Studies on the Oxy-acid Phosphors. III. Aluminate Phosphors (Part I)[*]

By Yoshihide KOTERA and Tadao SEKINE

(Received August 19, 1954)

Introduction

The aluminate phosphors were investigated for the first time by Lecoq de Boisbaudran who reported the emission of magnesium aluminate activated by manganese or chromium[1], and several other researchers[2-7] studied also about aluminate phosphors, but the full details of their preparations, charac-

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[*] Read before the Fourth Annual Meeting of the Chemical Society of Japan, 1951. Report II was published in this Bulletin, 27, 13 (1954).

1) Lecoq de Boisbaudran, *Compt. rend.* **105** 261 1887).

2) D. T. Wilber, *Phys. Rev.*, **20**, 101 (1922).

3) O. Deutchbein, *Ann. Physik*, **14**, 712, 729 (1932): *Z. Physik*, **77**, 489 (1938): *Physik. Z.*, **33**, 874 (1932).

4) E. Iwase, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **34**, 487 (1938).

5) H. W. Leverenz, *Proc. I. R. E.*, **32**, 256 (1944).

6) J. W. Strange and S. T. Henderson, *Proc. Phys. Soc.*, **58**, 369 (1946).

7) R. H. Clapp and R. J. Ginther, *J. Optical Soc. Am.*, **37**, 355 (1947).

teristics etc. are yet unknown. H. C. Froelich reported recently on the strontium aluminate which emits red light when excited by 3650 Å or cathode rays[8]. We have prepared various aluminate phosphors and found some remarkable results.

Experimental and its Results

(1) Purification of Sodium Aluminate and Metallic Salts.—In the preparation of aluminate phosphors, aluminum metal was used as one of the starting materials.

Aluminum metal, which is prepared by electrolysis and contains 99.81% Al, 0.10% Si, 0.07% Fe, 0.01% Ti and 0.01% Cu was dissolved in caustic soda solution and, after filtration, the filtrate was decomposed by pure carbon dioxide. Thus, the crystalline aluminum hydroxide was obtained, and its purity was established spectroscopically.

As for the other starting materials, respective metallic salts were used, which were purified by the process described in a previous paper[9].

(2) Mixing and Firing.—The purified aluminum hydroxide was mixed with the purified metallic salts, flux and activators.

When sodium fluoride was used for flux, its solution was purified by the addition of ammonium sulfide and, after filtration, the filtrate was added to the batch. After being mixed in the wet state, the product was dried and fired. Aluminum fluoride, which was used more frequently than sodium fluoride solution, was prepared from purified fluoride solution and aluminum salt solution, both being purified by the processes analogous to those described in a previous paper. It was precipitated by mixing the fluoride and aluminum salt solutions, washed, dried, and then mixed in the dry state in an agate mortar with the body materials and activators.

As for activators, commercial "chemical pure" grade of manganese sulfate, cerric oxide or lead oxide was used. When the activator was added in a considerably large amount, for example, in a case when lead was used as an activator, it was purified by processes similar to those described in a previous paper.

The batch was fired by the electric furnace. When the atmosphere had to be controlled, the tube furnace was employed, through the tube of which the gas purified by the method of Smith[10] was streamed.

TABLE II

THE OPTIMUM MIXING RATIO OF ALUMINATE PHOSPHORS

	$Al_2O_3 \cdot 3H_2O$: (MO or MC_2O_4 or $M(NO_3)_2$)	Flux(AlF_3's case) (mol.)
Mg aluminate	1 : 2 mol(MgO was used)	0.2
Ca aluminate	1 : 0.95 mol(CaC_2O_4)	0.3
Sr aluminate	1 : 0.9 mol(SrC_2O_4)	0.24
Ba aluminate	1 : 1.5 mol($Ba(NO_3)_2$)	0.048
Zn aluminate	1 : 2 mol(ZnO)	0.27
Cd aluminate	Wet process	0.27
Pb aluminate	1 : 1.2–1.3 mol($PbCO_3$)	0.25

(3) Properties.—The properties of some aluminate phosphors and their optimum mixing ratio were shown in Tables I and II respectively. The spectral curves measured by means of a quartz spectrograph, are shown in Fig. 1, no corrections

