

Nb(V) as an Electron Trap in the Storage Phosphor $\text{Ba}_5\text{SiO}_4\text{Br}_6:\text{Eu}(\text{II}),\text{Nb}(\text{V})$

W. J. Schipper and G. Blasse*

Debye Institute, Utrecht University, Postbox 80.000, 3508 TA Utrecht, The Netherlands

P. Leblans

Agfa-Gevaert N.V., Septestraat 27, B-2640 Mortsel, Belgium

Received April 4, 1994. Revised Manuscript Received July 5, 1994[Ⓞ]

Niobium-codoped $\text{Ba}_5\text{SiO}_4\text{Br}_6:\text{Eu}^{2+}$ acts as a photostimulable X-ray storage phosphor. The phosphor is also thermally stimulable. After X-ray irradiation, the EPR spectrum of Nb^{4+} is observed. UV irradiation at wavelengths between 250 and 340 nm has the same effect. It is concluded that an electron is trapped at the niobate group. The phosphor is optically stimulable between 300 and 650 nm. The corresponding absorption band is tentatively ascribed to a NbO_4^{4-} group. In the region between 300 and 340 nm, a competition between photoionization and stimulation takes place, resulting in characteristic thermoluminescence behavior.

Introduction

A great deal of research has been performed recently on photostimulable X-ray storage phosphors. A well-known example is $\text{BaFBr}:\text{Eu}^{2+}$.¹⁻³ Such materials find application in, for instance, medical X-ray imaging. Upon irradiation of a storage phosphor with high-energetic radiation, part of the absorbed energy is stored in the phosphor in the form of trapped electrons and holes. The stored energy can be released thermally or optically; this usually results in stimulated emission.

Europium-doped barium bromosilicate, $\text{Ba}_5\text{SiO}_4\text{Br}_6:\text{Eu}^{2+}$, is an efficient photoluminescent phosphor as well as a photostimulable X-ray storage phosphor. The luminescence of divalent europium in this lattice was studied by Garcia et al.⁴ and by Meijerink et al.⁵ The latter authors also studied the storage properties of this material and of the isostructural $\text{Ba}_5\text{GeO}_4\text{Br}_6$.^{6,7} They suggest that Br^- vacancies act as traps for the electrons that have been raised to the conduction band by X-ray irradiation. In this paper we describe the effect of codoping this material with niobium. This enhances the storage capacity considerably and changes the thermoluminescence (TSL) as well as the photostimulation (PSL) properties. We will show that niobium takes part in the storage process and propose a model for the mechanism involved on the basis of TSL and EPR measurements, using the recently elucidated crystal structure.⁸

Experimental Section

Powders were synthesized by firing an intimate mixture of BaCO_3 , SiO_2 (aerosil), $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$, Nb_2O_5 , and (optionally) Eu_2O_3 in air for 2 h at 750 °C. This was followed by two firings at 790 °C for 4 h each, in a 5% $\text{H}_2/95\%$ N_2 atmosphere, with intermediate grinding.

Photoluminescence and TSL measurements were performed on a SPEX 1680 spectrofluorometer equipped with a 450 W xenon lamp, two 0.22 m double monochromators, and a homemade high-temperature cell controlled by a WEST 3050 temperature controller.

X-ray irradiation was performed on a Philips PW 1729 X-ray generator operating at 40 kV, 20 mA (Cu K α radiation).

X-band EPR measurements were performed on a Bruker ESP3 setup.

Results

Thermoluminescence. $\text{Ba}_{4.98}\text{Eu}_{0.02}\text{Si}_{0.995}\text{Nb}_{0.005}\text{O}_4\text{Br}_6$ shows strong thermoluminescence after X-ray irradiation. The emission consists of a band with a maximum at 442 nm; the same band is also observed in photoluminescence⁵ and originates from Eu^{2+} .

The glow curve after X-ray irradiation is given in Figure 1a. By heating to 375 and 420 K, respectively, the first and second peak were removed (thermal cleaning) in order to make an initial rise fit⁹ possible. The thermal trap depth of the second and third peak found in this way are given in Table 1. It appears that the broad peak between 370 and 480 K consists of at least two different peaks which are unresolved in the complete glow curve. It was not possible to determine whether this peak consists of two discrete peaks or is caused by a continuous distribution in trap depths or frequency factors. The trap depth found is higher if the phosphor is thermally emptied at a higher temperature; at the highest emptying temperatures, the trap depth equals the value found after optical bleaching (see below). It appears that the peaks at higher temperatures in the glow curve correspond to the deeper traps.

