LUMINESCENCE OF F_2-DIMER CENTERS IN FAST-NEUTRON IRRADIATED Al_2O_3 SINGLE CRYSTALS

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Introduction: Elastic collisions of energetic neutrons with the ionic crystal nuclei (the knock-on mechanism) cause the displacement of lattice ions, creating stable point defects – empty sites (vacancies) and off-site ions (interstitials) – so-called "Frenkel defects", or "Frenkel pairs". Displacement of an anion creates positively charged anion vacancy (v_a) and negatively charged interstitial, which can capture electrons of holes, respectively, becoming electrostatically neutral. Anion vacancies with captured electrons are historically called "*F*-centers" and neutral anion interstitials are called "*H*-centers". In case of metal oxides with double-charged oxygen ions, oxygen vacancy v_a^{2+} can capture one or two electrons (v_ae^- or $v_ae^-e^-$; F^+ or F centers, respectively).

Prolonged irradiation leads to aggregation of point defects, which eventually causes undesirable changes in mechanical and optical properties of the material or even macroscopic cracking and brittle destruction. Therefore, commercial success of future fusion reactors (neutron radiation is a side effect of the fusion reaction) partially depends on the radiation resistance of the construction materials – the ability to withstand high fluences of particle radiation without significant changes in properties. Aluminium oxide single crystals is one of the promising candidates for optical window material, being transparent in the wide optical range, radiation-resistant and rather sturdy mechanically.

This study is devoted to radiation damage of single-crystal Al_2O_3 caused by the irradiation with fast fission neutrons. **The focus of the study** is luminescence related to absorption bands 2.75, 3.45 and 4.07 eV which are commonly attributed [1] to F_2-type dimers (F_2^{2+}, F_2^+, F_2) – simplest aggregates of *F*-type centers in various charge states. Luminescence spectra were measured at the excitation in each absorption band, and excitation spectra for most prominent emissions were also registered.

Complexity of defect distribution and their interaction in neutron-irradiated Al_2O_3 requires application of various complementary methods in order to fully understand related processes. This work is a continuation of our earlier studies of the same samples employing analysis of radiation-induced optical absorption (RIOA) and EPR [2,3].

Sample:

Pure **α-Al_2O_3** 3-mm-thick single crystal disc produced by the Union Carbide company and irradiated at Oak Ridge National Laboratory with fast neutron fluence of $6.91*10^{18}$ n/cm^2 ($T \leq 60°C$).

For this study, a ~7x7 mm^2 plate was cut out from discs (with main crystallogrpahic axis *c* parallel to the surface) and polished to thickness 0.77 mm.

Methods and equipment

Photoluminescent characteristics have been measured at room temperature and 78 K. Emission spectra have been registered in the region 1.6–4.4 eV (775–280 nm) and the excitation spectra – in the region 2.5–6 eV (496–206 nm).

Measurements have been performed on the custom setup with UV-enhanced Xe lamp as the light source and Hamamatsu H8259-01 photon counting head as detector.

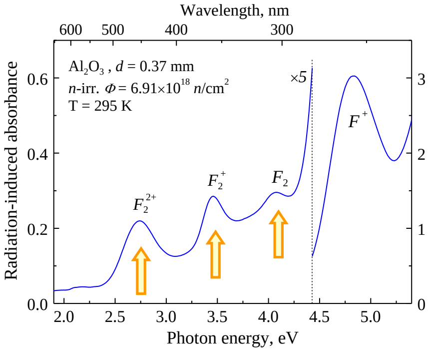


Fig. 1. Typical spectrum of radiation-induced (spectrum of non-irradiated sample subtracted) absorbance for our neutron-irradiated Al_2O_3 samples. As an example, a sample with thickness 0.37 mm was used. Locations for F_2-type band maxima are marked respectively.

Excitation in each of the marked bands

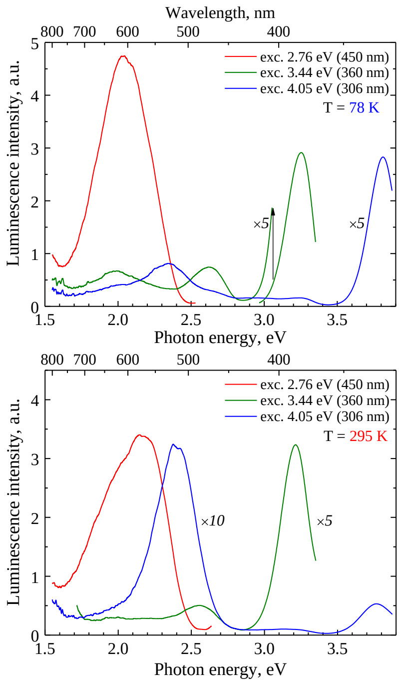
F-dimer luminescence at 78 and 295 K

Fig. 2 and 3. Luminescence spectra of the sample at 78 K and 295 K at the excitation in the maxima of dimer peaks marked on **Fig. 1**.