TABLE I

THE COLORS OF EMISSIONS OF ALUMINATE PHOSPHORS

Host lattice	Activators	3650 Å	2537 Å	X-rays	Cathode rays
Mg aluminate	none	orange f	none	none	none
,,	Mn (0.002)	orange m	orange f	green f	orange
,,	Pb (0.001)	yellowish green f	blue m	none	none
Ca aluminate	none	violet f	none	none	none
,,	Mn (0.0002)	orange m	orange f	yellow f	orange
,,	Pb (0.105)	none	blue m	none	none
,,	Ce (0.0008)	violet m	violet f	none	none
Sr aluminate	none	orange f	none	none	none
,,	Mn (0.002)	orange m	red f	green f	green
,,	Pb (0.1)	blue f	blue m	none	none
,,	Mn (0.001) Pb (0.02)	orange m	pink m	none	green
Ba aluminate	Pb (0.066)	none	blue	violet	violet
Zn aluminate	Mn (0.0015)	green f	green f	green m	green
Cd aluminate	Mn (0.0015)	orange f	orange f	orange f	orange
Pb aluminate	none	none	white blue m	white blue	white blue

The concentration of activator was expressed by mol ratio to the host lattice.
f = faint, m = medium.

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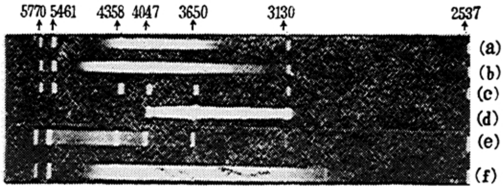
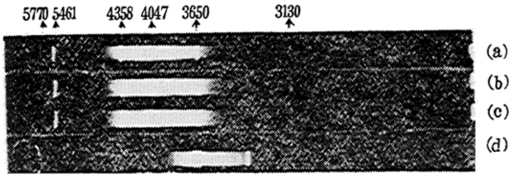
[8] H. C. Froelich, *U. S. Pat.* Spec., 2392814.

[9] Y. Kotera and T. Sekine, This Bulletin, 27, 13 (1954).

[10] A. L. Smith, *Trans. Electrochem. Soc.*, 93, 324 (1948).



(a) Ba aluminate Pb (2537Å)
(b) Ca aluminate Pb (2537Å)
(c) Mg aluminate Pb (2537Å)
(d) Sr aluminate Mn (3650Å)
(e) Pb aluminate (2537Å)
(f) Ca aluminate Pb (2537Å)



(a) Activated by Mn and Pb (Pb in large amount, 2537Å)
(b) Activated by Pb (2537Å)
(c) Activated by Mn and Pb (Pb in small amount, 2537Å)
(d) Activated by Mn and Pb (Pb in small amount, 3650Å)

Fig. 1.

being made on the spectral sensitivity of the photographic plate. The ranges of emission for aluminate phosphors activated by lead and lead aluminate were shown in Table III.

TABLE III

THE RANGES OF THE EMISSION FOR ALUMINATE PHOSPHORS ACTIVATED BY LEAD AND LEAD ALUMINATE (2537 Å EXCITATION)

Mg aluminate Pb	3700–4200 Å
Ca aluminate Pb	2900–4700 Å
Sr aluminate Pb	3200–4900 Å
Ba aluminate Pb	3300–4600 Å
Pb aluminate	4000–4700 Å

We have taken an interest in the preparation of doubly activated phosphors and continued the studies on the preparation of strontium aluminate phosphors.

(4) **The preparation of Strontium Aluminate Phosphors.**—According to Froelich strontium aluminate activated by manganese shows red luminescence when excited by long wavelength ultraviolet light, or cathode rays. We prepared it after his description and obtained a product which emits red light under the ultraviolet excitation, but all the products, emit green light when excited by cathode rays, although the conditions of preparation were varied as shown in Table IV.

