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Luminescence of Ytterbium(II) in Alkaline Earth Fluorohalides

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The luminescence properties of divalent ytterbium in alkaline earth fluorohalides are reported. In the Ca and Sr fluorohalides an emission is observed in the 400-nm region. The excitation spectrum of CaFBr : Yb^{2+} is different from those of the others, which is ascribed to a different coordination of the metal ion in this compound. The luminescence of YbFBr is also studied. In this compound energy migration to Sm^{2+} occurs. In BaFCl and BaFBr no Yb^{2+} luminescence is observed. From thermoluminescence measurements it is concluded that the Ca and Sr compounds act as storage phosphors and that the storage and recombination mechanisms are similar to those of the Eu^{2+}-activated compositions.

Introduction

The luminescence of divalent ytterbium has been studied in several hosts (*1–9*). In this paper the luminescence of Yb^{2+} in alkaline earth fluorohalides (MFX, where M = Ca, Sr, Ba and X = Cl, Br) is reported. Compounds of the type MFX doped with divalent europium are known to be efficient photoluminescent, X-ray and X-ray storage phosphors (*10–13*). The luminescence of divalent samarium in MFX compounds has also been studied (*14–17*). Therefore it seemed interesting to investigate the luminescence properties of divalent ytterbium in these hosts as well. The luminescence properties of the isostructural compound YbFBr were also studied. Furthermore the storage properties of the Yb-doped MFX compounds were studied, because they are expected to act as storage phosphors. Divalent ytterbium could play the same role as divalent europium in the trapping and recombination processes. There is a considerable controversy on the storage mechanisms in Eu-doped MFX compounds (*10, 11, 18, 19*). This is probably caused, among other reasons, by different preparation techniques, since the number and nature of trapping centers is known to depend strongly on preparation conditions. Therefore, we prepared Eu-doped samples in the same way as the Yb-doped materials for reasons of comparison.

MFX compounds have tetragonal symmetry (spacegroup $P4/nmm$); the metal ion is in a site with C_{4v} symmetry (*20*). It is coordinated on one side by a plane of four fluoride ions perpendicular to the c axis and by five chloride (bromide) ions on the other side. Four of these form a plane perpendicular to the c axis whereas the fifth is on the c

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axis. The luminescence properties of divalent ytterbium are due to 4*f*–5*d* transitions. The energy levels of the $4f^{13}5d$ excited configuration of Yb^{2+} in octahedral symmetry were elucidated by Piper *et al.* (*21*). The lowest excited levels are $T_{2u} + E_u$. These levels have mainly triplet character. About 3000 cm^{-1} above these levels is a T_{1u} level. Only transitions to and from T_{1u} are allowed (the ground state being A_{1g}). The lowest levels (T_{2u}, E_u), from which emission is to be expected, are further split into A_2, B_1, B_2 and E in C_{4v} site symmetry. From the ground state, only transitions to E are allowed.

In the case of Yb^{2+} in SrB_4O_7, a compound with approximately C_{4v} metal ion point symmetry, the decay time decreases steeply with temperature above 4.2 K. It has been concluded (*1*) that in this compound the E level is not the lowest excited level. The photoluminescence intensity of ytterbium in this host is weak, because the absorption strength of the transitions to the lowest T_{1u} levels is low, as was calculated earlier by Piper *et al.* (*21*).

In alkaline earth fluorides no intrinsic Yb^{2+} luminescence has been found (*7–9*); the luminescence in these compounds has been ascribed to an exciton bound to the ytterbium ions. These emissions consist usually of very broad bands. This study shows that in the calcium and strontium fluorohalides, the Yb^{2+} ion shows intrinsic luminescence. This emission is absent in the barium fluorohalides.

Experimental

Samples were prepared by heating an intimate mixture of the appropriate fluorides and chlorides or bromides and YbF_3 or EuF_3 for 5 hr at 500°C under a 25% hydrogen/75% nitrogen atmosphere. Solid solutions of the fluorochlorides and fluorobromides were prepared in the same way. Samples of $Ba_{0.99}Yb_{0.01}FBr$ and $Ba_{0.99}Yb_{0.01}FCl$ were prepared under a hydrogen atmosphere at 750°C. YbFBr was synthesized by heating a mixture of $YbBr_3$, YbF_3, and Yb metal for 7 days at 980°C under argon in a closed tantalum tube which had been sealed in an evacuated quartz tube. Powders were checked by X-ray powder diffraction.

