Activations by Anions in the Oxy-acid Phosphors. IV.
Activations by Sulfide and Sulfo-oxide Ions

By Yoshihide KOTERA and Tadao SEKINE

(Received August 10, 1961)

It was found in previous papers[1] that activation by sulfide occurs in alkali earth sulfate phosphors. Meanwhile, Gobrecht et al.[2] reported activation by polysulfide in alkali earth sulfides and alkali sulfides, and Kirk[3] reported the effect of sulfur in natural sodalite. We have prepared alkali earth sulfate activated by a sulfide ion or a sulfo-oxide ion and have obtained some remarkable results.

The Experiments and their Results

Preparation of Phosphors.—The alkali earth sulfides were prepared by the reaction between purified alkali earth sulfate and a reducing agent, for example, cane sugar, while the alkali earth sulfites were precipitated by the addition of a purified sulfite solution to a purified alkali earth salt solution. The optimum conditions for preparing the phosphors are shown in Table I; it was necessary to maintain the firing atmosphere in a neutral condition because oxidizing or reducing atmosphere causes a variation in the characteristics of the products.

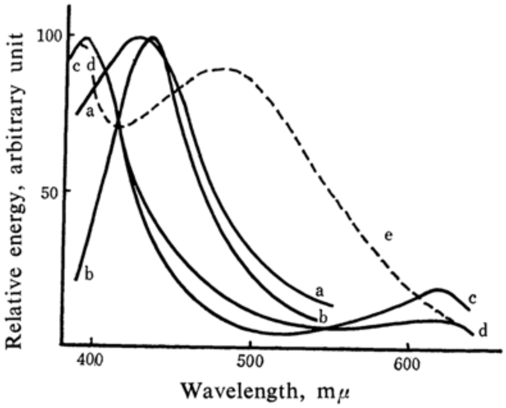

Fig. 1. Spectral distributions of alkali earth sulfate activated by sulfide and sulfite.

a: 0.01 g. $CaS/CaSO_4$ 1 g.
b: 0.1 g. $CaS/CaSO_4$ 1 g.
c: 0.035 g. $BaS/BaSO_4$ 1 g.
d: c+NaCl flux
e: 0.01 g. $SrSO_3/SrSO_4$ 1 g.

Spectral Distribution of the Emissions of the Phosphors.—The spectral distributions are shown in Fig. 1. It was difficult to obtain accurate distributions for calcium and barium sulfate activated by sulfite ion because of their weak emission, while that of strontium sulfate activated by sulfite is somewhat inaccurate. However, it was ascertained that activation by a sulfite ion gave a different product than that by a sulfide ion.

It is remarkable that the weak afterglow was detectable in the case of calcium sulfate activated by a sulfide ion.

---

[1] Y. Kotera, M. Yonemura and T. Sekine, This Bulletin, **35**, 577 (1962).

[2] H. Gobrecht and D. Hahn, *Z. Physik*, **132**, 111 (1952); **135**, 523 (1953).

[3] R. D. Kirk, *J. Electrochem. Soc.*, **101**, 461 (1954).

TABLE I. OPTIMUM CONDITIONS FOR PREPARATION OF SULFATE COMPOUNDS ACTIVATED BY SULFIDE AND SULFITE IONS

	Mixing ratio, mol.				Flux	Firing conditions
$CaSO_4$: S	$CaSO_4$	1	CaS	0.01	Na salt	1100°C, 4 hr. in N_2
$SrSO_4$: S	$SrSO_4$	1	SrS	0.01	—	
$BaSO_4$: S	$BaSO_4$	1	BaS	0.035	NaCl 10 mol. %	
$CaSO_4$: SO_3	$CaSO_4$	1	$CaSO_3$	0.01	—	
$SrSO_4$: SO_3	$SrSO_4$	1	$SrSO_3$	0.01	—	
$BaSO_4$: SO_3	$BaSO_4$	1	$BaSO_3$	0.1	NaF 10 mol. %	

Discussion

The spectral distribution of the emission of calcium, strontium or barium sulfate activated by a sulfide ion may differ from that of polysulfide, which was reported by Gobrecht et al.[2], but it is impossible to compare our results with theirs because they concluded that preparation by the reduction of sulfate salts is unsuitable for the preparation of their phosphors. Barium sulfate activated by a sulfide ion has an emission like that of barium polysulfide, but it is probable that barium sulfate is produced during the firing of barium polysulfide. Such comparisons are related to the fact the control of the atmosphere is important during the firing of sulfate salt phosphors. In our experiments it was possible to separate the activations by the sulfide ion and by the sulfite ion by precise control of the atmosphere.

Interesting facts were found in the phosphors activated by the sulfide ion; the flux has some effect on the intensity of the prepared phosphor, and the decay of some samples is relatively long. These facts show that the oxy-acid phosphors activated by the sulfide ion may be the intermediates between sulfide and oxy-acid phosphors. The fact that barium sulfate or calcium sulfate activated by sulfide ion emits, under the excitation of 3650 Å, a light of almost the same characteristics as when under 2537 Å, supports this idea. The excitation spectrum may be considerably longer than those of the oxy-acid phosphors, but it has not yet been measured precisely. It would be interesting to study the other matrices activated by the sulfide ion in relation to the studies by Gobrecht et al.[2], by Kirk[3] and by Thomson[4].

Government Chemical Industrial
Research Institute, Tokyo
Shibuya-ku, Tokyo

---

[4] S. M. Thomson, *J. Chem. Phys.*, **18**, 770 (1950).