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On the nature of the modification of luminescence spectra of alkaline-earth sulphides doped with cerium in the case of x-ray excitation

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Abstract. The luminescence spectra of CaS and SrS (as well as their solid solutions $\text{Ca}_{1-x}\text{Sr}_x\text{S}$) doped with cerium have been measured under excitation by x-ray tube and x-ray synchrotron radiation. The comparison of these spectra with those of photoluminescence has revealed two types of radiation-induced Ce^{3+} emission centre. We suppose that the first type is an activator ion displaced from the regular site as a result of the Coulomb interaction with charged defects (trapped electrons and holes) created in its neighbourhood by the excitation in the fundamental absorption range, whereas the second type is probably due to the creation, by x-ray exciting radiation, of sulphur vacancies in the first coordination shell of Ce^{3+} .

1. Introduction

Alkaline-earth sulphides doped with rare-earth ions have been known for a long time as excellent phosphors and have been studied by many investigators [1–12]. Because of their high cathodoluminescence efficiency, they have been successfully used for projection television and other electronic devices [6, 9]. Nowadays, they are considered as attractive candidates for application in high-definition television.

A detailed analysis of experimental results reported in the papers mentioned above reveals that the emission spectrum of these phosphors changes slightly with the variation in excitation energy. We did not, however, find a detailed discussion of this effect in the literature.

Cerium-doped alkaline-earth sulphides crystallize in the simple NaCl-type structure and are known to have a high emission brightness. Furthermore, Ce^{3+} ions incorporated in these crystals present a simple set of electronic levels sensitive to the crystal field. For these reasons, these phosphors are particularly suitable for use as model compounds in which to investigate the dependence of the emission spectrum on the excitation energy in ionic doped crystals.

In our previous paper [13], we established that the emission spectra of Ce^{3+} ions in CaS and SrS (as well as in their solid solutions $\text{Ca}_{1-x}\text{Sr}_x\text{S}$) are notably different when excited in the impurity band or at the fundamental absorption edge of the matrix. The origin of such behaviour was discussed in [14]. The study of this effect in the case of high-energy excitation is of a particular interest. Therefore, the present paper is devoted to the investigation of the x-ray-excited luminescence spectra of these phosphors.

2. Samples and experimental procedure

The method of preparing $\text{Ca}_{1-x}\text{Sr}_x\text{S}$ powder samples ($0 \leq x \leq 1$, $\Delta x = 0,05$) activated by cerium and the experimental apparatus used to measure their photoluminescence spectra have been described in [13]. To obtain the x-ray luminescence spectra the excitation sources that we used were an x-ray tube (30 kV; 10 mA) and also synchrotron radiation in the x-ray range from the wiggler of storage ring VEEP-3 (Institute Of Nuclear Physics, Novosibirsk). All luminescence spectra have been corrected with respect to the monochromator apparatus function and photomultiplier sensitivity.

3. Experimental results

Figure 1 shows luminescence spectra of $\text{CaS}:\text{Ce}^{3+}$ and $\text{SrS}:\text{Ce}^{3+}$ measured under different excitation energies. It is important to note that for $\text{CaS}:\text{Ce}^{3+}$ (figure 1(a)) the spectrum excited in the activator band (curve 1, open circles) is identical with that excited at the fundamental absorption edge (curve 2, full curve), whereas the spectrum excited by x-rays (curve 3) presents important modifications: the width and relative intensity of its long-wavelength wing increase. For $\text{SrS}:\text{Ce}^{3+}$ (figure 1(b)) a similar modification of the emission spectrum appears clearly with excitation of the fundamental absorption edge (curve 2) and is intensified with x-ray excitation (curve 3). Another interesting feature shown in this figure is the difference between the luminescence spectra excited by the x-ray tube (curves 3) and x-ray synchrotron radiation (curves 4). In the last case the width and relative intensity of the long-wavelength wing are more important.

Figure 2 depicts the Ce^{3+} emission spectra in the series of solid solutions $\text{Ca}_{1-x}\text{Sr}_x\text{S}$ obtained with x-ray tube excitation. As seen in this figure, with the increase in SrS concentration x in the solid solution, the modification of the spectrum shape (relative to the $\text{CaS}:\text{Ce}^{3+}$ emission spectrum) becomes more and more marked and reaches its culmination point for $\text{SrS}:\text{Ce}$. This is manifested as a broadening of the spectrum, an increase in the relative intensity of its long-wavelength wing and a more pronounced overlap of the two bands. Furthermore, on increase in x from 0 to 1, the spectrum shifts towards higher energies by about 0.15 eV.