Photoluminescence measurements were performed on a SPEX DM3000F spectrofluorometer equipped with two double-grating 0.22-m SPEX 1680 monochromators (resolution 0.1 nm). Thermoluminescence (TL) measurements were performed with the SPEX spectrofluorometer equipped with a high-temperature cell which has been described previously (*22*). Decay measurements were performed on a setup consisting of a frequency-doubled dye laser which was pumped by a Nd/YAG laser and a Spex 1269 monochromator. This setup was described previously in Ref. (*23*).

Results and Discussion

Compositions MFX : Yb^{2+} (M = Ca, Sr; X = Cl, Br)

Under UV excitation the calcium and strontium samples show a single, narrow emission band around 400 nm; the emission and excitation spectra are given in Figs. 1 and 2, respectively. The excitation and emission bands in all spectra are ascribed to transitions to and from states within the $4f^{13}5d$ configuration, since these are to be expected in this energy region. Like in SrB_4O_7 (*1, 24*), the Yb^{2+} emission is at slightly longer wavelength than that of Eu^{2+} (*12*). The photoluminescence intensity is weak due to the low absorption strength of Yb^{2+} in this spectral region. A low quantum efficiency can be excluded in view of other measurements to be discussed below.

The excitation spectra of $Ca_{0.99}Yb_{0.01}FCl$ (Fig. 2a) and $Sr_{0.99}Yb_{0.01}FCl$ (Fig. 2d) are comparable: they are dominated by two bands with maxima at about 285 and 320 nm. In $Sr_{0.99}Yb_{0.01}FBr$ (Fig. 2e) two similar bands are found at 290 and 340 nm. In addition

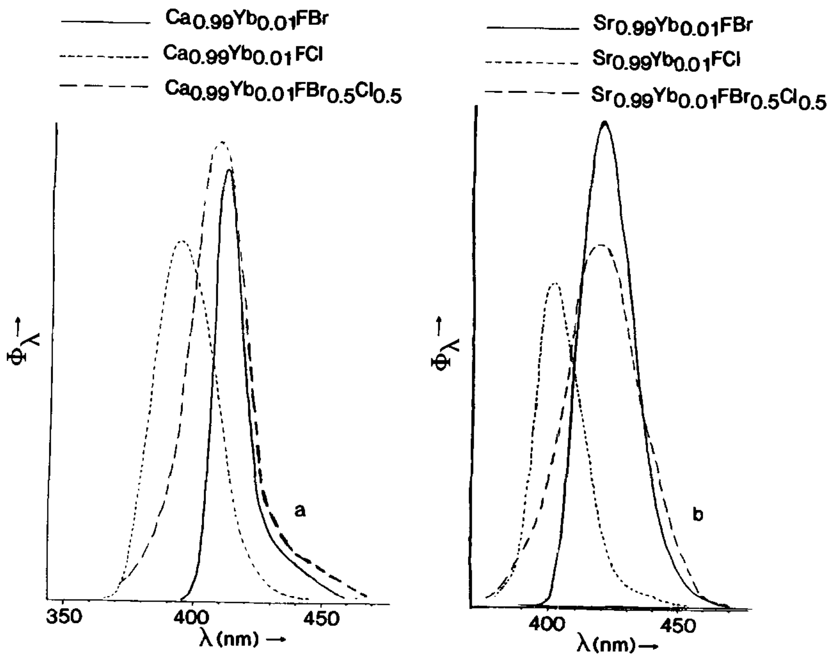

FIG. 1. Emission spectra of Yb-doped strontium and calcium fluorohalides at 4.2 K under excitation in the maximum of the strong band in the 290-nm region. Φ_λ denotes the radiant power per constant wavelength interval.

