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Luminescence of Phosphors Based on the Host Lattice $ABGe_2O_6$ (A, B = Ca, Sr, Ba)

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In the isostructural compounds $CaSrGe_2O_6$, $CaBaGe_2O_6$ and $SrBaGe_2O_6$ an efficient luminescence was found only in $CaSrGe_2O_6$, using Pb-activation (λ_{max}, 330 nm) and Mn-activation (λ_{max}, 610 nm). In $CaSrGe_2O_6$–Pb, 50% of Si can be substituted for Ge without any decrease in the quantum efficiency of the phosphor.

Introduction

Phosphors based on alkaline earth germanates were previously studied by Koelmans and Verhagen (*1*). With Pb-activation efficient phosphors were found with germanates of group II elements with composition $M^I_2M^{II}Ge_2O_7$ [e.g. $Ba_2MgGe_2O_7$–Pb, which has about the same efficiency as the corresponding silicate described by Klasens, Hoekstra and Cox (*2*)]. For the germanates of the type $M_2Ge_3O_8$ a noticeable emission could only be observed in $Ca_2Ge_3O_8$, activated with Mn, when excited with cathode rays.

New alkaline earth germanates with the general formula $ABGe_2O_6$ (A, B = Ca, Sr, Ba) were recently prepared by Grebenshchikov and Shirvinskaya (*3*). The three compounds, $CaSrGe_2O_6$, $CaBaGe_2O_6$, and $SrBaGe_2O_6$, are isostructural and, according to these authors, belong to a structure type similar to that of $Ca_2BaSi_3O_9$ (*4*).

We tried to activate these compounds with Pb, Mn, Ti, Tb and Eu. The most efficient phosphors were found with the compound $CaSrGe_2O_6$, when activated with Pb or Mn.

Experimental

Powder samples were prepared by heating intimate mixtures of luminescent grade Ca, Sr and/or Ba carbonate and GeO_2 at temperatures between 1000–1200°C in an atmosphere of nitrogen. The activator compounds used were: PbO, $MnCO_3$, TiO_2, Tb_4O_7 and Eu_2O_3. The mixtures were fired at least twice during 2 hrs. After each firing the reaction product was mortar ground. For $CaSrGe_2O_6$–0.02 Mn the optimum firing temperature was found to be 1075°C. In most cases a small excess of GeO_2 (about 1 mole%) was added to the firing mixture. The performance of the optical measurements has been described previously (*5*).

Results and Discussion

Activation with Pb. With Pb-activation the three alkaline earth germanates show about the same excitation spectrum, with a peak at 250–255 nm, as shown in Fig. 1 for $CaSrGe_2O_6$–Pb. The emission peak of this phosphor is situated at 330 nm, as shown in Fig. 1. With 250–270 nm excitation the highest quantum efficiency we observed for $CaSrGe_2O_6$–Pb was 40%, whereas that of the two other germanates was a factor 10 lower.

The optimum activator concentration was found at 0.02–0.04 gatom Pb per mole of $CaSrGe_2O_6$. Deviations from the Ca:Sr ratio from 0.75:1.2 to 1.2:0.75 in the firing composition had little effect on the brightness, although in the first case some nonluminescent $SrGeO_3$ and in the second case some nonluminescent $CaGeO_3$ was found as a second phase.

The substitution of Si for Ge in $CaSrGe_2O_6$–Pb gives a broadening of the excitation spectrum (Fig. 1), but the same emission spectrum (Fig. 1). No change is caused in the X-ray diffraction pattern of the reaction product by increasing x in $CaSrGe_{2-x}Si_xO_6$–Pb from 0 to 0.75, but the quantum efficiency of the phosphor becomes slightly higher.

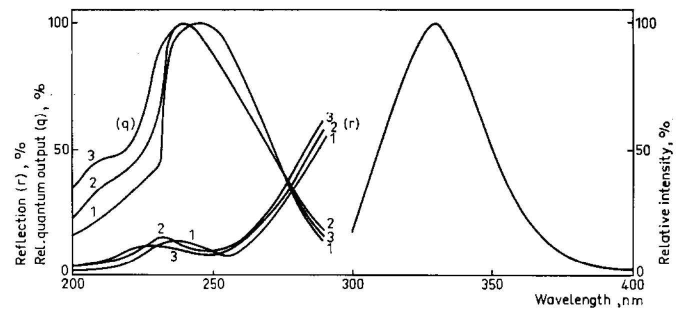

FIG. 1. Diffuse reflection spectra (r), excitation spectra (q), and spectral-energy distribution of the emission (mainly 254 nm excitation) of $CaSrGe_{2-x}Si_xO_6$–0.03 Pb phosphors. Curve 1, $x = 0$; curve 2, $x = 0.50$; curve 3, $x = 0.75$.

