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Abstract

Full Text

PHYSICAL CHEMISTRY

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TWO TYPES OF MANGANESE LUMINESCENCE CENTERS IN THE CADMIUM-LITHIUM ORTHOSILICATE PHASE

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In a brief communication by McKeag and Steward, among other phosphors, zinc-lithium and cadmium-lithium silicates activated by manganese were described (^{1}). Depending on the composition and preparation conditions, these phosphors exhibited green or red luminescence. We previously carried out a detailed investigation of zinc-lithium phosphors, which made it possible to clarify the reasons for the appearance of luminescence of one color or the other (^{5}); the present communication is devoted to cadmium-lithium phosphors.

On the basis of X-ray diffraction data, McKeag and Steward concluded that the green and red luminescence should be attributed to different crystalline phases, namely: the green—to cadmium-lithium orthosilicate activated by manganese, of composition $\mathrm{CdO} \cdot \mathrm{Li_2O} \cdot \mathrm{SiO_2} \cdot \mathrm{Mn}$, and the red—to cadmium-lithium metasilicate activated by manganese, of composition $\mathrm{CdO} \cdot \mathrm{Li_2O} \cdot 2\mathrm{SiO_2} \cdot \mathrm{Mn}$. We prepared a series of samples of cadmium-lithium orthosilicates activated by manganese with the general formula
$(6-x)\mathrm{CdO} \cdot x\mathrm{Li_2O} \cdot 3\mathrm{SiO_2} \cdot 0.015\mathrm{Mn}$; here x was taken equal to 0; 0.5; 1; 1.5; 2.0; 2.5; 3.0; 3.5; 4.0; 4.5; 6.0. The samples were prepared by two different methods: by sintering powders and by a method based on the use of orthosilicic ester and solutions of cadmium, lithium, and manganese nitrates. The starting materials were specially prepared cadmium and lithium carbonates of a high degree of purity, silicon dioxide of the grade "for phosphors," manganese nitrate of analytical reagent grade, and triply distilled orthosilicic ester. In preparing the charge for phosphors by the second method, the cadmium and lithium carbonates were dissolved in distilled nitric acid (the initial acid had chemically pure grade), and the manganese nitrate was introduced in the form of an aqueous solution.

The charge was subjected to high-temperature calcination, the temperature and duration of calcination being selected experimentally for each sample so that the luminescence brightness would be maximal. Depending on the composition, the temperature ranged from 800° to 1000°, and the calcination time from 2 to 3 hours. The use of different synthesis methods, as well as repeated syntheses by the same method, made it possible to assess the reproducibility of the luminescent properties of cadmium-lithium silicates with manganese; in doing so, we became convinced that phosphors of identical composition, but obtained by the indicated different methods or prepared repeatedly, did not differ in color or brightness of emission. Samples from the composition $5.5CdO \cdot 0.5Li_2O \cdot 3SiO_2 \cdot 0.015Mn$ to the composition $2CdO \cdot 4Li_2O \cdot 3SiO_2 \cdot 0.015Mn$ were capable of luminescing. Samples with still higher lithium oxide content had an intense coloration. Cadmium orthosilicate with manganese did not luminesce, although it had no coloration. The luminescence of cadmium-lithium orthosilicates with manganese is well excited by short ultraviolet and cathode rays.

Fig. 1. Photoluminescence spectra of cadmium-lithium orthosilicates activated with manganese, of different composition. Excitation by the mercury resonance line 254 mμ.
1—$5.5CdO \cdot 0.5Li_2O \cdot 3SiO_2 \cdot 0.015Mn$;
2—$5CdO \cdot 1Li_2O \cdot 3SiO_2 \cdot 0.015Mn$;
3—$4.5CdO \cdot 1.5Li_2O \cdot 3SiO_2 \cdot 0.015Mn$;
4—$4CdO \cdot 2Li_2O \cdot 3SiO_2 \cdot 0.015Mn$;
5—$3.5CdO \cdot 2.5Li_2O \cdot 3SiO_2 \cdot 0.015Mn$;
6—$3CdO \cdot 3Li_2O \cdot 3SiO_2 \cdot 0.015Mn$;
7—$2.5CdO \cdot 3.5Li_2O \cdot 3SiO_2 \cdot 0.015Mn$;
8—$2CdO \cdot 4Li_2O \cdot 3SiO_2 \cdot 0.015Mn$.

In Figs. 1 and 2 are presented the spectra, respectively, of photo- and cathodoluminescence of cadmium-lithium orthosilicates activated with manganese. Excitation was carried out either by the mercury resonance line 254 mμ, or by an electron beam with a voltage of 6 kV and a current density of $3 \cdot 10^{-7}$ A/cm^2. The spectra were measured using a UM-2 monochromator; the radiation detector was an FEU-32 photomultiplier.

