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Article

Confocal and time-resolved photoluminescence spectra of $MgAl_2O_4$ spinel crystals irradiated with swift heavy bismuth ions

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Abstract. Laser confocal microscopy technique (60 ps laser pulse excitation at 445 nm) and a time-correlated single photon counting (TCSPC) technique have been used to study photoluminescence (PL) in 710 MeV Bi ion irradiated MgAl2O4 single crystals. It was shown that radiation defects produced by swift Bi ions give rise to luminescence with peak at 1.9 eV. Gaussian deconvolution of the PL spectrum reveals that the band consists of three components: the first with a peak at 1.8 eV, the second at 2.1 eV, and the third at 2.35 eV. For the spinel sample irradiated to a fluence of $\Phi = 1\times10^{12}$ ions/cm², both PL and time-resolved photoluminescence (TRPL) spectra were measured as a function of depth within the irradiated layer using a confocal geometry. It was found that with increasing energy loss due to elastic collisions, the PL peak undergoes a redshift, which is more pronounced compared to surface emission measurements.
Keywords: MgAl2O4 single crystals, confocal and time-resolved photoluminescence, radiation-induced defects, swift heavy ions, tracks.

1. Introduction

Aluminum-magnesium spinel, $MgAl_2O_4$, is one of the most extensively studied optical materials due to its high radiation resistance, chemical and thermal stability, mechanical strength, and optical transparency across a wide spectral range—from infrared to ultraviolet. These properties make it suitable for use as an inert matrix for the transmutation of long-lived actinides, diagnostic windows in fusion reactors, and in dosimetry applications when doped with transition 3d elements or rare-earth ions to achieve desired optical properties, among other uses [1], [2], [3].

This potential for various applications has driven continuous and extensive research into the structure and optical properties of spinel using various radiation sources, primarily neutron and low-energy ion irradiation [3], [4], [5], [6], [7]. Notably, it has been found that $MgAl_2O_4$ does not amorphize under irradiation at temperatures above 300 K up to a radiation damage dose of approximately 100 dpa [7]. At the same time, spinel—with a relatively low threshold for specific ionization energy loss (~7.5 keV/nm) required to form latent tracks—is sensitive to swift heavy ion irradiation that simulates the impact of fission fragments [8].

A detailed analysis of ion track morphology in spinel was carried out in [9], [10][13-16], where the configuration of isolated ion tracks induced by 200 MeV Xe and 350 MeV Au ions in stoichiometric spinel, $MgO\cdot Al_2O_3$, was studied using high resolution transmission electron microscopy with bright-field imaging (HR-TEM) combined with high-angle resolution X-ray spectrometry. It was shown that a single ion track in spinel appears as a circle consisting of three concentric defect zones. At the center, a phase transformation to a NaCl-type rock-salt structure was observed (1 nm in radius). This rock-salt-like defect structure was surrounded by a strained region (radius of 3 nm) and a cation-disordered zone (approximately 5–6 nm in radius). Multiple overlapping non-amorphous discontinuous ion tracks led to full amorphization of the irradiated layer in $MgAl_2O_4$ [11].

X-ray diffraction analysis [10] revealed an order-disorder transition in $MgAl_2O_4$ irradiated with 765 MeV Kr ions at a high fluence of 10^{14} cm^{-2} and partial amorphization, without any change in the space group. However, there was no evidence of a phase transformation to a rock-salt structure, as the electronic stopping power of 765 MeV Kr ions (Se ~ 14 keV/nm) is significantly lower than that of 350 MeV Au ions (Se ~ 35 keV/nm).

As far as we know, photoluminescence of $MgAl_2O_4$ irradiated with high-energy heavy ions in the regime where electronic stopping exceeds the track formation threshold has not been reported.

The present paper deals with the photoluminescence and pulsed photoluminescence of spinel crystals irradiated with 710 MeV bismuth when tracks are also created.

