Studies on the Oxy-acid Phosphors. II. Vanadate Phosphors (Part 1)

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Introduction

Study of the vanadate phosphors was begun by R. Robl⁽¹⁾ who reported the emission of alkali-earth pyrovanadates. A. Schloemer,⁽²⁾ W. A. Weyl⁽³⁾ and L. Burns⁽⁴⁾ studied the magnesium and zinc vanadates, but the details of their preparations, characteristics, etc. are unknown. We prepared the vanadate phosphors and measured their brightness and emission spectra.

Experiments and Results

Purification of Ammonium Metavanadate and Metallic Salts.

In the preparation of the phosphor, a chemically pure grade of commercial ammonium metavanadate was used as one of the starting materials. The ammonium metavanadate was dissolved in a dilute solution of caustic soda (ca. 5%) until it was saturated. By the addition of recrystallized ammonium chloride to this solution, ammonium metavanadate was crystallized out, and filtered. After this purification procedure was repeated once more, the product was used as one of the batch materials for the dry process. For the wet process, the aqueous solution of this product was used.

Other batch materials were used for the purified metallic carbonate, oxide or hydroxide for the dry process, and for the wet one the aqueous solution of the purified metalic chloride or sulfate. A chemically pure grade of commercial metallic salts was purified as follows. Calcium, strontium or barium chloride was dissolved in water, the impurities due to iron and other heavy metals were removed by the usual chemical methods. This purification procedure was repeated once more, and the filtrate was used for the wet process. The sodium carbonate solution, which was treated in almost the same way as the purification procedure described above, was added to the purified metallic salt solution and the precipitated carbonate thus obtained was used for the dry process. When metallic oxide was needed, the carbonate was heated. The purification of zinc or cadmium sulfate solution was carried out in almost the same way as the procedure described above, except that hydrogen sulfide was passed until a small amount of zinc or cadmium sulfide was precipitated, and that the metallic zinc or cadmium was added to remove the traces of heavy metals which might be present.

As to magnesium salt, magnesium sulfate solution was purified in the same manner. For the dry process, purified basic magnesium carbonate or Merck's unpurified magnesium oxide was employed.

The purity of these batch materials was tested spectroscopically and colorimetrically.

Mixing and Firing

In the wet process, each metallic salt solution was added to the ammonium vanadate solution, and the metallic oxide or carbonate was mixed to the precipitated metallic vanadate in the agate mortar. As for the dry one, crystal of ammonium vanadate was mixed well with the metallic oxide or carbonate in the dry state. The mixed batch was heated at 640°C. for 2 hours.

The firing was done in air in the electric furnace. Three weight percent of ammonium perchlorate was added before firing, because the rise of brightness was expected.⁽⁵⁾

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1) R. Robl, *Z. Angew. Chem.*, **39**, 608 (1926).

2) A. Schloemer, *J. prakt. Chem.*, **133**, 51 (1932).

3) W.A. Weyl, *U.S. Pat.* 2,322,265; *Ind. Eng. Chem.*, **34**, 1035 (1942).

4) L. Burns, *U.S. Pat.* 2,452, 518.

5) Y. Kotera and T. Sekine, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **54**, 625 (1951). (in Japanese)

TABLE I

THE COLOR OF EMISSION OF PYROVANADATE PHOSPHORS

	3650 Å	2537 Å	cathode-ray or X-ray	previous results
$Ca_2V_2O_7$	no luminescence	blue	no luminescence	red brown (U. V.)[1]*
$Sr_2V_2O_7$	yellowish green	blue	white	yellow (U.V.)[1]
$Ba_2V_2O_7$	bluish green	yellowish green	bluish green	yellow (U.V.)[1]
$Mg_2V_2O_7$	yellow	yellowish brown	orange	—— §
$Zn_2V_2O_7$	yellow	orange	yellow	yellow[3, 4]
$Cd_2V_2O_7$	yellow	orange	yellow	——

A. Schloemer reported that calcium metavanadate emits the very weak luminescence of wine red color.[2]

§ A. Schloemer reported that magnesium metavanadate emits the green luminescence at –180°C.[2]

