Activations by Anions in the Oxy-acid Phosphors. II. Activations by the Tungstate Ion

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In the previous paper⁽¹⁾ it was found that anionic centers are present in oxy-acid phosphors and that the activation by tungstate ion is a typical example of "intraionic activation", the luminescence originating from the electron transitions in tungstate ion and being rather strong. The activation by the tungstate ion has been reported by several researchers⁽²⁾, for example, for calcium borate⁽³⁾ or halophosphate⁽⁴⁾, though the activation is assumed to be caused by the tungsten ion. In these cases it has been found that the brightness of phosphors increases with the increase in the added amount of tungsten, but the highest brightness is only equal to or lower than that of calcium tungstate. It is desirable to obtain phosphors which have a higher brightness and,

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

2) F. A. Kroeger, "Some Aspects of the Luminescence of Solids", Elsevier Pub. Co., Inc., Amsterdam (1948), p. 107.

3) Y. Uehara et al., The 2nd Symposium on Photochemistry, Tokyo, September, 1954.

4) N. Ohtani et al., 8th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1955.

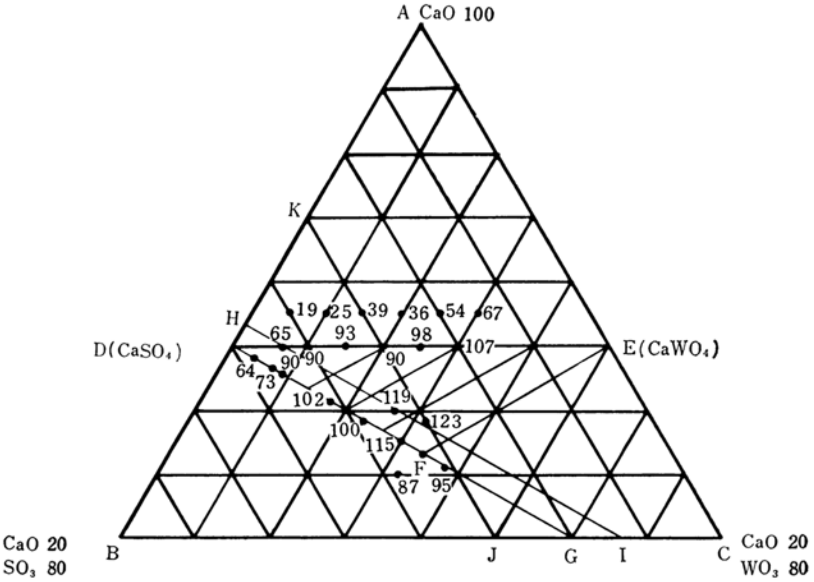

Fig. 1. Relation between the brightness of calcium sulfate activated by tungstate ion and the mixing ratio of batch component.
A : CaO ; B : CaO 20, SO_3 80 ; C : CaO 20, WO_3 80 ; D : $CaSO_4$, E : $CaWO_4$ (under 2537 Å excitation).

if possible, a cost cheaper than calcium tungstate, if calcium salts are to be activated by tungstate ion. In the various kinds of matrices discussed, it was expected that sulfate salts would satisfy this desire because of the similarity in crystal structure⁵⁾ between sulfate and tungstate salts. Among calcium salts the crystal structure of calcium sulfate is most like that of tungstate, the former being orthorombic with $a_0=6.21$, $b_0=6.95$ and $c_0=6.96$, whereas the latter is tetragonal with $a_0=5.24$ and $c_0=11.38$. Likewise, magnesium sulfate has an orthorhombic structure with $a_0=4.82$ $b_0=6.72$ and $c_0=8.35$, while magnesium tungstate is monoclinic, with $a_0=4.67$, $b_0=5.66$, $c_0=4.92$ and $\theta=89°35'$. An American patent⁶⁾ makes an interesting relevant suggestion. It is proposed by this patent that the brightness of calcium tungstate increases when sulfuric acid, in amounts corresponding to the excess calcium oxide in the tungstate, is added on firing for the purpose of preventing the formation of calcium oxide. Accordingly we have prepared various sulfate phosphors activated by tungstate ion and have so achieved some remarkable results.

