

RADIATION-INDUCED EFFECTS IN CORUNDUM SINGLE CRYSTALS

V.V. Harutyunyan¹, E.M. Aleksanyan^{1,*}, N.E. Grigoryan¹,
V.S. Baghdasaryan¹, and V.Jh. Yeghiazaryan²

¹*A.I. Alikhanian Yerevan Physics Institute, Yerevan, Armenia*

²*Armenian State Pedagogical University, Yerevan, Armenia*

*e-mail: aeduard@mail.yerphi.am

Received 15 April 2015

Abstract - 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_i⁺ F] type aggregate centers. A mechanism of “radiation memory” in corundum single crystals consisting in restoration of some optical absorption bands within 190-315 nm range after irradiation and thermal treatment at high temperatures with subsequent X-ray irradiation, is discussed.

Keywords: corundum, single crystal, “radiation memory”, absorption, defects.

1. Introduction

Aluminum oxide crystals, α -Al₂O₃, also called corundum, are of great scientific and practical importance due to their exclusive properties, namely, high hardness, refractoriness, chemical and radiation resistance, low electrical conductivity and high optical transparency in wide spectral range.

Due to excellent radiation resistance and availability of highly developed growth technology for large-sized single crystals, corundum is widely applied in optoelectronics, thermonuclear reactors, as scintillation detectors, containers of hazardous materials, etc. [1-12]. Besides, luminescent properties of the material are extensively used in medicine and astronomical dosimetry [3-6].

The increased radiation resistance of corundum crystals is of permanent interest in respect of the formation mechanisms of radiation defects (both point and complex ones), a part of which are color centers (CC), i.e. defects capable of absorbing or radiating quanta in ultraviolet (UV), vacuum ultraviolet (VUV), visual or infrared spectral ranges [7-10].

α -Al₂O₃ crystals are characterized by complex structure and have two molecules (10 atoms) in their unit cell (space group - D_{3d}⁶ - R3c). They are ionic crystals though their covalence is approximately 20 %. The important distinctive feature of their structure is lower symmetry of anion (oxygen) positions – C₂, compared to cation positions (Al³⁺) – C₃. According to calculations [13], the top of valence band is formed by 2p oxygen states, and in the crystal field of low symmetry positions, C₂, a complete splitting of p-states takes place. At the coordination number of 4 one of the oxygen p-orbitals appears as of nonbonding type and another one is located at an angle of 45 degrees to C₃ optical axis.

In our earlier works [7-12], the mechanisms of several optical effects, such as "effect of low doses" [14] and "multiplication of electronic excitations" (MEE) were investigated in the corundum crystals irradiated with high-energy particles (electrons, neutrons, ions).

It is known that energetic electron and neutron radiation results in structural changes and radiation defect formation [7-10, 15, 16], and as a consequence the absorption constant is increased in a wide spectral range. It is mostly considered that radiation "negatively" influences the crystal parameters. However under certain conditions the radiation could have a "positive" influence, particularly in case of lower (up to 10¹² e/cm²) irradiation doses, which results in ordering of crystalline structure and elimination of part of defects created during the crystal growth. This allows using the ionizing radiation for controllable modification of crystals properties.

The study of radiation influence on corundum resulted in revealing of the "radiation memory" phenomenon in the irradiated corundum single crystals. An analogous "radiation memory" phenomenon (but with somewhat different characteristics) was also detected in alkali-halide crystals in [13].

The purpose of this work is to reveal, at what stage of structural transformations the color centers are formed responsible for the "radiation memory" phenomenon, as well as to broaden the existing ideas on explanation of new and earlier obtained experimental results.

2. Materials and Methods

The subjects of study were samples of nominally pure (undoped) corundum (α -Al₂O₃) single crystals grown by various methods - by horizontal-oriented crystallization (HOC) and Verneuil method. Concentrations of uncontrollable impurities in the reaction mixture were less than: $3 \cdot 10^{-3}\%$ for Cr₂O₃, $10^{-4}\%$ for Ti₂O₃, $10^{-3}\%$ for Ca, Fe and Ni (in mass percent). HOC crystals had much smaller amount of as-grown defects compared to the crystals grown by other methods. The initial content of defects (particularly F and F⁺) in the material were mainly determined by thermal/chemical procedures during the crystal growth and post-growth treatments.

