EUROFUSION WPMAT-PR(16) 15743

E Feldbach et al.

Radiation resistance diagnostics of wide-gap optical materials

Preprint of Paper to be submitted for publication in
Optical Materials

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

Radiation resistance diagnostics of wide-gap optical materials

Eduard Feldbach[a*], Eliko Tõldsepp[a], Marco Kirm[a], Aleksandr Lushchik[a],
Kenichiro Mizohata[b], Jyrki Räisänen[b]

[a]*Institute of Physics, University of Tartu, W. Ostwaldi Str. 1, Tartu, Estonia*

[b]*Department of Physics, University of Helsinki, P.O. Box 43, Finland*

*corresponding author: Eduard Feldbach, eduard.feldbach@ut.ee

Abstract

Novel approach in the detection of radiation damage created by ion beams in optical materials was demonstrated. Protons of the energy of 100 keV and fluence of $10^{17}/cm^2$ create sufficient amount of crystal lattice defects in the thin surface layer for testing of optical materials needed for future fusion reactors. These structural defects can be detected and analysed using the spectra of cathodoluminescence excited in the irradiated layer by an electron beam with adjustable energy. The method was verified by the enhanced intensity of F-type luminescence that reflects the creation of radiation-induced oxygen vacancies in MgO and Al_2O_3 crystals. Low radiation resistance of nominally pure $(Lu_{1-x}Gd_x)_2SiO_5$ crystals was demonstrated by almost total suppression of intrinsic luminescence after the same irradiation.

Keywords: radiation resistance, wide-gap optical materials, cathodoluminescence

1. Introduction

Optical materials and insulators will play a substantial role in diagnostic systems of future deuterium-tritium fusion reactors, which have to withstand 14-MeV neutron irradiation of unprecedented intensity. The development of extremely neutron-resistant optical materials is an important task of the EUROfusion consortium research programme started in 2014 [1]. Neutron radiation induces numerous defects of different type in the materials. Radiation induced optical absorption and undesired light emission (luminescence) are the main problems/limitations for optical components (windows, lenses, fibers). The investigation of these optical phenomena under the operating conditions of future fusion reactors still lies ahead. According to rough estimations, optical elements in future fusion reactors should endure the irradiation with the damage level from 0.1 to 1 displacements per atom (dpa) [2]. However, at the moment there are no sources of 14 MeV neutrons with sufficient flux prohibiting experimental investigations. Fortunately, optical parameters can be determined in a very thin layer of tiny samples that enables to use ion beams for this task. The usage of protons or molecular hydrogen ion beams is most easy and convenient way to test some selected optical materials by the suggested diagnostic procedure. The level of proton energies used in standard implanters (hundreds of keV) differs considerably from 14 MeV, but enables to concentrate all the induced damage in a thin near-surface layer and, therefore, the needed fluence can be achieved within reasonable irradiation time using a standard high current ion implanter.

To detect elementary structural defects (vacancies and interstitials) within the proton-irradiated layer, a highly sensitive luminescence method can be used. A selected luminescence (impurity/defect related or intrinsic one) should be dependent, directly or in an indirect way, on the radiation creation of structural defects. For example, luminescence bands of F^+ and F centres (one or two electrons in the field of an oxygen vacancy, respectively) are well-known in most optical materials. It is important to excite the luminescence within the same near-surface layer that was previously irradiated by protons, and the most convenient excitation source for this task is an electron beam with adjustable energy, in other words, the cathodoluminescence (CL) technique.

2. Experimental

In the present study, the 200 keV hydrogen molecular beam (corresponding to protons of 100 keV) was applied using KIIA 500 kV ion implanter of Ion Beam Laboratory at the University of Helsinki. Molecular beam allows to get higher beam flux and, accordingly, to shorten the

irradiation time needed for a prescribed fluence. The Coulomb explosion of the H_2^+ molecule in the target material causes some depth profile spread for protons, but this circumstance is not substantial for the goals of our experiment [3]. The SRIM (www.srim.org) calculations for MgO target enable to estimate the irradiated thickness (400-600 nm) and the needed fluence (10^{17} protons/cm^2) to get the damage level of ~0.5 dpa at the maximum of damage distribution (see Fig. 1). Using molecular beam current of ~0.25 μA/cm^2, irradiation time of 8-9 h provides the fluence of 10^{17} protons/cm^2.