there is a small band at 250 nm. The excitation spectrum of $Ca_{0.99}Yb_{0.01}FBr$ (Fig. 2b) is substantially different from the other three. This might be due to the different coordination of the luminescent ion in $Ca_{0.99}Yb_{0.01}FBr$. Whereas the ratio c/a of the tetragonal unit cell of CaFCl, SrFCl, and SrFBr is close to 1.7, this ratio is 2.09 in CaFBr (*20*). This means that the bromide ion on the c axis in CaFBr is at a longer distance from the metal ion, making the structure more layer-like and the coordination number of the metal ion closer to 8. This may give rise to a different crystal field at the Yb^{2+} ion and to different transitions.

The excitation spectrum of the Yb^{2+} emission in a solid solution of CaFCl and CaFBr (Fig. 2c) looks like a sum of the spectra of the components, although the emission consists of a single band peaking at 400 nm under excitation in all bands; its maximum is between the emission maxima of CaFBr : Yb and CaFCl : Yb. The same seems to apply to a solid solution of SrFBr and SrFCl (Fig. 2f). X-ray diffraction shows a single phase in both cases, so that the sum effect in the excitation spectrum must be a coincidence. The emission band at 4.2 and 300 K in $Ca_{0.99}Yb_{0.01}FCl$ is broader than that of $Ca_{0.99}Yb_{0.01}FBr$ (see Fig. 1a). The same effect was observed for divalent europium in CaFCl and CaFBr. The reason for this could be a smaller offset of the excited state potential energy curve relative to the ground state curve. This could not be confirmed by analysis of the Stokes shifts, because it is impossible to identify the state from which the emission occurs in the excitation spectrum. However, if one simply considers the lowest excitation band, the Stokes shift would be 3060 cm^{-1} for $Ca_{0.99}Yb_{0.01}FBr$ and 3670 cm^{-1} for $Ca_{0.99}Yb_{0.01}FCl$. Perhaps this

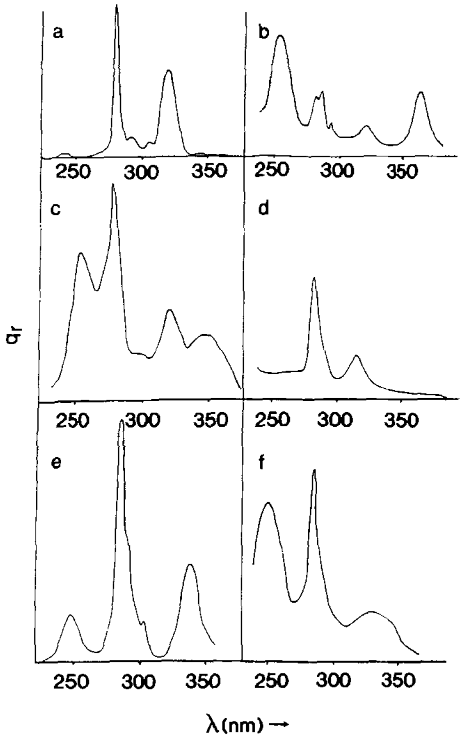

FIG. 2. Excitation spectra of $Ca_{0.99}Yb_{0.01}FCl$ (a), $Ca_{0.99}Yb_{0.01}FBr$ (b), $Ca_{0.99}Yb_{0.01}FBr_{0.5}Cl_{0.5}$ (c), $Sr_{0.99}Yb_{0.01}FCl$ (d), $Sr_{0.99}Yb_{0.01}FBr$ (e), and $Sr_{0.99}Yb_{0.01}FBr_{0.5}Cl_{0.5}$ (f) at 4.2 K. The excitation was measured at maximum emission intensity. q_r denotes the relative quantum output.

difference is also related to the structural difference mentioned above.

The emission intensity of Yb^{2+} in the compounds under consideration is the same at 4.2 and 300 K.