The samples of corundum (plane-parallel plates and cubes with C₃ optical axes parallel to the large side to within $\pm 3^\circ$) used for the measurement of optical absorption, photoluminescence and excitation of luminescence, were manufactured from specially selected perfect boles. The side surfaces of all samples were carefully mirror-finished using AM-1 diamond paste.

Crystals were irradiated with 50 MeV electrons from "ARUS" YerPhi linear electron accelerator with doses $3 \cdot 10^{17}$ e/cm², 2 MeV reactor neutrons with doses $\sim 10^{17}$ n/cm², X-rays and "white" beam of synchrotron radiation ($h\nu \sim 12$ keV). The propagation depth of such particles and quanta is much higher than the thicknesses of our crystals, therefore the defects created during ion bombardment and photoexcitation were accepted to be homogeneous throughout the crystals. The samples were heat-treated at various temperatures in air. The optical absorption spectra were measured within 190-330 nm range by means of a double grating monochromator.

3. Results

It is accepted, that 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 of the material. These centers are well identified by characteristic absorption, excitation and emission bands in visible-UV-VUV spectral range. A simple scheme of energy level distribution of F and F⁺ centers in corundum single crystals can be represented like in Fig. 1.

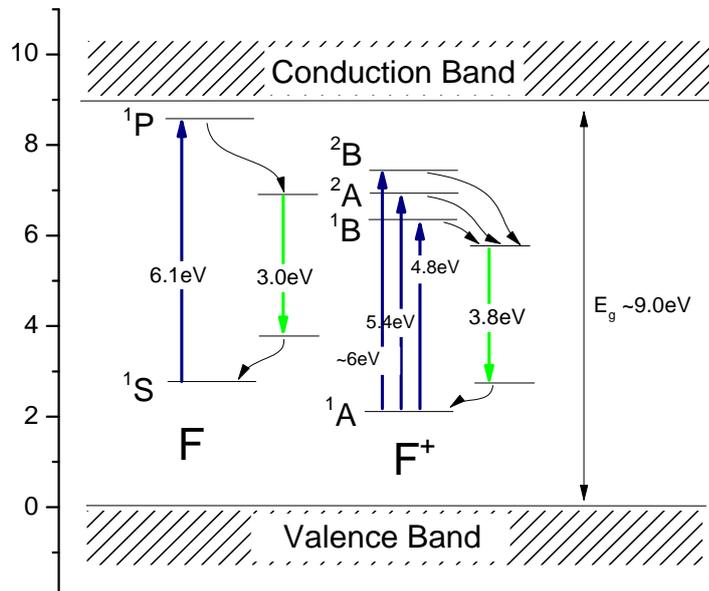


Fig. 1. Energy level diagram of F and F⁺ centers within the forbidden gap of corundum single crystal. Blue and green arrows show excitation and emission transitions with respective values, and curved arrows are non-radiative transitions between states.

A large Stokes shift between excitation and emission of centers (especially for F center the shift is more than 3 eV) is a result of cascade of non-radiative transitions between excited and relaxed states of defect centers.

Within the investigated range of optical absorption (Fig. 2, 3) the corundum single crystals are characterized by rather high transparency which decreases at higher energies (smaller wavelengths). As can be seen in the inset of Fig. 2, the optical absorption spectra (OAS) of non-irradiated and irradiated corundum samples differ significantly. The sample irradiation by high-energy electrons (50 MeV, dose of $3 \cdot 10^{17}$ electrons/cm²) results in the increase of absorption constant within the whole investigated spectral range. The spectra represent composite curves, superposition of all components of the induced absorption (IA) bands (i.e. the difference between the absorption constants before and after irradiation).