4. Discussion

In previous work [14], we analysed in detail the photoluminescence spectra of the phosphors $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Ce}^{3+}$. We then established that, for every sample, the spectrum measured under excitation in the high fundamental absorption range may be represented, with high accuracy, as the sum of two spectra: the first measured under direct activator excitation and the second with a similar shape but shifted relative to the former towards lower energies by a value which increases with increasing x and reaches 0.12 eV for $\text{SrS}:\text{Ce}^{3+}$ (figure 3).

We have assigned the first spectrum to the Ce^{3+} centres located in the sites with O_h cubic symmetry. The second spectrum was attributed to the contribution of another type of Ce^{3+} emission centre which is formed in the case of interband excitation and which we called a radiation-induced centre (RIC). We believe that these centres appear as a result of the displacement of Ce^{3+} ions from the sites of O_h symmetry (the centres of the octahedral complex $\text{Ce}^{3+}\text{S}_6^{2-}$) on account of their Coulomb interaction with radiative defects situated not far from them and created by the interband exciting radiation. In this case, the crystal

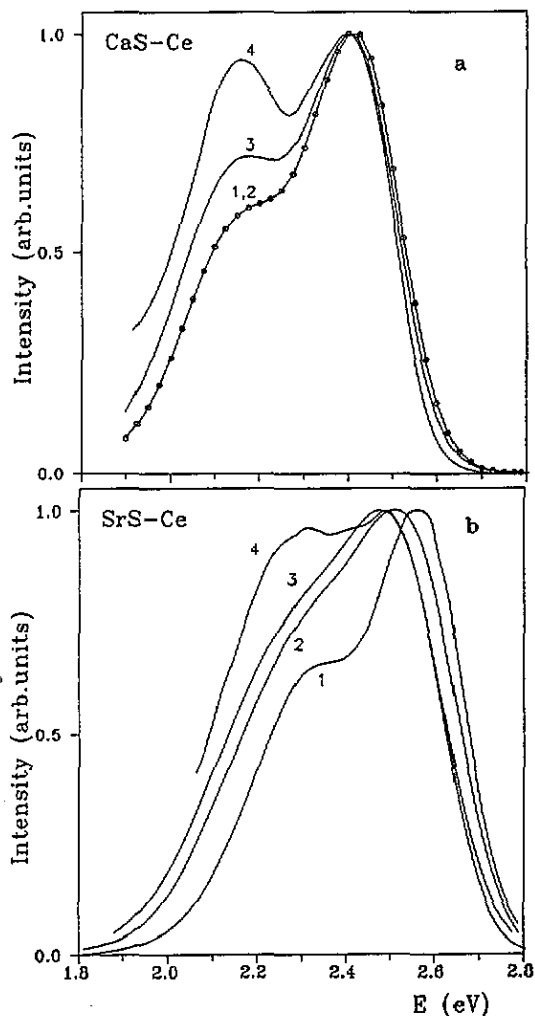


Figure 1. Luminescence spectra of (a) $CaS:Ce^{3+}$ and (b) $SrS:Ce^{3+}$ measured under different excitation energies: curves 1, activator excitation; curves 2, fundamental absorption edge excitation; curves 3, x-ray tube excitation; curves 4, x-ray synchrotron radiation excitation. The spectra have been normalized to the maximum intensity ($T = 300$ K).

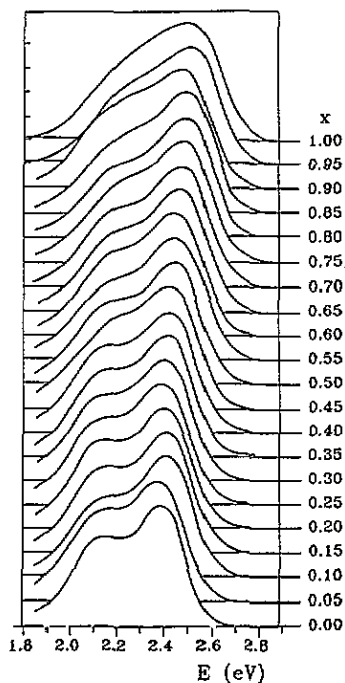


Figure 2. Luminescence spectra of Ce^{3+} in the concentration range of solid solutions $Ca_{1-x}Sr_xS$ (x-ray tube excitation; $T = 300$ K).

field may still be regarded as cubic, but with a contribution from a component with a lower symmetry. This causes a shift in the lower component of the Ce^{3+} excited level (the ${}^2T_{2g}$ ($5d$) state approached the fundamental $4f$ state) and therefore the spectrum attributed to RICs is shifted towards lower energies relative to the spectrum of the non-perturbed centres.

