Magnetic, thermal and luminescence properties in room-temperature nanosecond electron-irradiated various metal oxide nanopowders

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Abstract. By means of pulsed electron beam evaporation in vacuum of targets non-magnetic, in bulk state, Al₂O₃ and YSZ (ZrO₂-8% Y₂O₃) oxides, magnetic nanopowders (NPs) with a high specific surface were produced. The NPs were subsequently irradiated in air by electrons with energy of 700 keV, using a URT-1 accelerator for 15 and 30 minutes. The magnetic, thermal, and pulsed cathodoluminescence (PCL) characteristics of NPs were measured before and after irradiation. It was established that the electron irradiation non-monotonically changes the magnetization of the pristine samples. To the contrary, a clear correlation between the intensity of PCL and the irradiation doses is found in the oxides. There was a decrease in the intensity of PCL after irradiation. Luminescent and thermal properties reflect the transformation of structural defects in NPs more strongly after the exposure to a pulsed electron beam in comparison with corresponding changes of the NPs magnetic response.

1. Introduction

The magnetic properties of nanoparticles (NPs) depend on many factors - the chemical composition, type of the crystal lattice, degree of its deficiency, the shape and the size, morphology, interaction of particles with the matrix and neighboring particles, phase structure and type of structural defects, etc. [1]. By changing the size, shape, composition and structure of NPs, it is possible, within limits, to control the magnetic characteristics of nanomaterials.

The room temperature ferromagnetism (RTFM) is associated with lattice defects and / or added ions, whereas the added ions can be non-magnetic. This phenomenon is called defect-induced magnetism [2]. The identification of RTFM in non-magnetic dopant-doped oxide also attracts a lot of attention in connection with possible use of the oxides in semiconductor spintronics. Therefore, the search for a suitable non-magnetic additive, which makes non-magnetic oxides magnetic, is very important [3].

The study of the relationship between magnetic and luminescent characteristics (and the luminescence is a good tool for studying structural defects in solids) makes it possible to reveal the nature of magnetism in DMS, more deeply, in particular, in DMS based on nonmagnetic oxides. Presently, engineering of nanostructures using electronic irradiation has been widely used [4].

The possibility of improving properties by controlling the particle size can lead to potentially useful technological applications. There studies on the use of electron beam irradiation for controlling the
surface properties of NPles are very rare. There are few works related to the effect of electron irradiation on structural, optical and thermal properties of NPles [5].

In this work the magnetic, thermal, andoluminescent characteristics of oxide NPles obtained by pulsed electron evaporation in vacuum were studied before and after their exposure to the high-energy electron beam.

2. Experimental

Nanopowders of pristine Al₂O₃ [6, 7] and Y₂O₃-doped ZrO₂ (YSZ) oxides [8, 9] were previously obtained using the method of evaporation by a pulsed electron beam in a vacuum on NANOBEAM-2 apparatus [10]. NPles were deposited on the windowpanes of a large area placed around the target at a distance of 10-15 cm. The residual pressure in the evaporation chamber was 4 Pa. Next, the samples were irradiated on an electron accelerator URT-1M (700 keV, ~100 ns, 35 pps) [11]. The irradiation time was 15 minutes (1st series), then another 15 minutes (2nd series). The samples were placed on an aluminum plate cooled by fans. The samples irradiated at adsorbed dose (AD) of 0, 31.5 and 63 MGy are labeled as 1, 2 and 3, respectively.