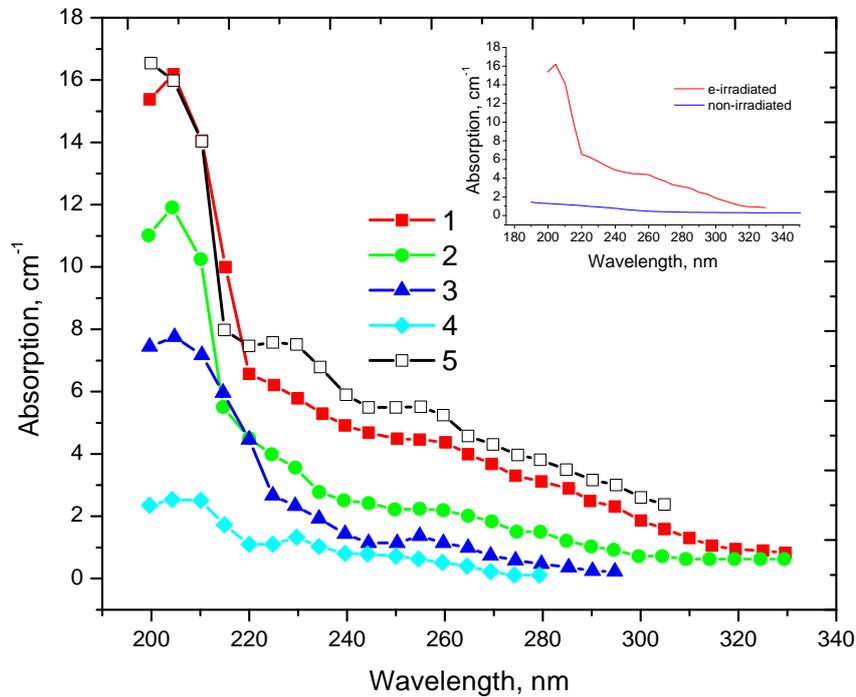


Fig. 2. Corundum optical absorption spectra (Verneuil crystal). Samples are irradiated with the dose of $3 \cdot 10^{17}$ electrons/cm². Curves: 1 – untreated sample; 2 – treated at 225°C for 15 min; 3 – 325°C for 15 min; 4 – 600°C for 15 min; 5 – untreated sample, measured at 77 K.

Evidently, the most intense is the 6.05 eV (205 nm) band in the spectrum. It is necessary to note that this absorption band is analogous to similar bands in the OA spectra of corundum grown by other methods. After heat-treatment of Verneuil crystals their OA spectra display distinct 5.4 eV (230 nm) and 4.86 eV (255 nm) bands. These bands are also well manifested when measuring OA spectra at 77 K (Fig. 2, curve 5). The appearance of these bands after annealing is probably related to different thermal stability of various bands forming the OA spectrum.

4. Discussion

It is known from previous publications [1-4, 8-19] that the most of detected absorption bands in corundum are caused by anion centers: F-centre (absorption at 6.05 eV - oxygen

vacancy with two localized electrons) and F^+ -centre (absorption at 5.4 eV, 4.86 eV - anion vacancy localized by single electron).

Figure 2 shows room and low temperature (curves 1 and 5 respectively) absorption spectra of Verneuil crystals irradiated with 50 MeV electrons and doses $3 \cdot 10^{17} \text{e/cm}^2$. The inset shows the difference between irradiated and non-irradiated crystals. The difference, which is additional absorption is evidently caused by defects created due to electron irradiation. However after annealing the absorption decreases, which is a result of reduction of defect concentration. As can be seen from the figure, the higher is annealing temperature, the less defects remain in crystal. It is important here to notice, that annealing at even as high temperature as 600°C will not completely remove all the defects from the material (fig 2, curve 4). The mechanism of defect elimination or transition from one type to another will be given below.

From the obtained results and other publications one can see that these bands well coincide in their location, half-width and thermal stability. To reveal the nature of the detected defects induced by electron irradiation, some samples irradiated by reactor neutrons with energy 2 MeV, dose of $10^{17} \text{neutrons/cm}^2$ and treated at 700°C were investigated as well.

The results shown in Fig. 3 are quite similar to those for e-irradiated samples. Even after 700°C annealing in neutron-irradiated crystal, a part of defects still exists with absorption at $\sim 255\text{nm}$ and $\sim 300\text{nm}$. The first one is ascribed to F^+ centers, while the origin of the second one is ambiguous and will be discussed later. X-ray irradiation causes increase of absorption in the whole investigated range, testifying to reappearance of defects. It is known that X-ray cannot create stable structural defects, therefore it is supposed that increased absorption is conditioned by recharging effects of initial defects.

