Activations by Anions in the Oxy-acid Phosphors. III. Activations by the Vanadate Ion

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In previous papers[1] it was found that anionic centers are present in the oxy-acid phosphors and that the activation by vanadate might be one of " intraionic activation ", then the luminescence would originate from the electron transitions in the vanadate ion. The activation by vanadate ions has been reported by a few researchers[2,3], but in most cases the activation has been assumed to be caused by vanadium ions[2]. We have prepared some magnesium compounds activated by vanadate ions and have obtained some remarkable results.

The Experiments and their Results

Preparation of Phosphors and the Measurements of their Characteristics.—The starting materials were MgO, $(NH_4)_2SO_4$, $SiO_2 \cdot nH_2O$, $(NH_4)_2HPO_4$, NH_4VO_3, As_2O_3, Sb_2O_3, H_3BO_3 and H_2WO_4, which had been purified by the process previously reported[3]. They were mixed in a dry state and fired in air. The spectral distribution was measured by means of a spectroradiometer[4], the brightness was measured by a photocell, and the crystal structure was determined by an X-ray diffractometer.

Activation of Magnesium Compounds by Vanadate Ions.—Magnesium sulfate, silicate or pyrophosphate, was prepared by the reaction between magnesium oxide and oxy-acidic compound. Other phosphates (orthophosphate or halophosphate) or silicates were proved to be worse than those described above. Their spectral distributions are almost the same as that of magnesium vanadate, and their brightnesses are shown in Table I, while their X-ray patterns are shown in Fig. 1.

Effect of the Addition of other Components to Magnesium Silicate Activated by Vanadate Ions.—Magnesium silicate was activated by two ions among the vanadate, phosphate, arsenate, antimonate, germanate and borate ions. Magnesium oxide and amorphous silica were mixed in the molar ratio of 1 : 1.1, and two

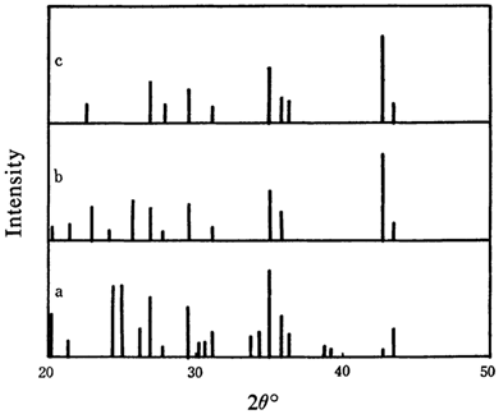

Fig. 1. X-Ray diffraction patterns of magnesium compounds activated by vanadate ions.

		g.		g.		g.
(a)	MgO	1.0	$(NH_4)_2SO_4$	0.7	NH_4VO_3	0.3
(c)	MgO	2.0	$(NH_4)_2HPO_4$	0.4	NH_4VO_3	0.3
(b)	MgO	1.5	SiO_2	0.7	NH_4VO_3	0.3

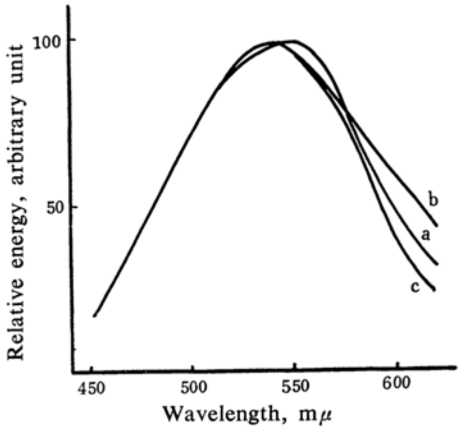

Fig. 2. Spectral distributions of magnesium silicate activated by vanadate and other ions.
(a) Activation by vanadate ions
(b) Activation by vanadate and phosphate ions
(c) Activation by vanadate and arsenate ions

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[2] H. Gobrecht and G. Heinsohn, *Z. Physik*, 147, 350 (1957).

[3] R. Robl, *Z. angew. Chem.*, 39, 608 (1926) ; A. Schloemer, *J. prakt. Chem.*, 133, 51 (1932) ; Y. Kotera and T. Sekine, This Bulletin, 27, 13 (1954) ; S. Rothschild, *Brit. J. Appl. Phys.*, 1955, Supplement No. 4, S. 32.

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

Table I. Optimum conditions for preparation of magnesium compounds activated by vanadate ions and their brightness

Matrix	Optimum mixing ratio mol.			Firing temp. °C	Relative brightness*
Mg silicate	MgO 1.5	SiO_2 0.7	NH_4VO_3 0.3	1050	70
Mg phosphate	MgO 2.0	$(NH_4)_2HPO_4$ 0.5	NH_4VO_3 0.2	1050	85
Mg sulfate	MgO 1.0	$(NH_4)_2SO_4$ 0.8	NH_4VO_3 0.2	1000	160

* The value of 100 corresponds to the brightness of a magnesium pyrovanadate phosphor.

