Studies on the Oxy-acid Phosphors. V. Stannate Phosphors (Part I)[*]

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Introduction

The stannate phosphors were investigated for the first time by E. Tiede and E. Villain, who reported magnesium stannate activated by manganese showing green emission under cathode rays excitation[1]. F. A. Kroeger[2] studied the alkali-earth and zinc stannates activated by titanium and calcium stannate activated by manganese, but the details of their preparation, characteristics, etc. are yet unknown. We have prepared various stannate phosphors and found some remarkable results.

Experimental and its Results

(1) Purification of Sodium Stannate and Metallic Salts.—In the preparation of stannate phosphors, a commercially available chemically pure grade of stannic chloride was used as one of the starting materials and purified as follows. The stannic chloride was dissolved in water and filtered. The sodium stannate solution was obtained by the reaction of the stannic chloride solution with solution of caustic soda in excess and by filtering off the resulting sediment. The precipitate, which was obtained by neutralization of this solution with conc. hydrochloric acid was filtered and dissolved again by addition of caustic soda solution. The filtrate was used as the purified sodium stannate solution.

The other starting materials were respective metallic salts, which were purified by the process described in a previous paper[3].

Each metallic salt solution was added to the sodium stannate solution, and respective metastannate salts were precipitated, their purity being established spectrographically.

(2) Mixing and Firing.—Each metastannate salt, respective metallic oxide or carbonate, flux

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[*] Read before the Sixth Annual Meeting of the Chemical Society of Japan 1953. Report IV was published in This Bulletin, 28, 132 (1955).

[1] E. Tiede and E. Villain, *Ber.*, 73, 274 (1940).

[2] F.A. Kroeger, "Some Aspects of the Luminescence of Solids", Elsevier Publishing Co. (1948), p. 158.

[3] Y. Kotera and T. Sekine, This Bulletin, 27, 13 (1948).

TABLE I

THE COLOURS OF EMISSIONS OF STANNATE PHOSPHORS

Host Lattice	Activator	3650Å		2537Å		Cathode Rays	
Mg_2SnO_4	Mn	none		green	ff	green	m
〃	Mn*1	none		none		blue	m
〃	Ti	none		bluish white	s	bluish white	s
〃	Ti*1	none		blue	s	blue	s
〃	Bi	blue	m	blue	ff	bluish violet	f
〃	Pb	none		green	ff	bluish violet	f
Ca_2SnO_4	Mn	none		none		orange	m
〃	Ti	none		blue	s	blue	s
〃	Bi	violet	m	violet	ff	bluish violet	m
〃	Pb	yellowish orange	m	none		yellow	m
〃	Ce	bluish white	f	red	ff	blue	m
Sr_2SnO_4	Ti	none		blue	m	blue	m
〃	Pb	none		orange	ff	orange	f
〃	Bi	none		none		yellowish orange	f
〃	Bi*2	none		none		red	f
Ba_2SnO_4	Ti	yellow	ff	yellowish orange	m	blue	m
〃	Pb	none		yellow	m	yellow	m
Zn_2SnO_4	Mn	yellowish white	f	none		yellowish white	f

s: strong, m: medium, f: faint, ff: very faint

*1. $Na_2B_4O_7 \cdot 10H_2O$ as a flux, other, NaF.

*2. $SrO : SnO_2 = 1 : 1$, others, see Table II.

TABLE II

THE OPTIMUM MIXING RATIO FOR THE PREPARATION OF STANNATE PHOSPHORS

Host Littice	SnO_2: MO or MCO_3	Flux	Activator
Mg_2SnO_4	1 : 2.2 (MgO)	NaF or $Na_2B_4O_7 \cdot 10\,H_2O$ 0.1 mol.	Mn 1 mol. %
Ca_2SnO_4	1 : 2–3* (CaO)		Ti 1–10 mol. %
Sr_2SnO_4	1 : 2 ($SrCO_3$)		Bi 1 mol. %
Ba_2SnO_4	1 : 2 ($BaCO_3$)		Pb 5 mol. %
Zn_2SnO_4	1 : 6 (ZnO)		Ce 1 mol. %

* There is a difference between the optimum ratio for ultraviolet excitation and that for cathode rays.

and activator were mixed in an agate mortar. Sodium fluoride, borax or some other salt was used as a flux. The solution of flux salt was purified by the addition of ammonium sulfide and, after filtration, the filtrate was added to the batch. As for activator, commercially available chemically pure manganese sulfate, ceric oxide, lead oxide, bismuth nitrate or titanium oxides were used. If necessary, they were purified by the process previously reported[3].

The batch was fired for two hours at 1100°C in air by an electric furnace.

(3) Properties.—The properties of some stannate phosphors and the optimum mixing ratios for their preparation were shown in Tables I and II respectively.