A detailed description of the preparation of specific oxide targets for electron evaporation is given in [6-10]. The following diagnostics of NPles were used in the experiments were used the following diagnostics of NPles. The XRD was made on diffractometers XRD 7000 Shimadzu (Japan) and D8 Discover (Holland). The morphology and the sizes of NPAs were observed by means of the on JEM 2100 microscope. Magnetic measurements were carried by Faraday's scales (sensitivity of scales ~ 10⁻⁵emu, the range of measurements on the magnetic field – to 12 kOe). The PCL spectra were recorded at room temperature on a KLAUI-1 spectral analyzer. TG and DSC measurements were performed on a Netzsch thermal analyzer at a heating rate of 10 °C min⁻¹ in air atmosphere. N₂ adsorption–desorption isotherms were obtained on a TriStar 3000 V6.03 apparatus at 77 K under continuous adsorption condition. BET and BJH analyses were used to determine the surface area, pore size distribution, and pore volume.

3. Results and discussion

3.1. Properties of NPles before irradiation

Some physicochemical characteristics of oxide NPles before irradiation are given in Table 1. All NPles, without exception, contained an amorphous fraction that was formed during the crystallization of NPles on a cold substrate. X-ray diffraction patterns of unirradiated oxide NPles and their analysis were performed in [6-10]. Measurement of adsorption isotherms showed that all powders obtained by the PEBE method belong to mesoporous NPles with disordered pores, a high pore volume and a relatively large pore diameter in the range of 15 to 20 nm.

Table 1. Some physical parameters of oxide NPles obtained by a PEBE, before irradiation

| Parameters                        | Al₂O₃   | YSZ     |
|-----------------------------------|---------|---------|
| S_BET (m²/g)                      | 124     | 98.7    |
| Phase composition                 | α, δ & amorphous | amorphous/cubic |
| Crystallinity (%)                 | not determine | 29      |
| BJH Desorption average pore diameter (4V/A) | -       | 20.4    |

3.2. Al₂O₃

The evolution of the specific magnetization (σ) and the PCL spectrum of the multiphase Al₂O₃ NP from the irradiation time are shown in Fig. 1 and 2.
The PCL spectrum is an important tool for obtaining fundamental information about structural defects in the lattice. The unirradiated Al₂O₃ sample showed (Figure 2) the maximum PCL intensity compared to samples irradiated with 700 MeV electrons. The PCL spectra of all samples are completely identical and have a similar morphology. All spectra consist of two bands in the red region of the spectrum, centered at ~ 620 and 720 nm. The narrow peak at 694.3 nm - R line, is from Cr³⁺ chromium impurity ions. Preservation of the PCL form of the non-irradiated sample Al₂O₃ after exposure to large doses of radiation indicates that there is no possible phase transformation in the sample with an electron irradiation. The absence of a peak in the defective green band at a wavelength of ~ 500 nm indicates the absence of oxygen vacancies (F centers) and/or copper ions in the Al₂O₃ sample.

The behavior of the dependences of the specific magnetization (σ) on the AD is more complicated. In the magnetization curves of the first arbitrary selection of NP, a decrease in σ with an increase in the AD was observed, which correlates with a change in the PCL spectrum.

3.3. Y₂O₃-doped ZrO₂

Fig. 3 shows that with the increase in the AD, the intensity of PCL emission of YSZ NP was reduced. The intensity is due to the formation of non-emission by-products or defects on the surface of NPles [12]. A decrease in the intensity of PCL indicates a decrease in the rate of recombination between electrons and holes. The location of the main peaks of the PCL spectra did not change significantly with increasing AD, which indicates the preservation of the pristine phase composition of the YSZ NP at the given irradiation levels.

The magnetization saturation (Fig. 4) of the YSZ sample increased by almost 20% after 15 minutes of irradiation and did not change later with an increase in the AD. This sample could contain insignificant magnetic impurities (the YSZ NP was collected from glass substrates using a steel razor), as indicated by the relatively high specific magnetization of the unirradiated sample, which is an order of magnitude higher than the magnetization of the YSZ sample from our early work [9]. It is possible that the increase in the magnetization of the YSZ sample was due to the effect of electron irradiation on the impurity magnetic iron particles. The magnetization of strong ferromagnets such as Fe and its oxides, as shown above, in the analysis of the effect of electron irradiation on particles with different types of magnetism, usually increases with the AD increase. The presence of magnetic impurities in the YSZ sample indirectly confirms the reach of saturation by all the magnetization curves at the same magnetic field and the uniformity of the magnetization curves, independently of the AD. The nature of the magnetic ordering in the YSZ NP requires further studies, but it is obvious that the irradiation
changed the concentration of defects in the NP, which was reflected in the growth of the magnetization of the NP.

