A Novel Preparation of Thiogallate-based Rare-earth Phosphors

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$EuGa_2S_4$ and $CaGa_2S_4$:Ce were prepared by a method of the decomposition of metal dimethyldithiocarbamates which provides a simple and safe technique desired for the phosphor production. UV-irradiation of such $EuGa_2S_4$ and $CaGa_2S_4$:Ce (in the Ce/Ca=1/20 ratio) polycrystallines gave green and blue emission with high yield, as exemplified by relative yields of 0.17 and 0.84 against a commercially available Y_2SiO_5:Ce blue phosphor at room temperature respectively.

It is a difficult problem to find a usable blue phosphor for full color electroluminescence displays, since wide bandgap materials are required and the eye sensitivity is quite low in the blue spectral region.[1] In the ZnS family of phosphors, activation with thulium produces a blue emission, but it is by far too weak to be useful. The next group of the blue phosphors to be investigated was the alkaline earth sulfides activated with rare-earth metals: the cerium-activated SrS (SrS:Ce) emits in the blue green light. However, none of these compounds have, as yet, shown enough emission intensity to be useful. A new approach to blue phosphor has been turned to more complex sulfide compounds, alkaline earth thiogallates, $CaGa_2S_4$, $SrGa_2S_4$, and $BaGa_2S_4$. All three of the thiogallate materials show blue emission when alkaline earth is replaced by cerium.[2] The alkaline earth thiogallates have been prepared from the elements at high temperature. In this procedure, an explosion of the sample occurs due to the strongly exothermic reaction among the elements. To avoid the explosion, alkaline earth metal alloys, $CaGa_2$ and $SrGa_2$ prepared at 1000°C, were heated with sulfur until 1200°C with a gradual slope of 30-50°C/h resulted in formation of $CaGa_2S_4$ and $SrGa_2S_4$, respectively.[3] Other method is the solid-state reaction between CaS and Ga_2S_3 at 900°C.[4] Rare earth metals were usually added to the thiogallates in the form of fluorides or oxides.[2]

This paper describes a novel preparation of thiogallate phosphors by a use of the thermal decomposition of metal dithiocarbamate precursors, which provides a simple and safe technique desired for the phosphor production. Metal-dimethyldithiocarbamate (Me_2dtc) complexes, well-known coordination complexes,[5] are easily prepared and decompose in argon at temperatures slightly below their melting points. Further heating in an atmosphere of sulfur in the range of 400-800°C produces metal sulfide phases that correspond to those obtained by direct combination of the elements at higher temperatures. To obtain a pure product it was necessary to pulverize the reactants thoroughly. Recently, other metal sulfides such as Sb_2S_3, Bi_2S_3,[6] and ZnS[7] have been prepared by heating corresponding metal-dtc complexes. Na[Me_2dtc]•$2H_2O$, $Ga(NO_3)_3$•7-$9H_2O$, $Eu(NO_3)_3$•$6H_2O$, $Ce(NO_3)_3$•$6H_2O$, [Me_4N]Cl, and CaH_2 were of reagent grade and commercially purchased from Tokyo Kasei or Kantoh Chemical Co. Commercial CaS and Sylvania P-47 Y_2SiO_5:Ce were received from Aldrich Chemical and Nilaco Co, respectively.