In the case of magnesium stannate activated by titanium, the change of flux caused the spectral shift of emission, as shown in Figs. 1 and 2 for 2537Å and cathode rays excitations respectively. In Fig. 1, the radiant energy curves were drawn in the same energy scale by arbitrary adjustment of the heights of the individual curves, to show relative spectral locations, while, in Fig. 2, the full lines were drawn relative to the value

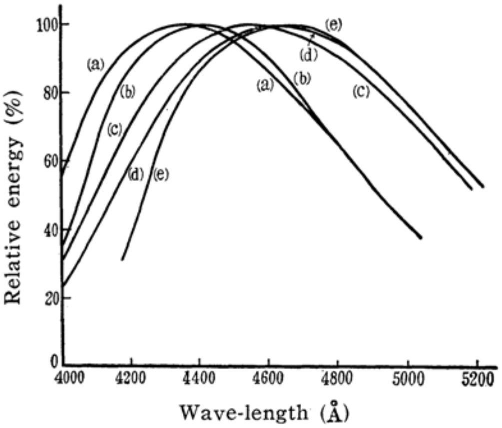

Fig. 1. The variation of emission spectra with different fluxes in Mg_2SnO_4: Ti (ultraviolet light).
(a) $Na_2B_4O_7$ (b) H_3BO_3 (c) $Na_2B_4O_7$ (Ti 1%) (d) NaF, MgF_2 or Al_2O_3 (e) KH_2PO_4 (Ti 10 mol.% (except (c)), 1100°C ×2 hrs, MgO : SnO_2 = 2.2)

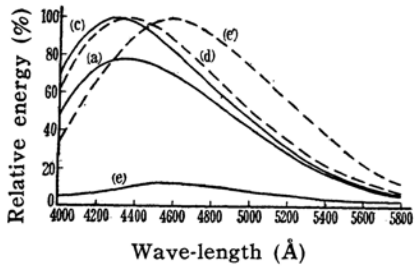

Fig. 2. The variation of emission spectra with different fluxes in Mg_2SnO_4: Ti (cathode rays)
(a) $Na_2B_4O_7$ (c) $Na_2B_4O_7$ (Ti 1%) (e) KH_2PO_4 (8 kV, 200 μA)

of 100 for the highest energy of sample (a) and the dotted lines were drawn in the manner analogous to Fig. 2. Both flux and activator amounted to 0.1 mol. per 1 mol. of the host crystal, and the other conditions were the same as the previous ones. Although lithium, sodium or potassium halides was used as a flux, the emission spectrum was found to be identical with that of sodium fluoride. Magnesium stannate showed itself to be a weak bluish emission when borax was employed as a flux, but it was difficult to determine the emission spectrum.

The emission spectra and the brightness of calcium stannate activated by titanium under cathode rays excitation were shown in Fig. 3 and Table III. In these measurements, the ratio of CaO to SnO_2 was varied from 1: 1 to 6: 1, and the generation of cathode rays was made at 5 kV., 50 μamp., the current density being $5 \cdot 10^{-5}$amp./cm^2. Taking a zinc silicate activated by manganese as the standard sample for the measurements of brightness, commercial calcium magnesium silicate activated by titanium had the value of 35.0. The same measurements were carried out on calcium stannate activated by cerium, in which case the amount of cerium was varied from 0.001 to 0.05 mol. per mol. of the host crystal. The results were shown in Fig. 4 and Table IV, the fourth column of the latter expressing the relative value of radiant energy at the wavelength 4350Å.

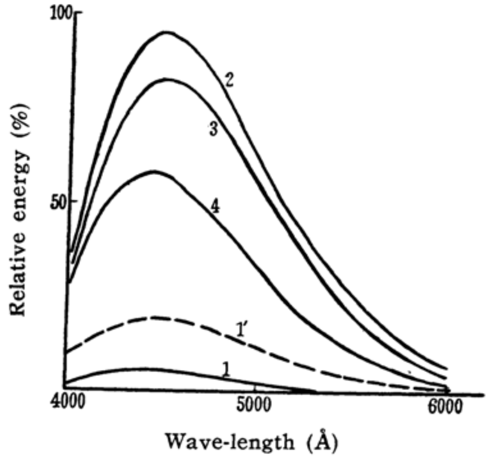

Fig. 3. The variation of emission spectra with CaO : SnO_2 in Ca_2SnO_4: Ti (5 kV, 50 μA, current density, $5 \cdot 10^{-5}$A/cm^2, 1′ : measured with higher sensitivity for sample 1. See Table III).