The temperature dependence of the decay time of the Yb^{2+} emission in the *MFX* compounds is given in Fig. 3. All decays are single exponential. At 4.2 K the decay time is extremely long for a (parity allowed) *f–d* transition. The value for $CaFBr : Yb^{2+}$ is particularly extreme ($\tau > 30$ ms). This might be related to the different surroundings of the metal ion which also causes the excitation spectrum to be different. The decay times show about the same temperature dependence as the decay time of $SrB_4O_7 : Yb^{2+}$: at relatively low temperatures (around 20 K) the decay time drops considerably. The room temperature decay times are 20 μs ($Ca_{0.99}Yb_{0.01}FCl$), 35 μs ($Ca_{0.99}Yb_{0.01}FBr$), 75 μs ($Sr_{0.99}Yb_{0.01}FCl$), and 85 μs ($Sr_{0.99}Yb_{0.01}FBr$). These are still relatively long for a 5*d*–4*f* transition; this can be explained by the fact that the lowest excited states have mainly triplet character (*21*), so that the emission is spin-forbidden. This is in accordance with the low absorption strength of these transitions.

The temperature dependence of the decay time was fitted to a three-level model following a similar approach for $SrB_4O_7 : Yb^{2+}$ (*1*). This could only be performed reliably for $CaFBr : Yb^{2+}$. For this case the metastable emitting level is found to be 70 cm^{-1} below the third level. The energy difference for $Sr_{0.99}Yb_{0.01}FCl$ and $Sr_{0.99}Yb_{0.01}FBr$ must be of the same order of magnitude, since the temperature dependence of the decay time is about the same as in $Ca_{0.99}Yb_{0.01}FBr$. Only in $Ca_{0.99}Yb_{0.01}FCl$ must the levels involved be closer together, because the decay time starts to drop at 5 K. In view of the complicated nature of the $4f^{13}5d$ configuration we have not tried to assign the transitions any further.

Compositions BaFX : Yb^{2+} (X = Cl, Br)

When $Ba_{0.99}Yb_{0.01}FBr$ and $Ba_{0.99}Yb_{0.01}FCl$ are synthesized in the same way as the strontium and calcium analogs, no luminescence is observed, not even at 4.2 K. Only when the samples are prepared at 750°C under a 100% hydrogen atmosphere, an efficient photoluminescence appears. It consists of a broad emission band with a maximum at 525 nm (BaFCl, 4.2 K) and 495 nm (BaFBr, 4.2 K) (Fig. 4). At room temperature the emission has the same intensity; the maxima are 510 nm (BaFCl) and 475 nm (BaFBr). This emission also appears in undoped samples, but only after prolonged firing under hydrogen at 750°C, and

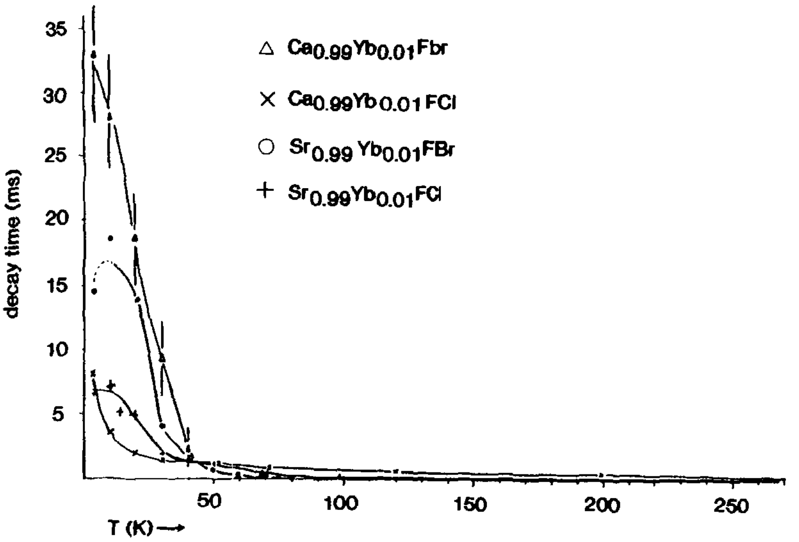

FIG. 3. Temperature dependence of the decay time of the Yb^{2+} emission in MFX compounds. Error bars are shown for $Ca_{0.99}Yb_{0.01}FBr$. The data points are connected with a solid line for clarity.

much less so at 500°C. An emission of this type was observed previously for BaFBr and BaFCl by Crawford *et al.* (*25*). They ascribed these emissions to $(Cl_2)^-$ and $(Br_2)^-$ V_k centers, respectively. Unlike in the present study, they found other emissions for the BaFCl case at considerably shorter wavelengths (300 and 370 nm, the latter of which is dominant at room temperature). They also found another emission in BaFBr at 300 nm which appears at about 150 K and vanishes at higher temperatures. These 300-nm emissions were ascribed to $(F_2)^-$ V_k-centers.