Nominally pure single crystals of MgO and α-Al_2O_3, well-known compounds of high radiation resistance as well as one representative of scintillator materials – single crystals of $(Lu_{1-x}Gd_x)_2SiO_5$, were used as test samples. Electron beam of 10 keV energy and 0.5 μA current was the luminescence excitation source, which, according to the CASINO simulation [4], overlaps well with the penetration depth of protons into above mentioned compounds (an example for MgO is shown in Fig. 1, together with the penetration depth distribution for 7 and 10 keV electrons, for comparison). As one can see, the 10 keV electrons cover the whole spatial depth of ion irradiation enabling maximum luminescence intensity. CL setup at the Institute of Physics in Tartu is equipped with a vacuum cryostat (5-400 K) and two monochromators covering spectral range from NIR (~1700 nm) to VUV (~110 nm) – ARC SpectraPro 2300i monochromator with various gratings and detectors or a self-made vacuum double monochromator with a Hamamatsu photomultiplier R6836. Electron gun (Kimball Physics EGG-3101) can be used both in steady and pulse (10 ns, 5 kHz) mode. The Becker&Hickl MSA-300 multiscaler allows to detect luminescence kinetics (decay curves). To avoid surface charging under electron beam excitation, the 3-nm Pt films were deposited on all samples. It was also possible to observe by the naked eye a visible luminescence through windows of the sample chamber of the implanter during proton irradiation (see text below and Fig. 3).

3. Results and discussion

It is generally accepted that several radiation-induced absorption bands in wide gap metal oxides manifest the creation of oxygen vacancies that capture one or two electrons each and are known as F^+ and F centres, respectively. The photoexcitation in the region of these absorption bands leads to the appearance of so-called F^+- and F-emission. The optical characteristics of F^+ and F centres were thoroughly studied in MgO and Al_2O_3 single crystals, thermochemically coloured or irradiated with fast neutrons and swift heavy ions (see, e.g., [5-11] and references therein).

Thermally coloured MgO crystals contain high concentration of F centres (absorption peak at 5.03 eV, emission – 2.4 eV), fast neutrons mainly create F^+ centres (absorption peak at 4.95 eV, emission band at 3.15 eV), while oxygen vacancies (V_O) dominate in ~GeV-ion-irradiated samples. It is worth noting that the detected F- or F^+-emissions in the CL spectrum definitely confirm the presence of V_O, although an additional analysis is needed to estimate a selective contribution of F, F^+ and V_O. An electron beam forms numerous electron-hole pairs and these carriers interact with the existing F-type defects. As a result, for example, the F-emission arises at the recombination of conduction electrons with F^+ centres, while the F^+-emission dominates in the CL spectrum of a neutron-irradiated sample with a large amount of V_O serving as efficient radiative traps of electrons [9, 10].

Figure 2 presents the CL spectra measured for virgin and proton-irradiated MgO and Al_2O_3 single crystals at 78 K. Because of a highly sensitive luminescence method, as-grown F-type defects are detected in the CL spectrum of a nominally pure MgO crystal in the form of F- and F^+-emissions. The intensity of CL related to F-type defects at 2.3-3.9 eV significantly increases in a proton-irradiated sample. Similar to the case of heavy-ion irradiation, the enhanced F^+-emission confirms the radiation-induced creation of V_O. In addition to the F- and F^+-emissions, CL of the irradiated MgO sample also contains a component (decomposition gives the additional maximum at ~2.9 eV) tentatively ascribed to the crystal lattice stress (presence of bivacancies) [12, 13]. A similar increase of F-type centres intensity in CL has been detected in an irradiated α-Al_2O_3 crystal (Fig. 2b), where the absorption bands of F and F^+ centres are peaked at 6.1 eV (F-emission at 3 eV) and 4.8 eV (F^+-emission at 3.75 eV), respectively [6, 7, 10, 11].

In addition to the detection of a typical emission of F-type centres, the radiation damage of wide gap metal oxides can be estimated via comparison of the intrinsic emission intensity in a virgin and an irradiated sample. It is well established that excitons are very sensitive to structural defects of solids (see, e.g., [14]). Two types of excitons were revealed in solids long ago. Besides free excitons (FEs) that manifest themselves at the long-wavelength edge of fundamental absorption as narrow emission lines and are thoroughly studied in semiconductors, in wide-gap crystals there can exist self-trapped excitons (STEs) with typical broadband emission arising after interaction of FEs with the field of acoustic phonons. The behaviour of excitons in wide gap oxides (e.g., existence/coexistence of FEs and STEs) is of great variety (see [15] and references therein). In MgO and α-Al_2O_3, the luminescence of excitonic origin

located in vacuum ultraviolet region (see the corresponding parts of CL spectrum in Fig. 2) was thoroughly investigated (see [15-21] and references therein).