TABLE II

THE OPTIMUM MIXING RATIO OF PYROVANADATE PHOSPHORS

	Wet process (Metallic vanadate) : (MO or MCO_3)	Dry process (NH_4VO_3) : (MO or MCO_3)
$Ca_2V_2O_7$	10 : 1 (wt., CaO was used)	1 : 1.5 (mol., CaO was used)
$Sr_2V_2O_7$	10 : 1 (wt., $SrCO_3$)	1 : 1.25 (mol., $SrCO_3$)
$Ba_2V_2O_7$	10 : 1 (wt., BaO)	1 : 1.25 (mol., BaO)
$Mg_2V_2O_7$	2.5 : 1 (mol., MgO)	1 : 3.5 (mol., basic Mg carbonate)
$Zn_2V_2O_7$	1 : 1 (mol., ZnO)	1 : 2 (mol., ZnO)
$Cd_2V_2O_7$	1 : 1 (mol., $CdCO_3$)	——

TABLE III

THE RESULTS OF THE CHEMICAL ANALYSIS OF PYROVANADATE PHOSPHORS

	Experimental		Theoretical for $R_2V_2O_7$	
	V_2O_5	RO	V_2O_5	RO
Strontium pyrovanadate	36.4	56.0	46.74	53.26
Barium pyrovanadate	34.1	62.3	37.24	62.76
Zinc pyrovanadate	—	55.0	52.78	47.22

The Properties of Phosphors.

The colors of emissions of the heated products were listed in TAB. I, and the optimum ratios of mixing, when excited by the 2537Å excitation, were shown in TAB. II. It is common that, when oxy-acid phosphors were prepared, the nonstoichiometric compound gives the brightest phosphor by the ultraviolet excitation, and the results obtained might be explained by this rule. Especially, magnesium pyrovanadate showed the brightest value, when prepared with a great excess of magnesium oxide. For the upper three in TAB. II, the precipitates have the form of pyrovanadate ($R_2V_2O_7$), while, for the lower three, metavanadate ($R(VO_3)_2$).[6] The phosphors would be in the pyrovanadate form, and the results of the chemical analysis of some products in TAB. III support this idea. For zinc pyrovanadate, the results in TAB. III were near to the theoretical value for $Zn_3V_2O_8$, which was reported by W. A. Weyl,[3] and contains 57.20% of ZnO, but we consider that the phosphor itself would be in the form of pyrovanadate, in which the excess of ZnO might be present as solid solution.

The emission spectra of some phosphors were shown in Fig. 1, no correction being made on the spectral sensitivity of the photographic plate, and, since their exposure times were not the same, their relative intensity can not be compared strictly. Their spectral range is fairly wide, and this property may be advantageous for practical uses. Further, the emissions of zinc and cadmium pyrovanadates are rather stronger than the others.

As zinc pyrovanadate seemed to be better from the standpoint of application, the preparation of zinc pyrovanadate was studied in detail.

The Preparation of Zinc Pyrovanadate Phosphors.

Both dry and wet processes were tried and the brightness of the samples produced was measured by the apparatus as illustrated in Fig. 2, under the excitation by a low-pressure mercury discharge lamp through the filter Corning No. 7–54, whose spectral transmission is shown in Fig. 3. The reflections from samples were calibrated by measuring the reflection from magnesium oxide, which shows no luminescence. The relative value of

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[6] J.W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry" (1922) Vol. IX p. 768.

