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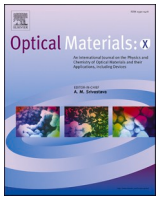

Influence of swift heavy ions irradiation on optical and luminescence properties of $Y_3Al_5O_{12}$ single crystals

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ABSTRACT

Optical and luminescence properties of $Y_3Al_5O_{12}$ (YAG) single crystals preliminary irradiated by swift heavy ions were studied. Swift heavy Xe ions with fluences ranging from $6{\cdot}10^{10}$ to $2{\cdot}10^{12}$ ions/cm^2 were utilized for the irradiation of nominally undoped YAG single crystals. A stable strong induced absorption observed in the 200–600 nm spectral range correlates with the irradiation fluence. It is suggested that several centers are responsible for this induced absorption in YAG single crystals and their possible origin (F-type centers) is proposed and discussed. The swift heavy ions irradiation strongly modifies the luminescence properties of YAG, namely, the excitonic emission at liquid helium temperature is drastically suppressed in heavily irradiated crystals.

1. Introduction

Yttrium aluminum garnet (YAG) single crystal is a well-known optical material. Undoped YAG has broad optical transparency, high hardness, and chemical and heat resistance and therefore it is widely used for a variety of optics [1–3]. Since this crystal does not exhibit birefringence, YAG crystals doped with rare-earth impurities are actively used as laser media [4]. On the other hand, YAG doped with cerium ions is one of the popular scintillators for detecting ionizing radiation [5–7]. For many applications especially in the case of utilization of YAG crystals as a laser material or as a scintillator the knowledge about induced defects and radiation resistance of YAG single crystals is important. The whole point is that radiation induced damages drastically modify the optical characteristics of crystals deteriorating their laser and scintillating performances. The same applies to optical components based on undoped YAG when used in radiation-aggressive environments, for example in space or fusion applications.

In the current research, radiation defects and radiation damage in undoped YAG have been induced by swift heavy ions (SHI). Such irradiation is capable of producing radiation defects similar to those generated by neutrons, i.e., it is a good alternative to neutron irradiation, which needs a significantly longer time for samples' relaxation after neutron treatment. It is generally accepted that elastic collisions of incident energetic particles with material nuclei/atoms are mainly responsible for radiation damage (formation of Frenkel pairs) in metal oxides as well as in complex oxides including YAG [8–10]. This displacement (impact, knock-on) mechanism solely describes radiation damage under complex oxide irradiation by fast neutrons. This displacement (impact, knock-on) mechanism solely describes radiation damage under complex oxide irradiation by fast neutrons. On the other hand, ion irradiation can yield high damage rates with negligible or no residual radioactivity and at a very low cost. One of the advantages of ion irradiation is the attained damage, which is 10^4 times greater than that of reactor irradiation. In turn, this allows us to reach 200 dpa (displacements-per-atom) in days instead of decades [11,12]. Therefore, it is suggested that the irradiation of SHI produces stable radiation defects in the lattice of the YAG crystal. The elucidation of the role of induced radiation defects on optical and luminescence properties in undoped YAG single crystals is the main goal of the current study. For this purpose, the irradiated YAG crystals have been examined by means of optical and luminescence spectroscopy including vacuum ultraviolet (VUV) excitation spectroscopy. Taking into account that YAG belongs to the class of wide bandgap materials VUV photons are needed in order to excite intrinsic luminescence in YAG, thus we have utilized synchrotron radiation, which is the best VUV source for luminescence experiments in wide bandgap materials [13–20].

Taking into account that the YAG single crystal is a well-known model garnet, the results obtained in the current research will be

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useful for understanding and interpretation of SHI-induced radiation damage in other relevant garnets that have high potential in high-energy physics and fusion applications [21].