Neither self-trapped holes nor electrons and excitons are found in an MgO crystal. Even at low temperatures electrons, holes and excitons are highly mobile and participate in the energy transfer to impurity/defect centres. Radiative decay of large-radius Wannier type FEs results in a narrow line of fast singlet emission with life time below 200 ps [22] resonant to the low-energy component of exciton absorption doublet [16, 17]. In addition, there are formed several bound excitons (connected with different metal impurities) that cause the appearance of a similar line emissions. Because of insufficient spectral resolution, all these exciton-like emissions are presented in the CL spectrum of a virgin MgO crystal as a single unresolved peak at ~7.6 eV (see Fig 2a). The proton-irradiation does not practically affect the intensity of this complex CL peak. On the other hand, we succeeded to detect, via enhanced F^+-emission, some amount of radiation-induced V_O, the presence of which (as well as other defects/impurities) should strongly attenuate the FE resonant emission. Therefore, the MgO is qualified as rather radiation-resistant material, and the radiation-induced amount of V_O is significantly smaller than that of as-grown impurities responsible for the formation of bound (near-impurity localized) excitons with typical emission at ~7.6 eV.

Similar to MgO, neither electrons nor holes undergo self-trapping in α-Al_2O_3 single crystals. At the same time, the broad luminescence band at 7.6 eV was detected long ago and ascribed to a specific type of STEs – medium-radius so-called self-shrinking excitons [18-20]. Although Al_2O_3 belongs to radiation-resistant wide gap materials and the amount of proton-induced V_O is comparable to that in MgO, the irradiation causes a practically total suppression of STE luminescence in our Al_2O_3 sample (see Fig 2b). In our opinion, this strong intrinsic luminescence attenuation can be explained by a significantly longer lifetime of exciton emission in Al_2O_3 compared to that in MgO. The decay time of singlet STE emission in Al_2O_3 in case of excitation by 200-keV electron pulses at 80 K is about 20 ns [19], while exciton-like emissions of MgO are faster than 200 ps [22]. A search for other reasons of radiation-induced suppression of STE luminescence in Al_2O_3 still lies ahead.

It was shown recently that scintillation characteristics of $(Lu_{1-x}Gd_x)_2SiO_5$ single crystals doped with trivalent cerium ions depend on cation composition, Lu/Gd ratio [23]. From our standpoint, it was important to analyse the dependence of Lu/Gd ratio on the efficiency of radiation damage caused by ion-irradiation in such mixed oxyorthosilicates. The results of this investigation will be presented in a separate paper. Here we only briefly demonstrate the preliminary results of irradiation of a set of $(Lu_{1-x}Gd_x)_2SiO_5$ crystals with same proton fluence

of 10^{17} cm^{-2} (see Fig. 3). Already during proton-irradiation, it was evidenced by the naked eye and documented by a photocamera that the intensity of steady luminescence (excited under ion beam irradiation) strongly decreases in time. The huge difference in the luminescence intensity between all silicates with different ratio of cations and an Al_2O_3 single crystal (the sample with triangle shape in a lower part of crystal holder) at the end of irradiation cycle is clearly seen in Figure 3.

The CL spectra of a nominally pure Lu_2SiO_5 sample before and after irradiation are presented in Figure 4. The sample contains a small amount of uncontrolled Gd^{3+} impurity ions responsible for a narrow CL band at 3.95 eV ($^6P_J \rightarrow {}^8S_{7/2}$ electron transitions in Gd^{3+}). The interpretation of the luminescence spectra can be found elsewhere (see, e.g., [23] and references therein), but the main result of proton-irradiation clearly manifests itself as a huge intensity drop (by approximately 300 times) and the change of spectral composition of CL spectra measured at 78 K. In complex with numerous experimental data obtained using different experimental methods, these CL results confirm that the considered class of silicates cannot withstand damage level of ~0.5 dpa caused by protons (and, tentatively, neutrons as well) and Gd/Lu oxyorthosilicates are not promising as optical materials for fusion application.