The Experiments and their Results

The starting materials are $CaSO_4$, $CaCO_3$, $WO_3 \cdot nH_2O$, $CaWO_4$, MgO, $(NH_4)_2SO_4$, ZnO, $CdCO_3$, $PbSO_4$, $BaSO_4$ and MoO_3, which had been purified by the process previously reported⁷⁾. They were mixed in a dry state and fired in air for 4 hr., at 1100°C for calcium sulfate and at 1000°C for magnesium sulfate. The spectral distribution was measured by means of a spectroradiometer⁸⁾, and the brightness, by a photocell.

Relation between the Brightness of $CaSO_4$: WO_4 and the Mixing Ratio.—The relation is

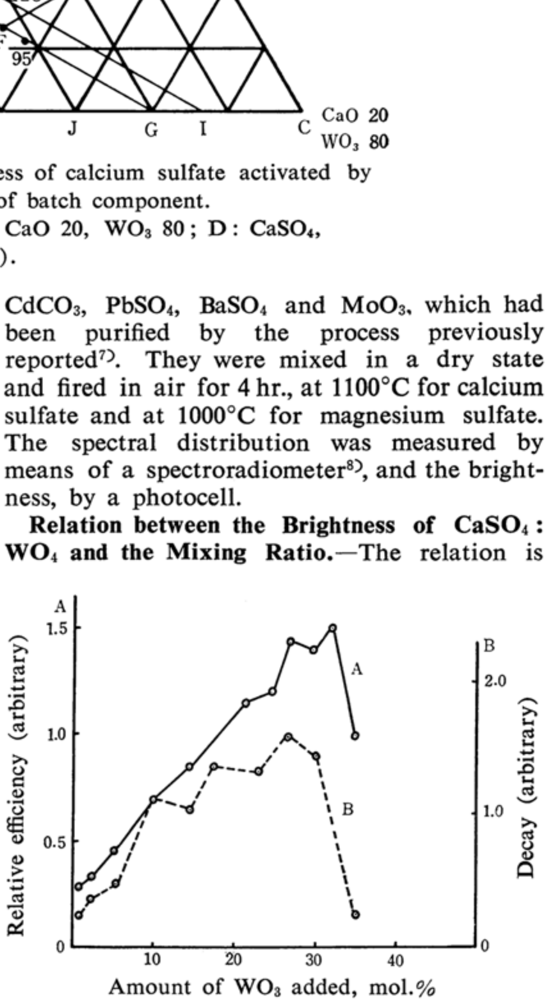

Fig. 2. Brightness and decay characteristics as the function of amount of WO_3 added to calcium sulfate (X-ray excitation). A, Brightness B, Decay

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5) R. W. G. Wyckoff, " Crystal Structures ", Interscience Publishers, New York (1948).

6) W. A. Roberts, U. S. Pat. 2312267 (1943).

7) Y. Kotera, T. Sekine and M. Yonemura, This Bulletin, **27**, 13 (1954).

8) Y. Kotera, *Rept. Govn. Chem. Ind. Research Institute, Tokyo*, **50**, 398 (1955).

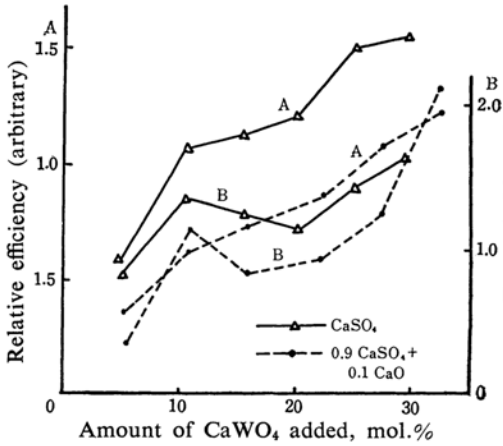

Fig. 3. Brightness and decay characteristics as the function of amount of $CaWO_4$ added to calcium sulfate and (0.9 $CaSO_4$ +0.1 CaO) (X-ray excitation).
A, Brightness B, Decay

