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## Abstract

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**PHYSICS**

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# ZINC-BORATE PHOSPHORS AND THEIR LUMINESCENT PROPERTIES

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The literature contains an indication that, depending on the ratio between zinc oxide and boric acid, the luminescence color of manganese-activated zinc-borate phosphors changes from yellow to green ($^1$). In the course of work with zinc-borate phosphors we observed that the change in the emission color of these phosphors depends, in addition, on other factors as well.

The system ZnO—$B_2O_3$ has been considered in several works ($^{2-4}$). We experimentally refined the existing data and established that in the system under consideration the compounds ZnO $\cdot B_2O_3$ and 3ZnO $\cdot B_2O_3$ can form. Their Debye diagrams are presented in Fig. 1. The compound ZnO $\cdot B_2O_3$ was prepared by calcining a mixture ZnO : $B_2O_3 = 1 : 1$ at 850° (a), and the compound 3ZnO $\cdot B_2O_3$ by calcining a mixture with an oxide ratio of 3 : 1 at 1000° (b). The duration of calcination was 15 min. The X-ray patterns were recorded by the Debye powder method in an RPK-57.4 camera using a BSV-4 electron tube (with a copper anticathode). The $K_\beta$ radiation was filtered out with a nickel filter. Boric anhydride, since it does not possess a crystalline structure, gives no diffraction pattern. Therefore, when interpreting the Debye diagrams, we compared them with the Debye diagram of zinc oxide only. In Debye diagram a, in addition to the well-defined lines characteristic of the compound ZnO $\cdot B_2O_3$, there are several lines of zinc oxide and of the compound 3ZnO $\cdot B_2O_3$; and in Debye diagram b, which mainly represents the compound 3ZnO $\cdot B_2O_3$, there are several lines of zinc oxide and of the compound ZnO $\cdot B_2O_3$. This is due to the incompleteness of the solid-phase reaction.

The most characteristic (reference) lines are the following: for ZnO $\cdot B_2O_3$: 2.98 (v.s.), 2.30 (m), 1.84 (m), 1.73 (s), 1.30 (m), 1.26 (m), 1.14 (m), 1.01 (m), 0.977 (m), 0.915 (m), 0.865 (m), 0.786 (m); for 3ZnO $\cdot B_2O_3$: 3.96 (m), 3.26 (s), 3.11 (s), 2.72 (m), 2.46 (m), 2.12 (m), 1.62 (m), 1.52 (m), 1.48 (m), 1.42 (m).

Our results on the formation of compounds with oxide ratios of 1 : 1 and 3 : 1 agree with the data of work ($^4$).

Fig. 2. Luminescence spectra of phosphors

Figure 1: Fig. 2. Luminescence spectra of phosphors

On the basis of these two compounds, phosphors were prepared. Figure 2 gives the spectra of the green emission of the phosphor $ZnO \cdot B_2O_3(Mn)$ (a) and of the orange emission of the phosphor $3ZnO \cdot B_2O_3(Mn)$ (b). The first phosphor was prepared by calcining a charge $ZnO : B_2O_3 = 1 : 1$ with 5 wt.% manganese sulfate at 850° for 15 min.; the second, by calcining a charge $ZnO : B_2O_3 = 3 : 1$ with 1 wt.% manganese sulfate at 1000° for 1 hour. The emission spectra were recorded on a photoelectric setup using an FEU-19. The phosphors were excited by light with a wavelength of 2537 Å, which was isolated from the total spectrum of a low-pressure mercury quartz lamp by means of a filter system: a UG-5 filter, transmitting the near-ultraviolet region, and a filter (bromine vapor), transmitting the 2537 Å line and blocking the remaining mercury lines.

