

Luminescent properties of alumina ceramics doped with chromium oxide

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Abstract. Ceramics doped with chromium oxide were synthesized from alumina nanopowder at high heating and cooling rates. XRD analysis of the obtained samples shows that they consist mainly of Al_2O_3 α -phase. Photoluminescence (PL) spectra in the visible spectral region and thermoluminescence (TL) curves were measured. An effect of the dopant concentration on the intensity and shape of the PL bands as well as on the TL yield was found. Annealing of the quenching defects which emerged during the synthesis changed the PL spectra. The centers responsible for PL and TL in the synthesized ceramics were identified.

1. Introduction

The investigation of optical properties of oxygen-deficient alumina ceramics synthesized by solid-phase method from nanopowder showed the opportunities of their use as phosphors, which can arouse interest in optoelectronics. It is known that photoluminescence (PL) properties of such ceramics depend on the concentration of the oxygen vacancies, which form the traps of charge carriers, and take part in recombination processes. It is established that the following conditions of synthesis influence the concentration of anion vacancies in the oxygen sublattice of alumina: the temperature of synthesis, the time of isothermal annealing, the pressure in chamber, and the presence of a strong reducing agent, such as graphite [1]. However, during the synthesis in the highly reducing medium (deep vacuum, the presence of graphite), the loss of mass and changing of the sample sizes take place, which leads to some particular difficulties of the usage of luminescent ceramics. In this regard, development of a synthesis method of luminescent Al_2O_3 -based ceramics which do not cause the abovementioned negative effects is an important task. One of the study directions is doping of ceramics with the introduction of different impurities. It is known that ions of Cr^{3+} can replace Al^{3+} in the crystal lattice of alumina. In this case one can expect the formation of new centers which can increase PL and TL without the use of strong reducing medium while synthesis. The purpose of this work is to study luminescence of oxygen-deficient alumina ceramics doped with chromium oxide.

2. Materials and Methods

α - Al_2O_3 nanopowder of high purity (99.99%) with the grain size of 50-70 nm and nominally pure microcrystalline powder of chromium oxide was used to produce blend. The powders were mixed and, after the addition of ethanol, the suspension was formed. Further mixing took place in an ultrasound bath. The mixture was dried at 343 K for 8 hours. After that the powder which consisted of oxides mixture was subject to uniaxial pressing at a pressure of 5 MPa. The obtained compacts 6.1 mm in diameter and 1 mm thick were annealed in the heating chamber of gas-analyzer EAO-220 (Balzers).



The device allowed us to get fast heating (200 K/s) of the samples put into carbon crucible due to transmission of high current. In this case the samples were heated to 1,773-1,873 K. The cooling rate of samples was 126 K/s. Quenching defects were annealed in the electrovacuum furnace SNVE 9/18 which heats the samples up to 2,073 K at a rate of 0.5 K/s. The annealed samples were cooled down to a room temperature with the furnace. The PL spectra were recorded by luminescence spectrophotometer Perkin Elmer LS-55 in the range of 200-900 nm. The excitation energy of quanta was 5.3 eV. Thermoluminescence was measured with an experimental unit at 2 K/s rate. XRD analysis was carried out on XPert PRO MPD (PANalitical) diffractometer in copper radiation with a beta-filter on the secondary beam. The voltage on the tube was 40 kV, the anode current was 30 mA. To exclude the effects of the sample texturing on XRD patterns, the samples were rotated in a horizontal plane at the angular rate of 0.25 revolution per second.

3. Results and Discussion

Figure 1 shows PL spectra of the synthesized alumina ceramics doped with chrome oxide. It can be seen that the intensity of the PL bands grows in the range of 2.2-3.4 eV with an increasing concentration of the impurity from 0.005 up to 0.01 weight %. Further increase in Cr_2O_3 concentration leads to decreasing emission in the given range due to concentration quenching. It is also noteworthy that PL yields grow in the 1.7-1.9 V band. Cr^{3+} ions which replace aluminum ions in the crystal lattice luminesce in the alumina single crystal in the reported range [2]. Increasing PL intensity in the given band indicates introduction of Cr^{3+} ions into Al_2O_3 crystalline lattice.

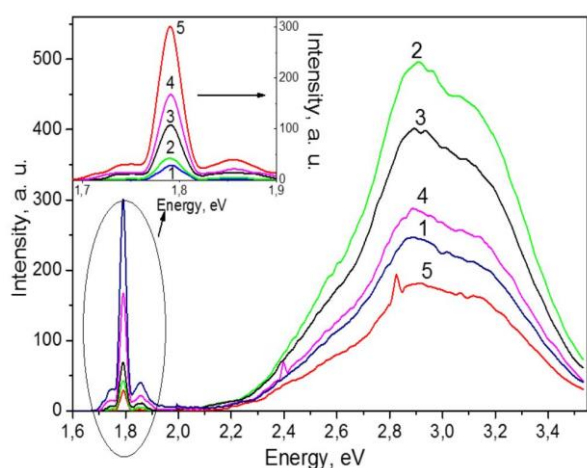


Figure 1. PL spectra of alumina ceramics ($E_{\text{ex}}=5.3\text{ eV}$, $T=300\text{ K}$) with different Cr_2O_3 concentrations (wt.%): 1 – 0.005; 2 – 0.01; 3 – 0.02; 4 – 0.03; 5 – 0.1.