As is seen from Figs. 1 and 2, the luminescence spectra consist of green or orange-red bands, or of their sum. The positions of the maxima of the green and red bands (514 and 615 mμ) do not depend on the method of excitation or on the composition of the luminophores. Depending on the ratio CdO/Li_2O in the orthosilicate, the ratio of the intensities of the green and red bands changes, and it does so differently under photo- and cathode excitation. The dependence of the intensities of these bands on composition has a complex character; therefore it is difficult to draw any conclusions solely on the basis of comparing the luminescence spectra shown in Figs. 1 and 2. To analyze the results obtained, we decomposed the luminescence spectra into their two constituent bands and, by measuring the areas under the corresponding spectral curves, determined the integral brightnesses of the green and red bands. Figure 3 presents the dependence of the integral brightness of both bands on the composition of the luminophores under photo- and cathode excitation. From these data it follows that, both under photo- and under cathode excitation, the maximum integral brightness of the green band, as well as of both bands together, is observed for samples whose composition is close to

$3CdO \cdot 3Li_2O \cdot 3SiO_2 \cdot 0.015Mn$.

For the green band, the maxima on the integral-brightness curves for both types of excitation coincide, but only under cathode excitation is green luminescence observed over a much broader range of sample compositions than under photoexcitation. In contrast

Fig. 2. Cathodoluminescence spectra of cadmium–lithium orthosilicates activated with manganese, of different composition. Excitation by an electron beam with a voltage of 6 kV at a current density of $3 \cdot 10^{-7}$ A/cm^2.
9—$1.5CdO \cdot 4.5Li_2O \cdot 3SiO_2 \cdot 0.015Mn$. The remaining curve designations are as in Fig. 1.

Therefore, the curves of the integral brightness of the red band differ fundamentally for different methods of excitation; namely, as part of the lithium in the phosphor $3CdO \cdot 3Li_2O \cdot 3SiO_2 \cdot 0.015Mn$ is replaced by cadmium, under photoexcitation the integral brightness of the red band increases sharply, and the curve passes through a maximum at the composition $3.5CdO \cdot 2.5Li_2O \cdot 3SiO_2 \cdot 0.015Mn$; whereas under cathode excitation the red band is almost completely absent in the luminescence spectrum of a sample of this composition.

The appearance in the luminescence spectra of cadmium–lithium orthosilicates with manganese of two bands would naturally be explained by the two-phase character of the phosphors, since in that case the change in the brightnesses of the bands would correspond to a change in the relative content of the phases in the system. To resolve this question, additional data were needed. We recorded X-ray diffraction patterns of several finished phosphors (Table 1).

The Debye photographs were taken in a camera of diameter 86 cm using a tube with a copper anticathode (the K_α line was isolated by means of a nickel filter). In the X-ray diffraction patterns presented one can distinguish three systems of lines: the systems of lines of cadmium and lithium orthosilicates (6:0 and 0:6) and, distinct from them, a system of lines appearing on the X-ray diffraction patterns of intermediate compositions. This system of lines undoubtedly belongs to the phase of the mixed cadmium–lithium orthosilicate. As cadmium is replaced by lithium in cadmium orthosilicate, the system of lines of cadmium orthosilicate is gradually replaced by the system of lines of cadmium–lithium orthosilicate. In the X-ray diffraction patterns of samples with compositions from $3.5CdO \cdot 2.5Li_2O \cdot 3SiO_2 \cdot 0.015Mn$ to $1.5CdO \cdot 4.5Li_2O \cdot 3SiO_2 \cdot 0.015Mn$, only the lines of this system are present, and the lines of the orthosilicates of cadmium and lithium are completely absent.

Fig. 3. Dependence of the integral brightness of the green and red bands in the spectra of photo- and cathodoluminescence on the molar ratio CdO/Li_2O in cadmium–lithium orthosilicate activated by manganese.
1 —green band, 2 —red band; *a* —cathode excitation, *b* —photoexcitation

It is evident from Fig. 3 that cadmium orthosilicate with manganese and lithium orthosilicate with manganese luminesce neither under photo- nor under cathode excitation; consequently, for sample compositions close to $3CdO \cdot 3Li_2O \cdot 3SiO_2 \cdot 0.015Mn$, both the green and the red luminescence should be attributed to one and the same phase of cadmium-lithium orthosilicate with manganese.

