Activations by Anions in the Oxy-acid Phosphors. I. General Consideration and Preliminary Experiments

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(Received August 10, 1961)

Activations by Anions in the Phosphors.—In the case of sulfide phosphors, it has been said that an anion of, for examaple, halogen, oxygen, phosphorus or arsenic ion, may act as an activator. Kroeger and Hellingman1) showed for first time that the ions Cl^-, Br^- and I^- play an essential part in the blue centers of ZnS phosphors. They introduced the orbital energy diagram for zinc sulfide with blue centers and attributed the blue emission to the electron transition between the conduction band and the activator level which is introduced by the blue centers. They assumed the following three possibilities for the configurations giving rise to the localized activator level, viz., A^+X^-, A^+ or X^-, together with their respective surroundings, where A^+ stands for metallic ion and X^- for halogen. Also they2) determined chemically the chlorine present in phosphors and claimed that this finding would support their assumption of a blue centers. Further, Kroeger and Dikhoff3) investigated the activation by the oxygen ion in zinc sulfide matrix. They established that the incorporation of zinc oxide in zinc sulfide causes the appearance both of a new absorption band and, in the presence of activators, of new fluorescence bands displaced about 150 Å toward long wavelengths with respect to the original bands. They explained these effects by the assumption of local oxygen levels and of new centers consisting of associated pairs of oxygen and activator ions. In addition, Bube, Riehl and several other researchers4) have also studied the action of halogen and oxygen ions. Subsequently McKeag and Ranby5) reported the activation of zinc sulfide by phosphorus and Prener6), its activation by arsenic; both phosphors were proposed for use as a single white screen for television and also for the preparation of transparent luminescent screens. Besides zinc sulfide, the activation by polysulfide ions in the matrix of sulfides and sulfates of alkali and alkali earth was found by Gobrecht and Hahn7). They assumed that in all cases the polysulfide compound was formed and that the red emission in these phosphors is to be attributed to the polysulfide formation, concluding that these emissions are the same as those occurring in pure tungstate or uranyl compounds. Meanwhile, Thomson8) assumed that the emission of pure zinc oxide required the presence of sulfide ion; Kroeger and Dikhoff3), however, denied this assumption on the basis of their investigations.

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2) F. A. Kroeger and J. E. Hellingman, ibid., **95**, 68 (1949).

3) F. A. Kroeger and J. A. M. Dikhoff, *J. Electrochem. Soc.*, **99**, 144 (1952).

4) R. H. Bube, *Phys. Rev.*, **80**, 655, 764 (1950); **90**, 70 (1953); *J. Chem. Phys.*, **19**, 985 (1951); **20**, 708 (1952); F. A. Kroeger, *Physica*, **16**, 297 (1950); H. A. Klasens, *J. Electrochem. Soc.*, **100**, 72 (1953); N. Riehl and H. Ortmann, *J. phys. radium*, **17**, 620 (1956); N. T. Melamed, *J. Phys. Chem. Solids*, **7**, 146 (1958).

5) A. H. McKeag and P. W. Ranby, *Trans. Electrochem. Soc.*, **96**, 85 (1949).

6) J. S. Prener, *J. Electrochem. Soc.*, **98**, 406 (1951).

7) H. Gobrecht and D. Hahn, *Z. Physik*, **132**, 111 (1952); **135**, 523 (1953).

8) S. T. Thomson, *J. Chem. Phys.*, **18**, 770 (1950).

Activations by Anions in the Oxy-acid Phosphors.—It has not yet been reported that activation by anions occurs in the oxy-acid phosphors. We can, however, find in the literature some experimental results which might be explained by assuming this activation, although the authors have not expressed this idea. One of them was described above; that is, Gobrecht and Hahn[7] found the activation by polysulfide ion in alkali earth sulfates. We suppose that the effect of the existence of sulfur upon the emission of aluminosilicate, which was reported by Kirk[9], might be the same activation as that reported by Gobrecht and Hahn. Tungstate, molybdate, vanadate and uranyl ions act as activators in the oxy-acid phosphors, and we could find some corroborative findings, one of which is that presented by Gobrecht and Weiss[10] regarding alkali earth tungstate and molybdate activated by the uranium compound, and another of which is reported for calcium borate[11] or halophosphate[12] activated by the tungstate compound. Further, we would like to propose that titanium or manganese ion in higher valency acts as an activator[13] which should be thought of as an anion. This idea might be partially supported by the fact that titanium in higher valency acts as an activator only when the matrix makes an eutectic compound with the titanate compound (Kroeger[13]). Also, we might explain the effect of the phosphorus[14] or arsenic[15] ion upon the emission of zinc silicate activated by manganese as the occurrence of anionic activation by the phosphorus or arsenic ion.

