

## BISMUTH AS ACTIVATOR IN FLUORESCENT SOLIDS<sup>1</sup>

F. A. KROEGER, J. TH. G. OVERBEEK, J. GOORISSEN,  
AND J. VAN DEN BOOMGAARD

*Philips Research Laboratories, Eindhoven, Holland*

### ABSTRACT

Trivalent bismuth forms fluorescence centers in its own compounds as well as in other systems in which it is present as an activator. The fluorescent emission consists of various bands lying between the ultraviolet and the red end of the spectrum. The relative intensity of these bands depends upon the nature of the host lattice and the temperature of observation.

Sulfates and phosphates of the alkaline earth group show predominantly red fluorescence. The red fluorescence of  $\text{Ca}_2\text{P}_2\text{O}_7:\text{Bi}$  shows the remarkable feature that its temperature dependence is different for excitation by cathode rays and by x-rays.

### INTRODUCTION

Bismuth is known to be responsible for fluorescence in its own compounds as well as in other systems containing it as an activator. Wiedemann and Schmidt (1) describe a blue fluorescence of  $\text{Bi}_2\text{O}_3$ , and Randall (2) mentions a blue fluorescence of  $\text{BiCl}_3$  at liquid air temperature. The activating properties of bismuth in foreign materials have been studied with the oxides, sulfides, and selenides of calcium, strontium, and barium (3-6), with aluminum oxide in which it produces a blue (7) or a red and blue (8) cathodofluorescence, with alkali halides (9), with tungstates and molybdates in which it produces yellow fluorescence (10-13), and with sulfates of the alkaline earth metals in which it produces a red cathodofluorescence (14). Finally, phosphate glasses containing bismuth show a bluish white fluorescence upon excitation by short wave ultraviolet (15).

In a preliminary investigation we prepared a number of oxides, phosphates, sulfates, silicates, and aluminates activated with bismuth. These products were prepared either by coprecipitation of the base material with the corresponding bismuth compound, followed by heating in a suitable atmosphere, or by mixing oxides, nitrates, carbonates, or other easily decomposed compounds and heating them at a temperature sufficiently high to assure reaction. A number of them showed cathodofluorescence at room temperature. Most phosphors that were not responsive fluoresced when cooled to lower temperatures. In all cases the fluorescence varied between blue, yellow, and red. The chemical and physical properties of some of the most interesting systems will be reported in this paper.

### PURE BISMUTH COMPOUNDS

Pure  $\text{Bi}_2\text{O}_3$  and  $\text{BiPO}_4$  both show fluorescence upon excitation by  $\lambda$  2537, x-rays, or cathode rays, at low temperatures. The emission of  $\text{Bi}_2\text{O}_3$  consists of two bands, one in the blue with a maximum at 3900 Å and the

<sup>1</sup> Manuscript received March 7, 1949. This paper prepared for delivery before the Philadelphia Meeting, May 4 to 7, 1949.

other in the yellow. The latter is too weak to be measured accurately. The emission of  $\text{BiPO}_4$  is white-blue with a maximum at  $4200 \text{ \AA}$  (Fig. 1). Both materials show strong absorption of ultraviolet radiation below  $3500 \text{ \AA}$ . Exact absorption measurements are difficult because radiation which is absorbed also causes some visible blackening of the material. Approximate reflection spectra are indicated in Fig. 1.

#### $\text{AlPO}_4$ , $\text{LaPO}_4$ , AND $\text{La}_2\text{O}_3$ PHOSPHORS

Lanthanum phosphate activated with  $3 \cdot 10^{-2}$  moles  $\text{BiPO}_4$  per mole  $\text{LaPO}_4$  shows a strong blue fluorescent band with a maximum at  $4400 \text{ \AA}$ ;