* Abstract published in *Advance ACS Abstracts*, August 15, 1994.

(1) Takahashi, K.; Kohda, K.; Miyahara, J.; Kanemitsu, Y.; Amitani, K.; Shionoya, S. *J. Lumin.* **1984**, *31*, 266.

(2) Thoms, M.; von Seggern, H.; Winnacker, A. *Phys. Rev. B* **1991**, *44*, 9240.

(3) Koschnik, F.; Spaeth, J. M.; Eachus, R. S.; McDugle, W. G.; Nuttall, R. H. D. *Phys. Rev. Lett.* **1991**, *67*, 3571.

(4) Garcia, A.; Latourrette, B.; Fouassier, C. *J. Electrochem. Soc.* **1979**, *126*, 1734.

(5) Meijerink, A.; Blasse, G. *J. Lumin.* **1990**, *47*, 1.

(6) Meijerink, A.; Blasse, G.; Struyve, L. *Mater. Chem. Phys.* **1989**, *21*, 261.

(7) Meijerink, A.; Blasse, G. *J. Phys. D, Appl. Phys.* **1991**, *24*, 626.

(8) IJdo, D. J. W.; Jansen, J.; Schipper, W. J. *Mater. Res. Bull.* **1992**, *27*, 45.

(9) McKeever, S. W. S. *Thermoluminescence of Solids*; Cambridge University Press: Cambridge, 1985.

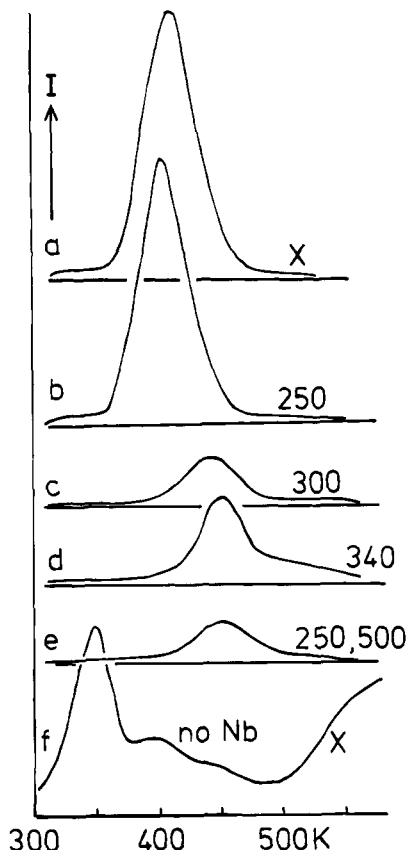


Figure 1. Glow curves for $\text{Ba}_{4.98}\text{Eu}_{0.02}\text{Si}_{0.995}\text{Nb}_{0.005}\text{O}_4\text{Br}_6$ (a–e) and $\text{Ba}_{4.98}\text{Eu}_{0.02}\text{SiO}_4\text{Br}_6$ (f) after 3 min. X-ray irradiation (a), 250 nm irradiation (b), 300 nm irradiation (c), 340 nm irradiation (d), 250 nm irradiation and 3 min 500 nm bleaching (e) and X rays (f). The emission wavelength was 442 nm. The heating rate was 10 K/min.

Table 1. Thermal Trap Depths Calculated with the Initial Rise Method from the Glow Curve of $\text{Ba}_{4.98}\text{Eu}_{0.02}\text{Si}_{0.995}\text{Nb}_{0.005}\text{O}_4\text{Br}_6$

T_{max} (K) after thermal cleaning	temp applied for thermal cleaning (K)	thermal trap depth (eV)	thermal trap depth (eV) after optical bleaching
340		0.98 ± 0.02	
415	375	1.19 ± 0.02	
440	420	1.25 ± 0.02	1.28 ± 0.03
> 500 ^a			

^a Not calculated due to the low intensity after thermal cleaning.

