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The Role of Ga_2O_3 in the Preparation of Y_2O_3:Eu^{3+} Phosphor from the Oxides

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It has been observed that Ga_2O_3 enhances the cathodoluminescence and the 2537 Å-excited photoluminescence, and also causes whitening of the body colour of Y_2O_3:Eu^{3+} prepared from the oxides. In both types of luminescence, these effects are apparently due to the Ga_2O_3 behaving as a mineraliser, i.e. a diffusion enhancer. In the case of photoluminescence, additional brightness enhancement resulting from incorporation of Ga_2O_3 is due to a type of sensitisation to the exciting wavelength.

1. Introduction

This paper reports that Ga_2O_3 enhances the photoluminescence and cathodoluminescence of Y_2O_3:Eu^{3+} prepared from the oxides, summarises studies carried out in an effort to determine the reason or reasons for this effect, and points out that one of the apparent causes, generally overlooked in phosphor preparation, could be of much more general application than simply the case described herein.

Optimised commercial Y_2O_3:Eu^{3+} phosphors (which are white, and emit principally in the red) usually contain about 5 mol % Eu_2O_3. Preparations are most often made by firing coprecipitated mixtures of the oxalates (or sometimes hydroxides) of yttrium and europium for 2 to 4 h in air at 1250° C after prefiring 1 h in oxygen at 800° C to decompose the oxalates (or hydroxides).

Alternatively, it is possible to prepare good Y_2O_3:Eu^{3+} phosphors by firing the oxides in the presence of molten fluxes which may or may not then be washed out of the product. One example of such a flux is $BaCl_2$ [1]. A recent patent [2] describes a process in which decomposition of coprecipitated oxalates on firing is followed by further heating in the presence of fluxes such as fluorides, vanadates, and borates. Direct preparation from oxides would be preferable because of the greater simplicity of the method.

2. Preparation and Luminescence

In the present work, the procedure employed was to fire mixtures of oxides† (thoroughly ground with mortar and pestle) for 3.5 h in covered platinum crucibles in air at 1250° C. It was found that Y_2O_3 containing 5 mol % Eu_2O_3 when prepared in this way had a yellowish-tan body colour and exhibited much poorer 2537 Å-excited photoluminescence than commercial phosphors prepared from coprecipitated oxalates, and that other preparations with less than 5 mol % Eu_2O_3 exhibited a similar body colour and were even poorer phosphors. Preparations with only 0.5 mol % Eu_2O_3 were in fact more deeply coloured than those with 5 mol % Eu_2O_3. However, when 2.5 mol % Ga_2O_3 was ground into raw mixtures of the yttrium and europium oxides, the fired products were colourless and

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†Sources and purities of materials used:
At Newark College of Engineering:
Y_2O_3 – Lindsay Rare Earths, Code 1118, 99.9999 %.
Eu_2O_3 – Ronson Metals Corp., Cubic, 99.97 %.
Ga_2O_3 – City Chemical Corp., 99.999 %, and Indium Corp. of America, 99.999 %.
At Zenith Radio Corporation:
Y_2O_3 – Lindsay Rare Earths, Code 1117, 99.999 %.
Eu_2O_3 – Lindsay Rare Earths, Code 1013, 99.9 %.
Ga_2O_3 – Penn Rare Metals, Inc., 99.99 %.

there was considerable enhancement of both photoluminescence and cathodoluminescence. A similar effect was noted when the additional oxide was Al_2O_3 rather than Ga_2O_3, but in this case the effect was somewhat weaker. Neither Ga_2O_3 nor Al_2O_3 can act as a flux because their melting points are too high.

Table I shows that a Y_2O_3 preparation with only 0.5 mol % Eu_2O_3 but with 2.5 mol % Ga_2O_3 also present is brighter on excitation with 2537Å radiation than one with 5% Eu_2O_3 in the absence of Ga_2O_3, and that one with 5% Eu_2O_3 and 2.5% Ga_2O_3 is much brighter still. However, none of these is quite as bright as an optimised Y_2O_3:5% Eu^{3+} phosphor prepared from coprecipitated oxalates. Cathodoluminescence brightness data (also in table I) indicate much the same trend, except that addition of Ga_2O_3 causes less enhancement of cathodoluminescence than of photoluminescence because the cathodoluminescence intensities of preparations without Ga_2O_3 are already considerably higher than the photoluminescence values. Addition of Ga_2O_3 to coprecipitated oxalates of Y and Eu prior to firing or to an already prepared optimised phosphor which was then refired did not increase the intensity of either photoluminescnece or cathodoluminescence.

The preparations listed in table I were made in two different laboratories, independently by all three authors, and results were reproducible. Other intermediate Eu concentrations were also employed and consistent results were obtained with them as well. It appears sufficient, however, to focus here on several key compositions.