The absence of intrinsic emission from Yb^{2+} in samples prepared at 500°C may be due to the large difference in ionic size between Ba^{2+} and Yb^{2+}, the latter being 0.33

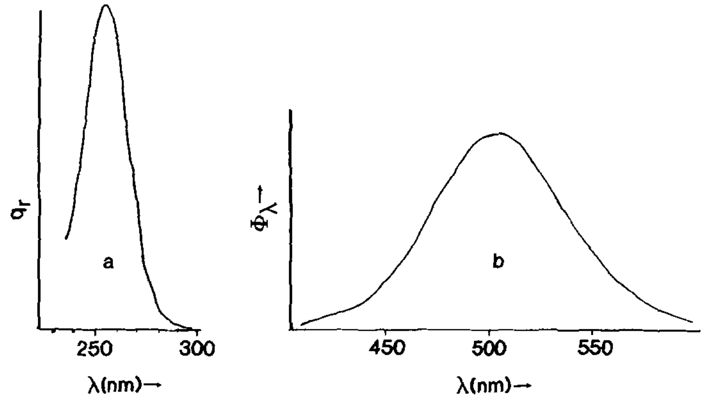

FIG. 4. Excitation (a) and emission (b) of $Ba_{0.99}Yb_{0.01}FBr$ at 4.2 K.

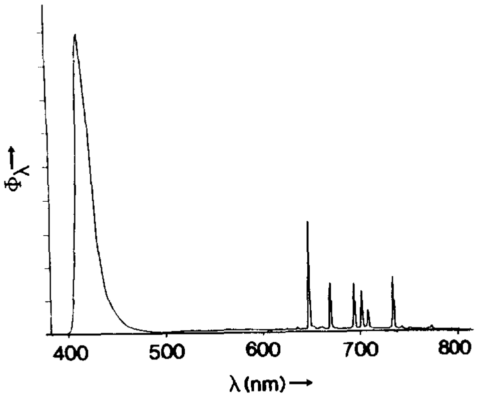

FIG. 5. Emission spectrum of YbFBr : Sm^{2+} upon excitation at 300 nm at 4.2 K.

Å smaller. This may lead to a low ytterbium solubility in BaFBr. Also, if Yb^{2+} is built in, its luminescence might well be quenched even at low temperatures due to the size difference. Finally, photoionization, followed by radiationless recombination, could take place. This process would be more favorable in the barium compounds (like in the alkaline earth fluoride series (*7–9*)). Bound exciton emission, however, like in, e.g., $BaF_2 : Eu^{2+}$, is not observed.

Although the luminescent center in $Ba_{0.99}Yb_{0.01}FCl$ and $Ba_{0.99}Yb_{0.01}FBr$ could not be identified, it seems that partial substitution of fluorine by hydrogen plays a role in its formation, as synthesis of the samples under hydrogen at 500°C or under 5% hydrogen at 750°C does not lead to this efficient photoluminescence. Compounds of the composition BaHBr and BaHCl are known (*26*); they have the same crystal structure and almost the same cell parameters as their fluorine analogs, so the assumption of substitution of some fluoride by hydride does not seem unrealistic. The formation of the center might further be enhanced by the presence of divalent ytterbium, because it takes a shorter firing time to obtain the photoluminescence in ytterbium-doped samples. Alternatively, the emission might originate from OH^- (which can substitute for both F^- and Br^-). IR absorption spectroscopy revealed the presence of OH^- in the samples. Why the luminescence is not observed after firing at 500°C is not clear; a detailed study is in progress. Firing of the ytterbium-doped calcium and strontium analogs at 750°C in hydrogen leads to irreproducible results.

