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Luminescent and dosimetric properties of magnesium oxide ceramics synthesized by a high–energy electron beam

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For the first time, samples of magnesium oxide ceramics were obtained by a method based on irradiation of the oxide powders with a beam of fast electrons. Luminescence centers associated with intrinsic and impurity defects were found in the obtained samples. A comparative analysis of the thermoluminescence (TL) curves and dose dependencies of TL of MgO ceramics obtained by the radiation and thermochemical methods is carried out. The linear dose dependence of the TL peak at 370 K excited by a pulsed electron beam (130 keV, 1.5–30 kGy) is shown to be the main advantage of MgO ceramics for their use in TL dosimetry. Possible reasons for improving the linearity of the dose characteristics of the newly created ceramics in comparison with analogs are discussed.

Keywords: magnesium oxide, thermoluminescent dosimetry, dose response, oxygen vacancies, pulsed cathodoluminescence.

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Luminophores based on ceramics made from nominally pure or doped magnesium oxide (MgO) are at present widely used in the laser engineering, optical engineering, optoelectronics, and also in luminescent dosimetry of ionizing radiations [1]. To achieve the optimal combination of operating luminescence and optical characteristics of the mentioned materials, the existing synthesis techniques are being improved, and new ones are being developed. A promising method for obtaining ceramics based on refractory materials is synthesizing them in the field of a high–power flux of energetic radiation. The radiation synthesis method was successfully implemented for producing ceramics based on MgF₂:W and YAG:Ce [2,3]. The ceramics were synthesized by the direct action of electron flux on stoichiometric mixtures of powders consisting of metal fluorides and oxides during less than 1 s. Among the method advantages there are unnecessary of adding any substances, extra process operations aimed at facilitating the process of the new phase formation, and high output (about 2 g/s under laboratory conditions). It is quite interesting to elucidate the possibility of synthesizing the MgO ceramics by the radiation method. Evidently, properties of such a ceramics are to differ from those of ceramics obtained by other methods.

Investigation of the MgO ceramics luminescent properties are interesting with regard to estimating the possibility of using this material in high–dose (more than 1 kGy) thermoluminescent dosimetry of ionizing radiations. Among such radiations there are, for instance, electron beams 130 keV in energy used in radiation technologies for surface sterilization of medical appliances and foods, and also in research work [4,5]. In this work, luminescent and

dosimetric properties of the MgO ceramics synthesized by the radiation method (type 1 ceramics) were studied in comparison with the same properties of other MgO ceramics (type 2 ceramics) obtained by high–temperature thermochemical coloring of nanostructured MgO compact in vacuum under reducing conditions for the purpose of creating anion defects in them [6].

The goal of this work was to synthesize MgO ceramics in the radiation field, investigate their luminescent properties, and estimate the possibility of using them in the thermoluminescent dosimetry of ionizing radiations.

The ceramics were synthesized by using oxide powder that was white powder with the particle size of about 10 μm. The basic material (MgO) mass percent in the oxide powder was not lower than 98.0%. The initial oxide powder contained such impurities as Cl (no more than 0.1%), SO₄ (no more than 1%), As (no more than 0.0003%), CaO (no more than 0.1%), Pb (no more than 0.002%), Fe (no more than 0.05%). To obtain the ceramics, the oxide powder was exposed to a 1.4 MeV electron flux with the power density of 20–25 kW/cm² generated in accelerator ELV–6 (INP RAS SB, Novosibirsk). The oxide powder was put into copper crucibles 120 × 60 × 40 mm in size; the oxide powder bulk density was 0.9–1 g/cm³, the oxide powder layer thickness was 7 mm. The crucible was moved with the speed of 1 cm/s relative to the plane of scanning electron beam 1 cm² in cross section; the scanning frequency was 1 cm². Thus, each section of the oxide powder surface was irradiated during 1 s. The total time of scanning the entire oxide powder surface was 10 s. The 1.4 MeV electrons penetrated into the MgO powder used in the experiments by

the depth of 5.7 mm. The maximum of the electron energy loss density falls on the depth of 2.5 mm.

