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Interrelation between magnetic and luminescent properties of aluminum oxide doped with copper and carbon

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ABSTRACT

The results of researches of structural, luminescent and magnetic properties nanopowders (NPs) of pure and carbon (copper)-doped aluminum oxide, obtained by the pulsed electron beam evaporation are presented below. The suppression of the R-line ions Cr³⁺ in photoluminescence spectra of all NPs is detected.

All NPs without an exception (pure and doped) showed room temperature ferromagnetism. The nature of the observed ferromagnetism is connected with high concentration of the structural defects, which are formed in NPs in the course of their synthesis by means of pulsed electron beam evaporation in vacuum.

The correlation between concentration of structural defects (oxygen vacancies) and ferromagnetic behavior of nanopowders is presented. The correlation was established between dependencies of the ratio integral intensity of the yellow and the red bands of photoluminescence spectra (the ratio integral intensity of the green and the red bands of pulsed cathodoluminescence spectra) and magnetization from carbon doping level.

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1. Introduction

Aluminum oxide in the form of nanoparticles [1], thin films [2], nanopowders [3], thin nano-structured coatings [4] shows unexpected ferromagnetic properties and considerable luminescent activity.

Sundaresan et al. [1,5] reported about detection of the room temperature ferromagnetism (RTFM) among nanoparticles (NPs) of certain oxides, in particular, of Al₂O₃. NPs of Al₂O₃ demonstrated RTFM with a clear hysteresis loop at the temperature of 390 K and specific magnetization of about $3.5 \cdot 10^{-3}$ emu/g at 300 K. Due to the better stability and high dielectric constant, thin films of aluminum oxide are widely used in the spintronic applications and in the future can replace the traditional SiO₂ semiconductor in MOS (metal-oxide-semiconductor) devices and in other areas [2].

Calculations from the first principles (ab initio) have shown that FM in Al₂O₃ can be induced at by means of carbon-doping of Al and O of the lattice sites, in which spin densities are localized generally on the C-dopant [6]. Doping C at the Al-site leads to band

gap narrowing and greatly modifies the upper valance band, while doping C at the O-site affects the band edges of α -Al₂O₃ slightly.

Magnetic properties of pure aluminum oxide [1–3,7] and doped by magnetic [8–11] and nonmagnetic elements [12,13] are poorly investigated.

Most RTFM researches were carried out on thin films, therefore it is important to investigate magnetic properties of the powdered Al₂O₃. Studying of magnetic properties of oxides and semiconductors in the powder form has some advantages over researches of films. Upon magnetic measurements, the interface between the film and the parameters mismatch between the film lattices and the substrate and impurity diffusion from the substrate do not influence the powders.

Carbon doped anion-deficient Al₂O₃ has also been widely used for a long time in solid-state dosimetry [14–16]. The last researches have shown the possibility to replace single-crystal TLD-500 dosimeters in the several directions of dosimetry on the basis of anion-deficient Al₂O₃, which are grown up from fusion by Stepanov and Chokhralsky's methods on thin films [17] or nanostructured coatings up to 20–40 μ m thick [18].

There are relatively few methods, by means of which it is possible to evaporate mechanical mixes of oxides with refractory carbon [19], i.e. to carry out the controlled carbon doping of the oxide matrix. Recently, use of the hybrid magnetron spraying system combining

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magnetron dispersion and generation of plasma by the electron beam on SiO₂ amorphous substrates with a seed layer of Cr₂O₃, it became possible to obtain single-phase coatings from α -Al₂O₃ of up to 1 μ m thick at the substrate temperature of 700 °C [20], which is indicative of the potential prospect to produce the anion-deficient α -phase of Al₂O₃ at the lower temperatures in the conditions of the lowered oxygen pressure by this method.

Thus, a steady tendency towards the increase of researches of nanodimensional Al₂O₃ oxide for the purpose of its further application in devices of spintronics, dosimetry, ceramic synthesis, catalysis, optics and other areas, is observed.

The purpose of this work consisted in the studying of interrelation between luminescent and magnetic properties of NP pure and doped by non-magnetic elements (copper and carbon) of Al₂O₃ obtained by the pulsed electron beam evaporation in vacuum, and establishment of interrelation between structural defects and magnetic-luminescent characteristics of NPs.

2. Materials and methods

NPs of pure and carbon- or copper-doped Al₂O₃ were obtained by the pulsed electron evaporation in vacuum [21] (electrons energy 40 keV, impulse energy 1.8 J, impulse duration 100 mcs, pressure in the evaporation chamber 4 Pa). Targets made of mechanical mixes of high-pure nanopowders of α -Al₂O₃ (corundum) of different manufacturers (Inframat Advanced Materials, the USA ($S_{\text{BET}}=8.8 \text{ m}^2/\text{g}$) and LLC Nanokorund Sarov, Russia) evaporated with powder of spectrally pure carbon obtained by grinding in the porcelain mortar (0.1–10.0 wt% C), or with copper NP ($S_{\text{BET}}=20 \text{ m}^2/\text{g}$) obtained by the method of the wire electric explosion [22] (1–5 wt% Cu).

Powders were deposited on the glass substrates placed around the evaporated target at the distance of 10–15 cm.