White precipitates of Ga[Me_2dtc]$_3$ (or orange crystallines of Na[Eu(Me_2dtc)$_4$]) were isolated from the solution by mixing 3 g; 7.5 mmol $Ga(NO_3)_3$•7-$9H_2O$ in 5 ml water (or 0.20 g; 0.45 mol $Eu(NO_3)_3$•$6H_2O$ in 2 ml water) and 4.3 g; 30 mmol Na[Me_2dtc]•$2H_2O$ in 100 ml water (or 5.0 g; 35 mmol Na[Me_2dtc]•$2H_2O$ in 8 ml water). Similarly, Na[Ce(Me_2dtc)$_4$] was obtained by mixing 0.5 g; 1.2 mmol $Ce(NO_3)_3$•$6H_2O$ in 2 ml water and 5.0 g; 35 mmol Na[Me_2dtc]•$2H_2O$ in 8 ml water.[8] [Me_4N][Eu(Me_2dtc)$_4$] (or [Me_4N][Ce(Me_2dtc)$_4$]) was precipitated from the solution by addition of 0.65 g; 5.9 mmol [Me_4N]Cl in 5 ml water into the solution containing 1.0 g; 2.2 mmol $Eu(NO_3)_3$•$6H_2O$ (or 1.0 g; 2.3 mmol $Ce(NO_3)_3$•$6H_2O$) and 1.6 g; 9.0 mmol Na[Me_2dtc]•$2H_2O$ in 10 ml water. The resulting crystalline solids were dried in vacuum at 120°C for 24 h before heating. X-ray-crystallographic analysis of Na[Eu(Me_2dtc)$_4$] (monoclinic, space group $P2_1/a$, $a=32.312(6)$, $b=10.524(2)$, $c=17.119(3)$ Å, $\beta=101.57(1)°$, $Z=8$, $R=0.094$ for 2118 independent data with $I>3\sigma(I)$) let us to formulate rare-earth-metal dtc anions as [Eu(Me_2dtc)$_4$]$^-$ and [Ce(Me_2dtc)$_4$]$^-$. Among the sulfides that can be prepared by this method are Ga_2S_3, Ce_2S_3, and EuS. A sample of Ga_2S_3 was prepared by decomposing Ga(Me_2dtc)$_3$ (1.0g; 2.3 mmol) for 30 min at 800°C on a silica boat with excess sulfur (2.7g; 84 mmol) in argon stream. Similarly, Ce_2S_3 and EuS were prepared by decomposing [Me_4N]$_4$[Ce(Me_2dtc)$_4$] and [Me_4N][Eu(Me_2dtc)$_4$] for 30-40 min at 600-650°C with excess sulfur, respectively. In the latter, the trivalent Eu^{3+} cation in [Me_4N][Eu(Me_2dtc)$_4$] is reduced to Eu^{2+} through the reaction. The samples of $EuGa_2S_4$ (or $CaGa_2S_4$) were prepared by solid-state reaction of 0.19 g;1.05 mmol EuS (or 0.08 g; 1.06 mmol CaS) with 0.25 g; 1.06 mmol Ga_2S_3 for 5 h in sealed evacuated silica tubes at 650°C (or 900°C). All samples obtained were confirmed to have X-ray-powder diffractograms in good agreement with the corresponding compounds in JCPDS data. Another interesting synthetic technique is double decomposition reaction with excess sulfur. $EuGa_2S_4$ and $CaGa_2S_4$ were prepared successfully by this procedure which can be used advantageously when the more common method becomes difficult. Bright yellow $EuGa_2S_4$ was obtained by heating Ga[Me_2dtc]$_3$ (0.50g; 1.16 mmol), [Me_4N][Eu(Me_2dtc)$_4$] (0.41g; 0.58 mmol), and sulfur (2.5g; 78 mmol) on a silica boat in the argon stream for 5 min at 650°C. The resulting sulfides were quenched to room temperature. White $CaGa_2S_4$ was obtained by heating CaH_2 (0.05g, 1.2 mmol), Ga[Me_2dtc]$_3$ (1.0g, 2.3 mmol) and sulfur (2.7g, 84 mmol) for 5 min at 850°C. The critical step of the preparation by the double decomposition is the short duration of the reaction. Such products seemed to give single phase well-crystallized sulfides, since their XRD patterns are coincident with the corresponding JCPDS data. The particle size (~350 Å) for the

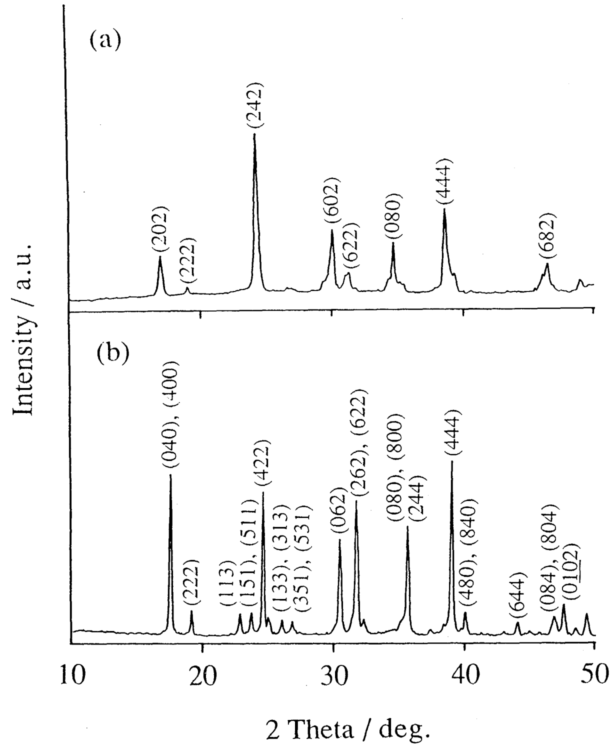

Figure 1. X-ray diffraction patterns of $EuGa_2S_4$ (a) and $CaGa_2S_4$:Ce (b) in the Ce/Ca=1/20 ratio, produced from the solid-state reaction of sulfide components.

