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The Luminescence of Pr^{3+} in $BaY_4Si_5O_{17}$

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The cell constants of four new monoclinic compounds $BaR_4X_5O_{17}$ ($R = Y$, Gd; $X = Si$, Ge) are given. The luminescence of various RE activators in the silicates is reported. Pr^{3+}-activated $BaY_4Si_5O_{17}$ shows efficient ultraviolet $5d \rightarrow 4f$ emission and weak $4f \rightarrow 4f$ emission (mainly red luminescence from the $^1D_2$ level). The $5d \rightarrow 4f$ emission is ascribed to Pr^{3+} on Y sites, the $4f \rightarrow 4f$ emission to Pr^{3+} on Ba sites. Energy transfer from Pr^{3+} to Gd^{3+} has been observed. Gd^{3+} plays an intermediate role in the energy transfer from Pr^{3+} to Sm^{3+} and to Dy^{3+} in $BaGd_4Si_5O_{17}$. Upon activation with Tb^{3+} the silicates show characteristic green Tb^{3+} luminescence with a quantum efficiency of 75% for ultraviolet excitation.

Introduction

Recently Wanklyn *et al.* (*1*) have reported on the existence of a new family of compounds $PbR_4Si_5O_{17}$ ($R = Y$, Er, Dy). These compounds have a monoclinic crystal structure. An X-ray crystallographic structure determination of $PbEr_4Si_5O_{17}$ (*2*) has revealed that the erbium ions occupy two crystallographic nonequivalent sites. The lead ions occupy only one crystallographic site.

In this paper we present the latttice parameters of four new compounds $BaR_4X_5O_{17}$ ($R = Y$, Gd; $X = Si$, Ge).

The luminescence of Pr^{3+} in $BaY_4Si_5O_{17}$ is also described. Next, the energy transfer from Pr^{3+} to Gd^{3+} and the role of Gd^{3+} in energy transfer from Pr^{3+} to Sm^{3+} and to Dy^{3+} in $BaGd_4Si_5O_{17}$ is demonstrated. Finally we mention the luminescence of Tb^{3+} in the silicates.

Experimental

Powder samples were prepared by the usual solid state reaction techniques. Starting materials were $BaCO_3$, Y_2O_3, Gd_2O_3, GeO_2, $SiO_2 \cdot xH_2O$, Pr_4O_7, Sm_2O_3, Dy_2O_3, and Tb_4O_7. Stoichiometric proportions of the starting compounds were intimately mixed together and then prefired at 1000°C for 1 hr. A second firing of a few hours was carried out at temperatures between 1250 and 1500°C. The samples activated with Pr^{3+} or Tb^{3+} were fired in a nitrogen atmosphere.

X-Ray powder patterns were obtained with a Philips diffractometer using Cu*Kα* radiation.

All optical measurements were performed at room temperature with equipment described elsewhere (*3*). The spectra given in Figs. 1–3 have been corrected for the characteristics of the experimental setup.

Results and Discussion

The X-ray powder patterns that we have obtained for fired mixtures with the compositions $BaR_4X_5O_{17}$ ($R = Y$, Gd; $X =$ Si, Ge) show a striking resemblance to those reported for $PbR_4Si_5O_{17}$ (*1*). Using the indexing given for the patterns of the latter

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compounds we have calculated the monoclinic cell constants of $BaR_4X_5O_{17}$ (see Table I). These are comparable to those of $PbEr_4Si_5O_{17}$. In view of these results we assume that the barium compounds are isostructural with the lead compounds.

The luminescence spectra of Pr^{3+}-activated $BaY_4Si_5O_{17}$ are shown in Fig. 1. The emission spectrum consists of two bands ($5d \rightarrow 4f$ luminescence) in the ultraviolet and of several lines in the green and red region ($4f \rightarrow 4f$ luminescence). The bands in the excitation spectra correspond to $4f \rightarrow 5d$ transitions. The energy of excitation depends to a large extent on the emission wavelength monitored. Three different excitation spectra have been obtained for 265, 330, and 625-nm emission. Excitation spectra recorded for the green (500 nm) and the red (625 nm) emissions are the same. The quantum efficiency of the $5d \rightarrow 4f$ emission is 30% for 245-nm excitation. The $4f \rightarrow 4f$ emission (from the $^3P_0$ and $^1D_2$ levels) has a low intensity and is dominated by the red luminescence from the $^1D_2$ level.

The difference in the excitation spectra indicates that the $5d \rightarrow 4f$ and $4f \rightarrow 4f$ emissions originate from different Pr^{3+} centers. We ascribe the efficient $5d \rightarrow 4f$ emission to Pr^{3+} on both types of Y sites. The lowest $4f\,5d$ level of these Pr^{3+} ions is situated near 40.8 kK. That of the Pr^{3+} ions showing $4f \rightarrow 4f$ emission is situated at 42.6 kK. This points to a weaker crystal field at the sites occupied by the latter Pr^{3+} ions than at the Y sites. Therefore the $4f \rightarrow 4f$ emission may originate from Pr^{3+} on Ba sites. This can also explain the low intensity of the $4f \rightarrow 4f$ emission: Pr^{3+} will occupy preferably the Y sites.