TABLE IV

THE CONDITIONS OF PRERARATION OF STRONTIUM ALUMINATE PHOSPHORS

Molar ratio($Al_2O_3:SrO$)	1 : 0.8–2.0
Flux(AlF_3)	0–0.5 mol/1mol. $SrAl_2O_4$
Center(Mn)	0–6 mol.%/1mol. $SrAl_2O_4$
,, (Pb)	0–20 mol.%/1mol. $SrAl_2O_4$
Firing temperature	1100–1200°C
Firing time	2–6 hours
Atmosphere	H_2, N_2, O_2, Air and Steam

We tried to decide whether this phosphor emits light even by the excitation of short wavelength ultraviolet light or not. We thought that the sensitization of this phosphor by secondary activator—or "sensitizer"—makes it possible, and added lead salt to the batch before firing. In this way we got strontium aluminate phosphor, which is activated by manganese and lead, and emits luminescence shown in Fig. 2, when excited by ultraviolet light. Its preparation was done under the conditions described in Table V. Though the emission curve did not show the red band, owing possibly to the poor spectral sensitivity of the photographic plate in this region, this phosphor emits weak red light also by short wavelength ultraviolet light. It emits red light by long ultraviolet, but green light by cathode rays. The observations of its properties will be made later.

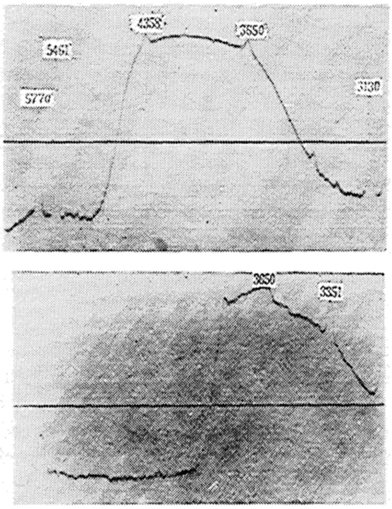


Fig. 2.

TABLE V

THE CONDITIONS OF PREPARATION OF STRONTIUM ALUMINATE PHOSPHOR ACTIVATED BY MANGANESE AND LEAD

Molar ratio($Al_2O_3:SrO$)	1 : 0.9
Flux(AlF_3)	0.24 mol./1 mol. $SrAl_2O_4$
Center(Mn)	0.1 mol.%/1 mol. $SrAl_2O_4$
,, (Pb)	2.0 mol.%/1 mol. $SrAl_2O_4$
Firing conditions	1200°C, 4 hours, in air

Discussion

Many reports were published on the aluminate phosphors, but all of these reports treated them as singly-activated ones. We tried to prepare the "doubly-activated" aluminate phosphors, and chose manganese as an emitting activator, because its emission is rather independent of the host crystal. At first, we prepared some aluminate phosphors, which were activated by manganese, lead and cerium, and confirmed that the manganese-activated phosphors show almost the same characteristics as those reported previously, except that strontium aluminate activated by manganese emits green light under cathode rays, although the conditions for its preparation were varied as shown in Table IV. As for the phosphors, which were activated by lead or cerium, we found that they have their characteristic emissions, which was not yet reported. Tables I and III show their characteristics. In Table II, it is interesting to note that the optimum mixing ratio is comparatively great in magnesium and zinc aluminates, the cause of which might be attributed to their spinel structure(1–3).

In the aluminate phosphors, which were prepared by us, strontium aluminate activated by both manganese and lead is the only one which might be considered as activated by double activators. It might be necessary to measure the absorption and excitation spectra in order to determine whether the red emission by 2537 Å is due to sensitization or not, and the facts that the lead-activated strontium aluminate emits blue light under shorter wavelength ultraviolet light and the manganese-activated one has no emission when excited by 2537 Å, but shows strong emission under 3650 Å, may be considered as a rather firm basis for the double activation. Calcium aluminate activated by manganese and lead or cerium was prepared by us, but in this case we could not obtain any doubly-activated phosphor.

Summary

Various aluminate phosphors were prepared and some of their emissions were measured. When activated by manganese, aluminate phosphors emit green, orange, or red light, while those activated by lead show blue or violet emission. Cerium acts as an activator only for calcium aluminate and emits violet light under ultraviolet excitation Strontium aluminate activated by manganese and lead shows a weak emission under short wavelength ultraviolet excitation. This may be caused by the double activation due to manganese and lead.

The authors wish to thank Mr. Shigeo Shionoya for the measurements of spectral distribution of emission, and Dr. Hiromi Nishida and Dr. Shoji Makishima for the general discussion on the subject and the experimental work they have done.

Government Chemical Industrial
Research Institute, Tokyo
Hatagaya, Tokyo