It is important to note that, although the spatial distribution of the charged defects created (which is responsible for the displacement of Ce^{3+} ions from their regular positions in the lattice) may differ from one activator ion to another, simulation of experimental spectra has revealed only one type of RIC. This may be related to the fact that, in different solid

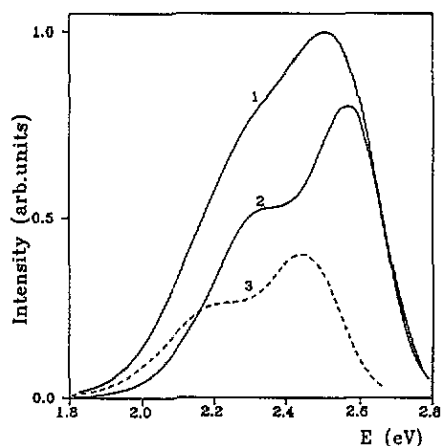


Figure 3. Decomposition of the SrS:Ce emission spectrum excited at interband excitation (curve 1) into two spectra: the first excited in the activator band (curve 2) and the second with a similar shape but shifted by 0.12 eV towards lower energies (curve 3). The relative intensity ratio of curve 3 to curve 2 is 0.50; the standard deviation between the experimental curve and a model curve is 0.62%.

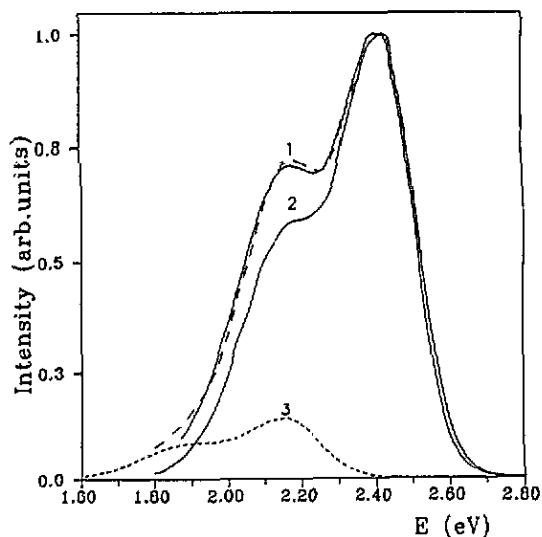


Figure 4. Decomposition of the luminescence spectrum of CaS:Ce³⁺ excited by x-ray tube (curve 1, full curve) into two spectra: the first excited in the activator band (curve 2) and the second with a similar shape but shifted by 0.25 eV towards lower energies (curve 3). Curve 1, broken curve, is the model curve, i.e. the sum of spectra 2 and 3; the standard deviation between the experimental curve and the model curve is 1.37%.

solutions, the displacement of Ce³⁺ ions from the sites of O_h symmetry is determined by the available space, i.e. by the difference between the ion radii of the activator (1.07 Å) and of the substituted cation of the matrix: Ca²⁺ (0.99 Å) or Sr²⁺ (1.13 Å).

So the possibility of the displacement of Ce³⁺ ions from the sites of O_h symmetry is very limited in CaS, and RICs are almost absent in this phosphor and hence their emission under interband excitation is identical with that obtained under activator excitation. In contrast the possible displacement of Ce³⁺ in SrS is substantial, and hence the spectrum assigned to RICs presents the highest value of shift towards lower energies in this phosphor (0.12 eV). The centres discussed above will be denoted as RIC1 (type 1). The properties of these centres (the dependence of their emission spectra shift on the sites of the Ce³⁺ ions) allows us to obtain new information on the local spatial structure of solid solutions Ca_{1-x}Sr_xS in the activator environment [15].

Naturally such centres must also be formed when the phosphors are excited by x-rays. However, the modification presented in the x-ray emission spectrum of CaS:Ce (figure 1(a)) cannot be explained by the contribution of RIC1s, because they are absent in this phosphor. Therefore it is reasonable to suppose that x-ray exciting radiation creates another type of emission centre (we shall call it RIC2). As RIC1s are almost absent in CaS:Ce, this sample is particularly appropriate for extracting the possible contribution of RIC2s. Thus, it has been found that its x-ray luminescence spectrum may be represented as a sum of two spectra (figure 4): the first similar to that measured under direct activator excitation and attributed to Ce³⁺ ions in regular sites, and the second with a similar shape but shifted by 0.25 eV towards lower energies. The integral intensity ratio of the latter to the former is 0.14. This allows us to assign the second spectrum to RIC2s which appear in the case of x-ray excitation

We have failed to represent the spectra of phosphors containing SrS as a sum of two spectra, as had been done in the case of photoluminescence. The appearance of an additional band on the long-wavelength side of x-ray-excited emission is indicative of the presence of RIC2s.