YbFBr

The emission of YbFBr at 4.2 K is given in Fig. 5. There is an emission band similar to that in the diluted systems, with an emission maximum at 415 nm; apart from this, line emission is observed in the 635–850 nm region. This emission is ascribed to transitions within the $4f^6$ configuration of divalent samarium, which was apparently present as an impurity in the starting materials. The excitation spectra of the Yb^{2+} emission and the Sm^{2+} emission are given in Fig. 6. The positions of the bands in the Yb^{2+} excitation spectrum coincide with those in CaFBr : Yb^{2+}. This similarity may be caused by the fact that the ionic radii of Yb^{2+} and Ca^{2+} are almost equal. The compound YbFBr also has an elongated unit

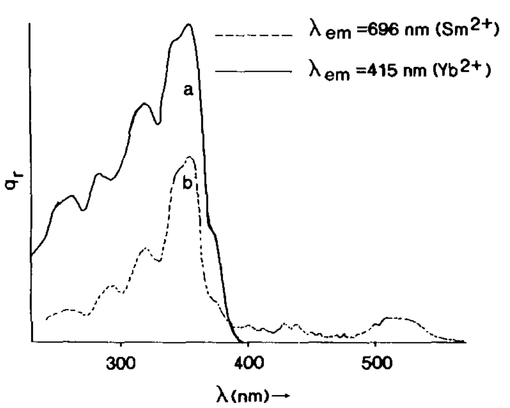

FIG. 6. Excitation spectra of the luminescence of YbFBr : Sm^{2+} at 4.2 K; emission wavelength at 415 nm (a) and 696 nm (b).

cell, though less so than CaFBr (c/a = 1.89 (*27*)). The excitation spectrum of YbFBr, however, shows less pronounced bands than the diluted systems. Because the total absorption strength is much higher in the former system, the exciting radiation has a smaller penetration depth, which could lead to less pronounced bands.

The shorter wavelength part of the Sm^{2+} excitation spectrum coincides with the Yb^{2+} excitation spectrum, indicating energy transfer from Yb^{2+} to Sm^{2+}. This transfer is probably a one-step process, because migration of excitation energy over the ytterbium lattice cannot have a long range at this temperature; the reason for this is the small spectral overlap (no zero-phonon lines are observed). This one-step transfer is expected to be efficient over large distances because the spectral overlap is large (higher crystal-field components of the Sm^{2+} $4f^55d$ configuration are present at 415 nm) and the Sm^{2+} excitation transition is allowed. Unfortunately the Sm^{2+} concentration is not known, which prevents an exact analysis; however, if a critical distance of 35 Å is assumed for energy transfer from Yb^{2+} to Sm^{2+}, a value taken from earlier work concerning energy transfer between inequivalent Eu^{2+} ions (*28*), it may be concluded from the relative intensities of the Sm^{2+} and Yb^{2+} emissions that the samarium concentration is of the order of 400 ppm.

At wavelengths longer than 390 nm the excitation spectrum of the Sm^{2+} lines shows a number of weak bands which are ascribed to $4f$–$5d$ transitions of Sm^{2+}. The very low Sm^{2+} concentration is reflected by the weakness of the $5d$ excitation bands of this ion.

At higher temperatures the spectral overlap between the ytterbium excitation and emission bands is no longer negligible. This makes migration of excitation energy over the ytterbium lattice possible, leading to a quenching of the 415-nm emission in favor of the Sm^{2+} emission, as observed experimentally. At room temperature the ytterbium emission is almost absent. As the nearest Yb–Yb distance in this lattice is 3.983 Å (*27*), efficient energy migration is to be expected. To the best of our knowledge, this is the first example of energy migration in an Yb^{2+} compound.

