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The effect of preparation method on the defect structure and luminescence properties of γ-Al_2O_3

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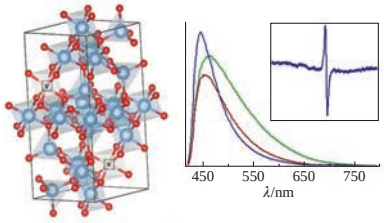
The photoluminescence properties of nanodimensional γ-Al_2O_3 produced by the thermolysis of aluminum hydroxoformate $Al(OH)(HCOO)_2$ under different conditions have been studied. In the EPR spectrum of γ-Al_2O_3 prepared by thermohydrolysis, a low-field signal was detected, whose shape depends on the amount of sample. The data were interpreted assuming the existence of paramagnetic centers having no inversion center.



Aluminum sesquioxide, possessing a high thermal conductivity, chemical stability, mechanical durability, radiation resistance, and optical transparency, is an inexpensive material widely used in modern engineering and technology.[1] The list of practical applications of Al_2O_3 covers a range of structural and functional materials including abrasives, ceramics, refractory materials, sorbents, solid electrolytes, catalysts, and phosphors.[2–4] The oxide α-Al_2O_3:C is a highly sensitive luminescent material, which is used in radiation dosimetry and radiotherapy.[5] In spite of the apparent advantage of α-Al_2O_3:C as a radiation-sensitive material, its production involves the long-term heating of a mixture of Al_2O_3 and carbon at very high temperatures.[6] Therefore, attempts are often made to use nanodispersed γ-Al_2O_3 with white-blue emission[7,8] as a luminescent detector. The oxide γ-Al_2O_3 is also an optical host for producing Ln^{3+} activated emission media.[9,10] As distinct from α-modification, the synthesis of γ-Al_2O_3:C does not require high temperatures and long-term annealing.[7,11,12] However, published data on the synthesis and luminescence properties of γ-Al_2O_3 are few in number.

The goal of this work was to establish the dependence of the luminescence properties of γ-Al_2O_3 on the synthesis conditions and intrinsic defectiveness. A precursor preparation method based on the heat treatment of aluminum hydroxoformate $Al(OH)(HCOO)_2$ was developed to obtain nanostructured γ-Al_2O_3 samples.[12,13]

The precursor $Al(OH)(HCOO)_2$ was synthesized by the addition of formic acid to a stirred solution of analytical-grade aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$ in distilled water at room temperature. The prepared solution was boiled; then, after a white film-like scurf appeared on the glass bottom, it was kept at 60 °C until a solid residue was formed. To obtain the γ-Al_2O_3 product, the precursor $Al(OH)(HCOO)_2$ was heat treated at 600–750 °C in helium and air atmospheres (samples 1 and 2, respectively) and in a thermal hydrolysis unit (sample 3). The annealing time was 3 h. The formation of the single-phase final products was confirmed by the X-ray powder diffraction (XRD) data.† According to the XRD analysis, the products of $Al(OH)(HCOO)_2$ thermolysis at 600 °C in an inert atmosphere and in air are X-ray amorphous. The crystalline γ-Al_2O_3 phase under these conditions was formed at 750 °C [Figure 1(*a*)]. At the same time, γ-Al_2O_3 was formed during thermal hydrolysis already at 600 °C. All the γ-Al_2O_3 samples were characterized by a low degree of crystallinity. The results of scanning electron microscopy (SEM) showed that the thermolysis of $Al(OH)(HCOO)_2$ is a pseudomorphical process irrespective of the heat treatment conditions, the particle shape