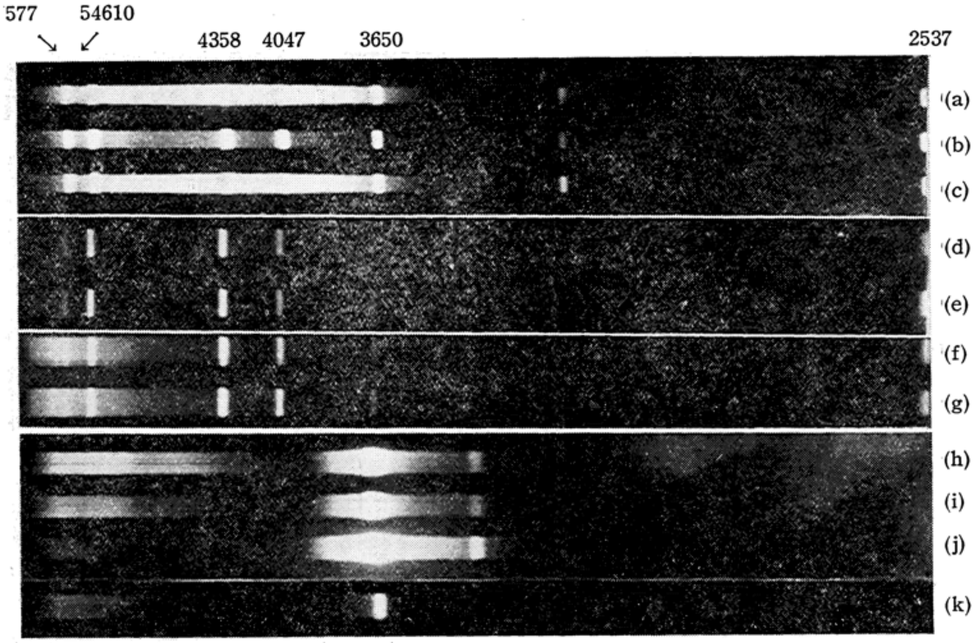


Fig. 1. The emission spectra of vanadate phosphors

(a) $Ca_2V_2O_7$, (b) $Ba_2V_2O_7$, (c) $Ca_2V_2O_7$, (d) $Sr_2V_2O_7$, (e) $Mg_2V_2O_7$, (f) $Zn_2V_2O_7$ (g) $Cd_2V_2O_7$ (h) $Ba_2V_2O_7$ (i) $Sr_2V_2O_7$ (j) $Mg_2V_2O_7$, (k) $Cd_2V_2O_7$

(a)—(g): excited by 2537Å

(h)—(k): excited by 3650Å

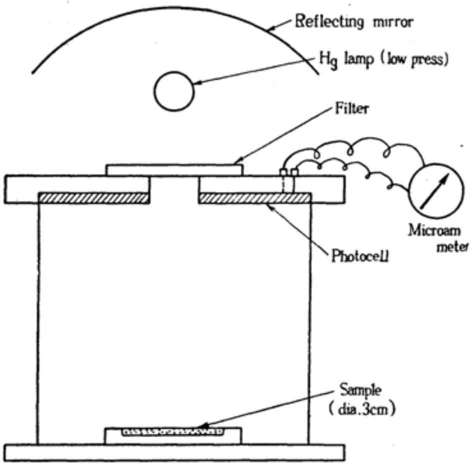


Fig. 2. The apparatus for the measurement of the relative brightness.

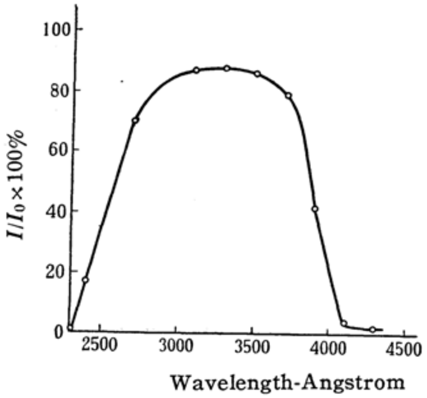


Fig. 3. The spectral transmission curve of the filter, Corning No. 7-54.

brightness was noted, the brightest sample being taken to be 10, while the value of commercial zinc beryllium silicate showed the value 17–20. In the dry process, purified ammonium vanadate and zinc carbonate were mixed well in the agate mortar, 1.2–3 folds of the latter being taken in the molar ratio, and fired 2 hours at 600°C. Results are listed in Tab. IV.