4. Concluding remarks

By the examples of MgO, α-Al_2O_3 and $(Lu_{1-x}Gd_x)_2SiO_5$ crystals we tested the luminescent approach in the detection of radiation damage in wide gap optical materials. The penetration depth of the 100-keV protons used as a radiation source determines a thin irradiated crystal layer (400-600 nm) with enhanced concentration of structural defects. A total amount of these defects is rather low in the case of MgO and α-Al_2O_3 but they can be easily detected using cathodoluminesce (directly by a typical emission or by an indirect way via influence on intrinsic luminescence) excited within the same irradiated layer by electrons with adjustable energy. The radiation-induced F-type defects have been directly detected in proton-irradiated MgO and α-Al_2O_3 crystals via typical emission from the excited states of F or F^+ centres. In addition, radiation defects strongly influence the intensity of intrinsic (excitonic origin) luminescence. However, the origin and specificity of intrinsic emission (e.g., luminescence of free or self-trapped excitons) as well as the peculiarities of related processes in a certain wide-gap materials should be taken into account. For example, it is not easy to interpret unambiguously the irradiation results of MgO and Al_2O_3. It is not straightforward which one has higher radiation

resistance. It is worth noting that the analysis is also affected by the partial reabsorption of CL by radiation-induced defects.

To estimate the prospects of material usage under heavy irradiation conditions it is possible to determine the needed fluence for amorphisation of compounds under investigation, but for samples of high radiation resistance it is usually time consuming and gives practically no information about processes taking place under real working conditions of optical elements. The number of created stable vacancies and interstitials per dpa would be much better criterion than the amorphisation dose. The number of anion vacancies can be derived from the luminescence intensity of F-type bands if applying calibrated setup and elaborated experimental methodology. However, the use of these intensities as the measure for two different compounds is still questionable because of unknown efficiencies of the energy transfer to luminescence centres in cathodoluminescence processes for different materials. So the comparison criteria of radiation resistance utilizing luminescence data can be used only as the first approximation, which should be subject to further investigations.

Acknowledgements

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission. The research leading to these results has received funding also from the Estonian Research Council – Institutional Research Fundings IUT02-26.

References

[1] www.euro-fusion.org/programme/

[2] S.J. Zinkle, Effect of H and He irradiation on cavity formation and blistering in ceramics, Nucl. Instrum. Meth. B 286 (2012) 4-19.

[3] A. Anttila, J. Räisänen, The use of H_2^+ and H_3^+ molecular ions as bombarding particles, Nucl. Instrum. Meth. 185 (1981) 601-602.

[4] D. Drouin, A.R. Couture, D. Joly, X. Tastet, V. Aimez, R. Gauvin, CASINO V2.42 – A fast and easy-to-use modeling tool for scanning electron microscopy and microanalysis users, Scanning 29 (2007) 92-101.

[5] L.A. Kappers, R.L. Kroes, E. Hensley, F^+ and F′ centers in magnesium oxide, Phys. Rev. B 1 (1970) 4151-4157.

[6] K.H. Lee, J.H. Crawford, Electron centers in single-crystal $A1_20_3$, Phys. Rev. B 15 (1977) 4065-4070.

[7] B.D. Evans, M. Stapelbroek, Optical properties of the F^+ center in crystalline Al_2O_3, Phys. Rev. B 18 (1978) 7089-7098.

[8] B. Henderson, Anion vacancy centers in alkaline earth oxides, Crit. Rev. Solids State 9 (1980) 1-60.

[9] A. Lushchik, T. Kärner, Ch. Lushchik, E. Vasil'chenko, S. Dolgov, V. Issahhanyan, P. Liblik, Dependence of long-lived defect creation on excitation density in MgO single crystals, Phys. Status Solidi C 4 (2007) 1084-1087.

[10] A. Lushchik, Ch. Lushchik, K. Schwartz, E. Vasil'chenko, T. Kärner, I. Kudryavtseva, V. Isakhanyan, A. Shugai, Stabilization and annealing of interstitials formed by radiation in binary metal oxides and fluorides, Nucl. Instrum. Meth. B 266 (2008) 2868-2871.

[11] I.I. Milman, V.S. Kortov, S.V. Nikiforov, An interactive process in the mechanism of the thermally stimulated luminescence of anion-defective α-Al_2O_3 crystals, Radiat. Meas. 29 (1998) 401-410.

[12] Y. Chen, M.M. Abraham, T.J. Turner, C.N. Nelson, Luminescence in deformed MgO, CaO and SrO, Philos. Mag. 32 (1975) 99-112.