Ceramics synthesized in such a way had a form of nontransparent glassy plates 2.5 mm thick. Preparatory to measuring the luminescent properties, the plates were cut in irregularly shaped pieces 0.03 g in weight.

To excite the thermoluminescence (TL), the synthesized ceramic samples were irradiated at room temperature with a pulsed electron beam (60 A/cm², 2 ns) of the „RADAN EXPERT“ accelerator with the electron energy of 130 keV. The irradiation dose was 1.5 kGy per pulse [7]. This accelerator was also used to excite pulsed cathodoluminescence (PCL). Notice that the electron energy used to excite PCL and TL (130 keV) differs significantly from the energies used in the ceramics synthesis (1.4 MeV). At the same time, it is considerably lower than the threshold energy of radiation defects formation in MgO, which is about 300 keV [8]. Therefore, the PCL and TL excitation in the ceramics under study does not promote formation of new centers in them, but only changes the charge state of already existing centers and trap occupation by charge carriers. TL was measured under linear heating with the rate of 2 K/s by using a photomultiplier tube FEU-142 with the spectral sensitivity range of 112–365 nm.

Fig. 1 presents PCL spectra of the MgO ceramics of two types. One can see that the PCL spectra have quite similar structures. Each spectrum exhibits a narrow band at 1.75 eV, and also the luminescence at 2.0–3.5 eV. According to the literature data, luminescence at 1.75 eV may be caused by relaxation of excited states of impurity ions, for instance, Cr³⁺ [9] and Fe³⁺ [10]. The last assumption is confirmed by the presence in the studied samples of a considerable amount of iron impurity (up to 0.05%). The difference in the 1.75 eV band width in the ceramics synthesized by the thermochemical and radiation methods may be caused by differences in their defect structures and extents of disorder. For instance, studies [11,12] revealed the effects of spreading, shift and emergence of asymmetry of the Cr³⁺ *R*-line in Al₂O₃:Cr³⁺ significantly damaged by ion irradiation. The Cr³⁺ *R*-line broadening was observed also in nanocrystalline MgO:Cr³⁺; the authors associated this with a high defect concentration in the material.

The MgO luminescence in the 2.0–3.5 eV range may be related to relaxation of the *F*-type centers [13]. So, *F*-centers that are oxygen vacancies with two captured electrons are characterized by a 2.5 eV luminescence band decay for a quite long time ($\sim 10^3$ s) [13,14]. Luminescence of *F*⁺-centers (oxygen vacancies with one captured electron) has an intensity maximum at 3.1 eV with a short decay time (~ 10 ns) [13].

To prove the presence in the studied samples of luminescence centers associated with oxygen vacancies, the PCL spectrum of the type 1 ceramics (Fig. 1, curve 1) was decomposed into elementary components (Gaussians). The decomposition results are presented in the table and Fig. 1.

One can see that the luminescence band at 2.0–3.5 eV is complex and consists of three elementary peaks: A (2.5 eV),

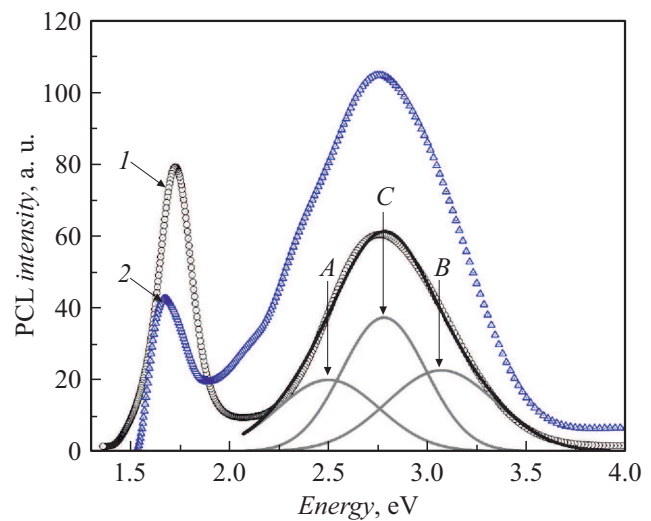


Figure 1. PCL spectra of the MgO ceramics synthesized by the radiation (1) and thermochemical [6] (2) methods.

