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Pulsed cathodoluminescence of nanoscale aluminum oxide with different phase compositions

V.S. Kortov [a,*,I], S.V. Zvonarev [a], A.I. Medvedev [b]

[a] *Ural Federal University, Ekaterinburg 620002, Russia*
[b] *Institute of Electrophysics, Ural Branch Russian Academy of Sciences, 620016 Ekaterinburg, Russia*

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ABSTRACT

The methods of pulsed cathodoluminescence have been used to study compacted powders and ceramics containing different phases of aluminum oxide. An intensive luminescence of the samples under study in the visible, NIR, and UV regions of the spectrum has been found. The luminescence bands are very broad and include a few components. The number of the bands depends on the phase composition of the samples. The oxygen vacancies, which capture one or two electrons, produce luminescence centers in the near UV region. The most probable in the visible region is the luminescence of aggregate defects, impurities, and surface centers.

1. Introduction

Aluminum oxide is a multifunctional material, which is widely used in science and engineering. Its defects, optical, and luminescence properties have been actively studied. The advancement of nanotechnologies stimulated interest in research of the luminescence properties of nanoscale materials, including powders and ceramics based on aluminum oxide. There are physical reasons to assume that a high concentration of surface atoms and defects on numerous boundaries of nanoparticles, a decrease in the probability of nonradiative recombination, a growth of the oscillator strength, and other factors can promote an increase in the quantum yield of the luminescence. The formation of new types of defects in nanostructures, a violation of the translational symmetry, and a limitation of the mean free path of electrons by the size of nanoparticles change the rules of selection and cause new optical transitions. As a result, the luminescence and excitation spectra can change [1].

Recently considerable study is given to the luminescence properties of the stable α-phase of nanoscale aluminum oxide [2,3]. At the same time, metastable phases in nanoscale alumina under study also present much scientific interest. The luminescence properties of mixed δ-, θ-Al_2O_3 nanopowders were investigated and luminescence bands due to intrinsic excitations, color centers, and transition metal ions were identified [4]. Also, investigations into specific features of the defect content and the luminescence properties of nanoscale aluminum oxide with different phase compositions provide a deeper insight into the physics of the nanostate of materials. Therefore, the aim of this work was to study the luminescence properties of nanopowders and ceramics of aluminum oxide, which contain metastable phases in comparison with the analogous properties of the stable α-phase and to use the results for identification of the luminescence centers.

2. Experimental

An Al_2O_3 nanopowder was produced by the method of electrical explosion of aluminum wire. Physical basics of the method, the experimental installation, and the nanopowder preparation techniques are fully described [5]. The method allows to prepare powders of metals and their oxides with an average particle size 20–100 nm, which do not show significant aggregation. In weekly aggregated powders, nanoparticles show their individual properties and effects depending on their size more significantly. We used in our experiments the powder contained metastable γ- and δ-phases in the ratio of 35 and 65 mass%, respectively. It was characterized by particles mostly of the spherical shape with the specific surface of 67 m^2/g ($d_{BET} \approx 25$ nm).

The luminescence samples 15 mm in diameter and 1 mm thick were produced by uniaxial magnetic pulsed compaction of the

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* Corresponding author. Tel.: +7 343 3754443; fax: +7 343 3754415.
E-mail address: v.kortov@mail.ustu.ru (V.S. Kortov).

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powders [6] at a pressure of up to 2 GPa and a temperature of 450 °C. To remove the stresses arising during compaction of the samples, they were annealed at a temperature of 500 °C for 2 h. A compaction temperature and subsequent annealing of the samples did not change the phase composition of the initial powders. The density of the samples accounted on the average for 55–60% of the theoretical density. An XRD analysis of the initial powders and the compacted samples was performed using a D8 DISCOVER X-ray diffractometer with CuK$_\alpha$ radiation and a graphite monochromator.

The pulsed cathodoluminescence (PCL) spectra were studied using prepared samples. The PCL method is highly effective in searching research when luminescence bands position and type of luminescence centers are unknown. Such situation is usual for luminescence properties study of nanomaterials. Most of the luminescence mechanisms, such as recombination, intracenter transition, exciton decay, etc. [7] occur in material studied by PCL because of very powerful excitation ($\sim 10^7$ W/cm^2), which lasts a few nanoseconds. Luminescence centers are exited not only by electrons but also because of absorption of shortwave optical and X-ray radiation, appearing during the deceleration of electrons in sample. In this case total specific excitation energy does not exceed 0.2–0.5 W/cm^3, and this makes the temperature condition much more easier than in case of stationary cathodoluminescence. Heating of sample in electron beam zone does not exceed 1–2 K, and destruction of sample does not occur. It is necessary to emphasize that a special preparation of samples is not required in the PCL method because they are exposed to electron beam in air. It is also seen that the rapidity of luminescence spectra measurement increases significantly. Therefore, PCL is the effective method for study of generation, interaction and migration of short-living excitations processes [7].