[13] A. Lushchik, Ch. Lushchik, K. Schwartz, F. Savikhin, E. Shablonin, A. Shugai, E. Vasil'chenko, Creation and clustering of Frenkel defects at high density of electronic excitations in wide-gap materials, Nucl. Instrum. Meth. B 277 (2012) 40-44.

[14] J. Cui, Defect control and its influence on the exciton emission of electrodeposited ZnO nanorods, J. Phys. Chem C 112 (2008) 10385-10388.

[15] A. Lushchik, M. Kirm, Ch. Lushchik, I. Martinson, G. Zimmerer, Luminescence of free and self-trapped excitons in wide-gap oxides, J. Lumin. 87-89 (2000) 232-234.

[16] E. Feldbach, I. Kuusmann, G. Zimmerer, Excitons and edge luminescence in MgO, J. Lumin. 24/25 (1981) 433-436.

[17] E. Feldbach, Ch.B. Lushchik, I.L. Kuusmann, Coexistence of large-radius and small-radius excitons bound on defects in solids, JETP Letters 39 (1984) 61-64.

[18] M. Kirm, G. Zimmerer, E. Feldbach, A. Lushchik, Ch. Lushchik, F. Savikhin, Self-trapping and multiplication of electronic excitations in α-Al_2O_3 and Al_2O_3:Sc crystals, Phys. Rev. B 60 (1999) 502-510.

[19] A. Lushchik, E. Feldbach, M. Kirm, P. Liblik, Ch. Lushchik, I. Martinson, F. Savikhin, G. Zimmerer, Spectral-kinetic study of self-trapping and multiplication of electronic excitations in Al2O3 crystals, J. Electron Spectrosc. 101-103 (1999) 587-591.

[20] A. Kuznetsov, B. Namozov, V. Mürk, VUV luminescence of self-trapped excitons in Al_2O_3 crystals, Proc. Est. Acad. Sci., Ph. 36 (1987) 193-196.

[21] J. Valbis, N. Itoh, Electronic excitations, luminescence and lattice defect formation in α-Al_2O_3 crystals, Rad. Effects Defect. S. 116 (1991) 171-189.

[22] M. Kirm, A. Lushchik, Ch. Lushchik, Creation of groups of spatially correlated excitations in wide gap solids, Phys. Status Solidi A 202 (2005) 213-220.

[23] O. Sidletskiy, V. Bondar, B. Grinyov, D. Kurtsev, V. Baumer, K. Belikov, K. Kartunov, N. Starzhinsky, O. Tarasenko, V. Tarasov, O. Zelenskaya., J. Cryst. Growth 312 (2010) 601.

[24] V.Yu. Ivanov, E.S. Shlygin, V.A. Pustovarov, V.V. Mazurenko, B.V. Shulgin, Intrinsic Luminescence of Rare-Earth Oxyorthosilicates, Phys. Solid State 50 (2008) 1692-1698.

Figure captions

Figure 1. Displacements per atom (dpa) caused by 100 keV protons (○○○) and penetration depth distributions for electrons (7 keV – ▽▽▽, 10 keV – ΔΔΔ) in a MgO crystal, calculated using SRIM code and CASINO software, respectively.

Figure 2. Cathodoluminescence spectra measured for MgO (a) and Al_2O_3 (b) single crystals at 78 K before (circles) and after (triangles) irradiation by 100 keV protons (10^{17} cm^{-2}) at room temperature. CL was excited by an electron beam of 10 keV and 0.5 μA.

Figure 3. Photos of the samples area (~3×3 cm^2) of the ion implanter taken at different stages of irradiation – at the beginning (a) and after proton fluences of 3×10^{16} cm^{-2} (b) and 10^{17} cm^{-2} (c). The triangle shaped sample is Al_2O_3, while all others are silicates $Lu_{2-x}Gd_xSiO_5$ with different Lu/Gd cation ratio.

Figure 4. Cathodoluminescence measured for a nominally pure Lu_2SiO_5 (contains some amount of Gd^{3+} impurity ions) single crystal under excitation by 10 keV electrons at 78 K before (circles) and after (triangles) irradiation by 100 keV protons (10^{17} cm^{-2}) at room temperature.