Results of the PCL spectrum decomposition (Fig. 1, curve 1) into Gaussians

Peak	Peak position, eV	FWHM, eV
A (<i>F</i> -center)	2.50	0.60
B (<i>F</i> ⁺ -center)	3.07	0.65
C (?)	2.78	0.50

B (3.07 eV) and C (2.78 eV). Parameters of peaks A and B (the maximum position and full width at half maximum (FWHM)) are close to those given in literature for the luminescence bands of *F*- and *F*⁺-centers, respectively [13]. There is no consensus on the nature of the 2.78 eV luminescence band. An opinion exists that the 2.81 eV luminescence band (with the decay time of 22–25 ms) is associated with the presence of either aggregate centers of the *F*₂-type [15] or strain-induced complex vacancy defects [16].

Fig. 2 (curves 1–5) presents TL curves for the type 1 ceramics irradiated with different doses. Comparative analysis of TL curves for the MgO ceramics of two types revealed the following facts. Ceramics of both types exhibit a dosimetric TL peak at 360–380 K that is scarcely shifted in the type 2 samples towards higher temperatures. The main feature of the TL curves for the type 1 ceramics synthesized by using fast electrons is that the dosimetric peak at 360–380 K is predominant and isolated, which is a doubtless advantage in dosimetric measurements. TL of deep trap emptied at $T = 450$ – 600 K in the type 1 ceramics is characterized by a lower intensity. The shape of the TL curve of deep traps in the type 2 samples is more complex (curve 6) and includes horizontal sections where the TL intensity depends on temperature only slightly. As shown in [6], the last feature is caused by the processes of tunnel recombination of electrons and holes observed at

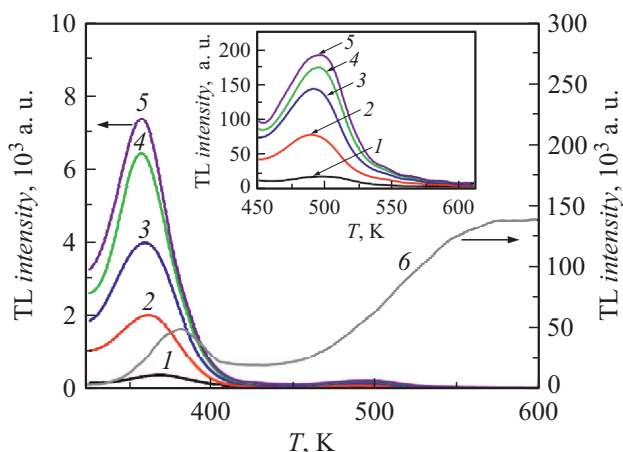


Figure 2. TL curves for the MgO samples synthesized by the radiation method and irradiated with doses of 1.5 (1), 7.5 (2), 15 (3), 30 (4), 60 kGy (5). 6 — the TL curve for thermochemically colored samples irradiated with the dose of 30 kGy [6]. The heating rate was 2 K/s.

high concentrations of traps and luminescence centers in thermochemically colored samples.

Fig. 3 demonstrates dose dependences of the TL peak intensity at 370 K for ceramics of two types (curves 1 and 3), and also those of the deep-trap TL peak intensity for the type 1 ceramics (curves 2). Apparently, the most linear dependence is observed for the TL peak at 370 K in the type 1 ceramics (curve 1). In the dose range of 1.5–30 kGy, the nonlinearity coefficient k of this dependence defined as a slope angle tangent of the curve plotted in logarithmic coordinates is close to 1.0 (more exactly, is equal to 0.98). Notice that this–range dose dependence of TL of the same peak in the thermochemically colored type 2 ceramics has a strongly pronounced nonlinear (sublinear) character with the nonlinearity coefficient k below unity, more exactly, 0.49 (Fig. 3, curve 3). The deep-trap TL dose dependence for the type 1 ceramics is also characterized by a pronounced sublinearity ($k = 0.81$, curve 2).