3. Band Spectra

3.1. Absorption Band Spectra

Unlike pure Y_2O_3, preparations from the oxides of Y_2O_3 doped with either Eu^{3+} or Ga^{3+} have been found to have very similar broad absorption bands in the ultraviolet (but they differ somewhat in that while the Y_2O_3:Eu^{3+} absorbs only below 3200Å, the Y_2O_3:Ga^{3+} absorption extends to 4000Å). In both cases, absorption reaches a maximum in the vicinity of the 2537Å mercury line by which these phosphors are strongly excited.

3.2. Excitation Band Spectra

Excitation spectra of Y_2O_3:Eu^{3+} phosphors prepared from coprecipitated oxalates consist of a rather narrow band peaking at 250 nm. On the other hand, the excitation spectra of corresponding preparations from the oxides peak at 240 nm, while those to which Ga has been added still peak at 240 nm but exhibit considerably increased excitation in the region from 250 to 260 nm.

TABLE I

Phosphor composition	Relative luminescence intensities	
	Photo-luminescence (2537Å excitation)	Cathodo-luminescence
Optimised Y_2O_3:5% Eu prepared from coprecipitated oxalates	100	100
Y_2O_3:5% Eu prepared from oxides	20	56
Y_2O_3:5% Eu, 2.5% Ga prepared from oxides	62	79
Y_2O_3:0.5% Eu prepared from coprecipitated oxalates	43	80
Y_2O_3:0.5% Eu prepared from oxides	5	24
Y_2O_3:0.5% Eu, 2.5% Ga prepared from oxides	32	36

4. Determination of Actual Concentration of Eu^{3+} in Solid Solution

4.1. Line Emission Method

In Y_2O_3, which has the cubic C-M_2O_3 structure, the cations are found at the centres of distorted cubelets with six of the eight corners containing oxide ions. Three quarters of the cations are in cubelets with the missing anions at the ends of a face diagonal (C_2 symmetry) and one-quarter in cubelets with the missing oxide ions at the ends of a body diagonal (S_6 symmetry). When Eu^{3+} ions are substituted for Y^{3+} ions, they enter the same sites in the same proportion. The strongest emission line observed on excitation with 2537Å ultraviolet is at 6112Å, but others are also seen at a number of wavelengths including 5804 and 5823Å; these latter two are due to a $^5D_0 \rightarrow {}^7F_0$ transition at a C_2 site and a $^5D_0 \rightarrow {}^7F_1$ transition at an S_6 site, respectively [3]. Although the 5804Å line is always sharper and more intense than that at 5823Å, the ratio of peak heights is very sensitive to concentration because in preparations containing higher percentages of Eu^{3+}, energy transfer occurs from S_6 to C_2 sites; thus, as the concentration of Eu is decreased from 5 mol %, the 5823Å emission becomes somewhat stronger relative to the 5804Å line than at the higher concentrations [4]. The relative peak heights of these two emissions on 2537Å excitation of phosphors prepared from Y_2O_3 and 5 mol % Eu_2O_3 with and without Ga_2O_3 present were actually characteristic of phosphors with much less than 5 mol % Eu_2O_3 (much less than 1 % in the absence of Ga and perhaps about 1 % or somewhat less in the one with Ga), as compared with optimised phosphors prepared from coprecipitated oxalates.

4.2. Line Absorption Method

The same conclusion is drawn from line absorption measurements on the same preparation in the blue and green regions of the visible spectrum [4]. The intensities of absorption lines due to Eu^{3+} indicate that there is not more than 0.5 to 1 % Eu^{3+} present in the C-M_2O_3 structure in or out of solid solution. The remaining Eu_2O_3 is presumably present in the monoclinic B-form.

4.3. X-Ray Diffraction Method

Although the excess B-form Eu_2O_3 cannot be detected in X-ray diffraction patterns because of its low concentration, the conclusion regarding its presence is supported by the observation that the Eu_2O_3 used, though originally in the cubic C-form, undergoes a phase transformation to the monoclinic B-form on firing under the same conditions used for the phosphor preparation.

The preparations from the oxides of Y_2O_3:2.5 % Ga^{3+}; Y_2O_3:5 % Eu^{3+}; and Y_2O_3:5 % Eu^{3+}, 2.5 % Ga^{3+} all have X-ray patterns indistinguishable from that of Y_2O_3, even in the back reflection region. This again indicates solution of 1 % or less Eu^{3+} or Ga^{3+} in Y_2O_3.