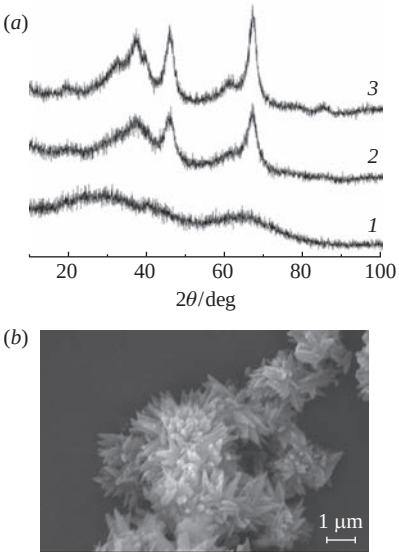


Figure 1 (*a*) X-ray diffraction patterns of γ-Al_2O_3 samples prepared from $Al(OH)(HCOO)_2$ (*1*) in air (600 °C), (*2*) in helium (750 °C), and (*3*) by thermohydrolysis (600 °C). (*b*) Typical SEM images of γ-Al_2O_3 powder obtained by thermohydrolysis.

† The XRD patterns were collected on a STOE STADI-P automated diffractometer using $CuK\alpha_1$ radiation in a 2θ range from 10° to 100°. The morphological characteristics of the samples were found by scanning electron microscopy using a Jeol JSM-6390LA instrument. To determine the excitation wavelength, the absorption spectra were recorded on a UV-2600 spectrometer in a range of 190–700 nm using $BaSO_4$ as a standard. The photoluminescence was measured on a Varian Cary Eclipse fluorimeter at an excitation wavelength of 260 nm. The EPR spectra were recorded in the X-band on a standard CMS-8400 EPR spectrometer (Adany) at room temperature.

being preserved. The particles of γ-Al_2O_3 samples have a crystal habit of flower [Figure 1(*b*)].

In the EPR spectrum of sample 1, obtained at 750 °C in a helium atmosphere, there is a single narrow symmetrical line with a *g*-factor of 2.002 (ΔH_{pp} = 8 G) [Figure 2(*a*)]. According to published data, the EPR signals in γ-Al_2O_3 with *g*-factors close to the spin value can be associated with carbonyl defects,[14] aluminum peroxyl radicals Al–O–O$^{\bullet}$ [15,16] and singly ionized oxygen vacancies V_O^+ (F^+-centers).[17,18] Earlier, we established that the observed signal is related specifically to oxygen vacancies rather than carbonyl defects.[12] The results of our *ab initio* calculations show that the carbon atoms, incorporated into the interstitial positions in γ-Al_2O_3 during the thermolysis of precursor, have no spin polarization, and they cannot be detected by EPR spectroscopy.[12] In the sample 2, isolated at 750 °C in air, there is no paramagnetic response [Figure 2(*a*)].

Unlike samples 1 and 2, an intense asymmetric signal with a *g*-factor of ~3.1 is recorded in the EPR spectrum of sample 3. In the course of the experiment, we noticed that the reduction of the sample volume from ~0.2 to ~0.02 cm^3 changed not only the signal amplitude but also the line shape [Figure 2(*b*)]. This behavior of the signal and the high *g*-value, which indicates a large contribution of the orbital angular momentum, can be connected, on the one hand, with the resonant effects on the band carriers and, on the other hand, with the features of the interaction of noncentrosymmetric systems with an alternating electromagnetic field.[19–21] In both cases, transitions between spin levels occur under the action of not only the magnetic component of a high-frequency field but also the electric component. Moreover, in some cases, the electric excitation of spin transitions can greatly exceed the magnetic excitation.[19] The pronounced dependence of the line shape on the amount of the sample is indicative of the electric nature of excitation. Apparently, a large-volume sample, when placed in the antinode of alternating magnetic field, partially exceeds its limits and interacts with the electric component of the high-frequency field. For small sample volumes, this does not occur, so the signal is lacking. Taking into account the large width of the band gap of γ-Al_2O_3 (~8 eV), we can assume that the low-field signal is not associated with the band carrier resonance but is caused by transitions between the spin levels of paramagnetic centers, whose local symmetry has no inversion center. This assumption is supported, in particular,