2. Methods

In this study, single crystals of stoichiometric $MgAl_2O_4$ spinel with a thickness of 500 μm and (100) orientation, purchased from CRYSTAL GmbH (grown using the Czochralski method), were used. The samples were irradiated with 710 MeV Bi ions at fluences ranging from 1×10^{10} to 2×10^{12} cm^{-2} at room temperature using the IC-100 cyclotron at FLNR, JINR, Dubna. The homogeneity of the ion beam across the irradiated sample surface was monitored via horizontal and vertical beam scanning and was better than 10%.

To exclude the influence of the unirradiated part of the crystal and to detect the stimulated emission solely from the near-surface layer of the sample, we employed laser confocal microscopy. As is well known, unlike standard photoluminescence measurement geometries, confocal microscopy provides spatial localization of the excitation light beam and enables luminescence detection with a spatial resolution of approximately 1 μm. In our case, this allows measurements to be conducted within the target layer, where structural modifications are predominantly driven by ionization energy loss.

Photoluminescence (PL) spectra and kinetics were measured using an Ntegra Spectra confocal scanning microscope (NT-MDT). The luminescence was excited by a picosecond laser diode head (PDL 800-D, PicoQuant) operating at an excitation wavelength of 445 ± 3 nm and a pulse duration of approximately 60 ps. The spectra were collected from a subsurface layer no thicker than 2 μm. The optical system provided a depth resolution of 1.7 μm, as determined by scanning the laser spot across the crystal edge and calculating the first derivative of the luminescence intensity. The decay of time-resolved photoluminescence (TRPL) at selected wavelengths within the 500–650 nm spectral range was measured using the time-correlated single photon counting (a time-correlated single photon counting (TCSPC) technique) technique. Decay curves were analyzed using Easytag 2 software [9]. The signal from the photomultiplier tube (PMA 175, PicoQuant), along with the synchronization signal from the diode laser, served as inputs for the TCSPC board (TimeHarp, PicoQuant). The temporal resolution of the system was approximately 200 ps.

3. Results and Discussion

Luminescence was excited at a wavelength of 445 nm (2.75 eV) using pulses with a full width at half maximum (FWHM) of less than 80 ps. Decay curves in the spectral range of 500–700 nm were recorded using a system based on a PMA-175 detector and a TCSPC module, with a temporal resolution of 300 ps. Figure 1 shows the PL dependence on fluence under irradiation with 710 MeV Bi ions, measured in a standard geometry. A broad PL band is observed in the range of 450–750 nm (2.76–1.6 eV). As the fluence increases, the luminescence intensity also increases. A slight redshift of the emission peak is observed. Figure 2 presents the Gaussian decomposition of the PL spectrum at a fluence of 2×10^{12} ions/cm^2. It consists of three bands: the first with a peak at 1.8 eV and FWHM of 0.3 eV; the second with a peak at 2.1 eV and FWHM of 0.4 eV; and the third with a peak at 2.35 eV and FWHM of 0.23 eV.

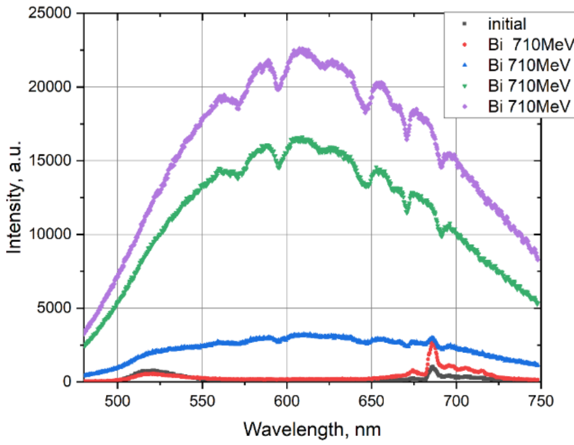


Figure 1 – Photoluminescence spectra of $MgAl_2O_4$ crystals irradiated with 710 MeV Bi ions under excitation at λ_{ex} = 445 nm