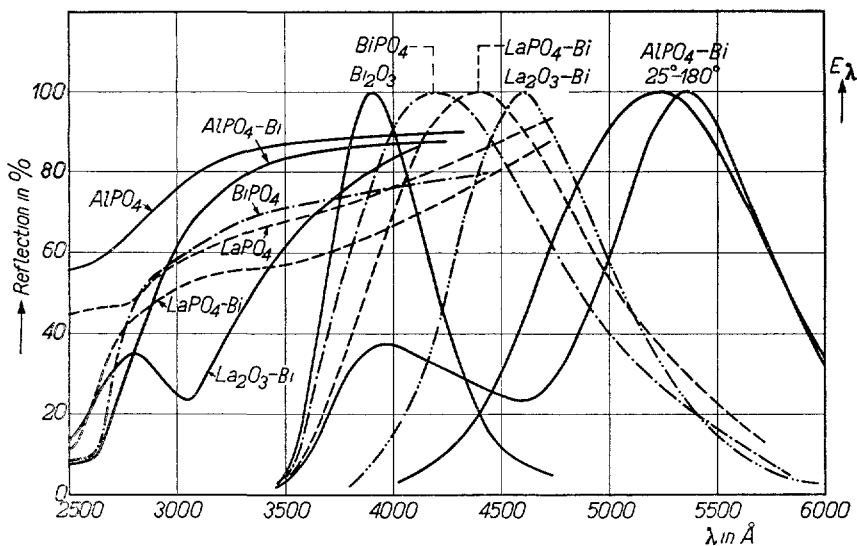


FIG. 1 Spectral distribution of the diffuse reflection and of the fluorescence, for  $\text{Bi}_2\text{O}_3$ ,  $\text{BiPO}_4$ ,  $\text{LaPO}_4:3 \cdot 10^{-2} \text{ BiPO}_4$ ,  $\text{La}_2\text{O}_3:10^{-2} \text{ Bi}_2\text{O}_3$ , and  $\text{AlPO}_4:10^{-2} \text{ BiPO}_4$ . The reflection for unactivated  $\text{LaPO}_4$  and  $\text{AlPO}_4$  is also shown. The curves are for excitation by  $\lambda 2537$  at  $-180 \text{ C.}$ , for  $\text{AlPO}_4:\text{Bi}$  also at room temperature.

lanthanum oxide with  $10^{-2}$  moles  $\text{Bi}_2\text{O}_3$  per mole  $\text{La}_2\text{O}_3$  shows blue fluorescence with a maximum at  $4600 \text{ \AA}$ ;  $\text{AlPO}_4$  with  $10^{-2}$  moles  $\text{BiPO}_4$  shows fluorescence in two bands, one at  $3950 \text{ \AA}$  and another more intense one with a maximum at  $5350 \text{ \AA}$  at  $-180 \text{ C.}$  or  $5180 \text{ \AA}$  at  $25 \text{ C.}$  The activator concentrations listed represent amounts close to the optimum for maximum intensity of fluorescence.

The pure base materials absorb only weakly in the ultraviolet, but the activated products do show strong absorption. Irradiation in these absorption bands leads to fluorescence. Absorption and emission bands are shown in Fig. 1. Fig. 2 shows the temperature dependence of the fluorescence, indicating the usual loss of efficiency with increasing temperature. The weak slope in the curve for  $\text{AlPO}_4:\text{Bi}$  below room temperature is due

to quenching of the blue band; the steep portion above room temperature indicates the quenching of the green band.

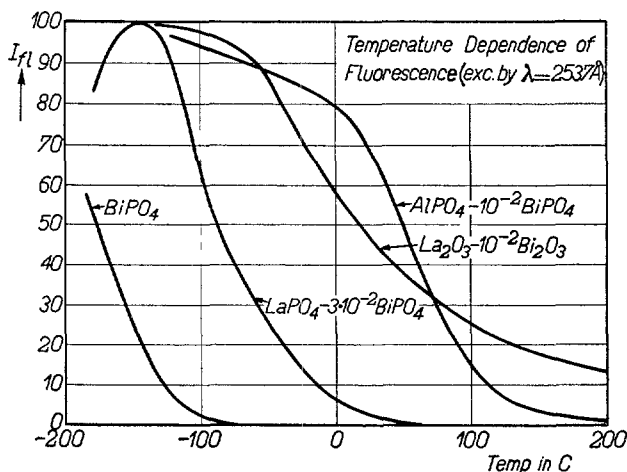


FIG. 2. Temperature dependence of the intensity of fluorescence of  $\text{La}_2\text{O}_3 \cdot 10^{-2} \text{Bi}_2\text{O}_3$ ,  $\text{LaPO}_4 \cdot 3 \cdot 10^{-2} \text{BiPO}_4$ , and  $\text{AlPO}_4 \cdot 10^{-2} \text{BiPO}_4$ , for excitation by  $\lambda = 2537\text{\AA}$ .