In (5) the phosphor $3ZnO \cdot 2B_2O_3(Mn)$ is described. Since in the $ZnO$—$B_2O_3$ system only two compounds can form, with oxide ratios of 1 : 1 and 3 : 1, it was natural to assume that, at a ratio of zinc oxide to boric anhydride equal to 3 : 2, a mixture of these two phosphors is formed. We prepared phosphors with this component ratio and recorded the spectrum (Fig. 2, b). Our assumption was confirmed: the spectrum of the phosphor obtained consists of two bands, which are the emission bands of both phosphors with $ZnO : B_2O_3$ ratios equal to 3 : 1 and 1 : 1.

A characteristic feature of zinc-borate phosphors is their ability to store light sums. It seemed interesting to check the correctness of our conclusion about the existence of two individual phosphors by comparing them also according to this property. For this purpose we recorded

Fig. 2. Luminescence spectra of phosphors. *a* —$ZnO \cdot B_2O_3(Mn)$; *b* —$3ZnO \cdot B_2O_3(Mn)$; *v* —phosphor obtained by firing a batch with $ZnO : B_2O_3 = 3 : 2$, 1% manganese; *g, d, e, zh* —phosphors obtained by firing a batch with $ZnO : B_2O_3 = 1 : 1$ at 840° for 15 min, with different manganese contents: *g*—1% Mn; *d*—3% Mn; *e*—5% Mn; *zh*—7% Mn (manganese was introduced in the form of chloride)

thermal-bleaching curves of the phosphor $ZnO \cdot B_2O_3(Mn)$ (Fig. 3, a) and of the phosphor $3ZnO \cdot B_2O_3(Mn)$ (Fig. 3, b). The first phosphor was prepared by firing a batch with $ZnO : B_2O_3 = 1 : 1$ and 0.01% Mn, the second by firing a batch with a component ratio of 3 : 1 and 0.05% Mn. The apparatus made it possible to work over a wide temperature interval: from the temperature of liquid nitrogen to 500°K. In this temperature interval the heating rate varied: from the temperature of liquid nitrogen to 213°K the phosphor was heated (by air) at a rate of 18 deg/min; from 213°K to the end of bleaching the phosphor was heated (by a furnace) at a rate of 5 deg/min. Excitation was carried out at the temperature of liquid nitrogen with the light of a PRK-4 mercury lamp

Fig. 3. Curves of thermal emission of phosphors. a—ZnO • $B_2O_3$(Mn); b—3ZnO • $B_2O_3$(Mn)

Figure 2: Fig. 3. Curves of thermal emission of phosphors. a—ZnO • $B_2O_3$(Mn); b—3ZnO • $B_2O_3$(Mn)

without a light filter, in a thick layer, to saturation. The operating regime of the mercury lamp was kept constant. The brightness of the glow was measured with a photometer (with a Lummer cube and an Allentsev diaphragm). As can be seen from Fig. 3, both phosphors have several common trapping levels, but there are also different levels characteristic of each phosphor separately*. The system of shallow trapping levels (peak at 203°K) belongs to the phosphor $3ZnO \cdot B_2O_3$(Mn); the color of luminescence at 203°K is orange. The trapping levels lying above 300°K belong to the phosphor $ZnO \cdot B_2O_3$(Mn); the color of the phosphor glow above 300°K is green. The trapping levels corresponding to the peaks at 240 and 280°K are common; they manifest themselves in both phosphors; accordingly, the color of luminescence upon emission from these levels may be either green or orange.

Thus, the totality of the data from X-ray analysis of the phosphors described, from study of their luminescence spectra, and from measurement of the curves of their thermal emission clearly proves the existence of two individual phosphors: $ZnO \cdot B_2O_3$(Mn) and $3ZnO \cdot B_2O_3$(Mn). However, it remained unclear why, for one and the same composition of the initial charge, the color of the phosphor' s glow changes depending on the synthesis conditions. To clarify this, we studied in detail the solid-phase reactions occurring in a charge of zinc oxide and boric acid, using for this purpose methods of thermal and X-ray analysis. In parallel, observations were made of certain luminescent properties (glow color, thermoluminescence). Heating curves with differential recording were taken on an N. S. Kurnakov pyrometer.