It is also possible to fill this storage phosphor efficiently with UV radiation. Irradiation at 250 nm for 1 min (in the setup described above) yields the same glow curve as X-ray irradiation for 3 min (Figure 1b). The intensities of the TSL signals are comparable. Irradiation at 275 nm gives approximately the same glow curve, but the filling efficiency at this wavelength is lower. For irradiation at 300 nm a different glow curve is obtained (Figure 1c): the high-temperature part is the same, but some intensity lacks at lower temperatures. When 340 nm irradiation is used, the glow curve is again different (Figure 1d); it consists of the highest temperature region of the original curve only. Irradiation at wavelengths longer than 350 nm does not lead to thermoluminescence. For each wavelength the filling efficiency was roughly estimated (see below).

It is possible to photostimulate the irradiated phosphor at all wavelengths between 375 and 650 nm. At shorter wavelengths no reliable measurements are

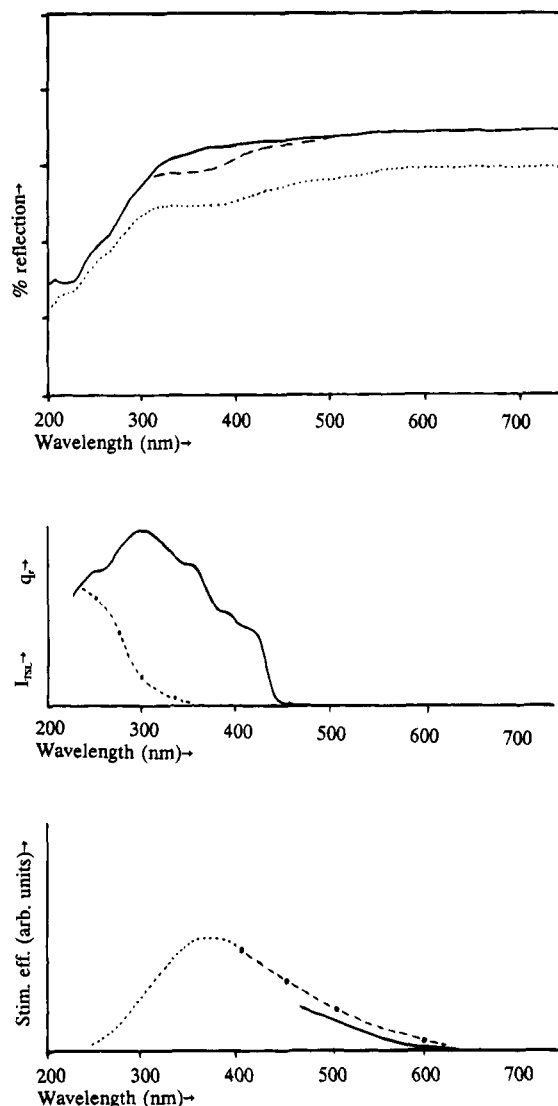


Figure 2. (a) Diffuse reflection spectra of $\text{Ba}_5\text{Si}_{0.995}\text{Nb}_{0.005}\text{O}_4\text{Br}_6$ before (solid line) and after 250 nm irradiation for 3 min (dashed line), and after X-ray irradiation (dotted line). (b) Excitation spectrum of the 442 nm emission of $\text{Ba}_{4.98}\text{Eu}_{0.02}\text{Si}_{0.995}\text{Nb}_{0.005}\text{O}_4\text{Br}_6$ (solid line) and filling efficiency (dashed line) estimated from TSL experiments. (c) Optical stimulation spectrum of $\text{Ba}_{4.98}\text{Eu}_{0.02}\text{Si}_{0.995}\text{Nb}_{0.005}\text{O}_4\text{Br}_6$ after 250 nm irradiation for 3 min (solid line), and bleaching efficiency estimated from TSL experiments (dashed line) and extrapolation of the bleaching efficiency (dotted line, see text).

possible, since the phosphor is refilled at the same time by the incident UV radiation. When the phosphor is first filled at 250 nm and then intensely photostimulated at 500 nm, the PSL signal drops to a nearly constant value after three minutes; its intensity is less than 1% of the signal at the start of the stimulation. However, a considerable TSL signal, about 25% of the original intensity, was measured after this bleaching procedure (Figure 1e). This glow curve is essentially the same as the glow curve obtained after 340 nm irradiation. Bleaching at other wavelengths also leads to this glow curve. From the time needed to eliminate the low-temperature part of the glow curve, the efficiency of bleaching was roughly estimated for several wavelengths (see Figure 2c).