The results are generally in agreement with flat-band diagram of *F*-type defects in Al_2O_3 proposed in [1], with the exception of lesser luminescence bands at 2.6 and 2 eV excited at 3.44 eV. The 2 eV band could be the result of luminescence reabsorption by the F_2^{2+} centers.

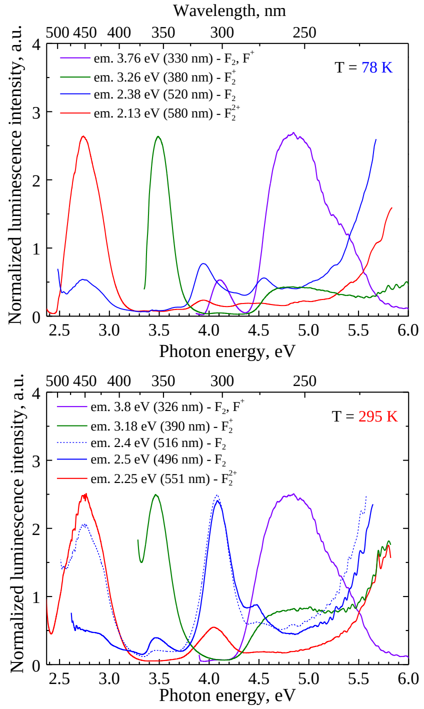
At both temperatures, emission spectra are qualitatively similar, especially for emission ~2 eV excited by the 2.76 eV photons, which does not undergo a significant quenching as opposed to emission excited in other two absorption bands. However, the shape of the 2 eV emission band becomes clearly asymmetric at room temperature.

Emission excited at 4.05 eV (F_2 band) demonstrates a drastic change in the ratio of two main bands at ~2.4 and 3.8 eV. This change could be explained by the stronger quenching of the 3.8 eV component compared to the 2.4 eV one.



F-dimer luminescence excitation spectra at 78 and 295 K

Excitation spectra for main luminescence bands



Excitation spectra on Figs. 4-5 are rather complicated, with several excitation bands expressed in spectra of different emissions. Most of this complexity arises from overlapping of close luminescence bands (~2 eV band related to 2.75 eV (F_2^{2+}) absorption band and ~2.4 eV band related to 4.05 eV (F_2) absorption band, the latter also overlaps with the 2.6 eV band related to 3.45 eV (F_2^+) absorption band). It is especially obvious when comparing excitation spectra for 2.4 and 2.5 eV emission at 295 K: slight shift towards larger overlapping leads to strong enhancement of "alien" excitation bands.

Like with emission spectra, most notable difference between 78 and 295 K is observed for F_2 centers. Unfortunately, the F_2 luminescence 3.8 eV almost fully coincides with F^+ emission in Al_2O_3, giving strong excitation bands at 4.8 and 5.3 eV, which correspond to F^+ transitions.

The origin of the weak excitation band at ~3.9 eV at 78 K is unclear yet. It is also unclear, why the 3.2 eV emission of F_2^+ centers has excitation band in the region of F^+ excitation (above 4.5 eV).

F_2^{2+} luminescence

In [2] we examined optical absorption of the band at 2.75 eV and changes in its shape after annealing at certain temperatures (Fig. 6). It became clear that this band consists of several components with different thermal stability. So it was interesting to compare luminescence excited in different regions of the band. The result on Fig. 7 shows that shifting excitation energy does not change the shape of emission spectrum, which could mean that either all absorption band components are transitions within the same center (which contradicts with different thermal stability), or that components correspond to different centers, but only one type of them has radiative transition in this region.

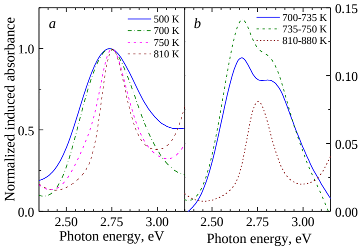


Fig. 6. *a* - normalized shapes of the ~2.75-eV band measured after preheating to different demperatures. *b* - Difference spectra representing the decrease of RIOA due to the preheating of the irradiated sample from *T*1 to *T*2. All spectra measured at 295 K. See [2] for details.

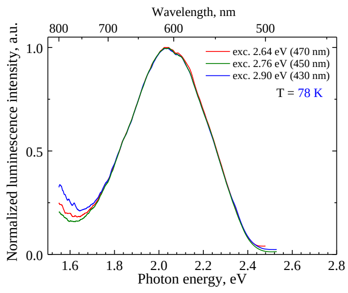


Fig. 7. Luminescence spectra excited in different regions of the non-elementary ~2.75 eV absorption band.

CONCLUSIONS

*** Luminescence of F_2-type dimers in our *n*-irradiated Al_2O_3 undergoes thermal quenching to different degree.**

*** Excitation spectra are complicated due to overlapping of luminescence from different centers.**

*** Emission and excitation spectra of each dimer type are rather similar at both 78 and 295 K, F_2 center spectra being the most influenced by temperature.**

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