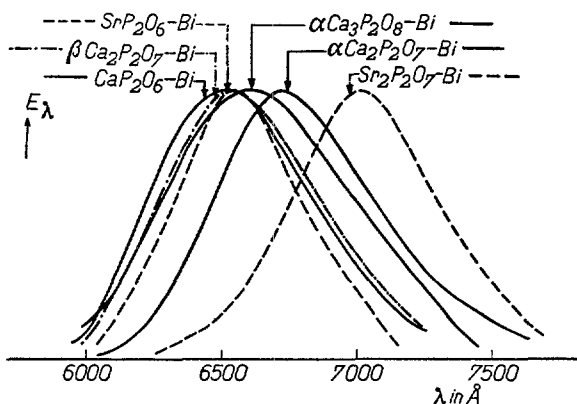


FIG. 3. Spectral distribution of the cathodofluorescence of  $\alpha$  and  $\beta$   $\text{Ca}_2\text{P}_2\text{O}_7$ ,  $\text{CaP}_2\text{O}_6$ ,  $\text{Sr}_2\text{P}_2\text{O}_7$ ,  $\text{SrP}_2\text{O}_6$ , and  $\text{Ca}_3(\text{PO}_4)_2$ , all activated with  $10^{-3}$  gram atoms Bi per mole.

#### PHOSPHATES OF THE ALKALINE EARTH METALS

Phosphates of calcium, strontium, and barium, activated with bismuth, were prepared by heating a mixture of the respective carbonates with ammonium phosphate. The completion of the solid state reaction and the crystal structure of the products were followed by means of x-ray diffraction patterns.

The meta- and pyro- phosphates of calcium and strontium show strong red cathodofluorescence; the orthophosphates of these elements show a similar but much weaker fluorescence, while the phosphates of barium did not fluoresce.

The spectral distributions of the most intense bands are shown in Fig. 3. The calcium pyrophosphates show different peaks depending upon the temperature of their preparation, i.e., above or below 1150 C. The difference in emission is related to a change in crystal structure from the  $\alpha$  to the  $\beta$  modification. Our value for the transition point agrees with that reported by Troemel and Moeller (16).<sup>2</sup> A similar difference in peak positions is also found in the cathodofluorescence of the calcium pyrophosphates activated with manganese (Fig. 4).

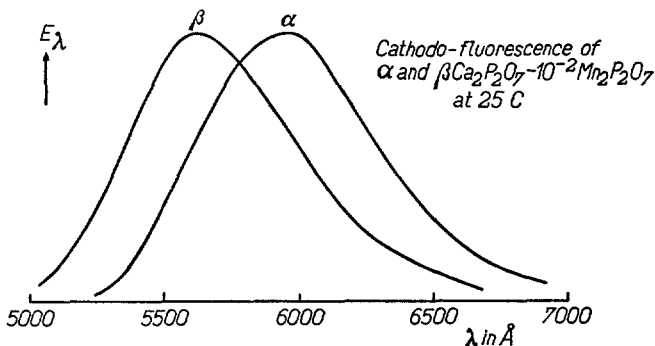


FIG. 4. Spectral distribution of the cathodofluorescence of  $\alpha$  and  $\beta$   $\text{Ca}_2\text{P}_2\text{O}_7$  activated with  $10^{-2}$  moles  $\text{Mn}_2\text{P}_2\text{O}_7$ .

Incorporation of bismuth produces an absorption band in the ultraviolet range which is not found in the pure base materials (Fig. 5). Even though absorption in this band is strong, it does not lead to fluorescence, whereas excitation by cathode rays does lead to strong red emission. To explain this, it is assumed that two types of centers are involved and that the absorption band is mainly due to centers which are not fluorescent at room temperature. This is demonstrated by the fact that products excited by  $\lambda$  2537 at liquid air temperature do develop a new ultraviolet fluorescence emission with a peak at 3180 Å, and also a weak blue band with maximum at 3980 Å (Fig. 5).

The red fluorescence is also excited by x-rays. The optimum concentration of bismuth is about  $10^{-3}$  gram-atoms Bi/mole, for x-ray as well as for cathode ray excitation (Fig. 6). The x-rays for this experiment were produced with a 60 kv Philips Practix tube and a filter of 1 mm Al. This gave a continuous spectrum from about 0.2 to 1 Å with a maximum intensity at about 0.3 to 0.4 Å. The intensity was 500 roentgens per minute.

