Eur. Phys. J. B **12**, 31–33 (1999)

THE EUROPEAN
PHYSICAL JOURNAL B
EDP Sciences

Luminescence quantum yield and multiplication of electronic excitations in the corundum crystals

V.V. Harutunyan[1,a], T.S. Hakobyan[1,b], V.A. Gevorkyan[1], and V.N. Makhov[2]

[1] Yerevan Physics Institute, Alikhanian Br. 2, 375036, Yerevan, Armenia
[2] Lebedev Physics Institute, Leninski prosp. 53, 117924, Moscow, Russia

Received 16 October 1998 and Received in final form 20 January 1999

Abstract. The excitation spectra of luminescence in irradiated and nonirradiated corundum crystals are investigated by means of highly polarised synchrotron radiation in 5 to 30 eV region. In the fundamental absorption region the double-exciton peaks are observed in the region 8.5–9.2 eV for irradiated (especially by neutrons) crystals at temperature 90 K. At 9.5 eV sharp drops appeared, in the luminescence spectrum space which were interpreted as nonirradiative near-surface recombination, the probability of which sharply increased at high absorption coefficients. The enhancement of the luminescence efficiency in the high-energy region was connected with the decay effect of electron excitations as well as with the influence of volumetric excitations leading to the enhancement of recombination glow.

PACS. 61.72.-y Defects and impurities in crystals; microstructure – 61.80.-x Physical radiation effects, radiation damage – 74.62.Dh Effects of crystal defects, doping and substitution

1 Introduction

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

The wide-band ion corundum crystals are of great interest because of their applications as optical materials in the UV-VUV region, as well as luminescence materials, such as scintillators for ion emission detectors, luminophors for memory screens, laser active media, materials for radiation defence. The development of radiation technologies needs materials stable to the effects of high energy particles — electrons, protons, neutrons, ions, γ-quanta, synchrotron radiation — (SR) [2–6]. So, the understanding of physics of luminescence in corundum crystals is very important.

Due to high intensity, wide-band spectra and impulse time structure, SR is a unique tool for investigation of luminescence spectroscopy of solids [5,6].

The goal of this work is the investigation of luminescence excitation in corundum crystals in the region 5–30 eV.

2 Experimental

Measurements of the luminescence excitation spectra were carried out using SR of C-60 accelerator ($E \sim 680$ MeV) with a modified Vodsvort set-up for monochromators of normal incidence ($10\,^\circ$). Spectral resolution of the monochromator was from 0.5 to 1 nm.

The main measurements were made using an Al coated diffraction grating with $N = 1\,200\,\mathrm{l\,mm}$, 4–30 eV working range of photon energy, and maximum concentration in the 8 eV region. To obtain more correct results in spectrum processing the measurements of the scattered light in the high energy spectral region were realised using MgF_2 filters which passed quanta with $h\nu < 10.5$ eV.

Registration of the sample irradiation was carried out using photomultiplier FEU-106 with the UFS-2 (3.1–5.2 eV filter in front of photocatode) operating in the photon counting mode [1,6].

The time-resolved luminescence spectra and excitation spectra (5–30 eV) for various emissions at 8 K and 17 K has been measured using the SUPERLUMI station (delay times of 1.5 or 5 ns after excitation and successive time windows of 5 or 23 ns were used in our measurements).

The nominally pure stoichiometric α-Al_2O_3 were grown by the horizontal-oriented crystallisation method (HOC). The optical axis C_3 was parallel to the large side of the samples. The crystals were irradiated in air with 50 MeV electrons and 2 MeV neutrons of temperatures 285 K and 370 K respectively.

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[a] e-mail: `arsen@moon.yerphi.am`
[b] e-mail: `hakob@lx2.yerphi.am`

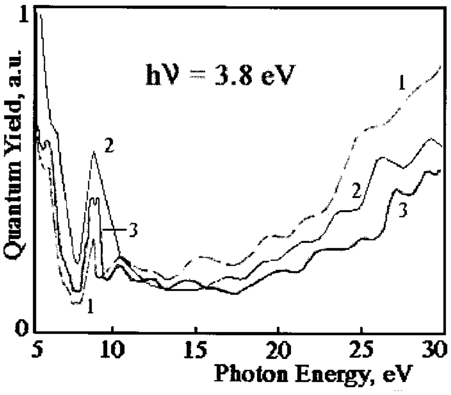

Fig. 1. Luminescence excitation spectra 3.8 eV of corundum monocrystals, measured at temperatures 300 K and 90 K: 1) unirradiated at 300 K; 2) neutron-irradiated with dose 10^{17} n/cm^2 at 300 K; 3) neutron-irradiated with dose 10^{17} n/cm^2 at 90 K.