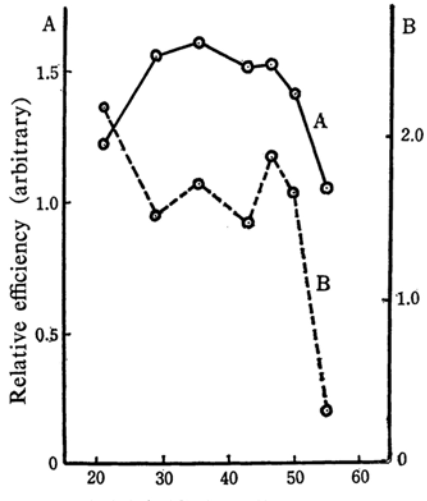

Fig. 4. Brightness and decay characteristics as the function of molar ratio of SO_3 to $CaSO_4$ (X-ray excitation).
A, Brightness B, Decay

shown in Fig. 1 between the brightness of the fired products under 2537Å excitation and the mixing ratio of $CaSO_4$, $CaCO_3$ and $WO_3 \cdot nH_2O$. The brightness and the decay characteristies of these products under X-ray excitation are shown in Figs. 2, 3 and 4.

In Fig. 1 the value of 100 corresponds to the brightness of the commercial product of calcium tungstate phosphor, while the brightness and decay characteristics under X-ray excitation were determined by the blackening of the photographic plate. The commercial product shows a brightness value of 1.40 for those prepared by the precipitation and the firing of calcium tungstate or 1.80 for those prepared by the solid-state reaction between calcium compound and tungsten trioxide, and 1.20 for the decay value.

In Fig. 2 the samples are selected for the mixing ratio from points on the straight line DG in Fig. 1, while in Fig. 3 the mixing ratios of samples are located on DE (A) and on the straight line parallel to DE (B), and in Fig. 4, on JK.

In these preparations it is probable that the reaction

$$CaSO_4+H_2WO_4 \rightarrow CaWO_4+H_2SO_4$$

proceeds; that this is the case is confirmed by the formation of white fume, which is presumed to be sulfur trioxide, and by the decrease in the weight of the samples. Then it has to be assumed that, for mixtures of compositions below the line DE (Fig. 1), the composition changes during the firing, along the straight line EF or parallel to EF, the reaction ending when the composition reaches line DE. The spectral distributions are shown in Fig. 5.

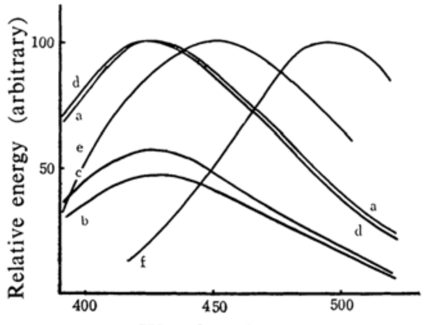

Fig. 5. Spectral distributions of calcium tungstate and calcium sulfate activated by tungstate ion.
a, $CaWO_4$; b, c, d, $CaWO_4$ activated by tungstate ion ($CaSO_4 : H_2SO_4$ (molar ratio)=99:1 (b), 9:1 (c), 7:3 (d)); e, $CaSO_4$ activated by tungstate ion with the addition of lead salt; f, $CaSO_4$ activated by tungstate ion with the addition of magnesium salt.

The Effect of the Addition of other Components than Calcium and Tungstate Compound to Calcium Sulfate Activated by a Tungstate Ion.—By the addition of lead salt to calcium sulfate activated by a tungstate ion, it might be supposed that the product would be about the same as that of calcium tungstate activated by lead. Actually, this is the case. The change in the spectral distribution by the addition of lead occurs in $CaSO_4 : WO_4$ as in the case of calcium tungstate; in this case it was also found that the brightness of the

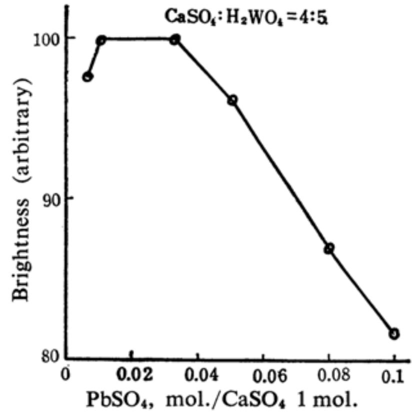

Fig. 6. Brightness as the function of amount of lead salt added to calcium sulfate activated by tungstate ion.