The analysis of experimental data presented in Fig. 2, 3 clearly proves the existence of absorption bands belonging to F-(absorption band at 205nm) and F^+ -centers (absorption bands at 230 and 255nm), as well as to other color centers ($\sim 300\text{nm}$). Here it is important to notice that the detected absorption bands are directly connected with the charge state of the CC. It is known that in real crystals there also exist uncontrollable impurities of some metals which stimulate the formation of growth defects to maintain the charge neutrality and which can not be annihilated even as a result of high-temperature treatment. Such defects are potential traps for the point radiation defects such as interstitial ions and their vacancies. A part of these new defects can become color centers (F, F^+, F^{2+}) [11-18]. The depth of the above-mentioned potential wells

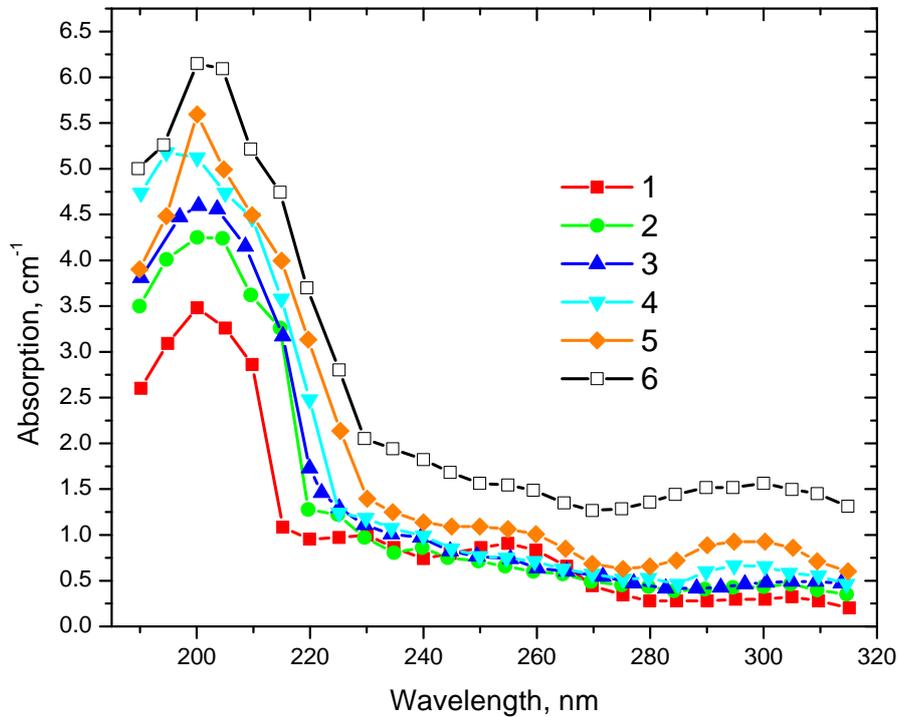
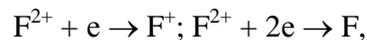


Fig. 3 - Optical absorption spectra of the irradiated (dose - $3 \cdot 10^{17} \text{ n/cm}^2$) and thermal treated corundum crystals (HOC sample). Curves: 1 – treated at 700°C ; 2 – X-ray irradiated during 90 sec; 3 – 150 sec; 4 – 300 sec; 5 – 450 sec; 6 – 600 sec.

sometimes can be so substantial that the interstitial ions are not capable to be released from these traps even at high temperatures (1000°C). Besides, irradiation with high-energy particles promotes an increase in density of such mechanical dislocations in the crystal matrix and, hence, the increase in the concentration of the localized interstitial ions which results in inhomogeneous concentration of vacancies and interstitial ions. There are inelastic interactions which modify the charge state of pre-irradiated defects according to the following reaction:



resulting in the formation of F – and F^+ – centers as well as other color centers and aggregate defects. Due to radiation-induced processes, a part of interstitial ions can migrate to the crystal surface because of their higher (in comparison with vacancies) mobility [18]. Hence, the OA bands - depending on the CC type and temperatures - become relatively stable. At 425°C a part of CC responsible for wide OAS, collapse and related bands become weaker. These CC are the

centers with an absorption band near 400 nm (not shown) caused by cation vacancies such as V^{\equiv} , V^{2-} , V^{-} , V^0 , where V^{\equiv} is a free cation vacancy and the others are cation vacancies with 1, 2, 3 localized holes, correspondingly.