It seems that the traps responsible for the remaining glow curve can be bleached as well; after 30 min of intense bleaching at 500 nm, the intensity of the

remaining glow curve has diminished by some 50%. Nevertheless it is clear that either these traps have a very low absorption coefficient, or the recombination probability for electrons from these traps is low.

All the glow curves obtained for this material are different from the curve obtained for niobium-free $\text{Ba}_5\text{SiO}_4\text{Br}_6\text{:Eu}^{2+}$ (Figure 1f).

Optical Measurements. The diffuse reflection spectrum of $\text{Ba}_5\text{SiO}_4\text{Br}_6\text{:Nb}$ is given in Figure 2a. It consists of a strong, broad absorption band in the short-UV range. The band is not present in undoped samples. Upon excitation into this band at 260 nm, no luminescence is observed, not even at 4.2 K. The band is also observed in samples containing Eu^{2+} ; in this case it is superimposed on the Eu^{2+} absorption.

The diffuse reflection spectrum after 250 nm and X-ray irradiation is also given in Figure 2a. An additional absorption band is present with a maximum at 360 nm after UV irradiation. The same band appears after X-ray irradiation, as well as an additional absorption in the whole spectral range. This gives the samples a brownish appearance. In europium-doped samples, the very broad absorption is also present. The presence of the 360 nm band could not be confirmed in this case, since the Eu^{2+} ion has a strong absorption in this spectral region.

The intensity of the Eu^{2+} emission under UV excitation diminishes by some 10% after prolonged irradiation. The extra absorption in the sample is probably responsible for this decrease, since the tail of this absorption band overlaps with the Eu^{2+} emission band. However, it cannot be excluded that the missing Eu^{2+} emission intensity is caused by the fact that some Eu^{2+} ions take part in the storage mechanism, so that they are not available for excitation.

No Eu^{3+} luminescence was observed after irradiation.

EPR. EPR measurements were first performed on samples doped with niobium only, since the strongly paramagnetic Eu^{2+} ion effectively obscures other signals present in the sample. Unirradiated $\text{Ba}_5\text{SiO}_4\text{Br}_6\text{:Nb}$ has no EPR signal in the range from 2600 to 4200 G. After irradiation with X-rays for 3 min, a clear EPR signal is observed. It consists of ten equally spaced lines with a spacing of 24 ± 3 G (Figure 3a). The g value is 2.00 ± 0.01 . In addition, weak lines at 3335 and 3650 G are present, as well as a large step between the fifth and the sixth line in the center of the spectrum at 3455 G. This latter value corresponds to $g = 2.01$.

In $\text{Ba}_5\text{SiO}_4\text{Br}_6$ doped with both europium and niobium the same signal is seen after irradiation (Figure 3b). However, in this case the signal is partially obscured by a strong Eu^{2+} background signal which is identical before and after irradiation. In the presence of Eu^{2+} the signal at $g = 2.01$ is stronger than in the sample without Eu^{2+} .

The 10 lines in the EPR spectrum do not appear in samples without niobium: in undoped $\text{Ba}_5\text{SiO}_4\text{Br}_6$ no EPR signal is observed before or after irradiation, whereas in $\text{Ba}_5\text{SiO}_4\text{Br}_6\text{:Eu}^{2+}$ the EPR spectrum before and after irradiation is the same.

Discussion

First we will discuss the thermoluminescence experiments and explain the glow curves on the bases of the TSL and optical experiments. In the second part of the