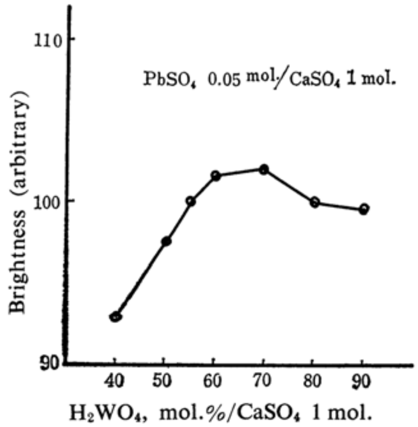

Fig. 7. Brightness as the function of amount of WO_3 added to calcium sulfate activated by tungstate ion with the addition of lead salt.

TABLE I. BRIGHTNESS AND DECAY CHARACTERISTICS OF CALCIUM SULFATE ACTIVATED BY TUNGSTATE ION WITH THE ADDITION OF BARIUM SULFATE (X-RAY EXCITATION)

No.	Mixing ratio, g.			Brightness*2	Decay*2
	$CaSO_4$*1	H_2WO_4	$BaSO_4$		
1	4.0	4.0	0.8	67.0	52.3
2	4.0	4.0	1.6	48.6	41.1
3	4.0	4.0	3.2	34.6	54.4
4	4.0	4.0	5.3	23.8	2.4
5*3	4.0	4.0	0.8	46.2	90.1
6	4.0	5.8	—	100	100
7	4.0	5.8	1.0	85.1	44.4
$CaWO_4$(Commercial material)				135	37.2

*1 $CaSO_4$ contains 1.02 H_2O.
*2 Relative value to that of No. 6.
*3 0.44 g. of $PbSO_4$ was added.

products is considerably higher than that of calcium tungstate activated by lead. In Figs. 6 and 7 the brightness of the samples under 2537 Å excitation is shown; the value of 100 means the brightness of commercial calcium tungstate activated by lead. The spectral distribution is shown in Fig. 5.

By the addition of barium sulfate, it might be presumed that the absorption of the X-ray increase and barium tungstate, which has no emission at room temperature, would be produced. The brightness and the decay characteristics of the products under X-ray excitation are shown in Table I. Under 2537 Å excitation the spectral distribution is almost the same as that of calcium tungstate, and the brightness decreases proportionally with the amount of the addition.

By the addition of magnesium oxide the products show an emission almost the same as that of magnesium tungstate, when the firing

TABLE II. BRIGHTNESS OF CALCIUM SULFATE ACTIVATED BY TUNGSTATE ION WITH THE ADDITION OF MAGNESIUM OXIDE

No.	Mixing ratio, g.			Brightness*2
	$CaSO_4$*1	H_2WO_4	MgO	
1	4.0	5.2	1.1	100
2	4.0	5.2	1.2	93
3	4.0	5.2	1.3	96
4	4.0	5.8	1.1	93
5	4.0	5.8	1.2	93
6	4.0	5.8	1.3	93

*1 $CaSO_4$ contains 1.02 H_2O.
*2 Relative value to that of magnesium tungstate.

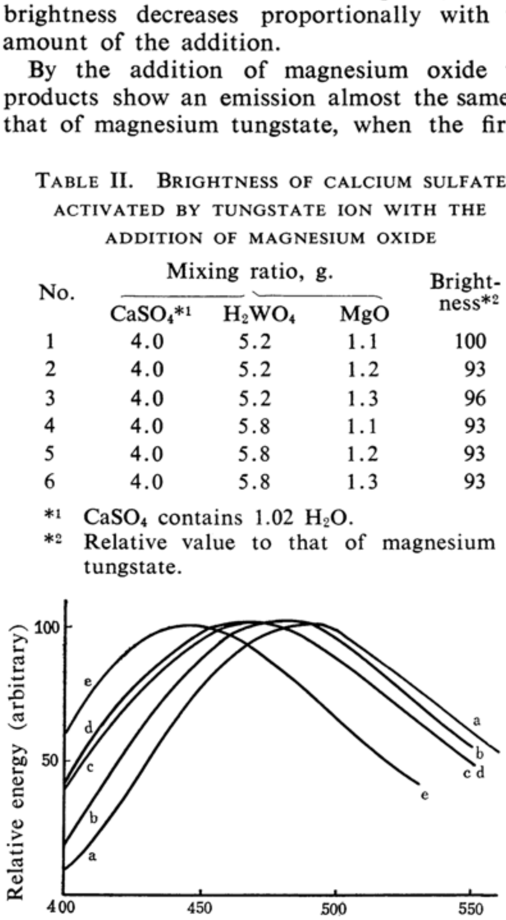

Fig. 8. Spectral distributions of calcium sulfate activated by tungstate ion with the addition of zinc oxide.