It is known that the linear dose dependence of TL ($k = 1.0$) is most preferable with regard to using this material in the TL dosimetry, since it provides the easiest calibration of the measuring instrument. Notice that the TL dose dependences in the ceramics of two types (Fig. 3, curves 1 and 3) were obtained for one and the same type of exciting radiation in almost identical ranges of absorbed doses and for the same peak at 370 K. Thus, it is possible to conclude that the type 1 ceramics, which were for the first time synthesized by the radiation method in this study, better meet the requirements for TL detectors with regard to the dose characteristics linearity than the type 2 ceramics.

At high doses, nonlinearity of the TL dose dependences in various materials is most often caused by the saturation of the trap charge–carrier occupation whose growth is limited by their concentration. According to literature data, the traps of the TL peak at 370 K are of the

hole nature and are associated with the V-type defects that are cation vacancies with one or several captured holes [17]. Those defects can arise in the studied samples during the radiation synthesis and also due to the charge compensation caused by the presence in the studied samples of the trivalent iron impurity. It may be assumed that the type 1 ceramics synthesis modes used in this work provide quite high concentration of traps responsible for the TL dosimetric peak, which causes linear dose dependences of their occupation by holes and, hence, of the TL intensity.

Another possible reason for the improvement of the TL dose dependence in the type 1 ceramics may be related to the influence of deep traps. Fig. 2 shows that the type 2 ceramics samples are characterized by a higher (by two or three orders of magnitude) intensity of deep-trap TL as compared with the type 1 ceramics, which may evidence their higher concentration. The competition between the traps able to capture different–sign charge carriers is known to lead to formation of sublinear sections of the TL dependences on the dose [18,19]; just this takes place in the type 2 ceramics (Fig. 3, curve 3). In the type 1 samples, the competing charge–capturing processes are less intense due to low concentration of deep traps. This may provide a near–linear dose characteristic of the dosimetric TL peak at 370 K (Fig. 3, curve 1).

Thus, this paper shows for the first time the possibility of the MgO ceramics synthesis by using a high–power flux of energetic electrons. PCL data has shown that their luminescence centers are oxygen vacancies and impurity ions. The main advantage of the ceramics obtained by the radiation method with regard to their use in high–dose TL dosimetry as compared with ceramics synthesized thermochemically is the linear dose dependence of the TL peak at 370 K in the case of irradiation with a pulsed electron beam (130 keV) in the dose range of 1.5–30 kGy. This feature may be associated with the high concentration of dosimetric traps and also with a lower intensity of competence in capturing charge carriers by deep centers. The results

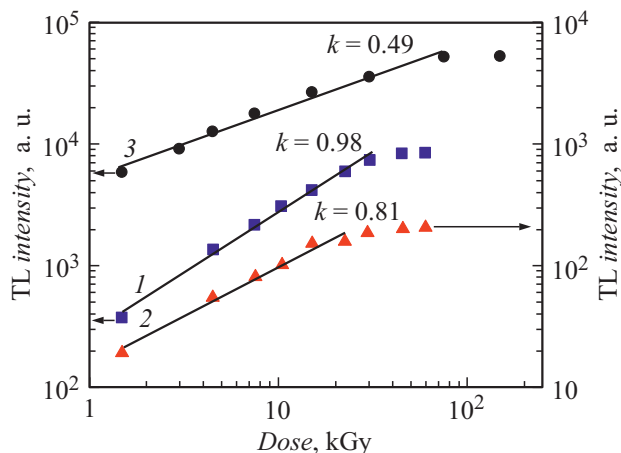


Figure 3. Dose dependences of intensities of TL peaks at 370 (1, 3) and 500 K (2) for the MgO ceramics synthesized by the radiation (1, 2) and thermochemical methods [6] (3).

we have obtained show that, using the radiation synthesis method, it is possible to vary the existing properties of the oxide–magnesium ceramics and also to give rise to their new properties. This allows assuming that the radiation synthesis may be used to produce ceramics with new improved properties based on other refractory oxide–based materials.

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Conflict of interests

The authors declare that they have no conflict of interests.

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