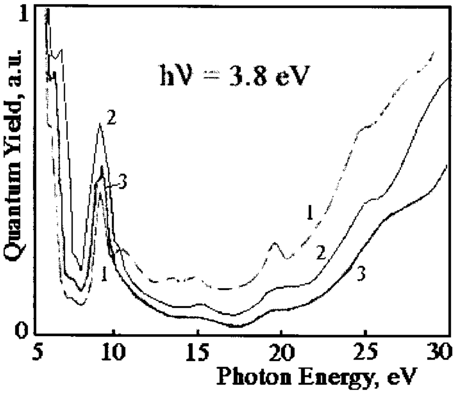

Fig. 2. Luminescence excitation spectra 3.8 eV of corundum monocrystals, measured at temperatures 300 K and 90 K: 1) unirradiated at 300 K; 2) electron-irradiated with dose 6×10^{17} e/cm^2 at 300 K; 3) electron-irradiated with dose 6×10^{17} e/cm^2 at 90 K.

3 Experimental results and discussion

The investigations have shown that in the fundamental absorption region in the luminescence excitation (LE) spectra one can see clearly pronounced relatively narrow bands of irradiated and nonirradiated corundum crystals. Some bands in the LE spectra up to the edge of fundamental absorption, within the experimental error of ±0.1 eV (Figs. 1, 2, 3, 4) correlate well with the absorption spectrum [7]. Hence in the LE spectra some of the bands are due to intracentre transitions. Additionally, a nonirradiative process with- out/with charge transfer is possible.

Figures 1 and 2 show (LE) spectra of 3.8 eV at temperatures 300 K and 90 K. It is known that the optical absorption bands of the F^+ center at high-energy quanta excitation give luminescence of 3.8 eV (UV) [7].

In the LE spectra (Figs. 1, 2) in the region from 5 to 8 eV one can observe the F and F^+-center bands [7–9].

The goal of this work is the investigation of radiation influence on electron excitation process peculiarities in corundum crystals in the region 5–30 eV.

In the fundamental absorption region band the double peaks of 8.5–9.25 eV are observed at temperature 90 K. The free exciton peak of 8.5 eV appeared as a result of valence electron transition from anion to cation in the presence of F-centers. The second peak of 9.25 eV is produced by self-trapped excitons (STEs).

The 7.5 eV emission can be effectively excited in a narrow region of 8.9 to 9.20 eV, where photons directly form excitons (Fig. 3). We consider 7.5 eV emission to be the luminescence of STEs. The emission of 3.8 eV was tentatively ascribed to the second luminescence band of STEs in Al_2O_3 (Fig. 4). The fast component of 3.8 eV emission is not excited in the region of extrinsic absorption 5–8.9 eV or at the generation of separated electrons and holes in the beginning of band-to-band transitions.

It is well known that the passage of high-energy particles through matter is accompanied by the exchange of energy and momentum between the atoms of the matter and the electrons. As a result, atoms are displaced from their equilibrium positions and genetic pairs appear: interstitial atoms and vacancies.

The concentration of knocked-out atoms is higher in the case of neutron irradiation than in the case of electron irradiation because of a cascade of elastic collisions, and it will be even higher if the loss of most of their electron energy in an inelastic interaction is taken into account. Therefore, the concentration of the corresponding color center will be different.

The decrease in effectiveness of energy transfer to emission centers can be explained as follows (Figs. 1–4). At the beginning stage of electron excitation, just immediately after the creation of electron-hole pairs, the main canal of relaxation of primary and secondary electrons is the relaxation on the optical phonons. During this process electron and hole move away by a distance which increases with the increase of their initial energy. The increase of this distance, in its turn, can decrease the probability of their recombination and increase the probability of nonradiative relaxation such as catching by traps, by decay centers, electronic excitation, etc.

The existence of these migration losses can stimulate the reduction of quantum yield of luminescence (QYL). The near-surface losses can be considered in the light of the diffusion model, according to which the QYL relates to reflection (absorption) coefficient [1,10,11]. The analyses of analogous phenomena in many luminophors shows that one of the causes of the losses should be increase of the absorption coefficient and, consequently, decrease of the depth of photon penetration into the crystals.