	$CaSO_4$ g.	H_2WO_4 g.	ZnO g.
a	0	4.8	1.9
b	4.0	4.8	1.6
c	4.0	4.8	1.2
d	4.0	4.8	0.8
e	4.0	4.8	0.4

temperature is below 1000°C. (See Fig. 5. Above 1100°C the emission is the same as for calcium tungstate, and the firing temperature between 1000 and 1100°C gives their mixture.) Also in this case the brightness is higher than that of an ordinary preparation, the results being tabulated in Table II.

By the addition of zinc or cadmium oxide, the spectral distribution shifts to a longer wavelength, which is shown in Figs. 8 and 9. Molybdenum oxide causes the same shift, which is shown in Fig. 10. This result is like that of Kroeger[2], but the details are not in accordance. The brightness of these samples under 2537Å is considerably high when compared with other commercial phosphors.

The Effect of the Precipitating Condition or Firing Condition.—Preliminary tests were carried out for the production of calcium sulfate activated by tungstate ion. Twelve kinds of samples were prepared as follows:

1. Pure calcium chloride ($CaCl_2 \cdot 2H_2O$ 80 g./l.) was mixed with a pure ammonium sulfate solution (($(NH_4)_2SO_4$ 80 g./l.), and precipitated calcium sulfate was mixed with tungstic acid.

The batch obtained was fired at different temperatures, viz., 1000, 1050 and 1100°C.

2. The same process as 1, except that the concentration of the ammonium sulfate solution was 40 g./l.

3. The same process as 1, except that tungstic acid was re-purified from the one used in process 1.

4. After the preparation by the process 1, the products were re-fired at 1100°C for 4 hr.

The relation between the relative brightness of these samples and the preparative condition

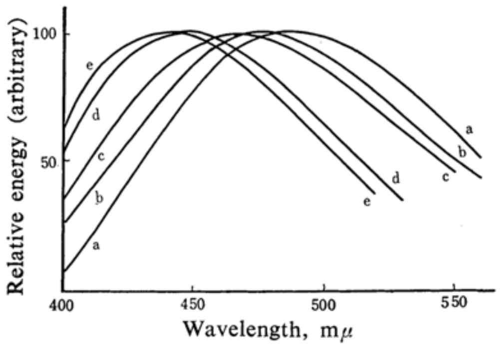

Fig. 9. Spectral distributions of calcium sulfate activated by tungstate ion with the addition of cadmium oxide.

	$CaSO_4$	H_2WO_4	CdO
	g.	g.	g.
a	0	4.8	4.0
b	4.0	4.8	3.4
c	4.0	4.8	3.0
d	4.0	4.8	2.0
e	4.0	4.8	1.0

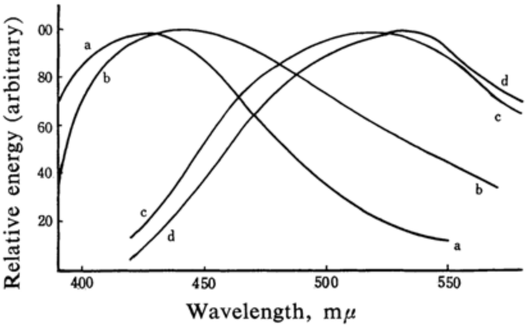

Fig. 10. Spectral distributions of calcium sulfate activated by tungstate ion with the addition of molybdenum oxide.