In order to understand the nature of these centres, we have to consider the splitting of the Ce^{3+} excited state (5d) by the crystal field. The Stark effect exerted by a cubic field results in the splitting of the 5d level into ${}^2T_{2g}$ and 2E_g states by $10Dq$ [7, 10]. We know [16] that, when Ce^{3+} is surrounded by six negative ions in an octahedral arrangement, the lowest excited state ${}^2T_{2g}$ is separated by $-4Dq$ from the non-degenerate 5d level, whereas the upper excited state 2E_g is situated at $+6Dq$ from this same position (in this case, $D > 0$). If, in contrast, Ce^{3+} is surrounded by four negative ions in a tetrahedral arrangement, D will be negative, which causes the inversion of the ${}^2T_{2g}$ and 2E_g level positions, and hence the separation between the ground state 4f and the lowest excited state (2E_g in this case) decreases by $2Dq$. As the splitting value of $10Dq$ is evaluated at a little more than 10^4 cm^{-1} (about 1.24 eV) in CaS and SrS [17], the shift in the RIC2 emission spectrum, being 0.25 eV, is in reasonable accord with $2Dq$. In our opinion, x-ray excitation results in a substantial displacement (much higher than that caused by Coulomb interaction with charged defects) of a definite number of Ce^{3+} ions from the sites of O_h symmetry and a reorganization of their local environment. This leads to the formation of RIC2s, affected by a crystal potential dominated by a component of tetrahedral symmetry. We believe that such an effect may be caused by the formation of sulphur vacancies in the first coordination shell of a definite number of Ce^{3+} ions.

However, in the case of inversion of excited levels, radiative transition probabilities will probably change and the intensity ratio of the two emission bands may be quite different from the ${}^2T_{2g}$ 4f transitions. For this reason we cannot confirm that the spectrum attributed to RIC2s has an identical shape with that measured under direct activator excitation. As we ignore the behaviour of the x-ray-excited spectrum (spectrum 1 in figure 4) for longer wavelengths, it is difficult to estimate the accuracy of the approximation in this region. It seems, however, that the intensity of the long-wavelength band of the shifted spectrum must be a little lower than shown in figure 4 to ensure a better approximation, which may be indicative of the modification of the transition probabilities.

It is difficult to evaluate the contribution of RIC2s to the emission spectra of samples containing SrS, because the contribution of RIC1s is unknown in the case of excitation by x-rays (obviously this contribution differs from that determined in the case of fundamental absorption edge excitation). Nevertheless, we have tried to extract approximately the contribution of RIC2s from the x-ray-excited luminescence spectrum of $SrS:Ce^{3+}$. For this purpose, we have subtracted from it the contributions of Ce^{3+} ions in regular sites (the spectrum measured under direct activator excitation) and of RIC1s (shifted spectrum). As a result, we have obtained a third spectrum with a similar shape to that excited under direct activator excitation but shifted relative to it by 0.2 eV towards lower energies. The ratio of its integral intensity to that of the x-ray spectrum is 0.1. The value obtained for the shift (0.2 eV) is in good accordance with the value of $2Dq$ for SrS, where the splitting of the 5d level by the crystal field ($10Dq$) is slightly lower than in CaS, because of the increase in the lattice parameter. The fact that the shift in the spectrum assigned to RIC1s is closer to $2Dq$ in CaS and SrS supports our hypothesis.

The increases in the width and relative intensity of the long-wavelength wing of the spectrum excited by x-ray synchrotron radiation with respect to that excited by x-ray tube may be explained by the fact that in the first case the flux of exciting photons is higher

by two to three orders of magnitude and therefore larger numbers of RIC1s and RIC2s are formed.

5. Conclusion

Usually, the omission spectra of activator ions are treated in terms of the splitting of their energy levels by the local crystal field. Sometimes the symmetry of the activator site is the same as that of the substituted ion, as for example in the relatively simple case of cubic symmetry O_h of the Ce^{3+} ions in CaS and SrS (and their solid solutions $Ca_{1-x}Sr_xS$). However, we have observed modification of the local symmetry of Ce^{3+} centres under the effect of exciting radiation. The luminescence was attributed to two new types of radiation-induced emission centres.

(1) RIC1s are created in the case of excitation by photons with energies $E > E_g$ owing to the Coulomb interaction between Ce^{3+} ions and charged defects formed in their neighbourhood (electrons and holes trapped by the intrinsic lattice defects), leading to a slight displacement of these ions from the sites of O_h symmetry.

(2) RIC2s are created in the case of x-ray excitation and are probably due to the formation of sulphur vacancies in the first coordination shell of the activator, leading to substantial displacement of the Ce^{3+} ions from their regular positions and reorganization of their local environment.

It is natural to assume that similar centres are created also in other doped ionic crystals. Their contribution to the formation of the luminescence spectrum must be taken into account, especially in the case of high-energy excitation.

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