The temperature dependence of the red emission excited by 6 kv cathode rays shows a remarkable difference from that excited by x-rays. Fig. 7 demonstrates this effect for  $\beta$   $\text{Ca}_2\text{P}_2\text{O}_7$ : $3 \cdot 10^{-3}$  Bi. The cathodofluorescence

<sup>2</sup> Bale, Bonner, and Hodge (17) report a transition point at 1270 C. This discrepancy may be due either to deviations from stoichiometry or to contaminations.

is nearly constant and of low intensity at low temperatures. From 0 to 150 C it increases strongly to reach a value about five times as high in intensity. It then levels off again and will probably be quenched at some temperature well above 300 C. On the other hand, the fluorescence excited by x-rays is constant over the entire temperature range. This constitutes

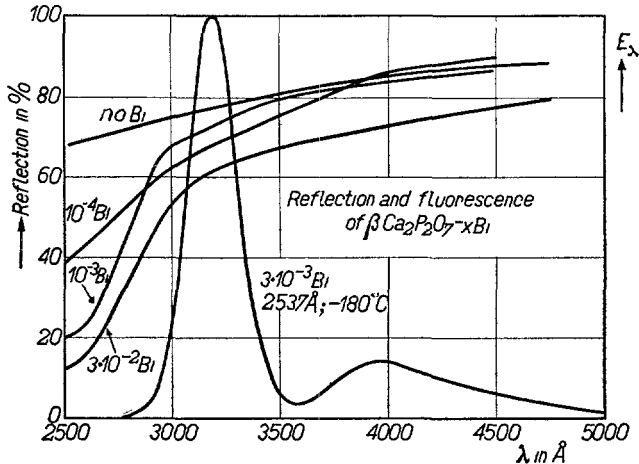


FIG. 5. Spectral distribution of the reflection of  $\beta$   $\text{Ca}_2\text{P}_2\text{O}_7$  containing various concentrations of bismuth, and of the fluorescence excited by  $\lambda$  2537 at  $-180^\circ\text{C}$ .

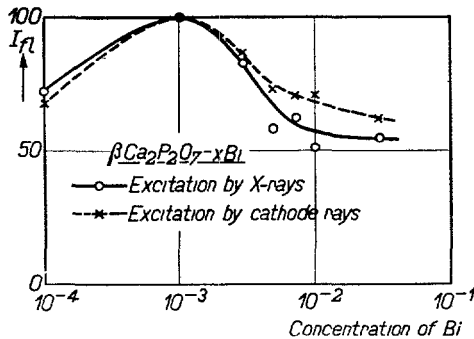


FIG. 6 Intensity of the red fluorescence of  $\beta$   $\text{Ca}_2\text{P}_2\text{O}_7:\text{Bi}$  as a function of the bismuth concentration, for excitation by 6 kv cathode rays and 60 kv x-rays (continuous spectrum with a maximum at 0.3 to 0.4 A)

the first case, of which we know, where such a marked difference occurs between the properties of the same fluorescence excited by x-rays and by cathode rays, respectively. This is of interest because the mechanism of excitation by these two agents is usually considered to be similar.

The difference is not due to an accumulation of charge on the phosphor in the case of cathode ray excitation. Exactly the same results were obtained with cathode rays of 20 kv, which proves that the difference is not

due to a surface layer of different properties. All measurements were carried out with a stationary electron beam of about  $2 \mu \text{ amp/cm}^2$ .

The difference might be explained with the assumption that the x-rays excite most of the centers directly, whereas excitation by cathode rays gives rise mainly to excited states in the base lattice, and to only a small number of directly excited bismuth atoms.

The directly excited centers produce a fluorescent emission which is independent of temperature (as long as characteristic quenching in the centers does not occur). The temperature-independent fluorescence excited by x-rays is then comparable with that excited by cathode rays at temperatures below 0 C. The main part of the cathodofluorescence,