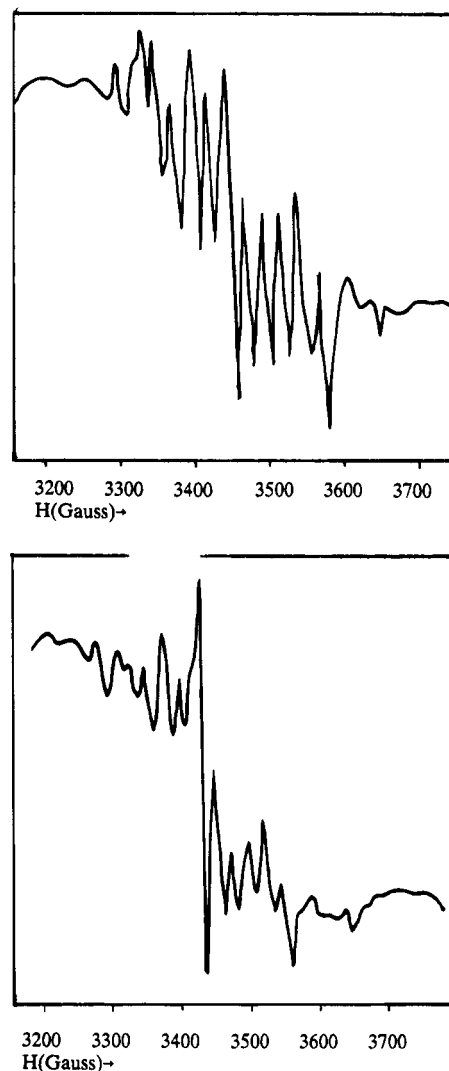


Figure 3. EPR spectrum of X-ray irradiated $\text{Ba}_5\text{Si}_{0.995}\text{Nb}_{0.005}\text{O}_4\text{Br}_6$ (a) and X-ray irradiated $\text{Ba}_{4.98}\text{Eu}_{0.02}\text{Si}_{0.995}\text{Nb}_{0.005}\text{O}_4\text{Br}_6$ (b) at room temperature. The microwave frequencies were 9.72 GHz (a) and 9.67 GHz (b).

discussion a physical model will be proposed using also the EPR results.

Glow Curves. The complete glow curve, viz. the curve obtained after X-ray or 250 nm irradiation, consists of at least four peaks. From Table 1 it becomes clear that the traps that cause these peaks appear in the glow curve in increasing trap depth order. The fourth, low peak at about 510 K could not be analyzed, but we assume that it is due to an even deeper trap than the other peaks.

The fact that UV irradiation induced thermoluminescence indicates that this type of irradiation leads to photoionization. The effect of this photoionization at 250 nm is the same as that of X-ray irradiation. However, 300 and 340 nm radiation seem to have a different effect. A possible explanation is the observation that upon irradiation with longer wavelengths, the deeper traps are filled selectively. If the filling process is local, i.e., the electrons enter the traps via a tunneling process, this seems a reasonable assumption.

Upon irradiation with higher energy irradiation, the electrons can also reach traps with energy levels closer to the conduction band. However, this sequence of trap depths would become apparent only if the recombination

took place via the conduction band. This conflicts with a local filling process. On the other hand, if the recombination process is also local, no relation is expected between the energy needed to fill the traps, and the energy needed to empty them. Recombination takes place after stimulation from the ground state of the trap to the excited (tunneling) state; the energy difference between these levels is independent of their position with respect to the ground state of the center from which the electron originates. Hence, the filling energy dependence of the peaks in the glow curve would be arbitrary.

In our opinion it is more obvious to assume that there is a competition between bleaching and filling at 300 and 340 nm. From Figure 2c one can infer that bleaching does not only take place between 650 and 375 nm. Although it is impossible to measure the bleaching efficiency curve for $\lambda < 375$ nm, it is unlikely that the bleaching efficiency drops sharply to zero at shorter wavelengths. Its form will be either a plateau or the mirror image of the slope between 650 and 375 nm. Indeed, after UV or X-ray irradiation a broad absorption band appears in the reflection spectrum with a maximum at 360 nm. The slope of this band at longer wavelengths fits the bleaching efficiency curve and the stimulation spectrum. This implies that bleaching also takes place at 350 and 300 nm. Here one should keep in mind that only the low-temperature part of the glow curve disappears under optical stimulation. Therefore, all traps are being filled at 340 nm, but the shallowest traps are emptied again more efficiently at the same time, leaving only the deepest traps filled. At 300 nm, also part of the shallow traps remain filled. At 250 nm, bleaching is apparently not as efficient as filling or may even be absent. From these observations, we have estimated the bleaching efficiency curve (for the lower temperature part of the glow curve) at wavelengths shorter than 400 nm (Figure 2c).