With further increase in quanta energy, $h\nu \geq 2\ E_g$ (9.5 eV), one can observe the increase of luminescence effectiveness. The structure of LE spectra at $h\nu > 17$ eV is stimulated by the fact that fast photoelectrons scatter on valent electrons and create slow secondary electron-hole pairs with small scattering and the number of decayed pairs monotonously increases ($h\nu \sim 23$ eV).

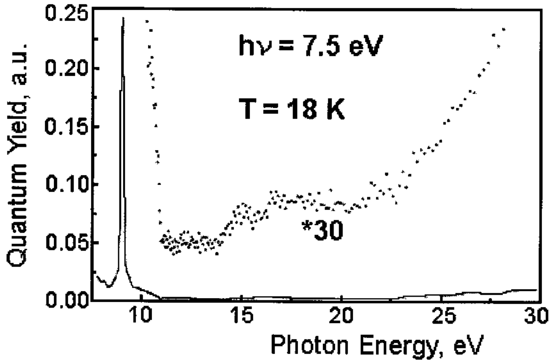

Fig. 3. Luminescence excitation for fast STE emissions of 7.5 eV (time delay + time window 6 + 23 ns) in corundum monocrystals-unirradiated.

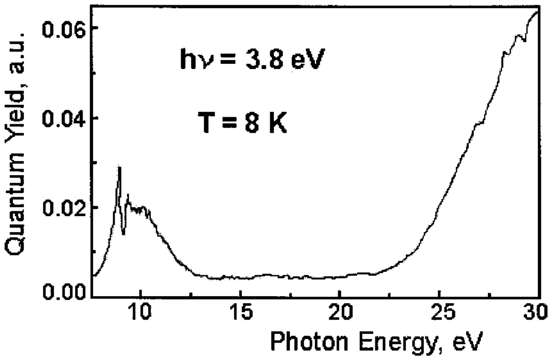

Fig. 4. Luminescence excitation for 3.8 eV fast emission (1.5+ 5 ns) in corundum monocrystals-unirradiated.

Beginning from $h\nu > 25$ eV some of the secondary particles also decay creating tertiary electron- hole pairs with small scattering and consequently, with high efficiency of electronic excitation energy transfer to photoemission centers. The described process is the process of multiplication of electronic excitations (MEEs) [1,6,7,11].

The effectiveness of LE at 90 K (Figs. 1, 2, curve 3), at 17 K Figure 3; at 8 K Figure 4 is not high because of the decrease of charge carriers' diffusion and the peaks become flat indicating that electrons stay longer in the traps.

So, it follows from the experimental results that the luminescence quantum yield strongly depends on level and type of irradiation and also on the temperature.

The investigation performed in this work was supported by grant A-102 of the International Science Technical Center.

References

1. I.M. Ternov, V.V. Mikhailin, *Synchrotron Radiation, Theory and Experiment* (Energoatomizdat, Moscow, 1986), p. 295.
2. I.H. Grawford Jr, Nucl. Instrum. Methods Sect. B **1**, 159 (1984).
3. G.W. Arnold, G.B. Krefft, C.B. Normis, Appl. Phys. Lett. **25**, 540 (1974).
4. M.L. Dalal, M. Rahmani, P.D. Townsend, Nucl. Instrum. Methods Phys. Res. Sect. B **32**, 61 (1988).
5. M. Casalboni, Rad. Eff. Def. Solids, **119-121**, 189 (1991).
6. V.V. Harutunyan, V.A. Gevorkyan, A.K. Babayan, H.M. Martorosyan, Phys. Stat. Solidi (b) **191**, K9 (1995).
7. V.V. Harutunyan, V.A. Gevorkyan, N.E. Grigoryan, Nucl. Instrum. Methods Phys. Res. A **308**, 200 (1991).
8. S.I. Choi, T. Takeuchi, Phys. Rev. Lett. **50**, 1474 (1983).
9. K.H. Lee, I.H. Grawford Jr, Phys. Rev. B **15**, 4065 (1977).
10. V.V. Harutunyan, V.A. Gevorkyan, A.K. Babayan, V.N. Makhov, Rad. Eff. Def. Solids, **136**, 257 (1995).
11. A.N Vasilev, V.V Mikhailin, *Introduction in Solid State Spectroscopy* (Moscow University Press, Moscow, 1987).