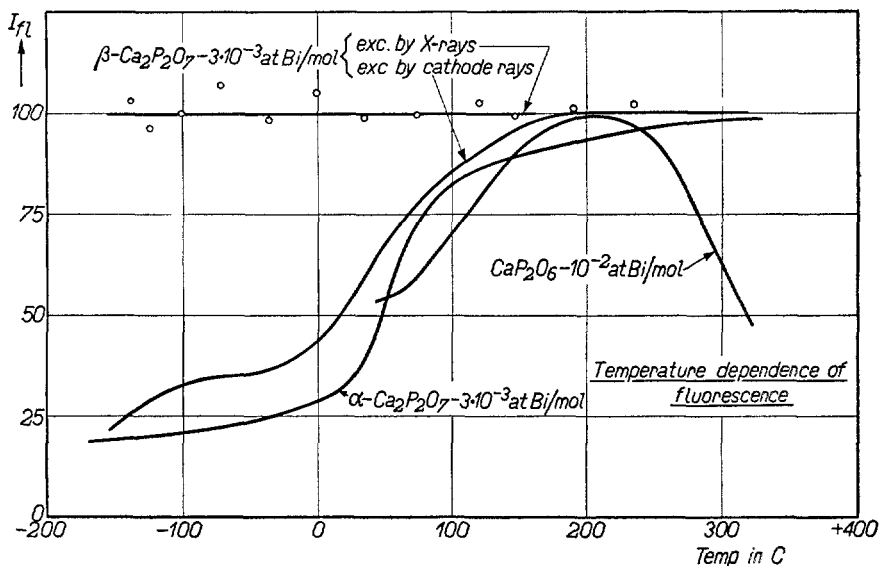


FIG. 7. Temperature dependence of fluorescence of calcium phosphates activated with bismuth, for excitation by 6 kv cathode rays and 60 kv x-rays.

however, requires the transfer of excitation energy from the lattice to the centers. If this process requires an activation energy, most of the excitation energy is lost without emission of light, at low temperatures. At a certain higher and critical temperature, the transfer process gains in prominence and the intensity of fluorescence increases. Similar effects have been observed with other systems in which the state reached in excitation is different from the state which leads to fluorescence ( $\text{Cd}_2\text{B}_2\text{O}_5:\text{Mn}$ ,  $\text{CdSiO}_3:\text{Mn}$ ) (18).

This explanation, however, is not fully satisfactory. In the first place, bismuth does not show exceptionally strong absorption for x-rays of the wavelengths used. Furthermore, the temperature dependence for excitation by x-rays does not show even a slight increase, and the optimum bismuth concentration for x-ray excitation is not observed to be higher than

it is for cathode ray excitation, as it would be expected to be. Therefore, this point is still open to question.

Fig. 7 also shows the temperature dependence for  $\alpha$   $\text{Ca}_2\text{P}_2\text{O}_7:\text{Bi}$  and for  $\text{CaP}_2\text{O}_6:\text{Bi}$ . It proves to be similar to that for  $\beta$   $\text{Ca}_2\text{P}_2\text{O}_7:\text{Bi}$ . With  $\text{CaP}_2\text{O}_6:\text{Bi}$ , the high temperature quenching range falls within our measuring region, the decrease setting in at 200 C.

#### SULFATES OF THE ALKALINE EARTH METALS

Sulfates of calcium, strontium, barium, magnesium, and zinc, activated with bismuth, were prepared by coprecipitation from solutions of the nitrates with sulfuric acid, or by evaporation of sulfate solutions. The filtered, washed, and dried materials were heated between 700 and 900 C.

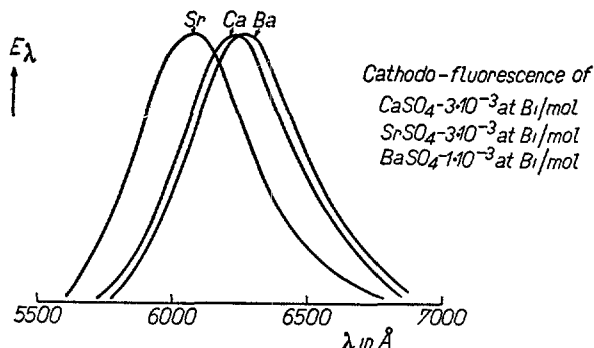


FIG. 8 Spectral distribution of the cathodofluorescence of bismuth activated  $\text{CaSO}_4$ ,  $\text{SrSO}_4$ , and  $\text{BaSO}_4$

If the firing was carried out in atmospheres of air, nitrogen, or oxygen, the products turned out grayish, particularly so at high concentrations of bismuth. This color is probably due to decomposition of bismuth sulfate with formation of basic compounds. The discoloration is prevented if the firing is carried out in an atmosphere containing  $\text{SO}_3$  such as is obtained by passing air through hot sulfuric acid. A mixture of  $\text{SO}_2$  and  $\text{O}_2$  may also be used.