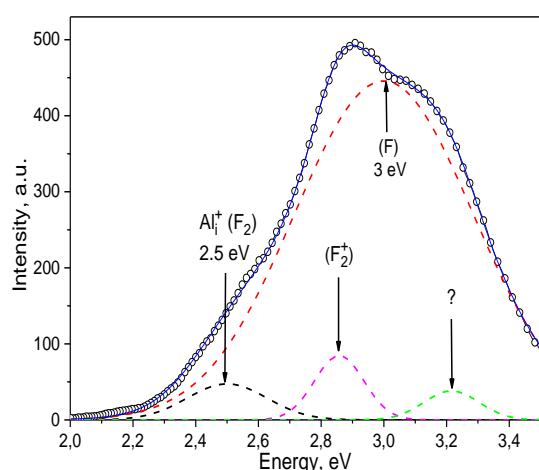


Figure 2. Gaussian decomposition of PL spectrum (curve 2, Figure 1).

Figure 2 features PL spectrum for the sample with the maximum intensity (curve 2, figure 1), which was deconvoluted into gaussians. It is known that in oxygen-deficient alumina the PL band with the maximum at 2.5 eV is caused by interstitial aluminum ions and F_2 aggregate centers (oxygen divacancies) [3]. Emission of F-centers (oxygen vacancies with two trapped electrons) is registered in the 3 eV band. The band with the maximum near 2.8 eV is associated with F_2^+ aggregate centers (oxygen divacancies with one trapped electron) [4]. The band with the maximum of 3.2 eV is presumably connected with deformation by (quenching) defects which emerged at high heating and cooling rates.

The analysis of the samples with a XRD method showed that they are $\alpha\text{-Al}_2\text{O}_3$ solid solution with the lattice parameters: $a(\text{\AA})=4,756(2)$; $c(\text{\AA})=12,987(4)$. The XRD pattern features traces of another phase in the form of weak reflexes on the angles of $20,85^\circ$, $28,8^\circ$, $38,9^\circ$, $42,6^\circ$ (Figure 3). Additional weak reflexes

in XRD may be caused by a presence of a small amount of chromium oxide which did not react with Al_2O_3 matrix while the samples were being synthesized.

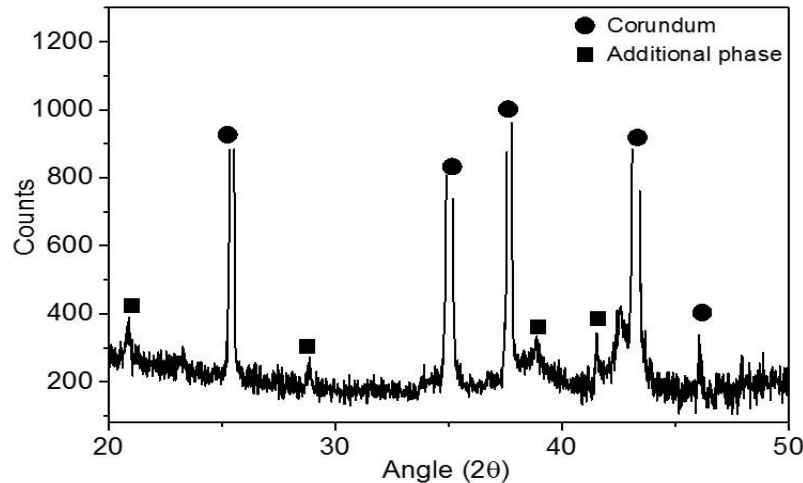


Figure 3. XRD pattern of the alumina ceramics doped with chromium oxide (0.02 wt.%).

To eliminate the effects of the tempering defects on the PL of the samples under study, thermovacuum annealing was carried out at $T = 1,773$ K for 180 min. The changes of PL spectra after annealing are shown in Figure 4. General decrease in PL yield and redistribution of the intensities of luminescence bands are observed both in the range of 1.7-1.9 eV and in the range of 2.2-3.4 eV. The maximum PL intensity is seen at the concentration of chromium oxide of 0.04-0.05 weight %. Deconvolution of the spectrum into gaussians in the range of 2.2 – 3.4 eV (Figure 5) allows singling out three components with the photon energies in the maximums 2.5 eV (Al_i^+ interstitial aluminium ions and F_2^- – centers), 2.8 eV (F_2^+ aggregate centers) and 3 eV (F-centers). It is also noteworthy that there is no band with the maximum 3.2 eV after annealing of the samples, which confirms the assumption on its association with the deformation defects.