$EuGa_2S_4$ crystallines prepared by the double decomposition reaction was slightly small compared with that (~460 Å) by the solid-state reaction of sulfide components but the particle size (~460 Å) of the $CaGa_2S_4$ crystallines was similar between the two preparation methods, when the particle size was estimated by X-ray diffraction line broadening.

Samples of $CaGa_2S_4$:Ce (in Ce/Ca=1/50, 1/20, 1/10, and 1/5 atom ratios) were prepared by heating Ce_2S_3, Ga_2S_3, and $CaGa_2S_4$ in a Ce_2S_3/Ga_2S_3=1/2 ratio in the sealed evacuated silica tubes for 5 h at 800°C. X-ray powder diffractograms of $CaGa_2S_4$:Ce in the Ce/Ca=1/50, 1/20, and 1/10 ratio were identical with the XRD pattern of $CaGa_2S_4$, whereas the XRD pattern in the Ce/Ca=1/5 ratio showed the existence of additional unidentified peaks. Figure 1 shows the powder X-ray diffraction patterns (orthorhombic, space group Fddd,[2] a=20.404(5), b=20.716(5), c=12.200(5) Å for $EuGa_2S_4$ and a=20.087(4), b=20.087(4), c=12.112(4) Å for $CaGa_2S_4$) of $EuGa_2S_4$ and $CaGa_2S_4$:Ce in the Ce/Ca=1/20 ratio prepared from the solid-state reaction of sulfide components. The crystallinities of the samples are similar. Figure 2 shows emission spectra of both $EuGa_2S_4$ and $CaGa_2S_4$:Ce in the Ce/Ca=1/20 ratio at 4.2 K, which were observed under 400- and 340-nm light excitation, respectively. For $EuGa_2S_4$ the emission spectrum exhibits a single band peaking at 545 nm due to a $^5D_1 \rightarrow {}^7F_2$ transition of Eu^{2+}. $CaGa_2S_4$:Ce gives the Ce^{3+} emission its typical double-band shape (λ_{max}=470 and 519 nm) which can be assigned to $^2D_{3/2} \rightarrow {}^2F_{5/2}$ and $^2D_{3/2} \rightarrow {}^2F_{7/2}$ transitions, separated by some 2000 cm^{-1} due to spin-orbital coupling.[9] The relative yield of emission (ϕ) decreased with increasing temperature; for example $\phi_{300K}/\phi_{4.2K}$=0.12 and 0.75 for $EuGa_2S_4$ and $CaGa_2S_4$:Ce in the Ce/Ca=1/20 ratio, respectively. Relative yields of emission at room temperature were high 0.17 and 0.84 relative to the commercially available blue phosphor Y_2SiO_5:Ce (Sylvania P-47), respectively. The preparation described here would be a simple and safe method of the preparation of the thiogallate-based blue phosphors.

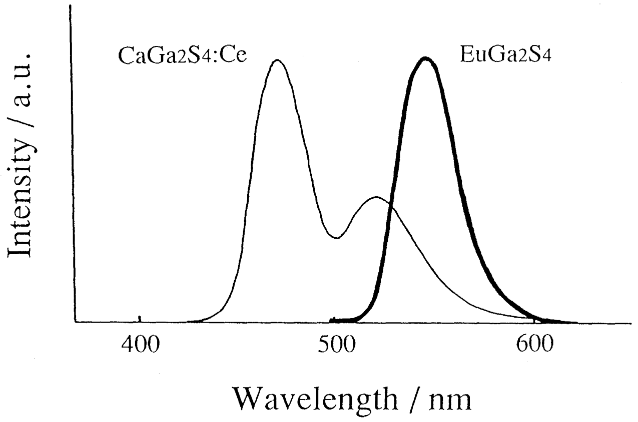

Figure 2. 4.2 K photoluminescence spectra of $EuGa_2S_4$ (λ_{ex}=400 nm) and $CaGa_2S_4$:Ce in the Ce/Ca=1/20 ratio (λ_{ex}=340 nm).

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