Against such a conclusion one may object that the phosphors of these compositions are two-phase and that in them one phase—responsible for the green luminescence—quantitatively predominates, under both photo- and cathode excitation, over the phase responsible for the red photoluminescence; in that case the lines of this second phase might not appear on the X-ray diffraction patterns because of the low sensitivity of the X-ray diffraction method as applied to systems of low symmetry. However, the ratio of the integral brightness of the red band to the integral brightness of the green band under photoexcitation, on going from the sample $3CdO \cdot 3Li_2O \cdot 3SiO_2 \cdot 0.015Mn$ to the sample $3.5CdO \cdot 2.5Li_2O \cdot 3SiO_2 \cdot 0.015Mn$, changes by more than a factor of 5; and if, in accordance with this, the concentration of the "red" phase increased by the same factor at the expense of the "green" one, this could not fail to be reflected in the X-ray diffraction patterns. In addition, it is known that the intensity of cathodoluminescence decreases sharply when non-luminescent mechanical admix-···

Table 1

Interplanar spacings of cadmium–lithium orthosilicates

CdO/Li_2O ratio	CdO/Li_2O ratio	CdO/Li_2O ratio	CdO/Li_2O ratio	CdO/Li_2O ratio	CdO/Li_2O ratio	CdO/Li_2O ratio	CdO/Li_2O ratio	CdO/Li_2O ratio	CdO/Li_2O ratio	CdO/Li_2O ratio	CdO/Li_2O ratio	CdO/Li_2O ratio	CdO/Li_2O ratio
6:0	5:1	3.5:2.5	3:3	2.5:3.5	1.5:4.5	0:6	6:0	5:1	3.5:2.5	3:3	2.5:3.5	1.5:4.5	0:6
–	–	–	–	–	–	5.26	–	–	–	–	–	–	1.52
–	–	–	–	–	–	3.96	1.44	1.44	–	–	–	–	–
–	3.62	3.62	3.62	3.62	3.62	–	–	–	1.37	1.37	1.37	1.37	–
–	–	3.18	3.18	3.18	3.18	–	1.32	1.32	1.32	1.32	1.33	1.32	–
–	–	–	–	–	–	3.15	–	–	–	–	–	–	1.31
2.73	2.73	–	–	–	–	–	–	–	1.20	1.19	1.19	1.19	–
–	–	–	–	–	–	2.62	–	–	1.10	1.10	1.10	1.10	1.10
2.58	2.58	–	–	–	–	–	–	–	–	–	–	–	1.07
2.27	2.28	–	–	–	–	–	–	–	1.03	1.03	1.03	1.03	–
–	–	2.13	2.14	2.14	2.14	–	–	–	–	–	–	–	0.93
–	–	1.95	1.95	1.95	1.95	–	0.85	0.85	–	–	–	–	–
–	–	–	–	–	–	1.83	–	–	0.82	0.82	0.82	0.82	–
1.73	1.73	–	–	–	–	–	0.81	0.81	–	–	–	–	–
1.66	1.66	–	–	–	–	–	–	–	–	–	–	–	0.79
–	–	1.55	1.55	1.55	1.55	–	–	–	–	–	–	–	–

case, in our case the appearance in the system of the "red"phase, i.e., a phase that does not luminesce under cathode excitation, should have been accompanied by a sharp decrease in the integral brightness of the cathodoluminescence of the "green" phase, which in fact is not observed.

Thus, comparison of the data obtained from the comparison of luminescence spectra with the data of X-ray phase analysis leads to the conclusion that, in the present case, both the green and the red luminescence are due to one and the same phase of cadmium—lithium orthosilicate activated by manganese. The molar ratio of cadmium oxide to lithium oxide in this phase can vary somewhat without disturbing phase homogeneity*.

At present the view is widespread that the color of the glow of manganese-activated oxygen-containing crystalline phosphors is determined by the environment of the manganese, namely: green luminescence arises when the manganese is surrounded by four oxygen atoms, and red luminescence by six oxygen atoms (2-4). Extending this point of view to cadmium—lithium orthosilicate activated by manganese, we believe that in this case also the green and orange-red bands in the luminescence spectra owe their origin to the two indicated types of luminescence centers. The change in the ratio of the intensities of the green and red bands, observed when the CdO/Li_2O ratio in the cadmium—lithium orthosilicate phase is changed, we attribute to the associated change in the probabilities of manganese being found in the environment of four or six oxygen atoms.

We previously encountered an analogous case of the formation by manganese of "green" and "red" luminescence centers in one phase in the study of a zinc —lithium silicate phosphor activated by manganese.

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* An exact determination of the limits of phase homogeneity of cadmium–lithium orthosilicate with manganese is beyond the scope of the present work.

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

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