Studies of thermal stimulated processes for both electron and neutron irradiated crystals have shown that when temperature increases to 1000°C, the optical absorption bands intensity decreases within the whole investigated spectral range (Fig. 2). The mentioned 6.2 eV absorption band (Fig. 3) was also detected by authors in [19] and ascribed to Fe^{3+} ions, but here it is caused by oxygen vacancies with two localized electrons - F-centers.

The appearance of several peaks in UV spectral range after X-ray irradiation - 205, 230 and 255 nm bands - specifies an incomplete annihilation of these centers at such high temperatures and hence the existence of a "threshold" for coloring.

The process of thermal ionization for color centers should be experimentally verified. With that end in view a series of experiments was carried out to reveal the state of some CC (Fig. 3, curves 2 - 4). It is seen from Fig. 3 that after X-ray irradiation, synchrotron radiation (SR) with $h\nu \sim 12$ keV (different exposure times) results in some changes of the absorption bands intensities. This experiment has shown that decrease in F^+ - center (230, 255 nm) band intensity in comparison with that of F - center takes place due to the formation of free electrons and holes in corundum after irradiation with high-energy SR photons. A part of electrons and holes are captured by single and complex CC (bands in near UV and visual spectral ranges), the others by F - and F^+ -centers. It is found [17] that in the case of neutron irradiation with energy 2 MeV as a result of a cascade of elastic collisions, the concentration of knocked-out atoms is higher by two orders of magnitude than in the case of electron irradiation with the same dose, and should be even higher taking into account the losses of the basic part of electron energy at inelastic scattering due to the Coulomb interaction.

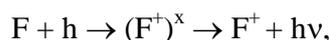
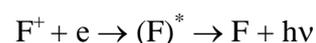
Before the collision with the atoms of material the accelerated electrons lose a considerable part of their energy due to ionization, that is why the number of generated vacancies, oxygen (O_i) and aluminum (Al_i) interstitial ions in the case of electron irradiation is much less than in the case of neutron irradiation.

The CC responsible for the 302 nm absorption band (4.1 eV) and the ions of uncontrollable impurities can be one of the reasons of increased absorption within the 290-320 nm spectral range (Fig. 3). Revealing the nature of this band is of much interest because the CC responsible

for this band play essential role in the corundum "radiation memory" phenomenon. According to [20], the 302 nm band is caused by F_2 - type complex centers. In [11] we have shown that the process of F –centers aggregation cannot be carried out even at temperatures above 1000°C. Migration of anion vacancies at the temperatures below 1800°C and their subsequent aggregation is impossible [16,21].

From the obtained experimental results it follows that the existence of F - centre and CC (302 nm absorption band) enables to present them as complexes. The CC energy states are related, basically, to the aluminum charge states and can only enter into the complexes with anion vacancies as $[Al_i^+F]$ centers [17].

The carried out photostimulation investigations (not brought here) have shown that when the F^+ - center captures electron, excited F centers are formed which participate in the following recombination processes (with various durations):



where e and h are free electron-hole pairs formed during X-ray irradiation.

Apparently, such high radiation resistance of corundum is caused by large radiation instability areas of genetic Frenkel pairs. The recombination of the anion genetic Frenkel pairs components in the investigated areas does not occur, which results in linear accumulation of CC at the radiation type dependent dose.

The luminescence and excitation spectra in the fundamental absorption region were investigated to analyze the participation of these CCs in the formation of luminescence quantum yield. It is found that the relative luminescence intensity is increased in the irradiated and thermal treated samples after their repeated irradiation with high-energy SR photons.

This assumption is confirmed by the fact that the electron-hole recombination processes occur in samples promoting the increase in concentration of the CCs participating in the formation of luminescence processes, i.e. the "radiation memory" phenomenon.

5. Conclusions

Thus, in the presented work the existence of radiation-induced defects is proved in corundum crystals, formed as a result of irradiation by high-energy particles. Spectral

distribution of the absorption spectra, the absorption band peaks caused by F, F⁺ color centers (Fig. 2 and 3) are determined.