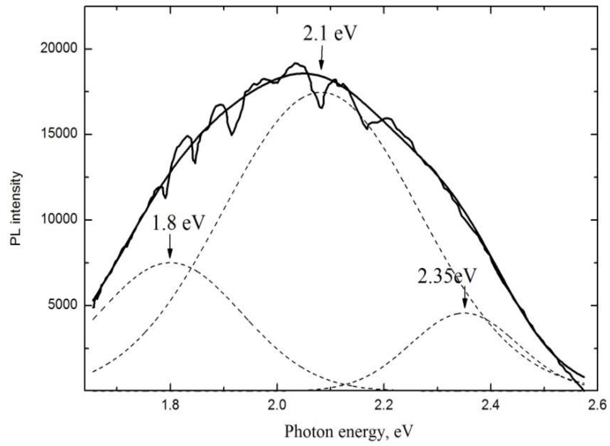


Figure 2 – Gaussian decomposition of the photoluminescence spectrum of $MgAl_2O_4$ crystals irradiated with 710 MeV Bi ions under excitation at λex = 445 nm

For the $MgAl_2O_4$ spinel sample irradiated to a fluence of $\Phi = 1\times10^{12}$ cm^{-2}, depth-resolved PL and TRPL spectra were measured using confocal geometry. Figure 3 shows PL spectra recorded on a cross-sectional cleavage at depths of 2, 12, and 24 μm from the irradiated surface. It was found that, with increasing energy loss due to elastic collisions, the PL peak shifts toward longer wavelengths. This redshift is more pronounced than in surface emission measurements, indicating that it is caused by defects generated via nuclear energy loss mechanisms.

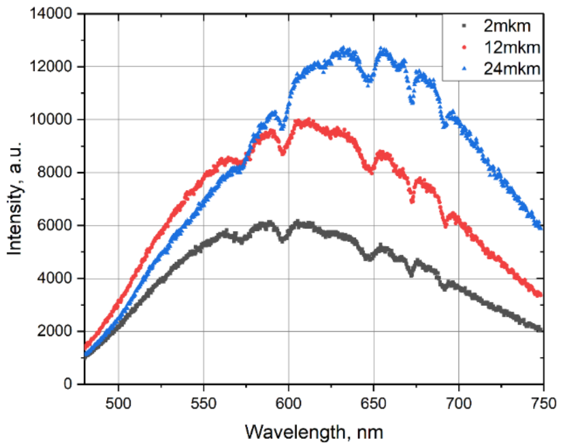


Figure 3 – Depth dependence of the photoluminescence spectra of an $MgAl_2O_4$ single crystal irradiated with Bi ions to a fluence of 1×10^{12} cm^{-2}. Excitation wavelength: λex = 445 nm

A similar effect was previously observed in LiF crystals [18], where enhanced PL from F_2 and F_3^+ aggregate color centers was detected. It was suggested that, at the end of the ion track—where elastic collisions dominate—vacancy production contributes significantly. In $MgAl_2O_4$, intrinsic luminescent centers include F^+ and F centers, antisite defects, and exciton-related emission. According to [12], at high concentrations of F^+ and F centers, PL with a peak at 2.7 eV is observed, attributed to radiative transitions from excited to ground states of F^+ and F centers. This 2.7 eV emission is predominantly excited through absorption by F^+ centers, likely surrounded by a high density of defects within their first and second coordination shells.

X-ray excitation of $MgAl_2O_4$ crystals results in a broad emission band in the spectral range of 3.15–4.2 eV (295–354 nm), which, according to [12], is attributed to antisite defects (AD). The origin of PL with a maximum at 5.3 eV remains unclear [13]. The most common impurities in the $MgAl_2O_4$ matrix are Cr^{3+} and Mn^{2+} ions [13], as confirmed by the photoluminescence of the as-grown, unirradiated $MgAl_2O_4$ crystals shown in Figure 4.