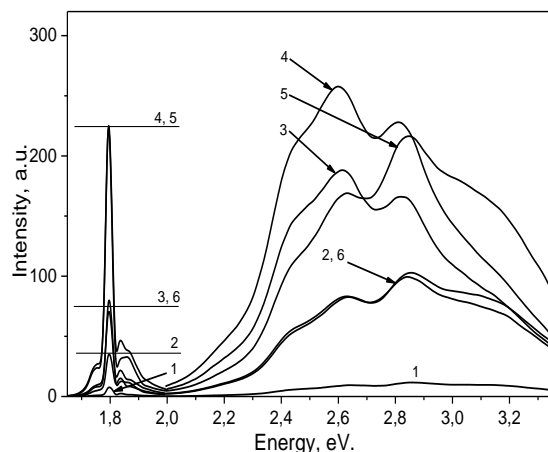


Figure 4. PL spectra of alumina ceramics ($E_{\text{ex}}=5.3\text{ eV}$, $T=300$ K) after annealing with different Cr_2O_3 concentrations (wt.%): 1 – 0.005; 2 – 0.01; 3 – 0.02; 4 – 0.04; 5 – 0.05; 6 – 0.1.

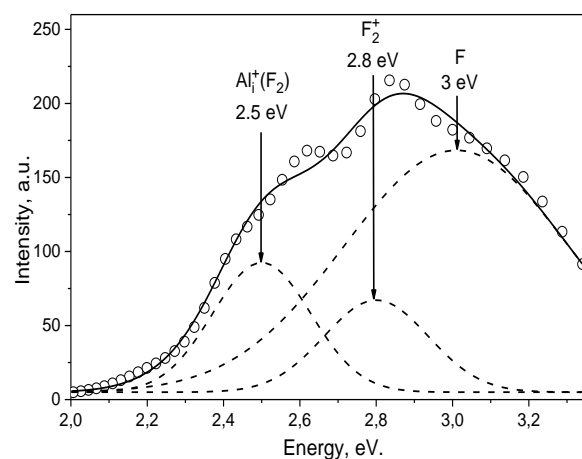


Figure 5. Gaussian decomposition of PL spectrum (curve 5, Figure 4)

A peak at 600 K is registered on the TL curve (Figure 6). It is known that impurity Cr^{3+} ions luminesce in alumina at this temperature. The intensity of TL at $T=600$ K correlates with spectroscopic PL measurements depending on the dopant concentration. In addition, on the TL curve one can single out a peak at 515 K associated with formation of F_2 centers, as well as a low-intensity peak at $T=430$ K which is caused by silicon impurity in the precursor nanopowder. The TL peak at 460 K is characteristic for oxygen-deficient alumina and is due to the presence of oxygen vacancies (F-centers) in the samples under study.

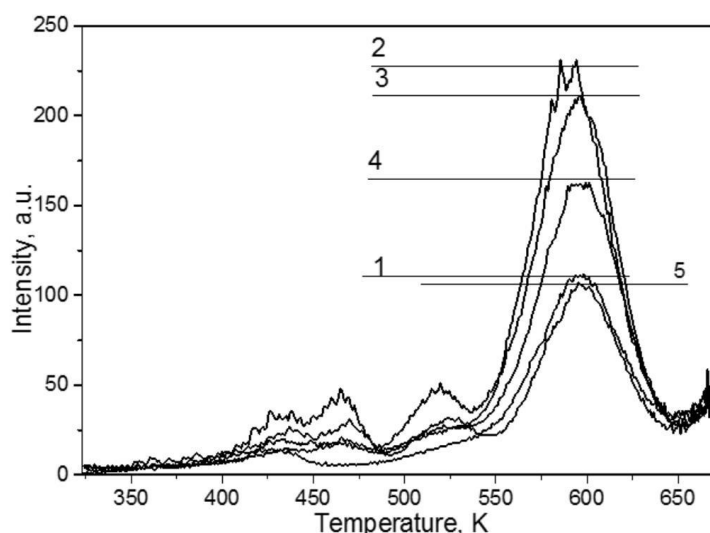


Figure 6. TL glow curves of alumina ceramics with different Cr_2O_3 concentrations (wt.%): 1 – 0.005; 2 – 0.02; 3 – 0.03; 4 – 0.05; 5 – 0.1.

4. Conclusions

Ceramics with photoluminescence in the wide region of visible light were synthesized from alumina nanopowder doped with chromium oxide. PL spectra and the curves of TL ceramics were measured; the main luminescence centers were identified. Concentration dependences of luminescence yield on Cr_2O_3 content were found. Functional materials for optoelectronic applications can be created on the basis of the obtained ceramics.

Acknowledgments

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References

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