[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Radioactive Tracer Study of Activator Distribution in Infrared Phosphor Systems: The Effect of Oxide and Calcium Ions[1]

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The distribution of the activators Eu^{2+} and Sm^{3+} in the system (Sr, Ca) S(s)—($Sr^{2+} + Cl^{-} + O^{2-} + Ca^{2+}$) (liq.) has been studied as a function of the concentration of calcium ions. It has been shown that the presence of calcium ion in the melt counteracts to some extent the influence of the oxide ion which lowers the concentration of the activators in the solid phase. The effect is more pronounced with Sm^{3+}. The phenomenon can be explained on the assumption of the formation of ion pairs or complex ions in the melt. The role played by these factors in the preparation of certain phosphors is indicated.

One of the problems in the art of phosphor preparation has been the selection of a suitable flux.[3] The method of selection has been largely empirical, guided by intuition and limited by specific properties of the phosphor system. The first, useful, infrared-sensitive phosphor produced by Urbach[4] was essentially strontium sulfide with samarium and europium as activators. The strontium sulfide was prepared by the Lenard method which was known to give a product containing large amounts of strontium sulfate. Calcium fluoride was the added flux but it was later shown[5] that the flux system was the reciprocal salt pair CaF_2–$SrSO_4$. The same flux system was originally used in the preparation of the strontium selenide, samarium–europium phosphor.[6] In subsequent investigations of these phosphor systems,[7,8] strontium chloride was substituted as flux mainly to eliminate the likely formation of oxide ion and to permit a more precise determination of activator concentrations. It had been observed, however, that the use of a calcium salt as flux frequently appeared to counteract the harmful effect of the presence of oxide in these phosphors. Since the effect of oxide on the efficiency of the phosphor has been shown to be due to its influence on the activator distribution between the flux and the strontium sulfide,[9] it appeared likely that the calcium ion was also capable of affecting the distribution of the activators. In this paper are presented the experimental data for the distribution of europium and samarium between solid strontium sulfide and a melt of strontium chloride containing various quantities of oxide and calcium ions.

The system is somewhat complicated. Starting with a mixture $SrS + SrCl_2 + SrO + CaCl_2$ we obtain on heating at 1000° a heterogeneous mixture consisting of a solid phase (Sr, Ca)S[10] and a liquid phase containing the ions Sr^{2+}, Ca^{2+}, Cl^{1-}, O^{2-}, S^{2-}. Changes in the distribution of the activator ions Eu^{2+} and Sm^{3+} between these two phases was to be determined with varying amounts of oxide and calcium ions. The composition of the solid phase was not determined, but precautions were taken to see that no solid calcium oxide would be formed in the equilibrium mixture.

Experimental

Materials.—The strontium oxide, sulfide and chloride, the calcium oxide and the radioactive tracers were the same as those previously described.[9,10] The anhydrous calcium chloride was made from purified calcium chloride hexahydrate by drying in a stream of hydrogen chloride the temperature being raised slowly to 600°.

The Solubility of Calcium Oxide in Strontium Chloride.—The solubility of calcium oxide in strontium chloride at 1000° was determined by the high temperature filtration method.[11] The oxide in the filtrate was estimated by adding excess standard hydrochloric acid and back titrating with standard sodium hydroxide. The chloride was determined by the Mohr method. The results of three determinations gave the value 9.4 ± 0.1 mole per cent. of calcium oxide in the melt.

An attempted application of the mass action law in the precipitation of calcium oxide from $SrCl_2$–SrO–$CaCl_2$ mixtures was not very satisfactory. Calculations indicated that a mixture of composition 24 moles SrO, 76 moles $SrCl_2$ and 22 moles $CaCl_2$ should on fusion at 1000° give a liquid phase having a ratio weight of oxide/weight of chloride = 0.0280. The experimental value was 0.0314. Another mixture containing 24 moles SrO, 76 moles $SrCl_2$ and 41 moles $CaCl_2$ should give a theoretical ratio of 0.0117 while the ratio actually found was 0.0260. These data are only approximate and are reported here because they indicate that the solubility of calcium oxide is somewhat greater in fused strontium chloride containing excess calcium ions than it is in strontium chloride alone. In the experiments on activator distribution, however, the oxide and calcium ion concentrations were always less than could be required for precipitation of calcium oxide assuming the solubility product of calcium oxide in strontium chloride to be 4.6×10^{-3}.

Pearlman, Goddard and Urbach[12] have shown conclusively that the activator ion Bi^{3+} is removed from strontium sulfide and transferred to strontium oxide when a mixture containing these two solid phases is fluxed with strontium chloride. The transfer is so complete that the emission spectrum of the phosphor SrS–Bi is supplanted by that of the phosphor SrO–Bi even with very small proportions of solid strontium oxide.

Mixtures of the compounds SrS, $SrCl_2$, SrO and $CaCl_2$ were made in a dry-box by grinding in a porcelain mortar. The strontium chloride contained the activator element. Europium was not reduced to the divalent ion prior to the heating process[13] so that direct comparison with the phosphor preparation could be made. The intimately mixed powders were placed in the high temperature filtration apparatus[9] and heated for 1.5 hours and filtered over a period of one hour. The samples were prepared for counting and the analyses were carried out as previously described.[9]

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[1] Abstracted from a thesis by Arthur Dreeben submitted to the Graduate School of the Polytechnic Institute of Brooklyn, 1950, in partial fulfillment of the requirements for the degree of Master of Science.

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[3] Discussions of fluxes in general will be found in H. W. Leverenz, "Luminescence of Solids," Chapter 3, John Wiley and Sons, Inc., New York, N. Y., 1950, and Peter Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., pp. 516, 594.

[4] F. Urbach, D. Pearlman and H. Hemmendinger, *J. Optical Soc. Am.*, **36**, 372 (1946).

