## *Studies on the Oxy-acid Phosphors. VI. Antimonate Phosphors**

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Few reports have ever been published on the antimonate phosphors. K. H. Butler et al. reported the formation of calcium pyro-antimonate during the preparation of calcium halophosphate phosphor, but he did not find any emission for this material[1]. R. Bernard and J. Janin observed recently the luminescence of calcium metaantimonate activated by manganese[2], and M. Tomono et al. reported the green luminescence of calcium metaantimonate activated by manganese[3], but the full details of their preparation, characteristics etc. remain still unknown.

In the preparation of antimonate phosphors, a commercially available pure grade of antimony chloride was used as one of the starting materials and purified by the process described in a previous paper[4]. As for the other starting materials, respective metallic salts were used, which were purified by the process described in another previous paper[5]. Their purity was established spectrographically. Purified antimony oxide and metallic oxide

TABLE I

THE OPTIMUM MIXING RATIO FOR THE PREPARATION OF ANTIMONATE PHOSPHORS

| | $Sb_2O_3$: (MO or $M(NO_3)_2$) | Firing Coditions |
|---|---|---|
| Ca antimonate | 1 : 2.4 mol. | 1100°C 2 hr. |
| Sr antimonate | 1 : 2.2 mol. | 1100°C 2 hr. |
| Ba antimonate | 1 : 2.2 mol. | 1100°C 2 hr. |
| Mg antimonate | 1 : 4.8 mol. | 1150°C 1 hr. |
| Zn antimonate | 1 : 2.2 mol. | 1100°C 1 hr. |

or carbonate were mixed in an agate mortar in the molar ratio as shown in Table I and, if necessary, an appropriate salt was also added as an activator; then the mixture was fired for one to two hours at 1100°C in air.

5 weight % of $NH_4NO_3$ was added to the batch so as to increase the brightness[6].

The properties of antimonate phosphors are shown in Table II. The $Ca_2Sb_2O_7$ : Bi

TABLE II

THE EMISSIONS COLOURS OF ANTIMONATE PHOSPHORS

| | 3650 Å | | 2537 Å | | Cathode rays | |
|---|---|---|---|---|---|---|
| $Ca_2Sb_2O_7$ | pink | f | pink | f | orange | f |
| $Sr_2Sb_2O_7$ | none | | bluish white | ff | none | |
| $Ba_2Sb_2O_7$ | none | | white | ff | none | |
| $Mg_2Sb_2O_7$ | none | | none | | orange | ff |
| $Zn_2Sb_2O_7$ | yellow | ff | none | | yellow | ff |
| $Ca_2Sb_2O_7$ : Bi | blue | m | blue | m | blue | m |
| $Sr_2Sb_2O_7$ : Bi | green | f | green | f | green | f |
| $Mg_2Sb_2O_7$ : Bi | green | f | green | f | none | |
| $Zn_2Sb_2O_7$ : Bi | green | f | none | | yellow | f |

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

phosphor gives the highest brightness among them, the spectral distribution of its emission under cathode-rays excitation being shown in Fig. 1. Data showing the X-ray diffraction pattern for $Ca_2Sb_2O_7$ are presented on Table III together with the results by K. H. Butler et al.[1].

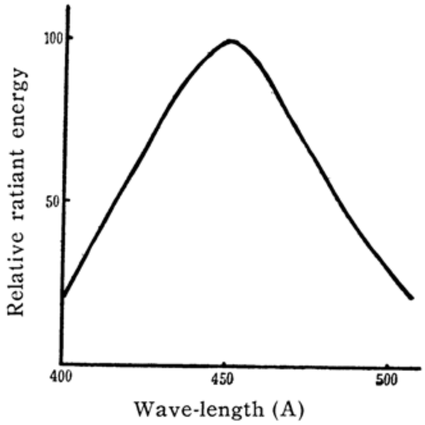


Fig. 1. Emission of $Ca_2Sb_2O_7$ : Bi with cathode-rays excitation.

The formation of $Ca_2Sb_2O_7$ during the preparation of calcium halophosphate phosphors was verified by K. H. Butler et al. 's X-ray diffraction analysis. We found that various antimonates without any intentional activator are able to luminesce and give blue, green or yellow luminescence when bismuth is employed as an activator. The emission of samples without activators might be due to the activation by antimony itself, although such a possibility is not definitely ascertained. From the mixing molar ratio shown in Table I and the X-ray diffraction patterns in Table III, it is concluded that these phosphors are composed of pyroantimonate. The emissions of haloantimonates are expected from the

TABLE III

X-RAY DIFFRACTION PATTERN OF $Ca_2Sb_2O_7$ PHOSPHOR

| Phosphor | | $Ca_2Sb_2O_7$* | | Phosphor | | $Ca_2Sb_2O_7$* | | Phosphor | | Phosphor | | Phosphor | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| d | I | d | I | d | I | d | I | d | I | d | I | d | I |
| | | 10.05 | 0.4 | 2.58 | s | 2.607 | 0.6 | 1.72 | w | 1.435 | w | 1.141 | m |
| 6.05 | m | 5.97 | 0.7 | | | 2.551 | 0.4 | 1.70 | w | 1.400 | w | 1.127 | vw |
| 5.13 | m | 5.19 | 0.6 | 2.37 | vw | 2.351 | 0.1 | 1.66 | vw | 1.364 | w | 1.092 | vw |
| 4.51 | w | | | 2.31 | m | 2.290 | 0.1 | 1.64 | vw | 1.344 | vw | 1.085 | vw |
| 3.99 | w | | | | | 2.132 | 0.1 | 1.61 | vw | 1.299 | m | 1.066 | m |
| 3.62 | m | 3.633 | 0.5 | 2.09 | vw | 2.106 | 0.2 | 1.57 | s | 1.266 | w | 1.049 | m |
| 3.29 | s | | | 2.00 | s | 2.009 | 0.4 | 1.55 | s | 1.225 | vw | 1.041 | w |
| 3.03 | w | 3.105 | 0.4 | 1.85 | w | 1.867 | 0.4 | 1.53 | m | 1.204 | vw | 1.029 | w |
| 2.97 | s | 3.009 | 0.9 | 1.81 | vs | 1.824 | 1.0 | 1.499 | m | 1.175 | vs | 1.015 | w |
| 2.93 | s | 2.960 | 0.9 | 1.74 | w | | | 1.475 | m | 1.157 | m | 1.003 | m |

* Data by K.H. Butler et al.

In all columns "d" and "I" represent the interplanar spacing in Angstrom and its intensity respectively. The abbreviations in columns "I" mean:

vs: very strong. s: strong. m: medium. w: weak. vw: very weak.

fact, that the change of emission colour was observed when halide was employed as a flux, but their details are not yet investigated.

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