	H_2WO_4	H_2MoO_4	MoO_3/WO_3 (mol.)
	g.	g.	%
a	0.732	0.0005	0.1
b	0.726	0.0053	1
c	0.696	0.0265	5
d	0.670	0.0530	10

$CaSO_4$: 4.0 g. (a—d)

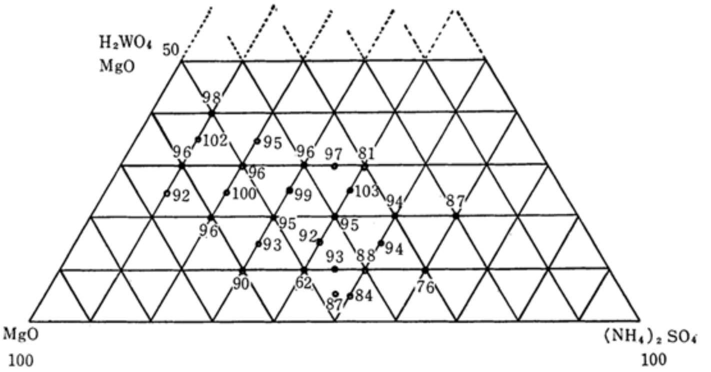

Fig. 11. Relation between the brightness of magnesium sulfate activated by tungstate ion and the mixing ratio of batch component (under 2537Å excitation).

TABLE III. RELATION BETWEEN THE BRIGHTNESS OF CALCIUM SULFATE ACTIVATED BY TUNGSTATE ION AND THE PRECIPITATING OR FIRING CONDITION

Firing temp. °C	Processes (1)	(2)	(3)	(4)
1000	85	87	90	84
1050	87	90	95	89
1100	88	90	93	87

is shown in Table III.

From these results we tried to investigate the effect of the precipitating condition of calcium sulfate and of the prefiring condition on the brightness of the products. The precipitation of calcium sulfate was carried out under the following conditions:

i. A calcium chloride solution (80 g./l.) was poured into an ammonium sulfate solution (80 g./l.).

ii. A calcium chloride solution (40 g./l.) was poured into an ammonium sulfate solution (160 g./l.).

iii. An ammonium sulfate solution (40 g./l.) was poured into a calcium chloride solution (160 g./l.).

iv. An ammonium sulfate solution (80 g./l.) was poured into a calcium chloride solution (80 g./l.).

Half a portion of precipitated calcium sulfate was prefired at 800°C for 2 hr., while the other half was not prefired. The batches were prepared with these eight calcium sulfate samples, the ratio of calcium and tungsten being the same. The relative brightness of these phosphors is shown in Table IV.

TABLE IV. EFFECT OF PRECIPITATING CONDITION AND PREFIRING UPON THE BRIGHTNESS OF CALCIUM SULFATE ACTIVATED BY TUNGSTATE ION

Prefiring	Precipitating conditions (i)	(ii)	(iii)	(iv)
Unfired	95	95	97	97
Prefired	98	100	100	101

It can be concluded from these experiments that the brightness becomes greater by the purification of tungstic acid or the prefiring of calcium sulfate, but that other factors are not so important as the former.

Relation between the Brightness of $MgSO_4$: WO_4 and the Mixing Ratio.—The relation is shown in Fig. 11 between the brightness of fired products under 2537 Å excitation and the mixing ratio of MgO, $(NH_4)_2SO_4$ and $WO_3 \cdot nH_2O$. The same is shown in Fig. 12, the brightness change being expressed as the function of tungstic acid proportion.

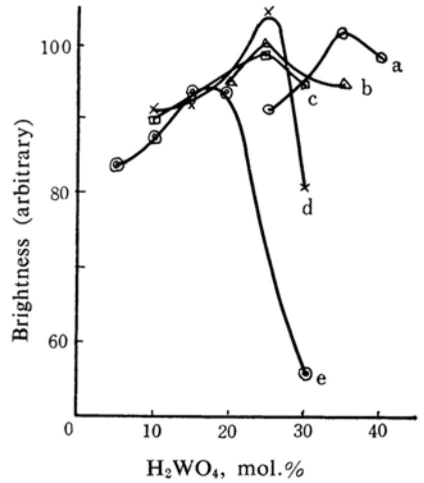

Fig. 12. Brightness of magnesium sulfate activated by tungstate ion as the function of ammount of WO_3 added to magnesium sulfate (under 2537 Å excitation).