It is, however, very difficult to conclude the anionic activation from these results because of the lack of reliable experimental facts for the occurrence of this activation. We thought that anions might be able to give localized levels between the filled and conduction bands in those matrices, and so act as activators, when they have a smaller electron affinity than that of the oxy-anions which compose the host crystal. We have prepared various oxy-acid phosphors activated by anions and have obtained some remarkable results[16].

Experimental

Selection of Matrices and Activators.—First, it was necessary to determine what kind of matrices and activators should be selected. Two types of matrices were used, the sulfates of alkali earth metals and magnesium, and the silicates of alkali earth metals, magnesium and zinc. It was thought that these anions might have a greater electron affinity; also, they were not expected to decompose during firing at relatively high temperatures. For the electron affinity of oxy-anions there are few data, but we presumed that, if two salts were prepared from two anions with a common metal ion and if the fundamental absorption of one salt has an edge at a shorter wavelength than the second, then the former would have a greater electron affinity than the latter. From this idea we supposed that a sulfate or silicate ion would have the greater electron affinity among the oxy-acid anions. As to decomposition during the firing, the facts that calcium[17] or magnesium[18] sulfate decompose partially above 1000°C and that strontium or barium sulfate behaves similarly, would be overcome by lowering their firing temperatures.

As activators, silicate, phosphate, borate, carbonate and sulfide were used, because they surely exist in the matrix as anions. Also tungstate, molybdate, vanadate and germanate ions were tried, as they probably exist in the matrix as anions; further, arsenate, antimonate[19] and aluminate[20] ions were tried, because they are anionic components of the phosphor matrix.

Preparation of Phosphors.—Sulfates of alkali earth metals were precipitated by mixing a purified ammonium sulfate solution with a purified solution of alkali earth salts. In the purification, precaution was taken, by the addition of distilled hydrogen chloride, that the residue of sulfide used for the purification was thoroughly decomposed. In the precipitation, the sulfate solution was poured into the metallic solution and the precipitation was stopped, when the latter solution was slightly in excess, in order to obtain a precipitate with an excess of cations. The silicate matrices were prepared by a well-known process. Magnesium sulfate was prepared by solid-state reaction between purified magnesium oxide and ammonium sulfate. The purity of raw materials was ascertained spectroscopically.

As activators, the following salts were used: $SiO_2 \cdot nH_2O$, $(NH_4)_2HPO_4$, H_3BO_3, metallic carbonate, metallic sulfide, $WO_3 \cdot nH_2O$ or metallic tungstate, MoO_3, NH_4VO_3, GeO_2, As_2O_3, Sb_2O_3 and $Al(OH)_3$. They were purified by a well-known process or by the process previously reported[19,20]. Metallic sulfides were prepared by the reaction between the metallic sulfate and a reducing agent, the details being described in the following report.

In general the amount of activators was optimum at 0.01 to 0.1 mol. per 1 mol. of sulfate and

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0.001 to 0.05 mol. for silicate. Some results were obtained in which emission colors were different among samples activated by different amounts of activator.

We could not obtain conclusive results for the form of activator. In the following tables we have used the form which is commonly found for an anion.

Flux was seldom used, and it was found in the following experiments that it has little effect.

Firing was done in air, except for special cases, for 2 to 4 hr. at 1100°C. For the activation of calcium sulfate by vanadate or carbonate ion, firing was done at 500°C, and for barium sulfate activated by carbonate ion, at 900°C, while the firing for the preparation of magnesium sulfate phosphors was carried out at 1000°C.

Results

The reselts are shown in Tables I and II for two kinds of matrices. Most of these emissions are excited both by 2537 and 3650 Å; some of them have the emissions only under 2537 Å excitation, whereas magnesium silicate activated by antimonate ion has emission only for the excitation by 3650 Å. In general, the emission under 2537 Å is stronger than that under 3650 Å.

Discussion

It was confirmed that in oxy-acid phosphors anionic centers are present, though their luminescence is weak in most cases. From the results obtained we suggest that anionic activators are to be divided into two group as follows:

1. The first group might be called "intra-ionic activation". They have emissions almost identical with those found in the matrices whose anion is identical with the activating one. The luminescence originates in this group from the electronic transition in the anions. The activations by tungstate and molybdate ions are typical examples of this group, and that by vanadate may belong to it too.