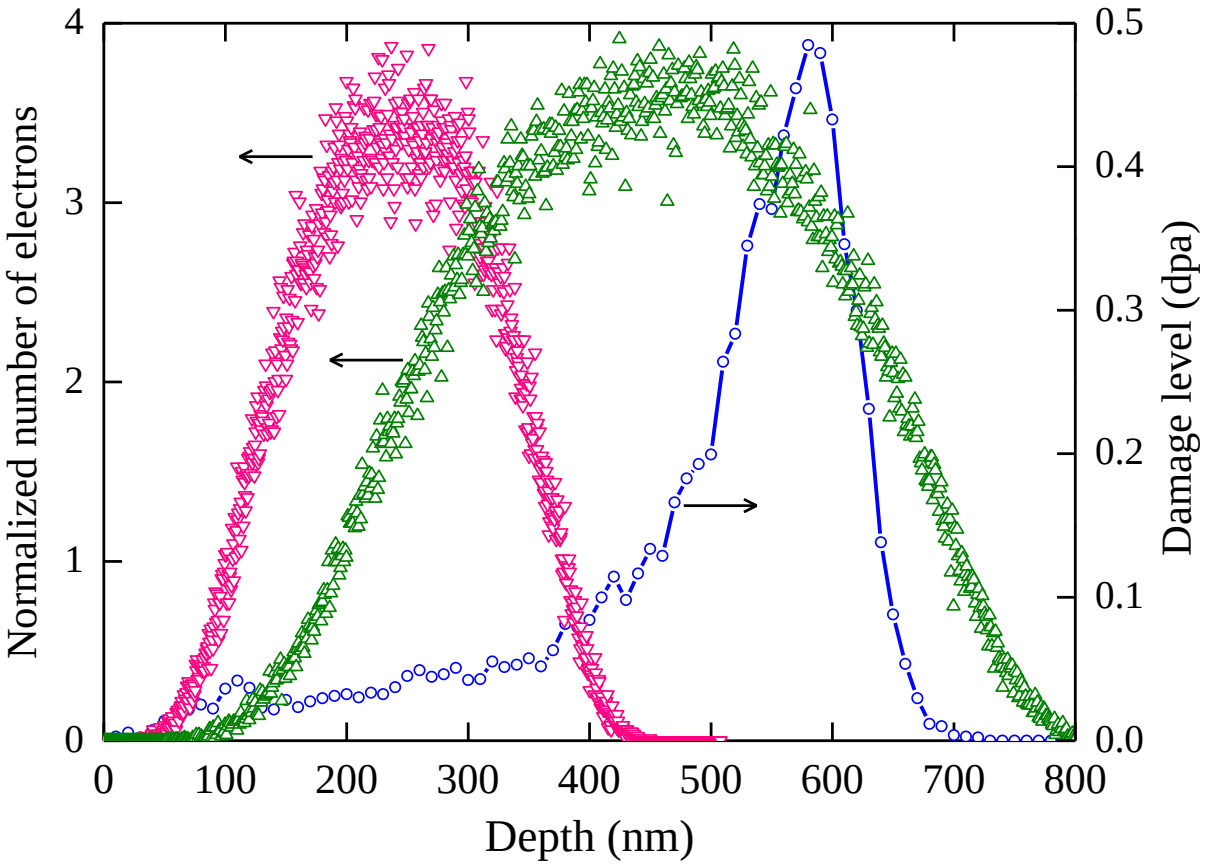

Figure 1. Displacements per atom (dpa) caused by 100 keV protons (○○○) and penetration depth distributions for electrons (7 keV – ▽▽▽, 10 keV – ΔΔΔ) in a MgO crystal, calculated using SRIM code and CASINO software, respectively.