The sulfates of calcium, strontium, and barium show a red emission upon excitation by cathode rays, x-rays, or ultraviolet. Fig. 8 shows the spectral distributions. The peaks are found to be at 6220, 6070, and 6270 Å in reasonably good agreement with the observations of L. de Boisbaudran (14) who reports the values 6180, 5980, and 6220 Å. The pure sulfates do not absorb in the near ultraviolet. Incorporation of bismuth produces an absorption band below 3600 Å which increases in intensity with the concentration of Bi. It is this absorption which is responsible for the excitation by  $\lambda$  2537.

For the various forms of excitation, the intensity of fluorescence depends upon the bismuth concentration in a different manner. For excitation with x-rays or cathode rays, the intensity increases with increasing bismuth content up to about  $5 \cdot 10^{-3}$  gram atoms Bi per mole sulfate. It then remains practically constant up to  $3 \cdot 10^{-2}$  gram atoms Bi per mole sulfate or

higher. For excitation by  $\lambda$  2537, there is an optimum concentration at  $10^{-3}$  gram atoms Bi per mole sulfate. Above this concentration the intensity decreases rapidly. The efficiency of the ultraviolet-excited fluorescence is extremely low, even at the optimum.

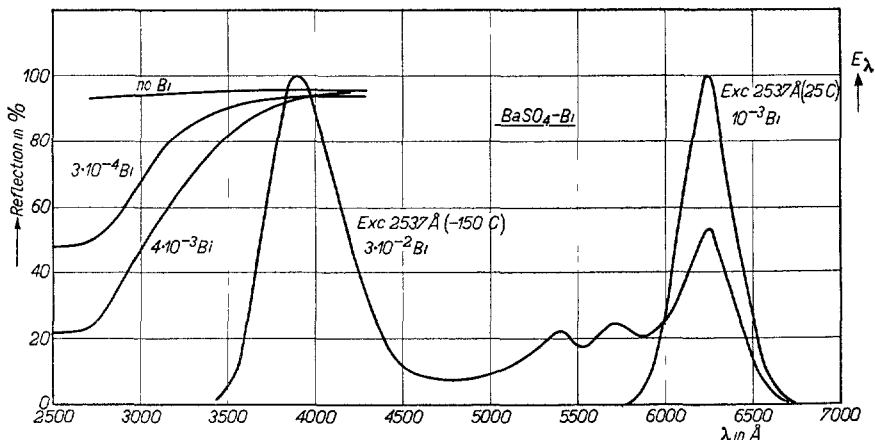


FIG. 9. Reflection of  $\text{BaSO}_4$  with various concentrations of  $\text{Bi}_2(\text{SO}_4)_3$ . Emission of  $\text{BaSO}_4$ : $3 \cdot 10^{-3}$  gram atoms Bi/mole, excited by  $\lambda$  2537 at room temperature, and of  $\text{BaSO}_4$ : $3 \cdot 10^{-2}$  gram atoms Bi/mole excited by  $\lambda$  2537 at  $-150$  C.

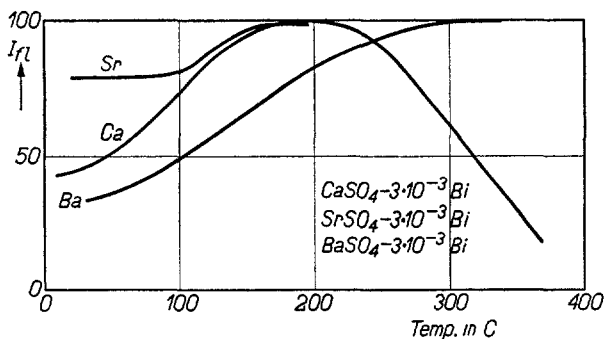


FIG. 10. Temperature dependence of the emission of  $\text{CaSO}_4$ ,  $\text{SrSO}_4$ , and  $\text{BaSO}_4$  activated with  $3 \cdot 10^{-3}$  gram atoms Bi/mole and excited with 6 kv cathode rays.