In the wet process, 2 parts of a 5% solution of purified ammonium vanadate were poured into 1 part of a 20% solution of purified zinc sulfate. In some cases alkali was added to the former, and in the other acid was added to the latter, and the effect of *p*H during the precipitation on the brightness of the fired samples was examined. 1 mol. of the precipated zinc metavanadate thus tobained was mixed with 1 mol. of purified zinc oxide, then fired for 2 hours at 600°C. Results are shown in TAB. V.

TABLE IV

THE BRIGHTNESS OF ZINC PYROVANADATE PHOSPHORS IN DRY PROCESS

The molar ratio	brightness
$NH_4VO_3 : ZnCO_3 = 1 : 1.2$	2
$= 1 : 1.5$	3
$= 1 : 1.8$	9
$= 1 : 2.0$	9
$= 1 : 2.5$	7
$= 1 : 3.0$	6

TABLE V

THE BRIGHTNESS OF ZINC PYROVANADATE PHOSPHORS IN WET PROCESS

pH by the precipitation	brightness
ammonia alkali	9
neutral	10
acidic	9

The effects of adding some heavy metals to phosphors were investigated on the samples obtained by the wet process. Various amounts of heavy metals were added to the precipitate and the mixtures were fired in the same manner as described above. TAB. VI shows the change of

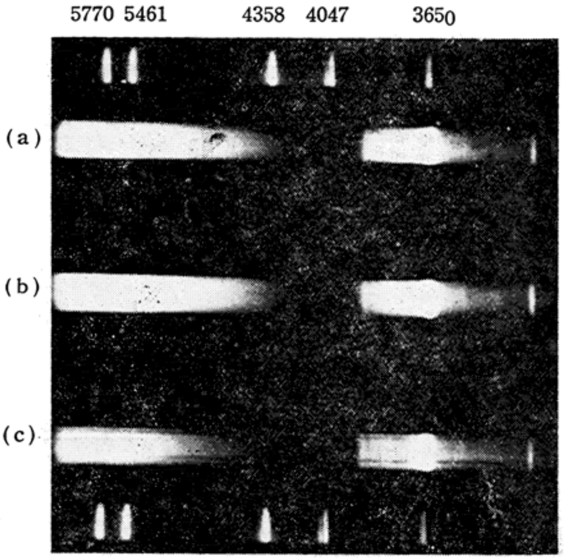


Fig. 4 The emission spectra of zinc pyrovanadate phosphors

Fig. 4—I. The emission spectra.