The filling efficiency curve (Figure 2b) was estimated from the glow curves and represents the excitation spectrum of the photoionization process responsible for the filling of the phosphor. It is different from the excitation spectrum of the Eu^{2+} emission (Figure 2b), but coincides with the absorption band which peaks at 250 nm in the diffuse reflection spectrum of unirradiated $\text{Ba}_5\text{SiO}_4\text{Br}_6:\text{Nb}$ (Figure 2a).

We ascribe this absorption band to a charge-transfer (CT) transition from oxygen to niobium in a niobate group (NbO_4 or NbO_6). The SiO_4 groups in the $\text{Ba}_5\text{SiO}_4\text{Br}_6$ structure are tetrahedral;⁸ since this crystal structure does not contain octahedral sites, the most obvious possibility for the incorporation of a niobate group in this lattice is substitution of a silicate group by a tetrahedral niobate group (NbO_4^{3-}). NbO_4 groups have been found in the rare earth niobates RENbO_4 ;¹⁰ the oxide ions form a distorted tetrahedron. An absorption band similar to the one observed here has indeed been observed for YNbO_4 ,¹¹ but in this case the niobate group luminesces efficiently. Other niobates usually contain octahedral NbO_6 groups.¹² Octahedral niobate groups can also have an absorption like the one observed

here,¹³⁻¹⁵ but the incorporation of an octahedral niobate group in this lattice seems improbable.

The absence of luminescence from the niobate group can be ascribed to the influence of the positive effective charge on the niobate group.¹⁶ A more obvious explanation, viz., quenching by photoionization will be discussed below.

If the niobium ions are pentavalent prior to irradiation, it is obvious to assume that they trap an electron during irradiation and become Nb^{4+} . The Nb^{5+} ion is known to trap electrons under X-ray irradiation in LiNbO_3 .¹⁷ Irradiation of this material with a xenon lamp (one-photon ionization) or with a Nd:YAG laser (ionization by multiphoton absorption) generates free electrons and produces Nb^{4+} as well.¹⁸⁻²⁰ In this lattice, tetravalent niobium is thermally unstable at room temperature.

So far, no absorption band could be unambiguously attributed to Nb^{4+} in LiNbO_3 ,²⁰ but some absorption spectra have been published for tetravalent niobium in other lattices. In K_3NbF_7 , Nb^{4+} has weak d-shell absorption bands at 16 500, 19 750, and 28 500 cm^{-1} .²¹ In octahedral chloride coordination, there are relatively weak d-shell absorptions in the visible, as well as a stronger CT absorption in the near-UV region.²² In ZrNbO_4 , the absorption lies in the blue region.²³ In the present case a band in the near-UV is observed after irradiation. This could be the CT transition in the NbO_4^{4-} group. Due to the low concentration of the filled traps, the parity-forbidden d-shell absorptions are probably too weak to be observed.

The origin of the extra, very broad absorption remains unclear; in LiNbO_3 , however, Schirmer and von der Linde¹⁸ observed a very broad band between 300 and 900 nm after photoionization. They ascribed this band to oxidic hole centers.

We note that the absorption band at 360 nm in the reflection spectrum coincides with the bleaching efficiency curve estimated from the TSL experiments (Figure 2c). The optical stimulation spectrum also seems to coincide with the bleaching efficiency and the onset of the absorption band, but it cannot be measured at wavelengths shorter than the emission wavelength of the phosphor.

Further evidence for the valence state of the niobium ion in the lattice is provided by the EPR experiments; this is discussed in the next section.

EPR Experiments and Physical Model. The 10-line EPR spectrum which is present after irradiation is

(13) Blasse, G.; de Haart, L. G. *J. Mater. Chem. Phys.* **1986**, *14*, 481.

(14) Blasse, G.; Dirksen, G. J.; Crosnier, M. P.; Piffard, Y. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 425.

(15) Blasse, G.; Dirksen, G. *J. Inorg. Chim. Acta* **1989**, *157*, 141.

(16) van der Voort, D.; Blasse, G. *Chem. Mater.* **1991**, *3*, 1041.

(17) Schirmer, O. F.; Thiemann, O.; Wöhlecke, M. *J. Phys. Chem. Solids* **1991**, *52*, 185.

(18) Schirmer, O. F.; von der Linde, D. *Appl. Phys. Lett.* **1978**, *33*, 35.