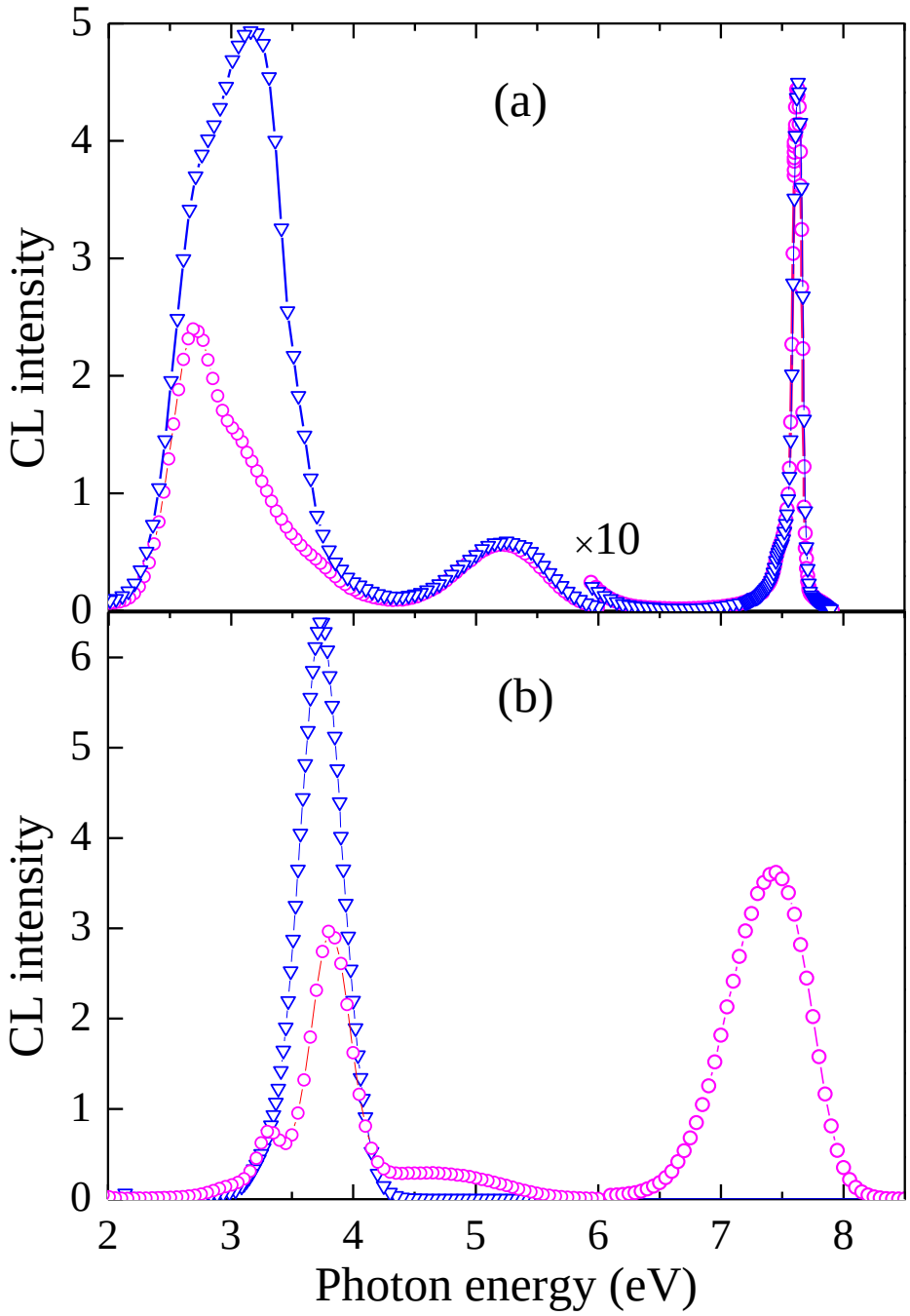

Figure 2. Cathodoluminescence spectra measured for MgO (a) and Al_2O_3 (b) single crystals at 78 K before (circles) and after (triangles) irradiation by 100 keV protons (10^{17} cm^{-2}) at room temperature. CL was excited by an electron beam of 10 keV and 0.5 μA.

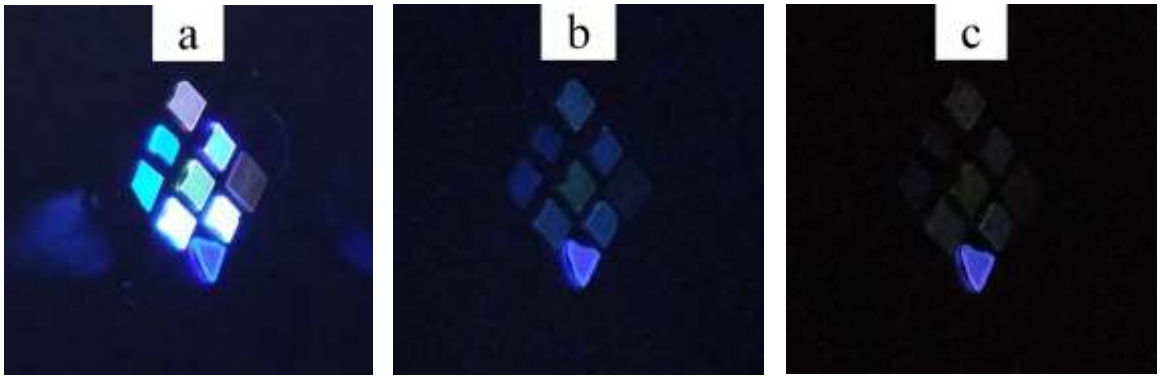

Figure 3. Photos of the samples area (~3×3 cm^2) of the ion implanter taken at different stages of irradiation – at the beginning (a) and after reached proton fluences of 3×10^{16} cm^{-2} (b) and 10^{17} cm^{-2} (c). The triangle shaped sample is Al_2O_3, while all others are silicates $Lu_{2-x}Gd_xSiO_5$ with different Lu/Gd cation ratio.