2. Experiments

2.1. Irradiation procedure

Nominally undoped YAG single crystals were produced by Alineason. The crystals were cut into small (5 × 5 mm^2) thin (1 mm thickness) pieces and polished for optical experiments. The crystals were irradiated with 156 MeV Xe ions to fluences from $6.6{\cdot}10^{10}$ to $2{\cdot}10^{12}$ cm^{-2} at the IC-100 at FLNR JINR (Dubna, Russia). Ion beam homogeneity over the irradiated specimen surface was controlled using beam scanning in the horizontal and vertical directions and was better than 10 %. Average Xe ion fluxes were less than 108 $cm^{-2}s^{-1}$ in order to avoid any significant heating of the specimens. To widen the ion energy range, Al degraders of varying thicknesses have been used. Using SRIM calculations the penetration depth of the Xe ions into YAG is estimated as 10.95 μm.

2.2. Characterization of irradiated crystals

Optical properties of the radiation-induced defects in the YAG single crystals were studied by means of Cary 7000 spectrophotometer and spectroscopic ellipsometer RC2-XI (Woollam). The main ellipsometric parameters Ψ and Δ were measured at the incident angles from 50° to 70° with the step of 5°. Dispersion curves of refractive index **n** were modeled using Cauchy oscillator functions. Regression analysis of experimental spectroscopic ellipsometry data was performed using the Woollam software CompleteEASE®. These experiments were carried out at room temperature.

In addition, the samples were tested by means of luminescence spectroscopy under synchrotron radiation excitations in the VUV range. These experiments were carried out at the Superlumi setup installed on the P66 beamline of the PETRA III storage ring at the DESY synchrotron facility (Hamburg, Germany). Some details of this experimental setup can be found elsewhere [22]. The excitation spectra were measured in the 330-100 nm excitation range at a low temperature (12 K). These spectra were corrected with respect to the sodium salicylate signal.

3. Results and discussion

Optical properties of the heavily irradiated ($2{\cdot}10^{12}$ ions/cm^2) and non-irradiated YAG crystals were obtained in the spectral range from 210 nm to 1690 nm (Fig. 1). For irradiated crystal, a slight decrease in refractive index is observed in the region of shorter wavelength. In further consideration, one can see that the induced radiation defects are mostly optically active exactly in the short wavelength spectral range.

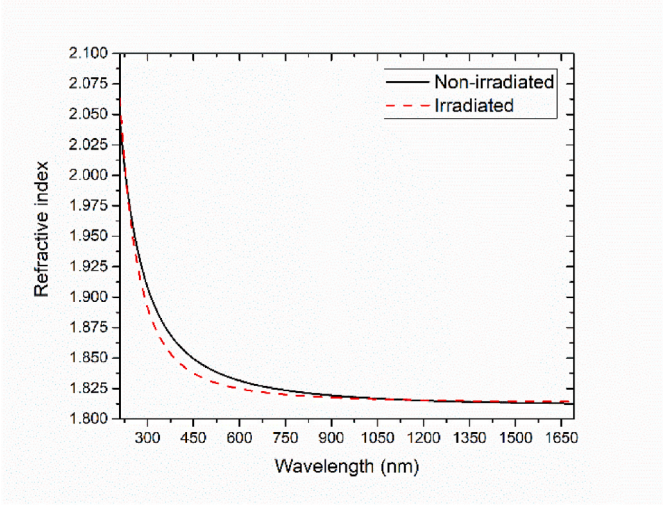

Fig. 1. Refractive index of non-irradiated and irradiated YAG single crystals. Extinction coefficient **k** = 0 in both cases.

Fig. 2 exhibits the comparison of absorption spectra (optical density) in the 200–600 nm spectral range of virgin and irradiated YAG single crystals. This picture clearly shows that the induced absorption is highly dependent on the irradiation fluences – if the irradiation fluence increases, the induced absorption becomes more intense. Obviously, the broad induced absorption observed in Fig. 2 is the result of the overlapping of several absorption bands, which belong to several types of radiation defect centers in YAG. It is well established that the main radiation defects in YAG are F-type centers, which are, in fact, oxygen vacancies with one, two, or three trapped electrons. It is known that the F-center (two electrons trapped by an oxygen vacancy) in YAG has absorption bands at 6.35 eV (195 nm) and 5.16 eV (240 nm) [23–25], while the F^+-center (an electron trapped by a vacancy) reveals absorption bands at 5.27 eV (235 nm) and 3.35 eV (370 nm) [23–25]. F^- center (three electrons trapped by oxygen vacancy) is supposed to have absorption bands at 3.44 eV (360 nm), 2.58 eV (480 nm), and 1.49 eV (830 nm) [23]. Known absorption energies of F-type centers are shown by arrows in Fig. 2(b). Based on these literature data we can suggest that the intensive induced absorption at wavelengths shorter than 220 nm is the onset of the intensive absorption band of F-center peaking at 6.35 eV (195 nm).