[5] W. Primak, R. K. Osterheld and R. Ward, THIS JOURNAL, **69**, 1283 (1947).

[6] A. L. Smith, R. D. Rosenstein and R. Ward, *ibid.*, **69**, 1725 (1947).

[7] K. F. Stripp and R. Ward, *ibid.*, **70**, 401 (1948).

[8] H. Texin, H. Williams and R. Ward, *ibid.*, **71**, 2494 (1949).

[9] J. Prener, R. W. Mason and R. Ward, *ibid.*, **71**, 1803 (1949).

[10] W. Primak, H. Kaufman and R. Ward, *ibid.*, **70**, 2043 (1948).

[11] R. W. Mason, C. F. Hiskey and R. Ward, *ibid.*, **71**, 509 (1949).

[12] D. Pearlman, P. E. Goddard and F. Urbach, *J. Optical Soc. Am.*, **39**, 695 (1949).

[13] J. Prener, THIS JOURNAL, **72**, 2692 (1950).

No attempt was made to separate calcium and strontium in the analyses, but the total cation was determined for residue and filtrate.

In most instances two determinations were made at slightly different temperatures. At the higher temperature the value of K_t was invariably smaller but only the average value is reported here.

The Effect of Calcium Ions on the Distribution of Europium.—To provide a basis for comparison, the compositions of the mixtures were made the same as those previously studied.[9] Each sample contained 1.4 g. of strontium sulfide; the total quantity of strontium chloride plus strontium oxide was 0.034 mole and the total amount of radioactive and non-radioactive europium was 1.4×10^{-4} g. The mole ratio of oxide to chloride (R), the amounts of calcium chloride, the temperature at which the mixture was filtered and the value of K_t obtained are given in Table I. K_t has been defined[9] as the ratio of the mole fraction of activator in the solid phase to that in the liquid phase. As previously described,[9] K_t can be expressed in terms of values obtained from the analysis of the solid and liquid phases. More recently[13] K_t has been derived in terms of ionic activity coefficients.

TABLE I

THE DISTRIBUTION OF EUROPIUM IN THE SYSTEM $SrS-SrCl_2-SrO$ WITH AND WITHOUT THE ADDITION OF Ca^{2+} IONS

R	$CaCl_2$, g.	Temp., °C.	K_t	K_t[a]
0	0	1030–1050	2.49	2.57
0	0.058	1038–1050	(2.60)	
0.0155	.058	1000–1023	2.38	1.68
0.170	.167	1025–1030	2.10	1.90

[a] Values of K_t in absence of Calcium was reported by Prener.[9]

The Effect of Calcium Ions on the Distribution of Samarium.—Samples similar to those used for the europium distribution were prepared. Each sample contained a total of 1×10^{-4} g. of radioactive and non-radioactive samarium. The details of composition and the experimental results are listed in Table II.

TABLE II

THE DISTRIBUTION OF SAMARIUM IN THE SYSTEM $SrS-SrCl_2-SrO$ WITH AND WITHOUT THE ADDITION OF Ca^{2+} IONS

R	$CaCl_2$	Temp., °C.	K_t	K_t[a]
0	0	1010–1025	5.52	5.38
0	0.058	1010–1020	5.36	
0.0155	.058	1010–1025	2.15	0.683
.0314	.1142	1035–1050	1.74	.088
.0802	.2820	1000	0.42	.12
.170	.2820	1000	1.09	.002

[a] Values of K_t in absence of calcium ions reported by Prener.[9]

Discussion

The results given in Table I would appear to indicate that the addition of calcium ions counteracts to some extent the effect of the oxide ion. The more recent values[13] for the distribution of Eu^{2+} in the same systems obtained by reducing the europium ion prior to fluxing, however, indicate that there may be some variation due to the persistence of some trivalent europium ions. Thus even though the changes in K_t due to the introduction of calcium ions are in the expected direction, the changes are slight enough to be questionable.

The data on the distribution of samarium, on the other hand, are quite conclusive. It can readily be seen that the introduction of calcium ions in the flux causes much more of the Sm^{3+} ion to enter the solid phase.

This might readily be explained on the assumption that the activity of trivalent rare earth ions in the melt is lowered by the addition of oxide ions due to the formation of a rare earth–oxide ion complex with a low instability constant. The calcium ion apparently also forms an ion pair or complex ion with oxide ion the instability constant of which is of the same order as that of the samarium complex. The net result of the introduction of the calcium ion to the melt is therefore an increase in the activity coefficient of the samarium ion. The divalent europium ion on the other hand does not appear to form such a stable complex with oxide ion so that the influence of the calcium ion is less pronounced. From consideration of ionic radius we would not expect the larger divalent ions to form such a stable complex with oxide ion.

A dual function is therefore served by the calcium fluoride in the Lenard Phosphors. It gives with the alkaline earth sulfate, a reciprocal salt pair which has a sufficiently low melting point so that a recrystallizing medium is provided for the phosphor base, and the calcium ions lower the concentration of oxide ions which might prevent certain activators from entering the phosphor base in sufficient concentration to provide a good phosphor.

In the samarium-containing infrared sensitive phosphors the samarium ion is known to introduce electron traps which cause both sensitization to stimulation by infrared radiation and a reduction of afterglow at room temperature. Thus, the calcium ion enhances these two important effects of the samarium ion by increasing its concentration in the phosphor base.

One would predict that similar effects would be produced by other small stable cations such as Li^+, Be^{2+}, Mg^{2+} and probably Sc^{3+} and that the activators which would be most affected would be Ce^{3+}, Sm^{3+} and Bi^{3+}. By some refinement of the technique described here, it should be possible to devise a procedure to investigate the nature of complex ions in melts.

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