![Figure 3.](image1.png)

**Figure 3.** Dependences of the change in the magnetization of the YSZ NP.

![Figure 4.](image2.png)

**Figure 4.** PCL spectra of pristine and irradiated samples of the YSZ NP.

The results of the thermal analysis of the YSZ NP by the synchronous DSC-TG method are shown in Fig. 5. On the TG curves of all samples in the temperature range from 100 to 430 ° C, water molecules and carbon-containing compounds adsorbed on the surface of mesoporous YSZ NPs were removed.

On the TG curve of the non-irradiated sample (Fig. 5), two temperature ranges are clearly visible: \( T_1 = 70-250 \) °C and \( T_2 = 250-430 \) °C, corresponding to evaporation of water and desorption of carbon-containing compounds, respectively. On the TG curves of irradiated samples, range \( T_2 \) is barely noticeable. The decrease in the endothermic peaks of the \( T_2 \) band in irradiated samples is caused by the influence of a strong oxidant-ozone on carbon-containing compounds adsorbed on the surface and in the pores of the samples (it is well known that ozone reacts with carbon at normal temperature to form carbon dioxide: \( 2C + 2O_3 \rightarrow 2CO_2 + O \)). In the \( T_2 \) temperature range from 430 to \( \sim 600 \) °C thermal peaks on the DSC curves were absent in all samples, with simultaneous, linear mass growth.

It is important to note that the increased mass growth (increase in the steepness of the TG curves) for all samples began at the same temperature around 430 °C and continued uninterruptedly up to 1400 °C. That indicates the same nature of the transformation starting at a temperature of 430 °C in all samples. It is likely that the growth of mass in the temperature range \( T_3 \) was mainly caused by thermal annealing of oxygen vacancies. In the \( T_3 \) range from 430 °C to 1030 °C, crystallization of the amorphous fraction in the monoclinic ZrO\(_2\) phase occurred in a wide temperature range in all samples. Synchronous growth of the TG and DSC curves for all samples in the \( T_4 \) temperature range from 1030 to 1130 °C shows that the completion of the crystallization of the amorphous fraction in the \( T_4 \) range promotes the acceleration of the annealing of oxygen vacancies.

In the \( T_5 \) range, the final polymorphic transformation of the monoclinic phase to tetragonal phase occurs at the same temperature of about 1130 °C in all samples. (The region of thermal stability of the bulk monoclinic phase is from 273 to 1160 °C [13]). The decrease in the temperature of the polymorphic transformation by 30 °C is exclusively due to the influence of the size factor and is not connected with the influence of the electron beam on the samples.

In the \( T_7 \) range, the growth of the mass of the samples in the TG curves, as a result of the annealing of the oxygen vacancies, continued until the end of the heating to 1400 °C (At the same time, there were no thermal transformations in the DSC curves).

The change in the mass of the samples at their heating from 430 to 1400 °C increased nonlinearly with an increase in the irradiation dose in the sequence 6.8 → 7.3 → 12.3%. An almost twofold increase in the mass of the sample at maximum irradiation clearly indicates that irradiation by electrons substantially changes the concentration of oxygen vacancies at the surface and inside of the volume of the YSZ mesoporous nanopowder. The decrease in the concentration of oxygen vacancies on the surface of irradiated samples as a result of radiation annealing confirms a consistent decrease in
the PCL intensity of the samples (Fig. 3) induced by electrons with an energy of 180 keV. In turn, the increase in the continuous growth of the mass of irradiated samples indicates an increase in the concentration of oxygen vacancies in irradiated samples as compared to the pristine concentration of vacancies in the unirradiated sample.