Furthermore, the induced absorption spectra have the well-resolved peak at 4.9 eV (250 nm) and the well-resolved absorption shoulder at about 3.9–4.1 eV (300–310 nm), which cannot be explained as standard F or F^+ centers. These absorption bands are marked by the block arrows in Fig. 2(b) and they have been observed before and reported in Refs. [26–30]. The origin of these two abortion bands was intensively discussed before. For instance, in Ref. [27] the absorption at 4.9 eV is explained as the absorption band of Fe^{2+}, but the band at 3.9 eV is due to O^{2-}-Fe^{3+} transition. However, the strong dependence of these absorption band intensities on SHI fluences cannot be explained extrinsic origin of such centers. Therefore, we are inclined to agree with the model that the 4.9 eV and 4.0 eV absorption bands are assigned to the F^+ centers near the *antisite* (Y^{3+}_{Al}) defect [24] and near the Fe^{2+} center [29] respectively.

Additional information about SHI radiation induced defects in YAG single crystals can be retrieved from the luminescence experiments. It is well known that YAG compound exhibits intensive intrinsic emission at 280 nm at low temperatures, which results from radiative recombination of the self-trapped exciton (STE) [31]. Fig. 3 exhibits the excitation spectra of STE luminescence observed in the virgin and the irradiated YAG crystals at liquid helium temperature. It is clearly seen that the intensity of the excitation spectra gradually decreases over the entire energy range with increasing irradiation fluences. This result indicates that the concentration of luminescence center – STE in the regular lattice of YAG – diminishes if irradiation fluence of SHI increases.

Upon a detailed analysis of the excitation spectra (Fig. 3), one can notice that the most significant changes are observed in the low-energy spectral range. The excitation intensity in the region of 6.5–6.6 eV (about 185 nm) drops down by a factor of 4 already at the smallest irradiation fluence, and at higher fluences the excitation intensity in this region tends to zero. We associate such change in the excitation spectra with the efficient reabsorption by the F-centers, which have an intense absorption band in this region (see discussion above).

The next feature in the excitation spectra in Fig. 3 is the spectral range 6.9–7.5 eV. In this spectral region, a significant dip in intensity is observed in the excitation spectra. By analogy with the reabsorption by F-centers discussed above, we assume that the characteristic degradation in the range of 6.7–7.5 eV in the excitation spectra may also be due to reabsorption by some radiation-induced center. Recently in SHI irradiated $MgAl_2O_4$ crystals the radiation induced absorption band at 7 eV was detected, which was explained by the formation of the exciton-