Table II. Emissions of magnesium silicate activated by two kinds of anions

	$V_2O_7^{4-}$	PO_4^{3-}	AsO_4^{3-}	$Sb_2O_7^{4-}$	GeO_4^{4-}	BO_3^{3-}
$V_2O_7^{4-}$	Yellow m*[1]	Yellow m (11)*[2]	Yellow m (15)	Yellow m (10)	Yellow m (10)	Yellow m (9)
PO_4^{3-}		Yellow ff*[1]	None	Pink ff	None	None
AsO_4^{3-}			Red f*[1]	Pink ff	White ff	Red f
$Sb_2O_7^{4-}$				Yellow ff*[1]	White ff	None
GeO_4^{4-}					Yellow ff*[1]	None
BO_3^{3-}						None*[1]

*[1] Activated by one kind of anions.

*[2] Relative brightness under 2537 Å excitation.

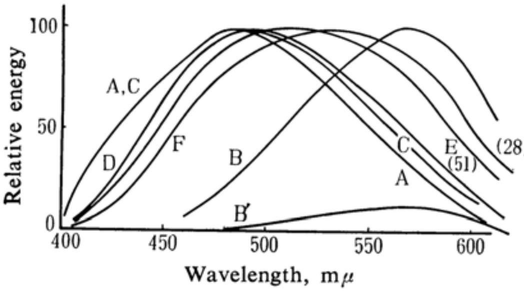

Fig. 3. Spectral distributions of the system of $MgWO_4$-$Mg_2V_2O_7$: A, $MgWO_4$; B, $Mg_2V_2O_7$; C, Calculated from A and B for the mixture of A and B with equivalent molar ratio; D, $MgWO_4$ 0.95+$Mg_2V_2O_7$ 0.05 (mol.); E, $MgWO_4$ 0.7+$Mg_2V_2O_7$ 0.3 (mol.); F, $MgWO_4$ 0.5+$Mg_2V_2O_7$ 0.5 (mol.); B′, Relative value of B to A.

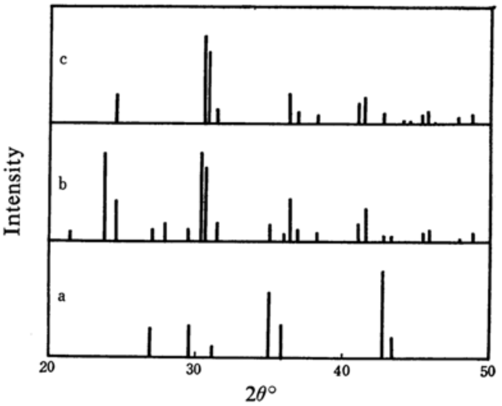

Fig. 4. X-Ray diffraction patterns of the system of $MgWO_4$-$Mg_2V_2O_7$.
(a) $Mg_2V_2O_7$
(b) $Mg_2V_2O_7$ 0.5+$MgWO_4$ 0.5
(c) $Mg_2V_2O_7$ 0.05+$MgWO_4$ 0.95

ions were added to it, each amount being 0.005 mol. per 1 mol. magnesium oxide. They were fired at 1100°C for 4 hr.; the spectral distributions measured are shown in Fig. 2, and the brightness of some of them, in Table II. The color of emission is tabulated in Table II.

The Spectral Distributions of Mixed Crystal $MgWO_4$-$Mg_2V_2O_7$.—The system of $MgWO_4$-$Mg_2V_2O_7$ was examined to clarify the activation effect of the vanadate ion. Mixtures of magnesium oxide, tungstic acid and ammonium vanadate were fired at 1050°C for 2 hr. The spectral distributions of these phosphors are shown in Fig. 3, in which the numbers attached to the curves represent the relative height at their peaks. The X-ray patterns of some products are shown in Fig. 4.

Discussion

The activation by the vanadate ion in alkali or alkali earth vanadate has been studied by us and by others[2,3], but for other compounds few patents[5] have been found. We prepared various magnesium compounds activated by the vanadate ion, and, when a large amount of vanadate compound was added to them, some of these compounds had a higher brightness than that of pure magnesium metavanadate. In the latter case, it might be concluded from a consideration of the case of the calcium sulfate-calcium tungstate system[6], in which the content of tungstic acid is high, that a

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[5] W. A. Roberts, U. S. Pat. 2312265; French Pat. 869448.

[6] Y. Kotera, T. Sekine and M. Yonemura, This Bulletin, 35, 580 (1962).

part of the product is activated by the vanadate ion. The formation of magnesium metavanadate was proved crystallographically in Fig. 1, in contrast to the calcium sulfate-calcium tungstate system, while it was difficult in the latter case to prove the formation of tungstate by means of X-ray analysis because of the structural similarity of the components.

The effect of the addition of other anions to magnesium silicate is relatively small, but it may be concluded that other anions cause the variation in brightness and a small shift in the spectral distribution of the emission.

The system of $MgWO_4$-$Mg_2V_2O_7$ shows almost the same characteristics as the results obtained when zinc or cadmium oxide is added to calcium sulfate activated by a tungstate ion[6]. Those results might be explained by the formation of a solid solution between the constituents, but it was difficult to know its formation from the X-ray pattern shown in Fig. 4.

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