irradiation by 2 MeV neutrons causes an 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 intensity, which is due to both the initial defect concentrations and their changes induced by 50 MeV electron irradiation at different doses. The luminescence of defects in α-Al_2O_3 is efficiently excited in the defect related absorption bands within the transparency range of the host crystal and is practically not observed in the fundamental absorption region of the host crystal including the region $h\nu \geq 15$ eV where inelastic scattering of hot photoelectrons can result in impact excitation of defect luminescence. The latter mechanism is not realized because of the specific profiles of defects in the irradiated samples.

Our dielectric studies have revealed that the radiation-induced defects and structural peculiarities play an essential role in the dielectric constant behavior. It is shown that the decrease of dielectric constant in neutron irradiated sapphire crystals is significantly stronger than in electron-irradiated crystals. The analysis of the obtained results shows that the variation of spectroscopic characteristics and dielectric parameters of corundum single crystals depending on the irradiation type and energies correlates well with each other. Such behavior is related to the creation of high concentrations of charged defects in irradiated crystals.

From the study of spectroscopic characteristics, it can be concluded that electron and neutron irradiation results in a strong decrease of the transparency over the entire spectral region due to the formation of radiation-induced defects in structure of materials. However, physical properties are maintained testifying to the radiation resistance of these materials.

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