The experimental results are presented confirming clearly the effect of thermal treatment on the behavior of the absorption bands, i.e. decrease of the absorption intensities within the investigated area. Based on these experimental regularities (irradiation, heat treatment), the mechanism of the “radiation memory” phenomenon as a result of repeated irradiation by X-ray quanta is offered.

The “radiation memory” phenomenon allows to explain the whole collection of experimentally revealed results of irradiation of solids from the united position. The study of radiation and optical properties of corundum single crystals in a wide spectral range has allowed to reveal and interpret the “radiation memory” phenomenon.

References

1. **S.W.S. McKeever**. Rad. Measurements 46, 1336 (2011).
2. **S.M.S. Damkjaer, C.E. Andersen**. Rad. Measurements 45, 671(2010).
3. **R.A.Z.M. Mohammad, T. Kobayashi, T. Awata, K. Atobe**. Rad. Effects Solids: Incorporat. Plasma Sci. Plasma Technol. **165**, 4, 290 (2010).
4. **G.O. Sawakuchi, Y.G. Yukihiro, S.W.S. McKeever, E.R. Benton**. J. Appl. Phys. 104, 124 903 (2008).
5. **X. Yang, H. Li, Q. Bi, Y. Cheng, Q. Tang, X. Qian, J. Xu**. J. Lumin. 129, 566 (2010).
6. **V.S. Kortov, I. I. Milman, S.V. Nikiforov, E.V. Moiseykin**. Phys.Stat. Sol. (c) 2, № 1, , 515-518 (2005).
7. **V.V. Harutyunyan**. Surface. X-ray, electron, neutron examinations. No7, 69 (in Russian) (2001).
8. **V.V. Harutyunyan, R.K. Ezoyan, V.A. Gevorkyan**. Phys. Stat. Sol., (b), v.149, # 77 (1988).
9. **V.V. Harutyunyan, V.A. Gevorkyan, V.N. Makhov**. The European Phys. Journal B, v.12, 31 (1999).
10. **V.V. Harutyunyan, M. Kirm, V.N. Makhov, G. Zimmerer**. Preprint DESY,HasyLab, Part I, 601 (2002).
11. **S.I. Choi, T. Takeyehi**. Phys. Rev. Lett., v.50, 19, 1474 (1983).

12. **V.V. Harutyunyan, T.S. Hakobyan, V.A. Gevorkyan**, Phys. Stat. Sol., (a), v.171, 2, 623, (1999).
13. **A. Lushchik, E. Feldbach, M. Kirm, G. Zimmerer**. J.of Electron spectroscopy and related phenomena. v.101-103, 587 (1999).
14. **R.R. Atabekyan, V.L. Vinetskii, V.A. Gevorkyan, R.K. Ezoyan, G.N. Eritsyan**. FTT, 9, 23, 1446 (1983).
15. **V.V. Harutyunyan, V.A. Gevorkyan, A.K. Babayan**. FTT, т.37, 4, 953 (in Russian) (1995).
16. **V. Makhov, A. Lushchik, Ch. Lushchik, M. Kirm, T. Vasilchenko, S. Vielhauer, V. Harutyunyan, E. Aleksanyan**. Nuclear Instruments and Methods in Physics Research B 266 P. 2949-2952 (2008).
17. **R.R. Atabekyan, R.K. Ezoyan, V.A. Gevorkyan, V.L. Vinetskii**. Cryst. Latt. Def. Amorph. Mat., v.14, 155 (1987).
18. **K.J. Caulfield, R. Cooper**. Phys. Rev. B.v.47, 55 (1993).
19. **E.R. Ilmas, A.I. Kuznetsov, I.A. Merilo**. J. of Applied Spectrometry, v. 24, No 4, 643 (1976). (in Russian).
20. **A.I. Surdo, V.S. Kortov, I.I. Milman**. Optics and Spectroscopy, v.64, 6, 1363 (1987).
21. **E. Aleksanyan, M. Kirm, S. Vielhauer, V. Harutyunyan**. Radiation Measurements, 56, pp.54-57 (2013).