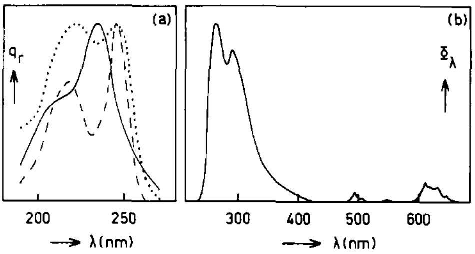

FIG. 1. (a) Excitation spectra of the emission of $BaY_{3.96}Pr_{0.04}Si_5O_{17}$. Solid line, 625-nm emission; broken line, 265-nm emission; dotted line, 330-nm emission. q_r in this and other figures denotes the relative quantum output. (b) Spectral energy distribution of the emission of $BaY_{3.96}Pr_{0.04}Si_5O_{17}$ for 235-nm excitation. Φ_λ in this and other figures denotes the radiant power per constant wavelength interval.

As pointed out by Hoefdraad and Blasse (*4*) the emission characteristics of Pr^{3+} are influenced enormously by the energetic position of the lowest $4f\,5d$ level and by Δr, the difference between the equilibrium positions of the ground state and the excited state. Since the lowest $4f\,5d$ levels of Pr^{3+} with $5d \rightarrow 4f$ luminescence and of Pr^{3+} with $4f \rightarrow 4f$ luminescence are situated at nearly the same energy, this indicates that the emission of the Pr^{3+} ions in $BaY_4Si_5O_{17}$ is influenced markedly by Δr.

TABLE I

CELL CONSTANTS OF COMPOUNDS $BaR_4X_5O_{17}$ (R = Y, Gd; X = Si, Ge)

Composition	*a* (Å)	*b* (Å)	*c* (Å)	β
$PbEr_4Si_5O_{17}$[a]	5.534	19.58	6.96	107.2°
$BaY_4Si_5O_{17}$	5.52 ± 0.01	19.59 ± 0.04	6.82 ± 0.01	107.0° ± 0.2°
$BaGd_4Si_5O_{17}$	5.14 ± 0.01	20.65 ± 0.08	7.17 ± 0.02	104.2° ± 0.2°
$BaY_4Ge_5O_{17}$	5.64 ± 0.01	20.05 ± 0.03	6.95 ± 0.01	106.8° ± 0.2°
$BaGd_4Ge_5O_{17}$	5.35 ± 0.01	20.92 ± 0.02	7.34 ± 0.01	103.8° ± 0.1°

[a] Reference (*1*).

The ultraviolet emission of Pr^{3+} in $BaY_4Si_5O_{17}$ has a large overlap with the absorption lines of Gd^{3+}. The Gd^{3+} ion has $4f \rightarrow 4f$ absorption transitions near 312 nm ($^8S_{7/2} \rightarrow {}^6P_J$) and 275 nm ($^8S_{7/2} \rightarrow {}^6I_J$). As can be expected, energy transfer from Pr^{3+} to Gd^{3+} occurs in $BaY_4Si_5O_{17}$. The phosphor $BaY_{3.66}Gd_{0.3}Pr_{0.04}Si_5O_{17}$ shows Gd^{3+} emission (Fig. 2b) with a quantum efficiency of 20% for 245-nm excitation. Additionally very weak red $4f \rightarrow 4f$ emission of Pr^{3+} is observed, whereas the $5d \rightarrow 4f$ emission of Pr^{3+} is negligible. The excitation spectrum of the Gd^{3+} emission (Fig. 2a) consists of $4f \rightarrow 4f$ excitation lines of Gd^{3+} ($^8S_{7/2} \rightarrow {}^6I_J$ transitions near 275 nm) and of the broad $4f \rightarrow 5d$ excitation bands of Pr^{3+}. The compound $BaGd_{3.96}Pr_{0.04}Si_5O_{17}$ shows Gd^{3+} emission with a quantum efficiency of 5%. For this composition the Gd^{3+} luminescence has a low intensity due to concentration quenching.