Discussion

In his brief studies on the luminescence of tungstates and molybdates, Kroeger²⁾ presumed from the absorption data of the molybdates that the absorption would be of the characteristic type caused by electronic transitions in the molybdate groups and that the same would be applied to the tungstates. He also assumed from his experiments the absorption and excitation bands on the one hand and the emission band on the other hand must be closely connected, both probably originating in one and the same atomic configuration, which might be tungsten and molybdenum with adjacent oxygen ions. In this case it was not determined whether any tungstate or molybdate group could give rise to an emission or not.

On the other hand, a few reports have been published on the emission of phosphors activated by tungsten or molybdenum. Calcium borate³⁾ or calcium halophosphate⁴⁾ activated by tungsten have been studied, but their details are uncertain, except that it has been explained that the emissions might be the same as those of calcium tungstate and that the brightness increases with the increasing amount of tungsten, its maximum value being the one which is obtained for calcium tungstate. Aluminum oxide activated by tungsten emits an orange light, while activation by molybdenum causes a blue emission⁹⁾; zinc silicate emits a green color when activated by tungsten¹⁰⁾. These reports are also uncertain but for the last case, where it is obvious that

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9) S. Izawa, *Sci. Pap. Inst. Phys. Chem. Res.*, **20**, 163 (1933).

10) Y. Uehara and U. Umekawa, *J. Chem. Soc. Japan* (Nippon Kwagaku Kwaishi), **61**, 107 (1940).

the emission corresponds to that of zinc tungstate. Meanwhile, Robert[6] has found that the brightness of calcium tungstate would increase when sulfuric acid, in amounts corresponding to the excess calcium oxide in the tungstate, is added on firing. This addition of sulfuric acid might cause the formation of calcium sulfate, reducing the amount of calcium oxide, which seems to cause the afterglow in calcium tungstate[11].

It is found that calcium sulfate is activated by the tungstate ion and that the brightness of this phosphor under 2537 Å excitation is higher than that of pure calcium tungstate. The spectral distribution of this emission is almost the same as that of calcium tungstate, although a small shift was found in some cases. However, as already stated, the reaction between calcium sulfate and tungstic acid might occur during the firing of their mixture. Further, it was found by us that the addition of ammonium persulfate to calcium tungstate causes its brightness to increase[12]. Thus the results might be explained by the findings of Robert and our above-written finding, that the addition of sulfate ion is favorable for the preparation of calcium tungstate phosphor.

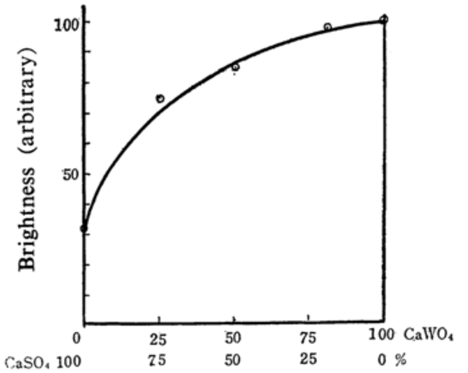

Fig. 13. Relation between the brightness and the mixing ratio of mechanical mixture of calcium sulfate and calcium tungstate.

For these problems it is proposed that, at low contents of tungstic acid, calcium sulfate is being activated by the tungstate ion, because the brightness is much higher than that obtained from a mixture of calcium sulfate and calcium tungstate, whose brightness is increased by the addition of sulfate. However, when the content of tungstic acid is high, a reaction with calcium sulfate occurs to produce calcium tungstae, while the activation by tungstate occurs simultaneously to increase the brightness of the product. In Fig. 13 the brightness of mechanical mixtures of calcium sulfate and calcium tungstate under 2537 Å excitation is shown; this clarifies the activation by the tungstate ion compared with Fig. 1. Some qualitative results which might clarify this assumption were obtained from crystallographic analysis by means of a recording X-ray diffractometer. In the phosphor, which was prepared by the firing of a mixture of 1 mol. calcium sulfate and 0.2 mol. tungstic acid, the patterns of both calcium sulfate and tungstate were found, while the pattern of the phosphor from the mixture of 1 mol. calcium sulfate and 0.05 mol. tungstate was almost the same as that of calcium sulfate. Because of this crystallographic similarity, it is quite difficult to determine the content of the constituent. On the other hand, absorption measurements were carried out to compare the spectra of pure calcium sulfate and that activated by tungstate ion, but the special peak was not found until 2800 Å, and the measurements at shorter wavelengths were disturbed by the emission which is excited by the light in this region. The final decision as to the occurrence of tungstate activation in the case of calcium sulfate phosphors must be based on measurements of excitation spectra.