TABLE III

THE BRIGHTNESS OF Ca_2SnO_4: Ti

No. of samples	CaO : SnO_2	Brightness
1	1 : 1	4.8
2	2 : 1	24.1
3	3 : 1	16.7
4	6 : 1	14.7

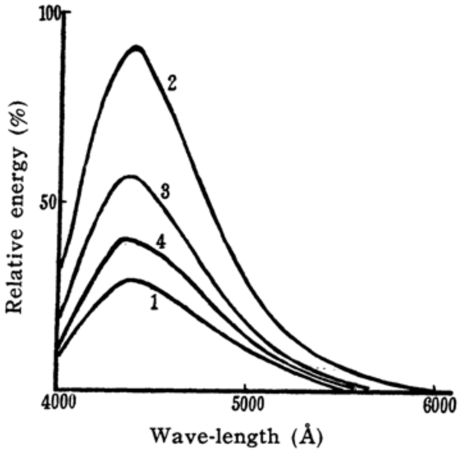

Fig. 4. The variation of emission spectra with Ce concentration in Ca_2SnO_4: Ce (5kV, 50 μA, current density 10^{-5}A/cm^2. See Table IV)

TABLE IV

THE BRIGHTNESS AND RADIANT ENERGY AT 4350Å OF Ca_2SnO_4: Ce

No of Samples	Ce Concentration mol./1 mol. Ca_2SnO_4	Brightness	Relative energy
1	0.001	4.4	30
2	0.01	8.8	90
3	0.02	7.7	58.5
4	0.05	4.4	39

See Fig. 4.

These measurements were carried out by means of an automatic recording spectroradiometer[4].

Discussion

The stannate phosphors activated by titanium were investigated by F. A. Kroeger[2]. He studied the function of titanium as an activator in the matrix of silicate, stannate or zirconate, and discussed the properties of stannate phosphors activated by titanium in detail. He found that titanium acts in the above-mentioned matrixes as an activator

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[4] Y. Kotera, *Rept. Gov. Chem. Ind. Research Institute, Tokyo*, 50, 398 (1955).

only when the preparation was made under oxidizing condition and it does not act as an activator in compounds of aluminium, phosphorus, or boron. From these facts he concluded that the luminescence effect correlated with titanium is attributed to tetravalent Ti^{4+} ions and the activator is built in isomorphously. Further he found that the amounts of titanium are considerably higher than is usual for activation; there is a certain relation between the spectral distributions of absorption and emission due to titanium and orthostannates and metastannates of Ca, Sr, and Ba present examples of the systematic change of the temperature quenching.

We found that some stannates, particularly orthostannates, show considerably strong emission when activated by several heavy metals including titanium. As may be seen in Table I, manganese acts as an activator in the matrix of zinc stannate, in addition to magnesium and calcium stannates[1,2] and the emission is also ascertained when activated by cerium, bismuth and lead. The optimum mixing ratio in Table II corresponds roughly to the highest value of brightness. It is remarkable that zinc stannate shows the strongest emission when prepared by employing zinc oxide in much excess, such result not being obtained in other matrixes. Probably this matrix is not composed of the compound which contains zinc oxide in much excess, but the formation of the matrix would proceed rather slowly and incompletely. Further it is noteworthy that the various emissions are observed for the preparations of magnesium stannate activated by titanium or manganese with different fluxes. In the case of magnesium stannates activated by titanium the emission changes are confirmed from the results shown in Fig. 1. These might be explained by an assumption that there are two kinds of centers, one is that of tin and the other that of titanium, each emission being intensified by different fluxes. It is expected that a longer wave-length emission might be caused by tin and a shorter one by titanium from the comparison of emission spectra of (a) and (c), but it is difficult to draw an accurate conclusion. Hoffmann[5] found that SnO_2 or glass containing SnO_2 luminesceses under excitation of ultraviolet light, but the colors of their emissions are mostly brown, and probably tin does not always act as an activator; it seems to be difficult to compare his results with ours. In the case of manganese activation, the blue emission is found under excitation of cathode rays when borax is used as a flux, and this result supports the above explanation. Kroeger[2] found that two different emissions occur, depending on the wave-length of the exciting radiation, and this fact might be explained by assuming the existence of two kinds of luminescence centers. The emission spectra under excitation of cathode rays for magnesium stannates with different fluxes look somewhat varied (Fig. 2), and such a phenomenon has not yet been observed.

From the practical viewpoint, it is important that calcium stannate activated by titanium with flux of borax shows the emission, the intensity of which is about 75% of that of $CaWO_4$. Furthermore, calcium stannate activated by titanium or cerium shows emission as indicated in Figs. 3, 4, Tables III and IV, and might be used as a blue component of color television.

Summary

Various stannate phosphors were prepared and some of their emissions were determined. Stannate phosphors emit green, blue or yellowish white light when activated by manganese, blue, violet or red by bismuth, orange, green or blue by lead, while those activated by cerium show blue or red emission. It is expected that the activation by tin also occurs in some cases. This is supported by the fact that the emission of magnesium stannate activated by titanium changes by the variation of flux. For different specimens of calcium stannate activated by titanium or cerium, emission spectra under excitation of cathode rays were measured.

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[5] J. Hoffman, *Sprechsaal*, 65, I, 82 (1932).