In our experiments PCL was excited by an electron beam of an accelerator (the current density of 1 A/m^2, the electron energy of 180 keV, and the pulse length of 3 ns). The PCL spectra were recorded in the visible region (350–800 nm) using a CCD camera, and in the violet and near UV region (240–430 nm) by an FEU-39A photomultiplier. The required wavelength was separated by a VMN-3 monochromator. The background signal of the airglow upon passage of the electron beam was subtracted during the computer processing.

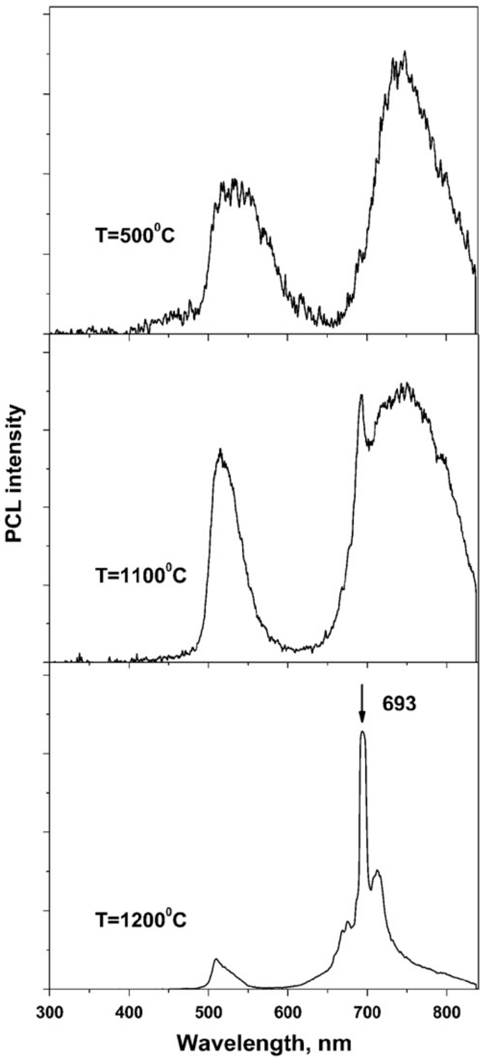

Fig. 1. PCL spectra of compacted nanoscale powders containing γ (35%) and δ (65%) phases of Al_2O_3 at different temperatures of annealing.

3. Results and discussion

Fig. 1a presents PCL spectra of the samples prepared by compaction of the initial nanopowders of aluminum oxide. A CCD camera (350–800 nm) was used. The spectra are characterized by two broad luminescence bands in the green region of the spectrum with a maximum near 520 nm and in the red region with a maximum near 750 nm. The red luminescence partly covers the NIR range.

The shape of the maximums points to a complicated structure of the luminescence bands. The band 520 nm can be related to the aggregate F_2-centers produced by double-oxygen vacancies and the centers formed by interstitial aluminum ions. It is known that these centers are responsible for the green luminescence in highly disordered crystals of aluminum oxide [8,9].

The broad red luminescence band with maximum at near 740 nm can be related with R-lines of Cr^{3+} impurity in metastable γ- and δ-phases of investigated alumina samples. It is known that very strong inhomogeneous broadening of ^2E–$^4A_2$ transition (R-line) is observed in photoluminescence (PL) spectra of mention above phases. The long-wavelength part of spectrum corresponds to vibronic transitions. Such spectra of R-lines are typical for highly disordered aluminum oxide crystals [10].

It is also to be noticed that PL spectrum of nanocrystalline Al_2O_3:Cr^{3+} powder with maximum at 740 nm can be observed under the UV-laser (λ=337, 1 nm) excitation with high average laser emission power density (0.2 W/cm^2) [11]. Authors supposed that excitation of alumina nanopowder by laser radiation of specified wavelength causes the $^4A_2$–$^4T_1$ transition in Cr^{3+} ions accompanied by phonon generation. In our experiments the influence of pulse electron beam on sample is also a high density excitation. In view of the foresaid PCL features it is possible to assume that transition $^4A_2$–$^4T_1$ occurs during the excitation of Cr^{3+} ion either by electron beam or laser radiation. This transition causes the growth of phonon density. In this case a red shift of phonon wing can be observed.

There are other mechanisms of red shift of PCL spectra. Also Ti^{3+} (λ_{em}=706 nm) impure ions and aggregate F^{+2} (2 Mg) centers (λ_{em}=750 nm) can luminesce in the red spectral region. The latter appear in aluminum oxide if oxygen vacancies and magnesium impurities exist in crystal [12]. It is possible that the foresaid luminescence bands superposition influences on the appearance of the wide band in red and NIR spectral region of investigated aluminum oxide samples containing metastable γ- and δ-phases.

The samples were annealed by higher temperature for further study of different phases luminescence in nanostructured