Thus, these results may be applied to the preparation of calcium tungstate phosphors. This phosphor is new prepared by two processes, one featuring the solid-state reaction between calcium carbonate or nitrate and tungstic acid, and the other consisting of the precipitation of calcium tungstate in an aqueous solution and its calcination. The former is now applied to the preparation of those phosphors which are used for fluorescent lamps, because they have good characteristics for 2537 Å excitation. In this case it might be claimed that better results might be obtained if calcium sulfate were used as a starting material for calcium salt. The advantages of this proposal may be summarized as follows:

1) Compared with the process in which calcium carbonate or nitrate is used as starting material, not so much calcium oxide remains after the firing, though the ratio ($CaO : WO_3$) is large enough, because calcium sulfate decomposes very slowly at 1000°C. (The vapor pressure of sulfur trioxide on calcium sulfate is a few millimeters at 1000°C[13].)

2) The calcium sulfate which might remain after the firing increases the brightness of the prepared phosphor as it is activated by tungstate.

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[11] T. Nishikawa et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **57**, 890 (1954); **58**, 256 (1955); **61**, 266 (1958).

[12] Y. Kotera and T. Sekine, ibid., **54**, 625 (1951).

[13] J. Zawadzki, *Z. anorg. u. allgem. Chem.*, **205**, 180 (1932).

3) The phosphor prepared by this procedure is in the form of very fine powder, the size being hardly measurable by an ordinary microscope.

These are advantages for 2537Å excitation, but for X-ray excitation different considerations are necessary. Under X-ray excitation it is necessary for the phosphor to absorb the X-ray, and it is clear that calcium sulfate has a smaller absorption coefficient than tungstate. From Figs. 2, 3 and 4 it is seen that calcium sulfate activated by tungstate has a weak emission when the amount of tungstate is small. However, advantage 1) mentioned above may, also be important in the case of X-ray excitation, because Nishikawa et al.[11] showed that the decay characteristic depends upon the residual amount of calcium oxide, while advantage 3) may be effective for the preparation of fine phosphor, which is used for X-ray intensifying paper with high resolution.

The effect of the addition of lead or magnesium may be considered for the preparation of calcium tungstate activated by lead or magnesium tungstate. In either case the results show that better phosphors could be prepared than by the ordinary process. It is remarkable that, when magnesium oxide is added to the mixture of calcium sulfate and tungstic acid, the firing temperature determines the characteristic of the product. It might be considered that a solid-state reaction between magnesium tungstate and calcium sulfate occurs. Similar results are obtained in the cases of zinc oxide and cadmium oxide, but in these cases the characteristic are determined by the mixing ratio, and these results could be explained by the formation of a solid solution between the products. The addition of molybdenum oxide causes a somewhat similar effect; the explanation for this case might be given by a combination of that one proposed by Kroeger[2] for the case of mixed crystals $CaWO_4 \cdot CaMoO_4$ and that other which may be concluded from the velocity difference between the solid-state reaction of calcium sulfate and tungstic acid and that of calcium sulfate and molybdenum oxide. It was unsuccessful to attempt to increase the sensitivity for X-ray excitation by the addition of barium sulfate.

The precipitating condition of calcium sulfate or the firing conditions has little influence upon the brightness, and it is shown that the repeated purification of tungstic acid or prefiring makes the brightness higher.

Magnesium sulfate, when activated by tungstate, shows the same characteristic as calcium sulfate. In this case it is necessary to lower the firing temperature, because magnesium sulfate decomposes thermally at a relatively lower temperature (the vapor pressure of sulfur trioxide on magnesium sulfate is reported to be 760 mmHg at 1213°C[14]), and so the firing must be done below 1100°C. It was possible to obtain a phosphor which has a higher brightness than that prepared by the ordinary process.

The authors wish to express their thanks to Dai-Nippon-Toryo Co. for the measurement of phosphor brightness under X-ray excitation.

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[14] H. J. Knopf and H. Staude, *Z. physik. Chem.*, **A204**, 265 (1955).