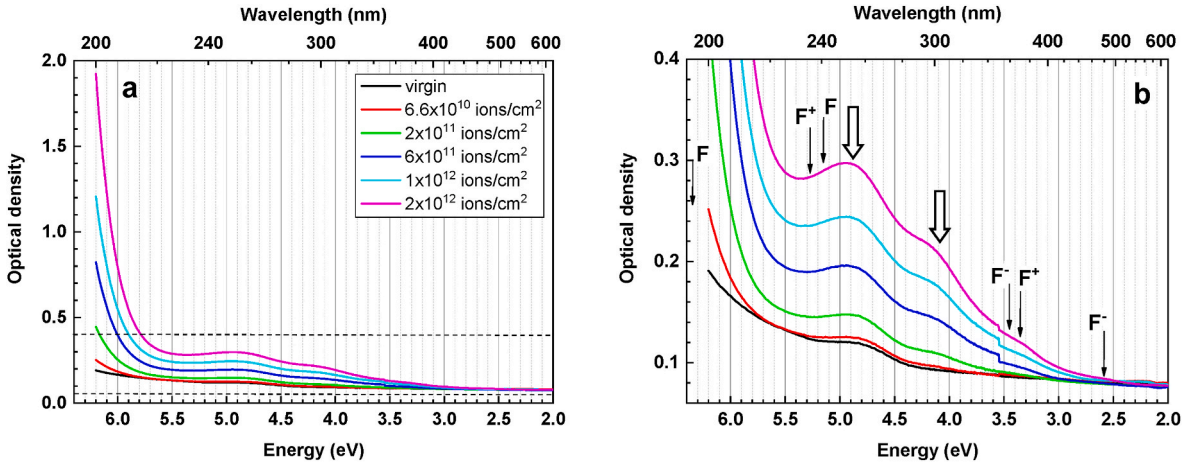

Fig. 2. Absorption spectra of YAG single crystals depending on the fluences of SHI **(a)**. The area between two horizontal dashed lines in **(a)** is shown in detail in **(b)**. The arrows show the absorption energies of F-type centers in YAG known in the literature, whereas the block arrows show the absorption bands discussed in the text.

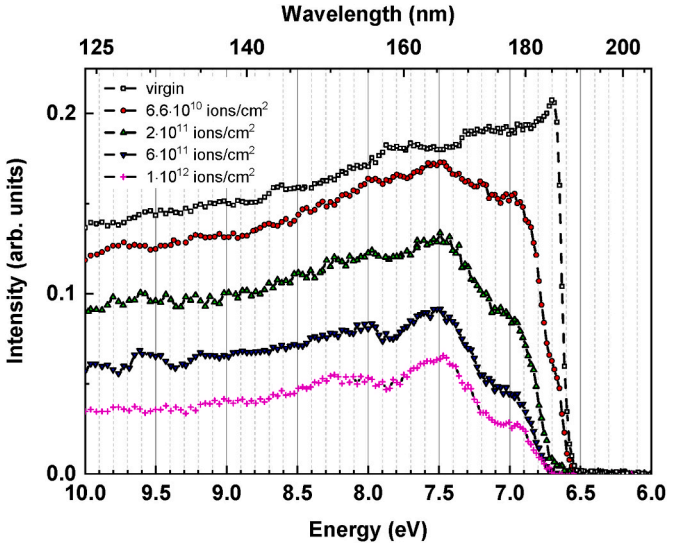

Fig. 3. Excitation spectra in virgin YAG as well as in YAG single crystals irradiated with different fluences of SHI at 12 K. Emission wavelength is monitored at 280 nm (4.42 eV).

like states (bound excitons) near the *antisite* defects [32,33]. We assume that such a center can be responsible for the reabsorption in the excitation spectra in Fig. 3 in the region 6.9–7.5 eV.

4. Conclusions

In the current paper, we demonstrated how the radiation defects induced by swift heavy ions modify optical and luminescence properties in YAG single crystals. It was clearly shown that the radiation defects due to the swift heavy ions irradiation are responsible for the broad induced absorption, which covers a wide spectral range (200–500 nm). The obtained induced absorption spectra were analyzed and we suggested that F-type centers in YAG are responsible for the induced absorption. In addition, swift heavy ion irradiations lead to the drastic degradation of the intrinsic excitonic luminescence in YAG single crystals. This degradation is thought to be related to a high concentration of induced radiation defects which, in turn, lead to a decrease in the number of self-trapped excitons in the regular lattice.

CRediT authorship contribution statement

V. Pankratova: Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **J. Butikova:** Validation, Methodology, Formal analysis, Data curation. **A. Kotlov:** Validation, Resources, Methodology, Data curation. **A.I. Popov:** Validation, Supervision, Project administration, Funding acquisition, Formal analysis. **V. Pankratov:** Writing – original draft, Validation, Supervision, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Vladimir Pankratov reports financial support was provided by University of Latvia Institute of Solid State Physics. Viktorija Pankratova reports financial support was provided by University of Latvia Institute of Solid State Physics. Anatoli I Popov reports financial support was provided by University of Latvia Institute of Solid State Physics. Aleksei Kotlov reports financial support was provided by DESY. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.omx.2024.100341.

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