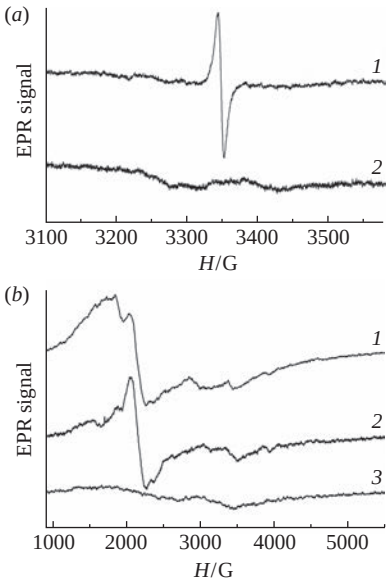


Figure 2 (*a*) EPR spectra of γ-Al_2O_3 samples prepared (*1*) in helium and (*2*) in air; (*b*) EPR spectra of γ-Al_2O_3 powder obtained by thermohydrolysis; sample volumes: (*1*) 0.2, (*2*) 0.08, and (*3*) 0.02 cm^3.

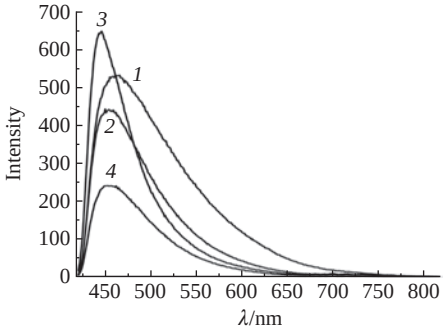


Figure 3 Emission spectra of γ-Al_2O_3 samples prepared (*1*) in helium (750 °C), (*2*) in air (750 °C), and (*3*) by thermohydrolysis (600 °C), (*4*) the photoluminescence spectrum of γ-Al_2O_3 sample 3 additionally annealed in air at 600 °C.

by the fact that the signal disappeared after the annealing of sample 3 in air (600 °C). Obviously, during such annealing, oxygen is embedded in the lattice whereupon the crystal structure around the centers changes and their environment becomes centrosymmetric. As a result, the resonance associated with the electrical effects is not observed. On the other hand, annealing in air can lead to the removal of defects responsible for a paramagnetic response. However, although the nature of the defect centers in γ-Al_2O_3 synthesized under thermohydrolysis conditions is not completely clear, it can be assumed that this sample has a fundamentally different defect structure as compared to the samples obtained in helium or in air.

The photoluminescence spectra of the γ-Al_2O_3 samples under excitation at the wavelength λ_{ex} = 260 nm exhibited wide bands with emission maxima in the blue-green region (Figure 3). The most intense emission at λ_{max} = 445 nm was observed in the sample obtained by thermohydrolysis. After annealing this sample in air, the emission intensity significantly decreased, and the emission maximum was slightly shifted toward large wavelengths (λ_{max} = 455 nm). The emission maxima of samples 1 and 2 correspond to 460 and 455 nm, respectively. Sample 1 prepared in a helium atmosphere, in comparison with sample 2, had a broader and more intense band extending up to the near infrared region.

According to published data, the blue-white luminescence of γ-Al_2O_3 is due to the presence of F^+-centers.[22] Y. Wakui *et al.*[11] proposed a photoluminescence mechanism involving carbon atoms in addition to oxygen vacancies. Previously, we found that the reduction in the concentration of oxygen vacancies and carbon removal from the structure during stepwise annealing of γ-Al_2O_3 in air lead to the suppression of emission up to its complete disappearance.[12] These data correlate with the results of this work: the intensity of γ-Al_2O_3 luminescence lowers with decreasing intrinsic defectiveness. In terms of the production of phosphors with intense emission in the blue spectrum region, the most effective method is synthesis based on the decomposition of the precursor in a water vapor atmosphere.

Thus, a relationship between the intrinsic defectiveness and the photoluminescence of γ-Al_2O_3 was revealed in this work. As shown by EPR spectroscopy, the intrinsic disorder of γ-Al_2O_3 depends largely on the synthesis method. The preparation method affects not only the intensity of γ-Al_2O_3 luminescence but also the width of the emission band and the position of the emission maximum in the spectrum.

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Spectroscopy and Analysis of Organic Compounds of the Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences.

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