5. Formation of Y_3GaO_6

Y_2O_3 and Ga_2O_3 in molar ratios $\geqq 3:1$ react to form Y_3GaO_6, leaving any excess Y_2O_3 as a second phase [5]. In order to obtain relevant information regarding the temperatures of formation and stability of Y_3GaO_6, a 3:1 mixture was heated for 24 h at 1350°C and the product cooled rapidly by air-quenching. Some of the product was then reheated for 4 h at 1250°C and cooled in the same way. Both were found to have the same X-ray diffraction powder pattern. Additional attempts to prepare this compound in 24 h periods at lower temperatures indicated that formation commences at about 1200°C and that it is definitely formed at 1250°C but to a lesser extent than at 1350°C.

6. Conclusions and Discussion

The results summarised above indicate that the Ga_2O_3 serves to enhance Eu^{3+} diffusion so that more Eu_2O_3 can dissolve in Y_2O_3 at a given temperature in a given time when one fires a ground mixture of oxides. The darkening of the body colour of preparations made in the absence of Ga_2O_3 is a typical impurity effect, probably due to non-equilibrium incorporation of at least some of the Eu^{3+} on interstitial sites which results in local electronic disturbances causing broad absorption in the shorter wavelength portion of the visible spectrum.

The amplitude shift in the excitation spectrum on addition of Ga^{3+} results in a better match with the 2537Å mercury line employed for excitation. However, this cannot be the entire explanation for the effect reported herein because the cathodoluminescence intensity is also increased (though relatively less than the photoluminescence) by the addition of Ga_2O_3; since the cathodoluminescnce is independent of absorption in the ultraviolet, Ga^{3+} must be more than a sensitiser in the usual sense. Certainly it does not sensitise Y_2O_3:Eu^{3+} in the same sense that Bi^{3+} does because Y_2O_3:Ga^{3+} has no emission in the visible like that of Y_2O_3:Bi^{3+}. The lack of effect of Ga^{3+} addition on optimised phosphors indicates that it is not an essential coactivator at all.

Ga^{3+} does not here act as a charge compensator because all cations involved are trivalent. Size effects are unlikely because the ionic radii of Y^{3+} and Eu^{3+} are not very different from each other so that Y_2O_3 and Eu_2O_3 should have no difficulty forming substitutional solid solutions under proper preparative conditions.

Possible explanations for the shift in excitation spectrum in the presence of Ga_2O_3 are: (1) the movement of greater amounts of Eu^{3+} ions into equilibrium substitutional positions (as in phosphors prepared from oxalates), thus creating a charge transfer absorption band slightly different from that resulting from Eu^{3+} on interstitial sites; (2) a dependence on total activator concentration; or (3) that, when Ga^{3+} is present along with Eu^{3+} whose concentration is too low to permit optimum absorption of the exciting 2537Å ultraviolet, the Ga^{3+} causes an increase in the absorption, following which energy is transferred to Eu^{3+} ions for eventual emission. In this last case, the Ga^{3+} would be a true sensitiser-type coactivator in the photoluminescence process. Even in the cases of the two other proposed possibilities, the ultimate effect may be thought of as a type of sensitisation to the exciting wavelength. More than one of the three may occur simultaneously, but in any case, it is this "sensitisation" which explains why the cathodoluminescence intensities of preparations from oxides in the absence of Ga_2O_3 (and those of other preparations with low Eu^{3+} concentration) are considerably greater than the photoluminescence values. Photoluminescence of such preparations benefits from the addition of Ga_2O_3 in two ways, as "sensitiser" and as diffusion enhancer, while cathodoluminescence does not require sensitisation and therefore starts out higher and is enhanced only by the improved diffusion in the presence of Ga_2O_3.

Although the preparation experiments indicate no structural oı compositional changes or equilibria at the reaction temperature which could perhaps explain increased mobility of ions, it is possible that the process of formation of Y_3GaO_6, even at 1250°C, would cause sufficient local agitation and thermal effects so that more Eu_2O_3 would be made to enter the Y_2O_3 lattice.

Another possibility is that the Ga_2O_3 simply lowers the melting point of the system and therefore permits greater diffusion at a given temperature even in the solid state (that is, the Tammann temperature concept). Y_2O_3 melts at 2410°C, while Y_3GaO_6 melts incongruently at 1770°C yielding Y_2O_3 and a liquid [6].

Even if the mechanism is not yet known, it seems quite clear that the Ga_2O_3 does enhance diffusion and acts as what is often called a "mineraliser", which, unlike a flux, does not melt at the temperature at which it is employed. (Examples of such mineralisers are given in references [7] and [8].) However, this term undoubtedly covers a multitude of unknown mechanisms. Regardless, mineralisers could probably be very useful in phosphor preparation generally; apparently they have not often, if at all, been so utilised.

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