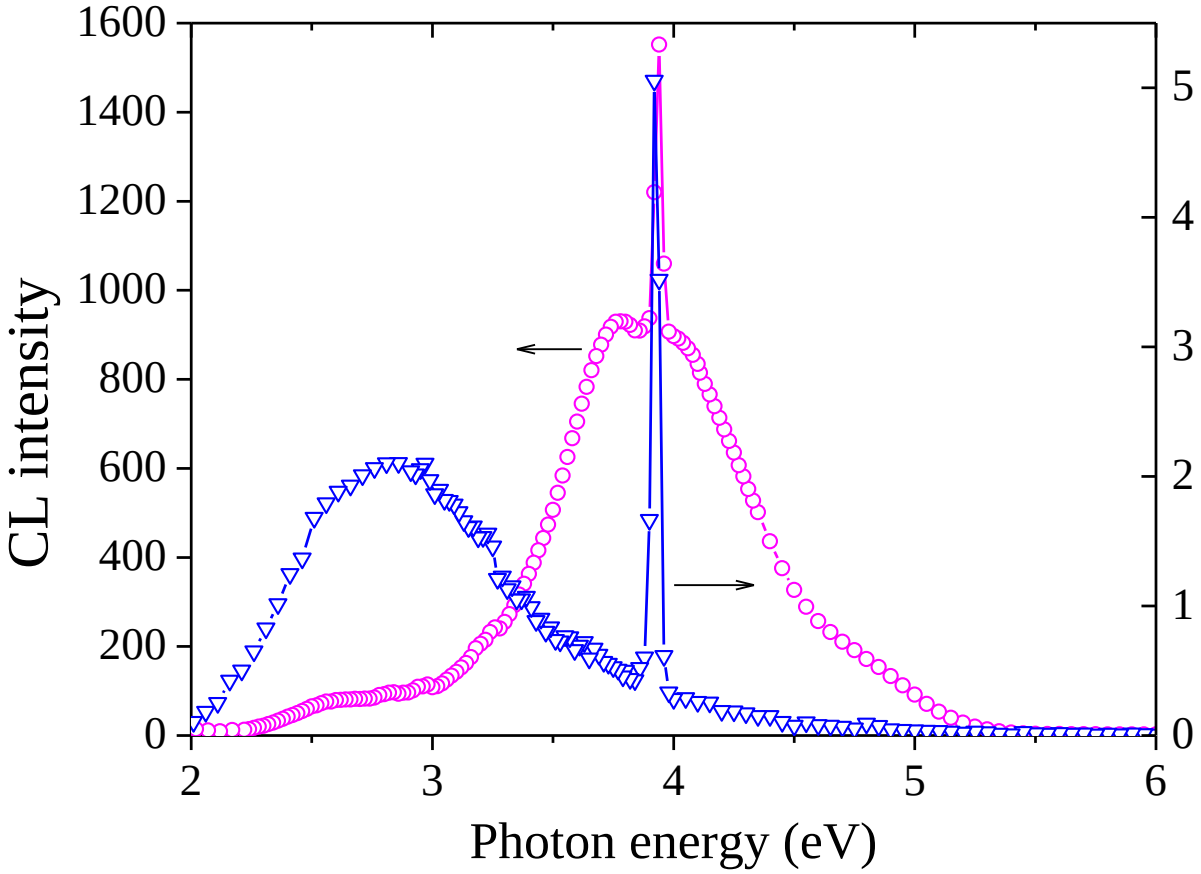

Figure 4. Cathodoluminescence measured for a nominally pure Lu_2SiO_5 (contains some amount of Gd^{3+} impurity ions) single crystal under excitation by 10 keV electrons at 78 K before (circles) and after (triangles) irradiation by 100 keV protons (10^{17} cm^{-2}) at room temperature.