At higher values of x the efficiency decreases (with $x = 1$ the quantum efficiency being about the same as for $x = 0$) and $SrSiO_3$ can be observed as a second phase.

At 77°K the peak height of the Pb-emission band is higher (up to 40%) than that at room temperature. At about 120°C the intensity of the luminescence has decreased to 50% of the value measured at room temperature.

Activation with manganese. By analogy with Pb activation the most efficient Mn-activated phosphor was $CaSrGe_2O_6$–Mn. This phosphor has an emission-maximum at 610 nm (Fig. 2) and a quantum efficiency (250–270 nm excitation) of about 60%. With cathode ray excitation (20 kV) an energy efficiency of 3–4% was measured. The quantum efficiency (ultraviolet excitation) of $CaBaGe_2O_6$–Mn (λ_{max}, 585 nm) and of $SrBaGe_2O_6$–Mn (λ_{max}, 585 nm) is about a factor 5 lower than that of $CaSrGe_2O_6$–Mn. It follows from the excitation spectrum, also given in Fig. 2, that $CaSrGe_2O_6$–Mn is strongly excited by the 254 nm radiation present in a low pressure mercury discharge lamp. The emission spectrum (halfwidth of the emission 75 nm) makes this phosphor suitable for colour rendering in the red. The emission band of $CaSrGe_2O_6$–Mn is narrower than that of $(Sr,Mg)_3(PO_4)_2$–Sn (6) (halfwidth of the emission 135 nm), which is commonly used in fluorescent lamps with a good colour rendering.

The optimum brightness in $CaSrGe_2O_6$–Mn was observed with 0.02 gatom Mn per mole. Adding more manganese resulted in a decrease of the brightness, probably because it was only partially dissolved in the germanate, since the reflection in the visible decreased. From the shape of the emission band it may be concluded that we are dealing with Mn^{2+} emission.

It follows from the diffuse reflection spectra of $CaSrGe_2O_6$–Mn (Fig. 2) and of $CaSrGe_2O_6$–Pb (Fig. 1) that the absorption of 254 nm radiation is much more intense for the Pb than for the Mn-activated phosphor. Although the addition of Pb to the $CaSrGe_2O_6$–Mn phosphor results in an increase of the 254 nm absorption, it did not influence the intensity of the Mn-emission band. This seems to exclude efficient energy transfer from Pb to Mn in $CaSrGe_2O_6$.

In contrast with the aforementioned Pb-activated phosphor, partial substitution of Si for Ge decreases the brightness of the Mn-activated phosphor.

The brightness at 77°K was found to be about

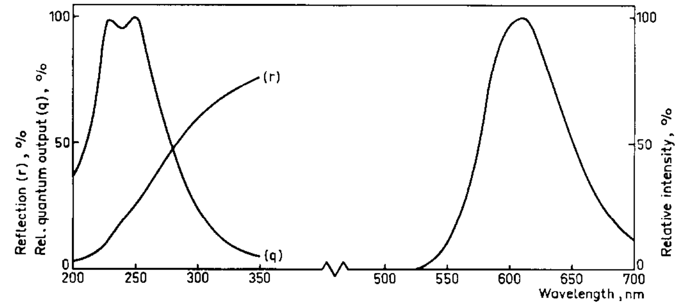

FIG. 2. Diffuse reflection spectra (r), excitation spectrum (q) and emission spectrum (mainly 254 nm excitation) of $CaSrGe_2O_6$–0.02 Mn.

the same as that measured at room temperature. At about 75°C the brightness has decreased to 50% of the value measured at room temperature.

Activation with Eu, Tb and Ti. With Eu as activator we found in $CaSrGe_2O_6$, $CaBaGe_2O_6$ and $SrBaGe_2O_6$ a weak luminescence, with a main emission peak at 611 nm. With Tb addition we observed a weak bluish green emission. With Ti as an activator a weak emission band at about 450 nm was found.

Concluding Remarks

A strong influence of the chemical composition of the host lattice on the luminescence efficiency has been observed in $CaSrGe_2O_6$, $CaBaGe_2O_6$ and $SrBaGe_2O_6$. For Mn as well as Pb activation the luminescence is the most efficient in $CaSrGe_2O_6$. Substitution of Si for Ge decreases the efficiency of the Mn-luminescence but not of the Pb-luminescence.

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