SHORT COMMUNICATIONS

Dependence of the Characteristics of Calcium Halophosphate Phosphors on the Condition for Preparing Secondary Calcium Hydrogen Orthophosphate

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The development of calcium halophosphate phosphors has been described by Jenkins, McKeag and Ranby[1] and Nagy, Wollentin and Lui[2]. Two main stages are involved in the preparation of calcium halophosphates: the first is the preparation of calcium phosphate of suitable purity and physical condition, the second being a thermal treatment in which the mixture of raw materials is fired in a suitable atmosphere at a temperature of 1050~1200°C. Doherty and Harrison[3] gave a detailed description of dry and wet syntheses, while Wanmaker, Hoekstra and Tak[4] and Wanmaker and Verheyke[5] investigated the second stage (thermal treatment) of the preparation. We have investigated the first stage and found the dependence of the characteristics of calcium halophosphates on the conditions for preparing secondary calcium hydrogen phosphate.

Three samples of calcium phosphate were prepared as follows:

Sample $\mathrm{I_a}$……Pure phosphoric acid, which was prepared by the reaction of the purified diammonium hydrogen orthophosphate with distilled nitric acid, was reacted with purified calcium carbonate at pH 3.6 and about 30°C.

Sample $\mathrm{I_b}$……The same as $\mathrm{I_a}$ except that the reaction between phosphoric acid and calcium carbonate proceeded under water cooling (about 10°C).

Sample II……Purified diammonium hydrogen orthophosphate solution was added to purified calcium nitrate solution at pH 3.6 and boiling temperature.

All raw materials were purified by the process described in a previous paper[6] and their purity was established spectrographically. The results of chemical analyses fos these samples are shown in Table I, where values in the forth column were calculated from those in the second one, while those in the fifth column were calculated from those in the second and fourth ones. Employing them as one of the starting materials for the preparation of calcium halophosphate, phosphors were prepared as follows:

$\mathrm{CaHPO_4}$ 27.0 $\mathrm{CaCO_3}$ 8.8(I) or 8.6(II) $\mathrm{CaCl_2 \cdot 2H_2O}$ 1.8 $\mathrm{CaF_2}$ 1.7 Mn phosphate 1.0 $\mathrm{Sb_2O_3}$ 1.1 (g.).

They are mixed by ball mill and fired at 1175°C for one hour (40 g. for one batch). The brightness of fired samples before and after grinding is shown in Table II, where the value of 100 is given for American commercial phosphor (Westinghouse 4500°K white). Their emission spectra illustrated in Figure 1 were obtained by means of spectroradiometer[7]. The residual amounts of activators after firing were determined polarographically[8] and the results are given in Table III.

Jenkins, McKeag and Ranby[2] found that the precipitate obtained from aqueous solutions of calcium chloride and diammonium hydrogen phosphate consists of

TABLE I

ANALYSIS OF SECONDARY CALCIUM HYDROGEN ORTHOPHOSPHATE

Sample No.	CaO	$\mathrm{H_2O}$	$\mathrm{P_2O_5}$ (calcd.)	$\mathrm{CaO/P_2O_5}$ (calcd.)	Density of Bulk
$\mathrm{I_a}$	40.30	7.78	51.92	0.776	0.71
$\mathrm{I_b}$	40.32	7.73	51.95	0.776	0.65
II	40.63	7.55	51.82	0.784	0.44
Theor.	41.21	6.62	52.17	0.790	

TABLE II

THE BRIGHTNESS OF CALCIUM HALOPHOSPHATE PHOSPHORS

Sample No.	Before Grinding	After Grinding
$\mathrm{I_a}$	90	88
$\mathrm{I_b}$	96	91
II	91	91

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[1] H. G. Jenkins, A. H. McKeag and P. W. Ranby, *Trans. Electrochem. Soc.*, **96**, 1 (1949) ; A. H. McKeag and P. W. Ranby, Brit. Pat., 578,192 (1942).

[2] R. Nagy, R. W. Wollentin and C. K. Lui, *Trans. Electrochem. Soc.*, **95**, 187 (1949).

[3] M. Doherty and W. Harrison, *British J. Applied Phys.*, Supplement No. 4, p. 11 (1955).

[4] W. L. Wanmaker, A. H. Hoekstra and M. G. A. Tak, *Philips Res. Repts.*, **10**, 11 (1955).

[5] W. L. Wanmaker and M. L. Verheyke, *Philips Res. Repts.*, **11**, 1 (1956).

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

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

[8] Y. Kotera, M. Yonemura and T. Sekine, This Bulletin, **28**, 132 (1955).

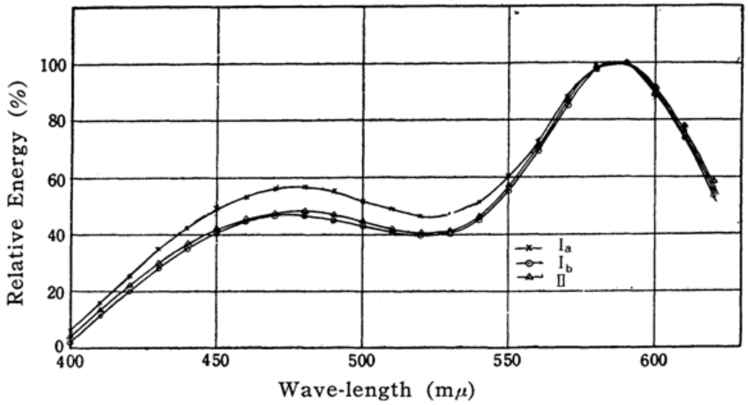

Fig. 1

TABLE III

ANALYSIS OF RESIDUAL AMOUNT OF ANTIMONY AND MANGANESE IN CALCIUM HALOPHOSPHATE PHOSPHORS

Sample No.	Antimony (g./g.)	Manganese (g./g.)
I_a	0.0056	0.0086
I_b	0.0057	0.0081
I_b (before grinding)	0.0059	0.0078
II	0.0049	0.0086
Westinghouse 4500°K white	0.0070	0.0069
Westinghouse 3500°K white	0.0040	0.0095

$CaHPO_4 \cdot 2H_2O$ when precipitated cold and $CaHPO_4$ when precipitated from boiling solutions. We found that, although calcium phosphate was prepared by almost the same processes, the ratio CaO : P_2O_5 changes according to small differences of the preparing conditions and chemical analysis is necessary for the determination of the mixing ratio for resulting phosphor (Table I). The characteristics of phosphors with the same mixing ratio (I_a and I_b) are however affected by the conditions for preparing calcium phosphate. In particular, the initial brightness and its decrease during grinding shown in Table II depend on these conditions, indicating that the imperfections of the phosphor crystal, which might be related to the brightness and its decrease, would be affected by the physicochemical properties of raw materials. This idea is supported from the analytical result for the residual activator amount as given in Table III. Whether the migration of antimony and manganese in the apatite lattice and the formation of active centers are easy or not, might depend upon the properties of integrants. The spectral energy distribution curves illustrated in Fig. 1 show a little difference between phosphor samples and this fact might be explained by the idea described above.

A detailed account of this work will be published elsewhere.

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