These properties indicate that, in addition to the centers responsible for the red fluorescence, the systems contain nonfluorescent centers which absorb ultraviolet strongly and which increase in relative concentration with increasing bismuth content. The presence of such centers is directly proven by the fluorescence of the sulfates at low temperatures: a product with  $3 \cdot 10^{-2}$  Bi which is only faintly luminescent at room temperature changes its emission upon cooling to liquid air temperature. It then shows two weak bands in the green and yellow region at 5400 and 5710 Å, re-



spectively, and one strong band in the violet at 3900 Å, in addition to the normal red band (Fig. 9).

The temperature dependence of the intensity of the red cathodofluorescence is shown in Fig. 10. As with the phosphates, the intensity increases with increasing temperature up to a constant value. With  $\text{CaSO}_4:\text{Bi}$ , the intensity decreases above 200 C owing to temperature quenching. The measurements were hindered by strong electron "burning," particularly so with  $\text{BaSO}_4:\text{Bi}$ . The burning is evident only as a decrease of the intensity of fluorescence; it is not accompanied by a discoloration of the material. Heating above 200 C restores the original state so far as burning is concerned. When the heating is carried out in a vacuum, however, a new effect is observed: the substance turns gray due to thermal decomposition of bismuth sulfate as discussed above. The two effects are readily separated because electron burning appears only at those spots where electrons reach the powder, whereas the discoloration occurs over the entire area, independently of electron bombardment.

#### THE VALENCY OF BISMUTH ACTING AS ACTIVATOR

As shown in the introduction and in the work reported above, bismuth produces fluorescence in a large number of substances, even in its own compounds. We are therefore inclined to attribute the fluorescence to characteristic electronic transitions in the configuration formed by bismuth and its nearest neighbors.

The appearance of violet, green, yellow, and red bands might be explained in two ways. For example, it may be due to bismuth atoms of different valencies. Bismuth occurs normally in the trivalent state, but pentavalent bismuth is also known (as in sodium bismuthate). Even though the free energy of pentavalent bismuth is rather large in its pure compounds, it may well be stabilized by incorporation in suitable host lattices, such as sulfates or phosphates. A second explanation would be that the fluorescence centers are formed only by trivalent bismuth and that variations in emission are due to the influence of the lattice fields on the energy levels of the  $\text{Bi}^{3+}$  ions. Such effects may reach considerable magnitude, as is shown with the corresponding case of divalent manganese, the fluorescence of which varies from green to infrared.

In order to determine whether or not different states of valence are involved, we have analyzed a few samples of red fluorescing  $\text{Ca}_2\text{P}_2\text{O}_7:\text{Bi}$  which was shown to contain ultraviolet emission centers (Fig. 5). To this end, about one gram of phosphor was dissolved in hydrochloric acid which had previously been freed from oxygen by passing a current of pure nitrogen through it, and which contained some KI and a few drops of a fresh solution of starch. If the products had contained pentavalent bismuth, the latter would have formed free iodine. However, no trace of a blue color was observed. In a variation of this test, the phosphors were dissolved in hydrochloric acid. A current of pure nitrogen passed through the liquid to carry liberated chlorine, if any, into an absorption vessel with a solution of KI,  $\text{H}_2\text{SO}_4$ , and starch. Again, the tests were negative. We, therefore, feel justified in our conclusion that the fluorescent effects observed are not due to bismuth atoms of different valencies, but to trivalent bismuth in different surroundings, as outlined above.

It remains to be seen what differences in surroundings would be necessary in order to cause a variation in emission ranging from blue to red, particularly in lattices which make both bands appear. The blue and ultraviolet bands of  $\text{Ca}_2\text{P}_2\text{O}_7:\text{Bi}$ ,  $\text{BaSO}_4:\text{Bi}$ , and  $\text{La}_2\text{O}_3:\text{Bi}$  are situated close to the absorption bands due to bismuth. They must be attributed to corresponding electronic transitions from the ground state to an excited state and vice versa. The red bands in the phosphates and sulfates, on the other hand, are far removed from these ultraviolet absorption bands. Absorption bands in the visible which might lead to red fluorescence have not been found. This indicates that the fluorescence must be attributed to an electronic transition between two excited states, the lower one being so high that it is not occupied at normal temperatures.

The same reasoning applies to the blue bands in the other systems, which are so widely separated from the absorption bands that the shift can not be accounted for on the basis of the Franck-Condon principle.

#### ACKNOWLEDGMENT

The authors wish to express their thanks to Dr. H. C. Froelich for applying numerous editorial improvements to the manuscript.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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