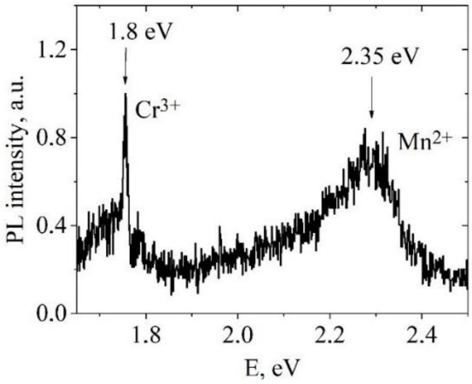
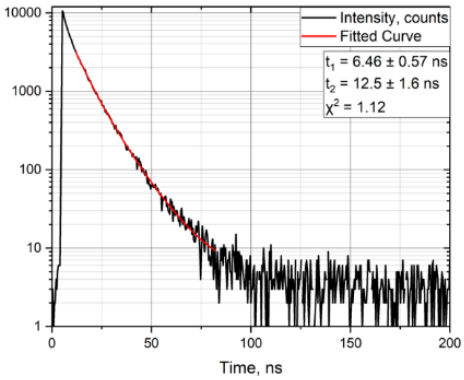


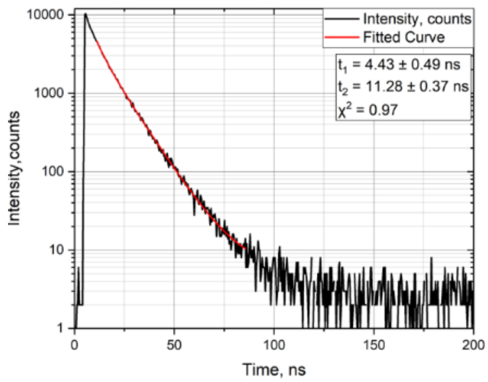
Figure 4 – Photoluminescence spectrum of an unirradiated $MgAl_2O_4$ crystal excited at 2.78 eV (445 nm)

A sharp shift of the maximum from 2.1 eV at a distance of 12 μm to 1.9 eV at the end of the ion path, accompanied by a surge in intensity, indicates that the stopped bismuth ion created a deformation field around itself. The track region is amorphized.

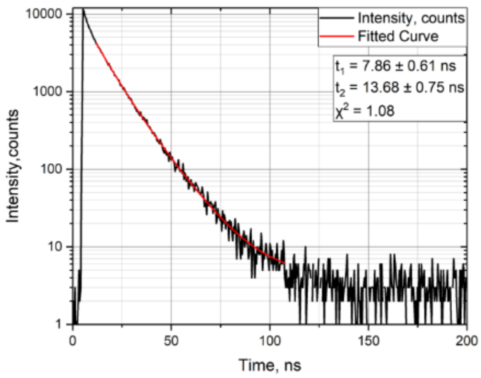
Figure 5 shows the kinetic decay curves measured at the same points as the PL spectra (Figure 4). The measurements were taken at the maximum of the PL band. The lifetimes of the excited states were determined.



a) Data measured at depths of 2 μm



b) Data measured at depths of 12 μm



c) Data measured at depths of 24 μm

Figure 5 – Photoluminescence decay kinetics of an $MgAl_2O_4$ single crystal irradiated with Bi ions to a fluence of 1×10^{12} cm^{-2}

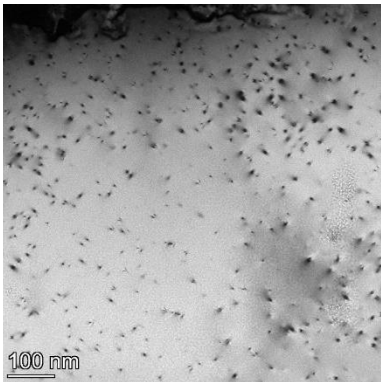
A distinguishing feature of the PPL band at 1.9–2.1 eV is its strong intensity at room temperature. The decay kinetics of the 1.9 eV band at T = 296 K can be described by a double-exponential function with two distinct characteristic lifetimes, as presented in Table 1. Based on the data in Table 1, it can be concluded that the characteristic decay times of both the fast and slower components of the PPL signal are independent of depth within the measurement uncertainty.