Fig. 4—II. The microphotometer curve

(a) $Zn_2V_2O_7$ Ag

(b) $Zn_2V_2O_7$ Pb

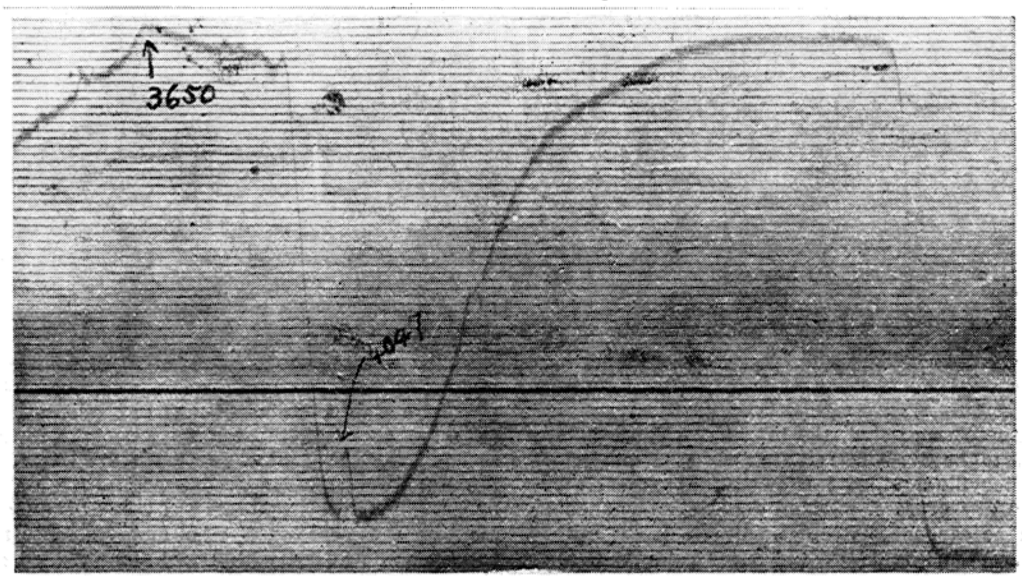
(c) $Zn_2V_2O_7$ Sn

TABLE VI

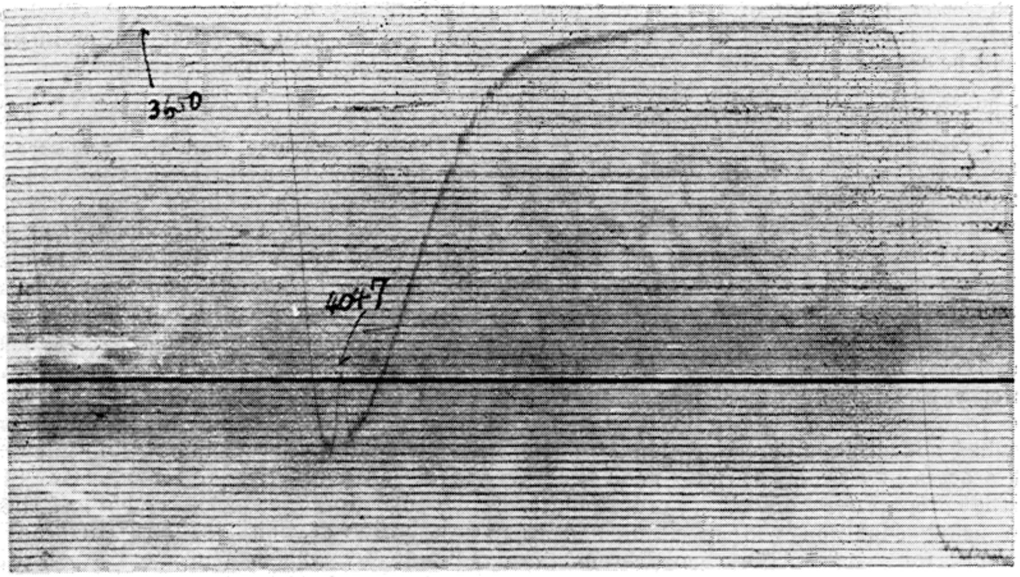
THE EFFECTS OF THE HEAVY METALS ON THE BRIGHTNESS OF ZINC PYROVANADETE

Concentration (mol %) Heavy metals	0.01	0.05	0.1	0.25	0.5	5
Ag	8	10	9	7	7	—
Cu	—	7	—	4	—	—
Pb	10	6	10	8	—	—
Bi	6	4	4	—	7	—
Mn	—	7	—	4	—	—
Sn	8	10	8	8	7	4
Ni	—	7	—	—	—	—
Ce	—	7	—	7	—	—