We have described recently the intermediate role of Gd^{3+} in energy transfer (*5*, *6*): if Gd^{3+} can be sensitized by a sensitizer, *S*, energy transfer from *S* to an activator, *A*, can occur almost exclusively via Gd^{3+} ions. This has been described in detail (*6*) for the case where Tb^{3+} is the activator. With Pr^{3+} as a sensitizer, however, the energy transfer from Pr^{3+} to Tb^{3+} via Gd^{3+} in $BaGd_4Si_5O_{17}$ cannot be demonstrated well, since the $4f \rightarrow 5d$ excitation bands of Pr^{3+} and Tb^{3+} are observed in the same wavelength region (see below). Since energy transfer from Gd^{3+} to Sm^{3+} and Dy^{3+} is known (*7*), and these ions do not have strong excitation bands in the region where the $4f \rightarrow 5d$ excitation bands of Pr^{3+} are observed, we investigated the intermediate role of Gd^{3+} in the energy transfer from Pr^{3+} to Sm^{3+} and to Dy^{3+} in $BaGd_4Si_5O_{17}$. Figure 3 shows luminescence spectra of $BaGd_{3.95}Pr_{0.04}Sm_{0.01}Si_5O_{17}$. The emission spectrum consists of red Sm^{3+} emission and Gd^{3+} emission near 312 nm. The latter emission is much weaker than that of the compound without Sm^{3+}. The excitation spectrum recorded for the Sm^{3+} emission is comparable to that recorded for the Gd^{3+} emission. The emission spectrum in Fig. 3b is the same for excitation of Pr^{3+} (235 nm) and for excitation of Gd^{3+} (275 nm). This means that the ratio of peak heights of the Gd^{3+} emission and the Sm^{3+} emission is not affected by whether Pr^{3+} or Gd^{3+} is excited. If direct $Pr^{3+} \rightarrow Sm^{3+}$ transfer were involved, we should observe a lower ratio (intensity Gd^{3+} emission/intensity Sm^{3+} emission) upon excitation of Pr^{3+}. Since this difference was not observed we conclude that the energy transfer from Pr^{3+} to Sm^{3+} in $BaGd_4Si_5O_{17}$ occurs almost exclusively via Gd^{3+} ions, and that direct energy transfer from Pr^{3+} to Sm^{3+} is negligible for the activator concentration used. The

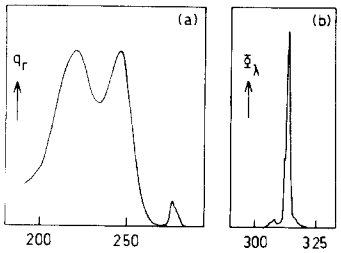

FIG. 2. (a) Excitation spectrum of the 312-nm Gd^{3+} emission of $BaY_{3.66}Gd_{0.3}Pr_{0.04}Si_5O_{17}$. (b) Spectral energy distribution of the emission of $BaY_{3.66}Gd_{0.3}Pr_{0.04}Si_5O_{17}$ for 245-nm excitation.

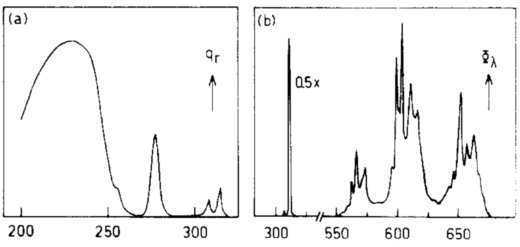

FIG. 3. (a) Excitation spectrum of the 605-nm Sm^{3+} emission of $BaGd_{3.95}Pr_{0.04}Sm_{0.01}Si_5O_{17}$. (b) Spectral energy distribution of the emission of $BaGd_{3.95}Pr_{0.04}Sm_{0.01}Si_5O_{17}$ for 235-nm excitation. The Gd^{3+} emission (near 312 nm) is shown reduced by a factor of 0.5.

quantum efficiency of the Sm^{3+} emission (40% for 235-nm excitation) is much higher than that of the Gd^{3+} emission (5%) of $BaGd_{3.96}Pr_{0.04}Si_5O_{17}$. This indicates that the energy transfer from Gd^{3+} to Sm^{3+} can compete successfully with the energy tranfer from Gd^{3+} to killer sites. In the same way as described for Sm^{3+} we have demonstrated the role of Gd^{3+} in the energy transfer from Pr^{3+} to Dy^{3+} in $BaGd_{3.95}Pr_{0.04}Dy_{0.01}Si_5O_{17}$. This phosphor shows characteristic Dy^{3+} line emission (near 475 and 580 nm) with a quantum efficiency of 20% for 235-nm excitation.

Finally, we give some results on the luminescence of Tb^{3+} in the silicates. As mentioned above, the $4f \rightarrow 5d$ excitation bands of Tb^{3+} are observed in the same region where Pr^{3+} $4f \rightarrow 5d$ excitation bands are found. The maxima of the excitation bands of Tb^{3+} in $BaY_4Si_5O_{17}$ and $BaGd_4Si_5O_{17}$ are situated at 235 and 230 nm, respectively. The luminescence of these Tb^{3+}-activated compounds consists of the characteristic green Tb^{3+} emission. The quantum efficiency of this emission amounts to 75% for ultraviolet excitation.

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References

1. B. M. Wanklyn, F. R. Wondre, G. B. Ansell, and W. Davison, *J. Mater. Sci.* **10**, 1494 (1975).
2. G. B. Ansell and B. Wanklyn, *J. Chem. Soc. Chem. Commun.* 794 (1975).
3. W. L. Wanmaker, J. W. ter Vrugt, and E. P. J. de Meester, *J. Electrochem. Soc.* **119**, 1237 (1972).
4. H. E. Hoefdraad and G. Blasse, *Phys. Status Solidi A* **29**, K95 (1975).
5. J. Th. W. de Hair, *J. Lumin.* **18/19**, 797 (1979).
6. J. Th. W. de Hair and W. L. Konijnendijk, *J. Electrochem. Soc.* **127**, 161 (1980).
7. L. Ozawa and S. Nishikawa, *Japan. J. Appl. Phys.* **7**, 1354 (1968).