Table 1 – Example of a table

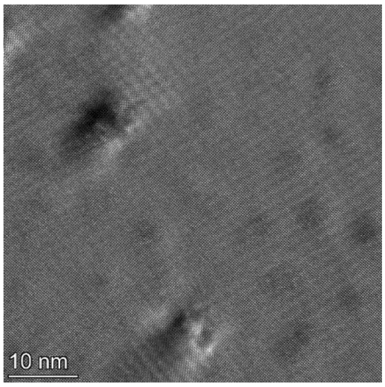
Depth, μm	t_1, ns	t_2, ns
2	6.46±0.57	12.5 ±1.6
12	4.43±0.49	11.28±0.37
24	7.86±0.61	13.68±0.75

The formation of tracks in $MgAl_2O_4$ spinel crystals irradiated with 710 MeV ions is beyond doubt, as track formation has been previously observed under irradiation with 100 MeV Xe, 200 MeV Xe, and 340 MeV Au ions [8], [14], [15]. For instance, the track diameter for 100 MeV Xe ions is reported to be 4.9–5.1 nm based on small-angle X-ray scattering data [15], which agrees well with the size of the deformed region observed via transmission electron microscopy [2].

Figure 6 shows transmission electron microscopy images of radiation-induced microstructural changes in spinel crystals irradiated with Bi ions to a fluence of 10^{11} cm^{-2}, obtained at the Joint Institute for Nuclear Research (JINR), Dubna.



a) Data measured at 100 nm



b) Data measured at 10 nm

Figure 6 – High-resolution transmission electron microscopy images of latent ion tracks in $MgAl_2O_4$ spinel irradiated with Bi ions

The track diameter for 100 MeV Xe ions, for example, is reported to be 4.9–5.1 nm based on small-angle X-ray scattering data [26], which coincides with the size of the deformed region observed by transmission electron microscopy [13, 23].

The observed photoluminescence is highly sensitive to structural disorder and is likely associated with the emission from aggregate electronic color centers, such as F_2^{2+} centers in Al_2O_3, which exhibit a luminescence peak at 2.2 eV [27]. These centers typically form at high fluences due to track overlapping. The 1.9 eV luminescence enhancement near the end of the ion trajectory may be related to the creation of vacancies.

4. Conclusions

A photoluminescence (PL) band at 1.9 eV is observed in $MgAl_2O_4$ spinel irradiated with 710 MeV Bi ions. Gaussian deconvolution of the PL spectrum reveals that the band consists of three components: the first with a peak at 1.8 eV and a full width at half maximum (FWHM) of 0.3 eV, the second at 2.1 eV (FWHM = 0.4 eV), and the third at 2.35 eV (FWHM = 0.23 eV).

For the spinel sample irradiated to a fluence of $\Phi = 1\times10^{12}$ ions/cm², both PL and time-resolved photoluminescence (TRPL) spectra were measured as a function of depth within the irradiated layer using a confocal geometry. It was found that with increasing energy loss due to elastic collisions, the PL peak undergoes a redshift, which is more pronounced compared to surface emission measurements.

A significant shift of the 2.1 eV peak to 1.9 eV at a depth of 12 μm—near the end of the ion range—accompanied by an intensity spike, indicates that the decelerated bismuth ion induces a local deformation field.

The observed PL is extremely sensitive to structural disorder and is presumably associated with the luminescence of aggregate electronic color centers, such as F_2^{2+} centers with a peak emission at 2.2 eV. These centers are typically formed under high fluence conditions due to overlapping ion tracks. The 1.9 eV luminescence spike near the ion stopping range may be related to vacancy creation.

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Nikita Kirilkin – resources, data collection, testing, modeling.
Meruert Mamatova – analysis, visualization, interpretation, drafting, editing.

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