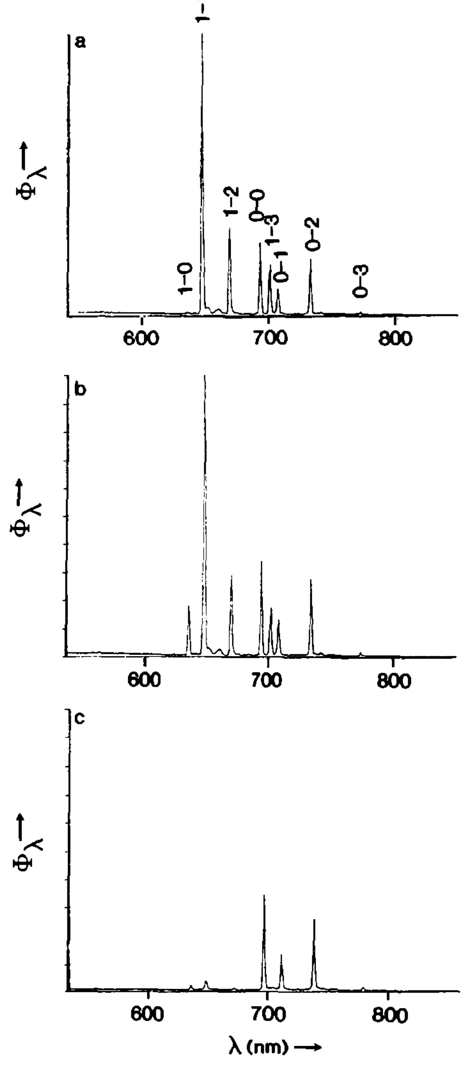

FIG. 7. Emission spectra of YbFBr : Sm^{2+} upon excitation at 520 nm at 4.2 K (a), 20 K (b), and room temperature (c). J labels are given for each ^5D_J–^7F_J transition.

The Sm^{2+} emission is due to $^5D_0$–^7F_J and $^5D_1$–^7F_J transitions (see Fig. 7). The crystal

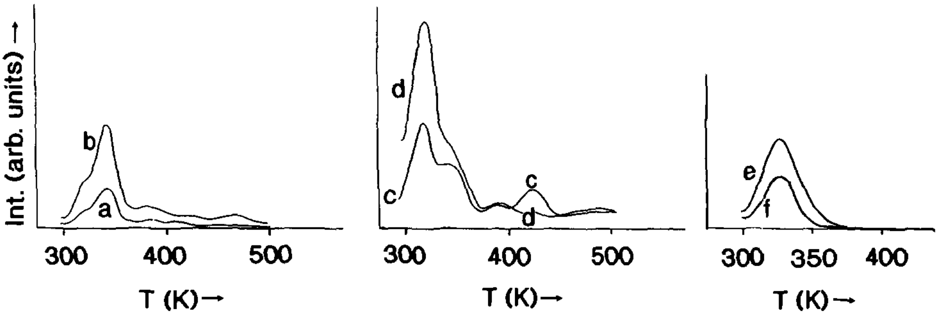

FIG. 8. Glow curves for $Sr_{0.99}Yb_{0.01}FBr$ (a), $Sr_{0.995}Eu_{0.005}FBr$ (b), $Sr_{0.995}Yb_{0.005}FCl$ (c), $Sr_{0.995}Eu_{0.005}FCl$ (d), $Ca_{0.995}Yb_{0.005}FCl$ (e), and $Ca_{0.995}Eu_{0.005}FCl$ (f) after irradiation with 40 kV, 20 mA Cu$K\alpha$ X-rays for 3 min. The heating rate was 10 K/min.

field is very weak in this compound because no splitting of the $^7F_{1-4}$ levels is observed with our setup (resolution approximately 0.1 nm). Very small splittings (of the order of 10 cm^{-1}) were found in SrFCl : Sm^{2+} (*14*) and BaFCl : Sm^{2+} (*15*). At 4.2 K some weak vibronic satellite lines are observed near the $^5D_1$–$^7F_0$, $^5D_1$–$^7F_1$, and $^5D_1$–$^7F_2$ emissions. Their energies are 55, 150, and 290 cm^{-1}. These energy values seem reasonable for vibrations in this host lattice.