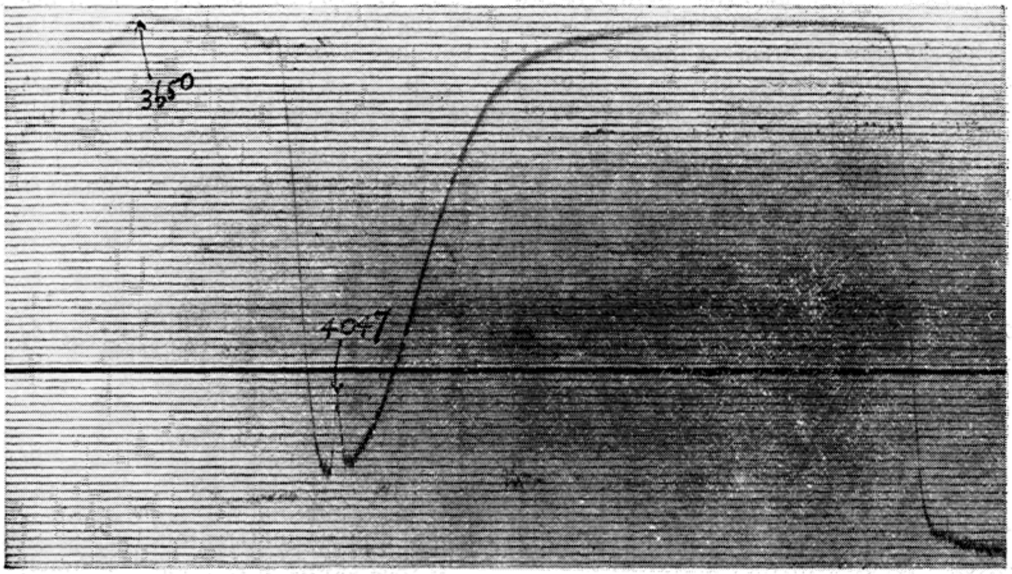
(a) $Zn_3V_2O_7$ Ag



(b) $Zn_2V_3O_7$ Pb



(c) $Zn_3V_2O_7$ Sn



brightness, when the amounts of heavy metals were changed from 0.01 to 5 mol. % for 1 mol. zinc pyrovanadate. The emission spectra of some samples were shown in Fig. 4, no correction being made on the spectral sensitivity of the photographic plate.

These results indicate that the wet process gives somewhat better results than the wet one in the preparation of zinc pyrovanadate phosphors and the greatest brightness is about a half of that of commercial zinc beryllium silicate, and the heavy metals scarcely change the emission spectra but have the effect of intensifying the brightness.

Discussion

According to Robl, calcium, strontium and barium pyrovanadates show the emission of colors listed in Tab. I. These discrepancies of colors with our results are difficult to explain. As for calcium pyrovanadate, we could recognize its luminescence at 3500–5850Å only by the 2537Å excitation, and could not obtain such a calcium pyrovanadate as emits the red-brown luminescence under any kind of excitation method. Robl found the range of luminescence of strontium pyrovanadate to be 6000–4830Å and that of barium salt 6000–4570Å, while we recognized the luminescence at 4370–5830Å and 3900–5850Å respectively. Strontium pyrovanadate phosphor may be of use for the single white luminescent material for the Braun tube, but its brightness is much lower than that of the current phosphors, and further studies of its preparation should be made.

We found that magnesium, zinc and cadmium pyrovanadates emit the luminescence whose characteristics are shown above. It is to be noted that magnesium pyrovanadate phosphor was prepared with a great excess of magnesium oxide, like the case of other oxy-acid phosphors, for example, tungstate phosphors. Zinc and cadmium pyrovanadate phosphors are excited both by 2537Å and 3650Å, and, if they are used in the fluorescent lamp, ultraviolet radiation from it will decrease, and this might be the reason why zinc pyrovanadate phosphor is used in the so-called nonactinic fluorescent lamp.⁴⁾ The wet process gives comparatively good results in the preparation of zinc pyrovanadate. The firing condition will be studied more precisely, for example, the atmosphere of the firing.

It is ascertained that zinc pyrovanadate shows a slight change of distribution of emission by the addition of heavy metals, and other pyrovanadate phosphors showed similar results. We conclude that the pyrovanadate salts belong to the phosphors of unactivated type similar to the tungstate phosphors. This conclusion is supported by other experiments, for example, by the measurements of the temperature dependence of the intensity of luminescence.⁷⁾ Their emission centers may be vanadium, or in precise expression, pyrovanadate radical.

Summary

The preparations and the measurements of the general characteristics of the pyrovanadate phosphors have been carried out. When excited by the ultraviolet, zinc pyrovanadate shows a relatively strong emission. Strontium pyrovanadate emits white color on irradiation by the cathode ray. Magnesium, calcium, barium, and cadmium salts show emission by the various methods of excitation. It has been suggested that pyrovanadate phosphors belong to the unactivated type similar to the tungstate phosphors.

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7) S. Makishima, J. Yamanouchi, T. Mukaibo, S. Shionoya; ***Ann. Rep. Eng. Res. Institute,*** University of Tokyo, 9, 33 (1951).