(19) Halliburton, L. E.; Sweeney, K. L.; Chen, C. Y. *Nucl. Instrum. Meth. Phys. Res.* **1984**, *B1*, 344.

(20) Sweeney, K. L.; Halliburton, L. E.; Bryan, D. A.; Rice, R. R.; Gerson, R.; Tomaschke, H. E. *J. Appl. Phys.* **1985**, *57*, 1036.

(21) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

(22) Horner, S. M.; Clark, R. J. H.; Crociani, B.; Copley, D. B.; Horner, W. W.; Collier, E. N.; Tyree, S. Y., Jr. *Inorg. Chem.* **1968**, *7*, 1859.

(23) diGregorio, S.; Greenblatt, M.; Pifer, J. H. *Phys. Status Solidi b* **1980**, *101*, K147.

(10) Ferguson, R. B. *Can. Mineral.* **1957**, *6*, 72.

(11) Wanmaker, W. L.; Bril, A.; ter Vrugt, J. W.; Broos, J. *Philips Res. Rep.* **1966**, *21*, 270.

(12) Blasse, G. *Struct. Bonding* **1980**, *42*, 1.

characteristic of Nb^{4+} .^{18,19,23,24} Niobium has one isotope (^{93}Nb) with a nuclear spin of 9/2. This leads to a hyperfine splitting of the EPR signal of Nb^{4+} into 10 equally spaced lines of the same intensity. It is striking that the signal can be detected at all, since for other systems a considerable anisotropy of the hyperfine structure has been observed.^{17,23} The anisotropy in those systems arises from the fact that the unpaired electron occupies a d orbital (the electron configuration of Nb^{4+} is $4d^1$). If the system under study had such an anisotropy, the hyperfine structure would not be clearly observed in a powder sample. Moreover, the isotropic hyperfine splitting of 24 G is also considerably smaller than that in a tetrahedral organic complex ($A_{\text{iso}} = 80 \text{ G}^{24}$). Presumably the paramagnetic electron in the system under study is delocalized in a molecular orbital on the niobate group, rather than localized on the niobium itself. This could explain the apparent isotropy of the signal as well as the relatively small interaction with the niobium nucleus. The g value, which is that of a free electron, also points into this direction. Indeed, Sweeney et al.²⁰ indicate for LiNbO_3 that the notation Nb^{4+} is only formal, since the electron is strongly delocalized over the oxide ligands due to a high degree of covalency in the niobate group. The covalency may be enhanced in the present case due to the fact that the niobate group substitutes for a considerably smaller silicate group, which shortens the Nb–O distances.

It should be noted that the TSL experiments point to at least four different trapping centers. However, in the EPR spectra the signal seems to arise from one center only. If more centers were present, the EPR spectrum is expected to be a sum of several spectra with different hyperfine splittings. It is not clear whether the additional features at 3335 and 3650 G belong to another paramagnetic Nb species. Perhaps the relative broadness of the lines is due to the presence of several closely-resembling trapping centers. In the crystal structure, there is only one crystallographic site for the SiO_4^{4-} group,⁸ the incorporation of a NbO_4^{3-} group, however, requires local charge compensation. Since there are four different sites for Br^- and three sites for Ba^{2+} , it can be easily understood that several different NbO_4^{3-} electron traps are present.

The additional signal in the EPR spectrum at 3455 G indicates the presence of another, different paramagnetic species. The fact that its g value is almost 2 indicates that it is due to an electron or a hole with little interaction with its surroundings. This center could, for instance, be another electron trap, like an electron in a bromine vacancy (F_{Br} center). However, this is unlikely since in $\text{Ba}_5\text{SiO}_4\text{Br}_6:\text{Eu}^{2+}$, where the electron traps are probably F_{Br} centers,^{6,7} no additional EPR signal after irradiation is observed. A second possibility is a trapped hole. From the optical experiments, it has become clear that the europium ion itself is not the hole trap. Also, the presence of europium is not essential for the trapping of electrons at the niobium sites, since materials without Eu clearly exhibit a niobium EPR signal. However, the presence of Eu^{2+} probably enhances the number of these traps, since the signal at $g = 2.01$ is relatively stronger in $\text{Ba}_5\text{SiO}_4\text{Br}_6:\text{Eu}^{2+}, \text{Nb}^{5+}$ than in $\text{Ba}_5\text{SiO}_4\text{Br}_6:\text{Nb}^{5+}$ (Figure 3). Perhaps the Eu^{2+}