At 4.2 K emission from the $^5D_1$ and $^5D_0$ levels is observed. Already at slightly higher temperatures (20 K) the $^5D_1$ emission intensity drops considerably. This is not consistent with the multiphonon emission model (*29*), since in that case the decrease would be less pronounced at low temperatures. We ascribe the decrease to a radiationless transition to the $^5D_0$ level via the lowest excited level of the $4f^55d$ configuration as has been described before for BaFCl : Sm^{2+} (*17*), $BaBr_2$: Sm^{2+}, and $BaCl_2$: Sm^{2+} (*30*). The closeness of this level is also reflected in the low $4f^55d$ excitation onset (550 nm), in the absence of $^5D_2$ emission, and in partial quenching of the $^5D_0$ emission at higher temperatures (its intensity does not increase as much with temperature as is expected by direct feeding from the $^5D_1$ state).

This also helps to explain the striking difference in $^5D_1$–$^7F_0$ emission intensity between 4.2 and 20 K (Figs. 7a and 7b). Whereas this emission is almost absent at 4.2 K, its intensity increases sharply as the temperature increases to 20 K. Above this temperature the emission intensity has the same temperature dependence as the other $^5D_1$ emissions. In C_{4v} symmetry the $^5D_1$ level splits into $E + A_2$, A_2 being the lower level in this symmetry (*14, 15*). Transitions between these levels and the ground state ($^7F_0$, A_1) are both allowed as magnetic dipole transitions, but only E–A_1 is allowed as a (forced) electric-dipole transition. Therefore, the emission intensity at 4.2 K reflects the magnetic-dipole transition probability, since only the A_2 level is populated. At 20 K the E level is populated because the crystal field splitting is small. The intensity of the emission from this level is much higher, reflecting the contribution of the (forced) electric-dipole transition. This must be caused by the closeness of the $4f^55d$ state to the $4f^6$ levels. The $4f^55d$ state is still high enough in energy, however, to observe emission from the $4f^6$ levels at room temperature.

Thermoluminescence

Glow curves for samples of $Ca_{0.995}Yb_{0.005}FCl$, $Sr_{0.995}Yb_{0.005}FCl$, and $Sr_{0.995}Yb_{0.005}FBr$ and the same hosts doped with an equal amount of europium are given in Fig. 8. From Fig. 8 it is clear that divalent ytterbium in CaFCl plays the same role in the storage process as divalent europium in this compound. For the other compounds there are some differences in the glow curves, but the maximum and the form of the peaks are the same. Afterglow at room temperature and poor resolution of the peaks prevent an analysis for the Sr compounds. For both CaFCl samples a thermal trap depth of 1.0 eV was found with the initial rise method and from the peak shape after thermal cleaning (*31*). The geometrical factor μ_g of the peak is 0.43 ± 0.01, indicating, within the experimental error, a kinetic order of 1 for the recombination process. A first-order process was also found in BaFBr : Eu^{2+} (*18, 19*).

In $Ca_{0.995}Yb_{0.005}FBr$ and $Ca_{0.995}Eu_{0.005}FBr$ no storage was found. The reason for this is not clear, but, since these are by far the most hygroscopic compounds in the series, decomposition might play a role because our present TL setup does not allow the complete exclusion of moisture. For the same reason no attempts were made to measure storage in YbFBr as this compound decomposes very rapidly in moist air.

In the barium fluorohalides no thermoluminescence is found either. If the luminescent center in these compounds is a V_k center, it cannot be excluded that recombination of electrons with these V_k centers during X-ray irradiation is efficient. This would inhibit the trapping of large numbers of electrons and holes, causing the thermoluminescence to be very weak.

The fact that Yb^{2+} plays the same role as Eu^{2+} in the storage process implies that Yb-doped fluorohalides may be good storage phosphors when prepared in the correct way. Major drawbacks for application of these materials in X-ray imaging systems, however, are the long Yb^{2+} decay time, causing extremely long readout times, and the fact that Yb^{2+} does not luminesce in the most suitable host materials for this application, viz. BaFBr and BaFCl. They may, however, find use as data storage materials in applications where no fast readout is needed.

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