Thus, the use of a complex approach to study the nature of defects induced by irradiation in multiphase mesoporous NPs allows a qualitative estimation of the change in the concentration of oxygen vacancies after exposure. From the obtained data, the following conclusions can be drawn:

- irradiation with high doses of high-energy electrons significantly changes the concentration of oxygen and, possibly, cationic vacancies, which clearly demonstrates the continuous increase in the
mass of irradiated samples at heating in comparison with the change in the mass of the unirradiated sample;

- the impact of electrons does not change the temperature of the various phase transformations (crystallization temperature of the amorphous phase, the temperature of the polymorphic transformations), which indirectly indicates the absence of a significant change in the original size of the nanocrystallites after irradiation;

- the kinetics of the sample mass transformation (mass reversal) significantly changes after irradiation. The temperature at which the mass of the sample, after the initial weight loss, returns to its original level (Tr), successively decreases 895 → 760 → 530 °C with the dose increase, which confirms that the irradiated samples contain significantly less amount of adsorbed water and carbonaceous impurities;

- the unchanged location of the PCL peaks indicates the absence of phase transformations caused by irradiation.

4. Conclusions

Thus, the preliminary investigation of the effect of a pulsed electron beam with a high electron energy on the NPs of some nonmagnetic metal oxides showed the following:

- the effect of electron irradiation on the magnetic properties of NPs is less pronounced than the effect on structurally sensitive PCL spectra and thermal properties;

- the specific magnetization of NPs of non-magnetic oxides varies nonmonotonically from the AD of irradiation and varies arbitrarily for each particular sample;

- there is a general tendency to decrease the PCL intensity of NP of various metal oxides with an increase in the irradiation dose, probably caused by a decrease in the concentration of structural defects;

- synchronous thermo-gravimetric analysis of the behavior of the samples before and after irradiation by the electrons significantly expands the idea of the formation and change of the defect structure of NP samples of nonmagnetic oxides as a result of their irradiation with low-energy electrons, in the synthesis process by the PEBE method, and with further irradiation by high-energy 700 keV electrons.

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References

[1] Gubin S, Koksharov Y, Khomutov G, Yurkov G 2005 Russ. Chem. Rev. 74 489
[2] Peng H, Xiang H, Wei S, Li S, Xia J, Li J 2009 Phys. Rev. Lett. 102 017201
[3] Hsu H, Tung Y, Chen Y, Chen M, Lee J, Sun J 2011 Phys. Status Solidi RRL 5 12 447
[4] Gonzalez-Martinez I, Bachmaituk A, Bezugly V, Kunstmann J, Gemming T, Liu Z, Cuniberti G, Rummeli M 2016 Nanoscale 8 11340.
[5] Nagase T, Umakoshi Y 2005 Materials Transactions 46 616
[6] Il’ves V, Sokovnin S, Zuev M 2016 J.Lumin. 179 474
[7] Sokovnin S, Il’ves V, Surdo A, Mil’man I, Vlasov M 2013 Nanotechnologies in Russia 8 466
[8] Sokovnin S, Il’ves V 2009 Tech. Phys. Lett. 35 1026
[9] Sokovnin S, Il’ves V 2012 ISRN Nanomaterials Article ID 504634 11
[10] Sokovnin S, Il’ves V 2012 J. Ferroelectrics 436 101
[11] Sokovnin S, Balezin M 2016 Radiation Physics and Chemistry S0969-806X(17)30918-0
[12] Chethan P, Joshi P, Raj Mohan S, Dhami T, Jayakrishna K, Koteshwar Rao K, Kukreja L, Ganesh S 2013 Adv. Mat. Lett. 4 454
[13] Kumar S, Ojha A, 2016 Materials Chemistry and Physics 169 13.