ions stabilize a hole trap in the lattice. The hole could be trapped at an oxide site (forming O^-) as has been found in LiNbO_3 .¹⁸ Here, O^- has a single, rather broad EPR line at $g = 2.0294$. Other possibilities for the hole trap are an europium-stabilized $V_{\text{K}}(\text{Br}^-)$ center, as has been proposed for $\text{BaFBr}:\text{Eu}^{2+}$ by Rüter,²⁵ or an oxide ion substituting for Br^- , compensating the excess positive charge of the niobate group. Koschnik et al.³ found that the oxide ion can trap holes in $\text{BaFBr}:\text{Eu}^{2+}$. On the basis of the present results it is impossible to attribute the signal to one of these traps.

These observations lead us to the following physical model. Upon irradiation with UV, an electron is excited from an oxide ion to niobium in a NbO_4 group. Due to the large relaxation which follows the CT excitation, the niobate group returns nonradiatively to its ground state as the electron returns to the oxygen. However, there is a second possibility: the electron stays on the niobium, or rather the niobate group, while the hole, which is left on one of the oxide ligands, moves away from the niobate group and is trapped elsewhere in the lattice. If this is the more probable process, it may explain the absence of photoluminescence in the niobate group. Thus, a metastable situation is created, where Nb^{5+} acts as an electron trap, becoming Nb^{4+} (or NbO_4^{4-}); the hole could be trapped as a $V_{\text{K}}(\text{Br}_2)^-$ center. Irradiation with X-rays has the same effect. Photoionization of a charge-transfer state has been observed before for $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$,^{26,27} where a hole leaves the Eu^{3+} ion, which becomes Eu^{2+} . This state has a high stability.

Upon stimulation, the electron is stimulated and recombines with the hole. The stimulation spectrum and the reflection spectrum after irradiation seem to indicate that indeed Nb^{4+} is the trap which is stimulated. The energy that is released during recombination is transferred to an Eu^{2+} ion, which gives the stimulated luminescence. This type of energy transfer from an electron–hole pair to Eu^{2+} has also been proposed by Rüter and von Seggern.²⁵ This mechanism implies that the europium ion and the niobate group should be associated. Since the Eu^{2+} ion is too small for the barium site and the niobate group too big for the silicate site, this does not seem unrealistic.

In this context we note that some of our nominally europium-free samples contain Eu^{2+} in trace quantities; the Eu^{2+} photoluminescence is very weak, but these samples exhibit a considerable Eu^{2+} emission under thermal stimulation. When the europium ions and the niobate groups are statistically distributed through the lattice, an efficient transfer from the recombination center to Eu^{2+} seems improbable.

Of course it is also possible to imagine a mechanism where the hole is stimulated, but this would probably lead to recombination at the electron trap, viz., the niobate group; the recombination energy would then be lost nonradiatively before it could be transferred to Eu^{2+} , since the luminescence of the niobate group is quenched at all temperatures.

(25) Rüter, H. H.; von Seggern, H.; Reininger, R.; Saile, V. *Phys. Rev. Lett.* **1990**, *65*, 2438.

(26) Struck, C. W.; Fonger, W. H. *J. Lumin.* **1970**, *1*, 456.

(27) Forest, H.; Cocco, A.; Hersh, H. *J. Lumin.* **1970**, *3*, 25.

(24) Sanchez, C.; Vivien, D.; Livrage, J.; Sala-Pala, J.; Viard, B.; Guerschais, J. E. *J. Chem. Soc., Dalton Trans.* **1980**, 64.

Conclusion

In conclusion, we have shown that excitation into the niobate absorption band of $\text{Ba}_5\text{SiO}_4\text{Br}_6:\text{Eu}^{2+},\text{Nb}^{5+}$ leads to photoionization. The Nb^{5+} ion acts as an electron trap, becoming Nb^{4+} after irradiation. The phosphor

is thermally and optically stimuable; a competition between filling and bleaching takes place between 300 and 340 nm.

Acknowledgment. We thank our colleague H. Eviatar for her kind assistance with the EPR experiments.