**Fig. 3.** Curves of thermal emission of phosphors.
*a*—$ZnO \cdot B_2O_3$(Mn);
*b*—$3ZnO \cdot B_2O_3$(Mn)

Figure 4 shows one of the heating curves obtained by us, namely the heating curve for a mixture of composition $ZnO : B_2O_3 = 1 : 1$. On this curve, the low-temperature effect at 95—140° is due to the removal of water from boric acid; the remaining effects, with the exception of the last one (920—980°), reflect interaction of the components of the mixture. The beginning of the interaction of boric anhydride with zinc oxide (exothermic effect at 515—600°) is associated with softening of boric anhydride and its transition to the liquid phase (500—600°). This seems quite natural if the role of the liquid phase in the in-

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* The same characteristic difference in the thermal-bleaching curves we observed for both phosphors also at the same manganese concentration in them.

Fig. 4. Heating curve of a mixture of zinc oxide and boric acid
($ZnO \cdot B_2O_3 = 1 : 1$)

Figure 3: Fig. 4. Heating curve of a mixture of zinc oxide and boric acid ($ZnO \cdot B_2O_3 = 1 : 1$)

teraction of components during solid-phase reactions is taken into account (6). The effect at 920—980° is due to melting of the reaction product formed.

On the basis of comparison of thermograms, Debye diagrams, and the luminescent properties of the phosphors obtained, we arrived at the following conception of the mechanism of the reactions taking place. Independently of the composition of the initial charge, first of all (upon heating to 780° for 15-20 min.) a small amount of the compound $3ZnO \cdot B_2O_3$ is formed and, consequently, in the presence of an activator, the phosphor $3ZnO \cdot B_2O_3(Mn)$ (orange glow). With an increase in the calcination temperature, the compound $ZnO \cdot B_2O_3$ is formed in the charge, and on its basis the phosphor $ZnO \cdot B_2O_3(Mn)$ (green glow). However, if boric anhydride has reacted completely, while zinc oxide still remains in the mixture, then in this case, with further increase of the calcination temperature, the amount of $3ZnO \cdot B_2O_3(Mn)$ increases (orange glow). As a result of

as a result, with a gradual increase in the firing temperature, a change occurs in the color of the phosphor luminescence, caused by the fact that, as a result of solid-phase reactions, the ratio of the phosphors $3ZnO \cdot B_2O_3(Mn)$ and $ZnO \cdot B_2O_3(Mn)$ changes. These data are in agreement with the proposition that the priority of formation of one compound or another is determined not by the ratio of the components taken, but by the thermodynamic conditions (7).

Considerable assistance in understanding the causes that produce changes in the luminescent properties may be provided by state diagrams of the system of batch components from which the phosphor base is formed, since they make it possible to know precisely which phases can form in the system under consideration and what the conditions of their existence are. However, it should be remembered that conclusions following from the state diagram are valid only for the equilibrium state. Phases formed in solid-phase reactions in many cases do not reach a state of equilibrium, and therefore the regularities expressed by the state diagram are fulfilled only in part (8). With an increase in the firing temperature, as equilibrium is approached, the state diagram more and more fully reflects the processes occurring in the system being studied. This is especially clearly manifested in the case considered by us.

**Fig. 4.** Heating curve of a mixture of zinc oxide and boric acid
($ZnO \cdot B_2O_3 = 1 : 1$)

It is interesting to note that the ratio of both phosphors (3 : 1 and 1 : 1) is not the same at different concentrations of the activator manganese chloride (Fig. 2, *c, d, e, g*) and, moreover, changes depending on whether the activator is introduced into the initial batch or into a batch that has been preliminarily fired. Accordingly, the luminophors formed in the two cases also differ both in the color of luminescence and afterglow and in the light sums stored.

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*Note: Figure translations are in progress. See original paper for figures.*