Ultraviolet cathodoluminescence of pure zinc aluminates ZnAl$_2$O$_4$

S V Lisovskii$^1$, A V Meganov$^1$, V R Khrustov$^{1,2}$, V V Ivanov$^1$

$^1$Phystech School of Electronics, Photonics and Molecular Physics, Moscow Institute of Physics and Technology, Dolgoprudny 141701, Russia
$^2$Institute of Electrophysics, Ural Branch of the RAS, Ekaterinburg 620016, Russia

E-mail: lisovskii@phystech.edu

Abstract. The features of the intrinsic cathodoluminescence of pure zinc aluminates ZnAl$_2$O$_4$ having a radiation maximum in the range 250-270 nm are studied. The kinetics of the afterglow of a sample excited by short (~ 2 ns) pulses is analyzed. Analysis and possible explanation of the influence of the type and composition of the atmosphere, in which zinc aluminates were annealed, is given. Possibilities for a multiple increase in the cathodoluminescence intensity of zinc aluminates for use in bactericidal lamps are demonstrated.

1. Introduction

Zinc aluminates (ZnAl$_2$O$_4$) is well known for use as a matrix for a phosphor with an activator emitting in the visible range. However, it has recently been discovered that pure zinc aluminates also have a rather intense intrinsic cathodoluminescence (CL) in the ultraviolet region (250-270 nm) [1]. It is shown that the device based on this phosphor and cold cathode has bactericidal properties comparable to the UV mercury lamp [2]. Zinc aluminates are chemically stable, sufficiently resistant to overheating and charging, and can be used to create radiating devices with a long service life. To create competitive devices based on zinc aluminates, it is necessary to achieve high CL intensity of zinc aluminates and the position of the spectrum most effective for sterilization tasks.

According to the assumption of scientists who discovered the phenomenon of intrinsic CL of zinc aluminates, this phenomenon is associated with the appearance of oxygen vacancies in zinc aluminates crystals [1, 2]. This assumption is based on the enhancement of the luminescence of a phosphor synthesized in a reducing atmosphere, i.e. in conditions of oxygen deficiency. There is another method for obtaining oxygen vacancies in spinel [3]. At the same time a certain shift in the spectrum is observed, depending on the synthesis conditions, on the composition of the atmosphere and on the artificially created excess of zinc or aluminium. It is known that zinc aluminates contain three types of own defects on which the corresponding luminescence is possible: oxygen vacancies and zinc substitutions with aluminum or aluminum with zinc [4], also associated with the formation of oxygen vacancies.

Another group of researchers found the dependence of the intensity of useful cathodoluminescence on the purity of zinc aluminates as well as on the particle size of the phosphor powder [5]. In addition, there are reports of the enormous influence of the composition of the auxiliary substances used during the synthesis on the intensity of cathodoluminescence [6].
This work continues exploring the features of the cathodoluminescence of zinc aluminate: the influence of the quasistationary and pulsed excitation regime on the intensity of cathodoluminescence, the effect of the annealing atmosphere on the cathodoluminescence spectrum, the afterglow kinetics, and the phenomenon of sample burning.

2. Materials and Methods

Zinc aluminate powders were synthesized by solid-phase synthesis from chemically pure zinc oxide and aluminum oxide powders with a 2% excess of zinc oxide (air, 5 hours, 1200 °C). The XRD analysis confirmed that the sample was zinc aluminate. Then the samples were further annealed in a reducing atmosphere (H₂ and CO, 5 and 10 hours, 1200 °C). Samples were studied in a scanning electron microscope (SEM) Quanta 200MK2 (FEI). The CL spectra were collected with the help of a special Chroma CL mirror (Gatan) and HR4000CG-UV-NIR (Ocean Optics). The electron beam standing time at a single point varied from 50 ns to 30 μs to estimate the effect of the quasistationary excitation regime of zinc aluminate on the intensity of CL. The applied accelerating voltage of the electron beam varied from 10 to 30 kV. In addition, the samples were studied with a pulsed cathodoluminescent analyzer of materials (pulse duration ~ 2 ns, accelerating voltage 140-160 kV) [7], and the kinetics of the afterglow of the samples was studied with the help of a streak camera (Princeton Instruments).

3. Results

Although for all samples cathodoluminescence was observed in the ultraviolet range, the radiation spectrum of different samples was somewhat different (Figure 1). It can be seen that samples that have undergone additional annealing in CO show a shorter wavelength spectrum, while annealing in H₂, on the contrary, shifts the spectrum to the right. Also worth noting is the steepness of the left edge of the spectrum in CO and its some bimodality.

![Figure 1](image)

**Figure 1 (a, b).** Cathodoluminescence spectra of zinc aluminate samples synthesized in an air atmosphere and subjected to additional annealing for 5 and 10 hours (a) in CO; (b) in H₂.

From the point of view of the change in the spectrum, the result demonstrated by burning the sample (sample temperature reached 1000 °C or more) in a vacuum of the SEM under the intense electron beam current of 1 μA is also of interest. The sample displayed a gradually attenuating cathodoluminescence within a few minutes after burning out; the spectrum of cathodoluminescence was shifted to a large extent in the long-wave region (Figure 2). Visually, the place of burning was blackened.
Remaining measurements of cathodoluminescence in the SEM were carried out at lower electron beam currents (10–100 nA), which do not lead to a sample burning (sample temperature did not reach 300 °C). The averaged cathodoluminescence intensity as a function of the standing time at each point (from 50 ns to 30 μs) from a certain fixed scanning site yielded the result shown in Figure 3. It can be seen that the increase in the intensity of cathodoluminescence occurs inversely proportional to the standing time at the point (excitation time), i.e. the dependence is close to hyperbolic.