2. The other group might be called "inter-ionic activation". Their emissions have various colors, depending upon the matrices, even for the same activator. This activation occurs when the electron affinity of the activating anions is smaller than that of the host crystal anions. Some ions of this group show a tendency for the emission color to shift to a longer wavelength in the order of calcium, strontium and barium. Phosphate, germanate,

TABLE I. EMISSIONS OF SULFATES ACTIVATED BY ANIONS

Matrix	Activator						
	WO_4^{2-}	MoO_4^{2-}	$V_2O_7^{4-}$	PO_4^{3-}	AsO_4^{3-}	$Sb_2O_7^{4-}$	GeO_4^{2-}
$CaSO_4$	Blue s	Yellowish green	None	White f	Yellow f	Red m	Greenish white f
$SrSO_4$	Bluish white m	Yellow m	None	White ff	White ff	Pink ff	White ff
$BaSO_4$	None	None	None	Yellow f	Blue ff	Blue ff	Red m
$MgSO_4$	Bluish white s	—	Yellow m	Red f	Red f	—	Red f

Matrix	Activator					
	SiO_4^{2-}	CO_3^{2-}	BO_3^{3-}	AlO_2^-	S^{2-}	SO_3^{2-}
$CaSO_4$	Greenish white f	Blue ff	White ff	Blue ff	Blue m	Bluish white
$SrSO_4$	White ff	Yellow ff	White ff	White ff	Bluish white f	Yellow f
$BaSO_4$	Blue f	None	White f	White f	Orange m	Orange f
$MgSO_4$	Yellow f	—	None	Blue f	—	—

TABLE II. EMISSIONS OF SILICATES ACTIVATED BY ANIONS

Matrix	Activator					
	$V_2O_7^{4-}$	PO_4^{3-}	AsO_4^{3-}	$Sb_2O_7^{4-}$	GeO_4^{4-}	BO_3^{3-}
$CaSiO_3$	Yellow ff	None	None	None	None	Yellow ff
Ca_2SiO_4	None	Red m	Red m	Red ff	Red m	Red m
$BaSi_2O_5$	Yellow f	Yellow f	Yellow f	Bluish white f	Yellow f	Bluish white f
$Ba_2Si_3O_8$	Yellow m	Yellow f	Yellow f	Yellow f	Yellow f	Yellow f
$MgSiO_3$	Yellow m	Yellow ff	Red f	Yellow ff	Yellow ff	None
Zn_2SiO_4	Yellow f	Yellow f	Yellow f	Yellow f	Yellowish white	Yellow f

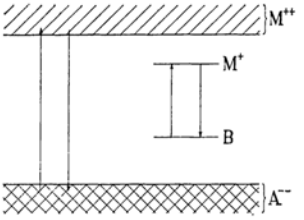

Fig. 1 Energy band model for intraionic activation.

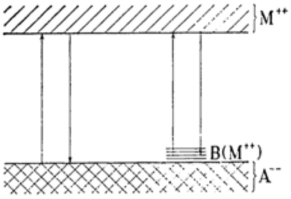

Fig. 2. Energy band model for interionic activation.

aluminate, sulfide and sulfite ions tend to show this tendency.

Phosphors with intraionic activation have a rather strong emission and it might be found that such activation occurs in phosphors which have been studied by other researchers who have assumed them to be activated by other sources[11,12] We assume an energy band model for this group like the one in Fig. 1. This activation may correspond to the activation by divalent manganese or rare earth ions in the case of cationic activation.

In interionic activation, it is difficult to find the relation between the emission and the composition of phosphors because of the weak emission intensity. However, in some cases the regularity is found according to the ionization potential of the cations which compose the matrices. In many cases the emission of this group shows a wide distribution. Such an activation has rarely been found before, the sulfide activation being the only case in this group, but it is not clear whether the sulfide activation belongs to this group or not. We assume an energy band model for the interionic activation as in Fig. 2. Because of the complex structure of the activating anions, their energy levels may be complicated, in turn causing the broadening of the spectral distribution of emission.

Compared to cationic activation, it was found that the amount of activators is considerably large in anionic activation; this may be due to the more complex structure of the anions.

The authors wish to express their thanks to Professor S. Makishima for his general discussions on the subject and on some of their experimental work.

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