The specific surface area of NPs (S_{BET}) was defined by the BET method on the Micromeritics TriStar 3000 unit. Chemical analysis was made by methods of the inductive-connected plasma (ICP) and nuclear-absorbing spectroscopy (AAC). The X-ray diffraction (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 translucent electronic microscopy (TEM) on JEM 2100 microscope. Magnetic measurements were carried out by the vibration magnetometer Cryogenic CFS-9T-CVTI at the temperature of 300 K and magnetic fields of ± 5 T and by Faraday's scales (sensitivity of scales $\sim 10^{-5}$ emu, the range of measurements on the magnetic field – to 12 kOe). Photoluminescence spectra (PL) are recorded at the room temperature on the spectrometer MDR-204 (deuterium lamp, photoelectronic multiplier R928 by Hamamatsu firm). The pulsed

cathodoluminescence (PCL) spectra were recorded at room temperature on a KLAIVI 1 spectral analyzer.

3. Results and discussion

By means of evaporation in vacuum of the compacts from NPs of α -Al₂O₃ from different manufacturers (IAM and Corund) and the annealed at 1000 °C mixes of α -Al₂O₃ (IAM)–C (0.1–10 wt% C), multiphase amorphous-nanocrystalline powders of pure and C (Cu)-doped Al₂O₃ were obtained. S_{BET} measurement results and determination of the element and phase composition of ANC powders are presented in Table 1.

It follows from Table 1 that NP S_{BET} changed not monotonic for different types of dopants; the content of the impure Fe in NPs generally didn't exceed $(3-6) \cdot 10^{-2}$ wt%; limit of solubility of copper in the lattice of Al₂O₃ was below 11.19 wt% Cu. The limit of carbon solubility in the lattice of Al₂O₃ didn't exceed 1.06 wt% C.

XRD patterns of non-doped NP samples (Nos. 1 and 2, Table 1) and carbon-doped NPs (Samples nos. 3–5 in Table 1) Al₂O₃ are presented in Fig. 1. Samples nos. 1 and 2 had essentially different phase structure. NP no. 1 consisted of three crystal phases: α -Al₂O₃ (corundum), the cubic phase γ -Al₂O₃, the monoclinous phase θ -Al₂O₃ and the amorphous phase [13], at the same time, relative concentration of crystal phases amounted to 65:24:11, respectively. NP No. 2 consisted of two crystalline phases, rough estimate of crystalline phases ratio α : δ has shown the ratio 2:1.

The parameter ϵ varies within experimental error (Table 2). Doping small carbon atoms do not significantly affect the lattice parameters Al₂O₃.

All NPs based on Al₂O₃ formed by electron evaporation, had similar morphology and consisted of the agglomerates of up to several hundred nm in size formed by nanoparticles close to spherical shape with an average size from 5 to 15 nm. The TEM image of non-doped Al₂O₃ NP in Fig. 2 (No. 2, Table 1) has the characteristic appearance. We shall note complete absence of crystalline NPAs on TEM images of sample No. 2, though according to XRD in sample No. 2 there are crystalline phases (Fig. 1b). Strong agglomeration of nanoparticles between each other is clearly visible in Fig. 2b and c.

In Fig. 3a the bands of photoluminescence spectra (PL) of the samples of pure and C (Cu)-doped Al₂O₃ are presented. PL spectra of all samples contain two mutually overlapping bands with maxim values at (581–585 nm) (2.1 eV) and (661–664 nm) (1.87 eV). We can note the intensification of PL Al₂O₃–C at a small carbon doping level ($x_{\text{C}} \leq 1.19$ of wt% C), with a further intensity decrease at the x_{C} growth. Lack of R-lines of ions Cr³⁺ in PL spectra of all samples (irrespective from matrix material) is indicative of the volumetric samples doping by carbon, which, as already

Table 1

Specific surface area (S_{BET}), Fe concentration (x_{Fe}), carbon concentration (x_{C}), cuprum concentration (x_{Cu}) and phase composition NP based on Al₂O₃.

No. sample	Target composition (factory)	S_{BET} , m ² /g	x_{Fe} , wt% (ICP)	$x_{\text{C(Cu)}}$, wt% (AAC)	^a NP phases(XRD)
1	α -Al ₂ O ₃ (IAM)	270	0.06	–	α, γ, θ
2	α -Al ₂ O ₃ (Nanokorund)	124	–	–	α, δ
3	α -Al ₂ O ₃ (IAM) 0.1 wt% C	128	–	1.07	α, δ
4	α -Al ₂ O ₃ (IAM)–1.0 wt% C	295	–	1.19	α, δ
5	α -Al ₂ O ₃ (IAM)–10.0 wt% C	140	0.03	6.60	α, δ
6	α -Al ₂ O ₃ (Nanokorund)–0.1 wt% Cu	101	–	–	α, δ
7	α -Al ₂ O ₃ (Nanokorund)–0.6 wt% Cu	149	–	–	α, δ
8 ^a	α -Al ₂ O ₃ (IAM)–1 wt% Cu	338	0.13	1.72	α, γ, θ
9 ^a	α -Al ₂ O ₃ (IAM)–3 wt% Cu	80.7	0.05	11.19	$\alpha, \gamma, \theta, \text{Cu}_2\text{O}$
10 ^a	α -Al ₂ O ₃ (IAM)–5 wt% Cu	68.7	0.06	17.22	$\alpha, \gamma, \theta, \text{Cu}_2\text{O}$

^a [13].

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