Figure 2 (a, b). (a) Spectra of cathodoluminescence of a sample of zinc aluminate before and after burning; (b) an image of burning in the SEM.

Figure 3. Integral intensity of cathodoluminescence from the sample area of zinc aluminate as a function of the time of electron beam standing at a point.
Measurements with the help of a streak camera and a pulsed cathodoluminescent analyzer of materials made it possible to evaluate the nature of the afterglow kinetics and compare the cathodoluminescence intensities for various samples. It was found that the sample with the highest intensity is prepared in an atmosphere of CO – 5 hours of additional annealing increased intensity by 1.5 times, 10 hours – by 3.5 times. At the same time, additional annealing in the H₂ atmosphere led to the opposite results – after 5 hours the intensity decreased by 8 times, after 10 hours by 7 times. As for the afterglow kinetics, the sample annealed in the air has the largest characteristic afterglow time – ~30 μs (the time after which the cathodoluminescence intensity falls by a factor of e). For CO samples, characteristic afterglow time was 13 to 21 μs, for H₂ it was 5-10 μs. After a short increase in the intensity of the luminescence, it begins to subside. At the time of decline, the character of the dependence of the intensity of the afterglow on time is close to hyperbolic (Fig. 4, for example); although in the early stages (less than 0.1 ms) the data may be fitted with the exponent as well.

![Figure 4. Intensity of afterglow of zinc aluminate as a function of time.](image)

4. Discussion

The hyperbolic character of the dependence of the afterglow intensity on time will indicate that the luminescence does not occur inside a single luminescence center and is not recombination but occurs between charge carriers localized on electron and/or hole traps and free charge carriers in the valence band/conduction band [7].

The time scale of the afterglow can also be estimated from the dependence of the integrated cathodoluminescence intensity on the sample area of the zinc aluminate on the time of the electron beam standing at the point. Dependence is hyperbolic because the number of afterglow excitations for...
individual points (pixels) depends on the scanning speed of the section. Respectively, the integral intensity of the afterglow from the site is inversely proportional to the time at the point. If we assume that the integral value of the current that excites the section does not depend on the standing time at the point, then the total intensity of the cathodoluminescence at the moment of excitation and after will be a hyperbola, shifted upward by a constant \( I = b / t + a \), where \( t \) is equal to the time at a point, \( a \) characterizes the intensity of cathodoluminescence at the instant excitation, and \( b \) characterizes the afterglow. The value \( b / a = \tau \) corresponds to the characteristic afterglow time. For Figure 3 \( \tau = 0.4 \mu s \), which is two orders of magnitude lower than the characteristic time measured with the help of a streak camera. Such discrepancies may be due to incomplete illumination of the afterglow of cathodoluminescence in the quasi-stationary excitation regime (pulse time greater than 50 ns) in comparison with the pulsed excitation regime (pulse time \( \sim 2 \) ns).

A different shift in the spectrum and a different change in the intensity of the cathodoluminescence for various reducing annealing atmospheres indicates that not only the reducing character of the atmosphere matters, but also its composition does. Taking into account the fact that the intensity grew and the spectrum shifted to the left during annealing in the CO atmosphere, we can assume an increased value of carbon proper in these phenomena. First, this is consistent with a decrease in intensity and a shift in the right-hand side of the cathodoluminescence spectrum after annealing in an \( \text{H}_2 \) atmosphere in which a part of the carbon obtained by annealing in air could be lost. Secondly, it conforms to a decrease in intensity and a shift to the right side when the sample is burned, which judging from the visual blackening is accompanied by the release of carbon. Thirdly, this is in agreement with the data of the researchers who found a 25-fold increase in the intensity of zinc aluminate in the case when the carbon containing \( \text{Li}_2\text{CO}_3 \) was used as a flux in the course of chemical synthesis [6].

The mechanism of carbon influence can be the following: a carbon atom due to high temperatures is able to dope zinc aluminate, penetrating some depth of the crystal lattice and localizing near oxygen vacancies as, for example, here [8, 9]. Then the luminescence shift is explained by the change in the energy level of the trap in the band structure due to the carbon localized nearby; the bimodal character of the spectrum can be associated with the presence of both types of oxygen vacancies – with and without a localized carbon series, and the ratio of these types of oxygen vacancies should vary with depth; an increase in the intensity of the cathodoluminescence may be due to the immobilization by the carbon of the oxygen vacancy and, as a consequence, the shift of the thermodynamic balance of the number of oxygen vacancies in the sample in the direction of increase (the carbon-immobilized oxygen vacancy becomes incapable of vanishing, but carbon does not affect the creation of new oxygen vacancies). The ability of carbon to immobilize the oxygen vacancy in some other oxides is discussed, for example, here [10].

5. Conclusions

Ultraviolet cathodoluminescence of zinc aluminate occurs from own defects, which are traps for free charge carriers. Probably, these are oxygen vacancies.

The use of a quasistationary cathodoluminescence excitation regime makes it possible to increase the intensity of cathodoluminescence by a factor of at least three, but this increase is several orders of magnitude lower than that which can be achieved in the pulsed excitation regime according to the kinetics of the afterglow of cathodoluminescence of zinc aluminate.

The annealing atmosphere affects the spectrum and intensity of cathodoluminescence, and the effect is not only on the reducing nature of the atmosphere, but also on its composition. Probably the cathodoluminescence of zinc aluminate is affected by carbon, which interacts with oxygen vacancies.
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