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Effect of γ-radiation on optical properties of Eu^{2+} ions in the $KCl:Eu^{2+}$ system

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Emission spectra and luminescence time decay of Eu^{2+} ions in KCl crystals annealed at 873 K and quenched to room temperature before irradiation were measured at 80 K after γ-irradiation which was performed at 295 and 200 K. The results are consistent with radiation-induced aggregation of the original isolated europium dipoles.

1. Introduction

The effect of irradiation Eu^{2+}-vacancy dipoles in quenched KCl crystals was recently the subject of a systematic investigation. By using different experimental techniques, it was shown [1–4] that γ-irradiation of $KCl:Eu^{2+}$ crystals at 80, 200 and 295 K induces aggregation or precipitation of isolated Eu^{2+}-vacancy dipoles. On the other hand, the aggregation or precipitation of Eu^{2+} dipoles can be produced by thermal annealing. In the as-grown $KCl:Eu^{2+}$ crystals, which were stored for a long time at room temperature, the occurrence of Eu^{2+} precipitates has been shown [4].

Annealing of the as-grown crystals at high temperatures (up to 600° C) and quenching to room temperature brings about the dissolution of these precipitates, resulting in the appearance of isolated Eu^{2+} dipoles of nn type (substitutional divalent Eu^{2+} ions bound to the nearest cation vacancy to retain the electrical neutrality) [5].

The isolated Eu^{2+} dipoles, present in the quenched crystals, aggregate at elevated temperatures, giving rise to the formation of different kinds of aggregates or precipitates depending on annealing time and temperature. For short-term annealing at a low temperature (below 100° C), the formation of dimers and trimers takes place [6]. For long-term annealing, the precipitation of a Suzuki-type metastable phase is supposed [7]. There are some suggestions that the same phase exists in as-grown crystals [9].

The annealing at higher temperatures (about 200 to 250° C) results in the formation of precipitates of a more stable phase of $EuCl_2$ structure [7, 8].

The aim of this work was to compare the results of emission and time-decay measurements obtained for γ-irradiated $KCl:Eu^{2+}$ crystals and thermally annealed ones.

2. Experimental procedure

$KCl:Eu^{2+}$ crystals were grown in vacuum-sealed quartz ampoules, by the modified Bridgman method, using pre-purified materials. The pre-treatment of molten $KCl–Eu_2O_3$ mixture with gaseous CCl_4 ensures the reduction of oxygen impurities below the optically detectable limit [10].

The dopant enters the crystal lattice substitutionally in the form of divalent ions. In all samples examined, the concentration of Eu^{2+} ions was determined from the absorption coefficient of the high energy absorption band as suggested, for example, by Opyrchał *et al.* [1] and resulted in 100 p.p.m.

The samples were annealed at 873° C for 1 h in order to dissolve the Eu^{2+} precipitates in as-grown crystals and were irradiated by γ-rays (^{60}Co source, dose rate $10^6\,R\,h^{-1}$) at 200 K (sample S_1) and at room temperature (RT) (sample S_2). The concentration of Eu^{2+} dipoles in irradiated samples was checked by the ionic thermocurrent (ITC) method. The dipole concentration decreases with increasing irradiation time. It disappeared at RT or reached a saturation value for long irradiation times [3] at 200 K.

The optical measurements were performed after irradiation times (for example 44 h) ensuring lowest dipole concentrations in both samples. The F centre concentration, as estimated from the absorption band using the Smakula equation (oscillator strength of the F band = 0.55) [11] turned out to be 90 p.p.m. in sample S_1 and 32 p.p.m. in sample S_2.

Emission spectra and luminescence time decay signals were measured by the single photon counting techique. The complex emission spectra obtained were decomposed into gaussian-shaped bands, using a numerical analysis based on non-linear least squares method, according to the procedure described by Bevington [12].

3. Results and discussion

The emission spectra of γ-irradiated $KCl:Eu^{2+}$ crystals taken at liquid nitrogen temperature (LNT) for samples S_1 and S_2 are shown in Fig. 1. Because of the presence of a high concentration of F centres absorbing the emitted light, the intensity of Eu^{2+} emission measured after irradiation was rather low

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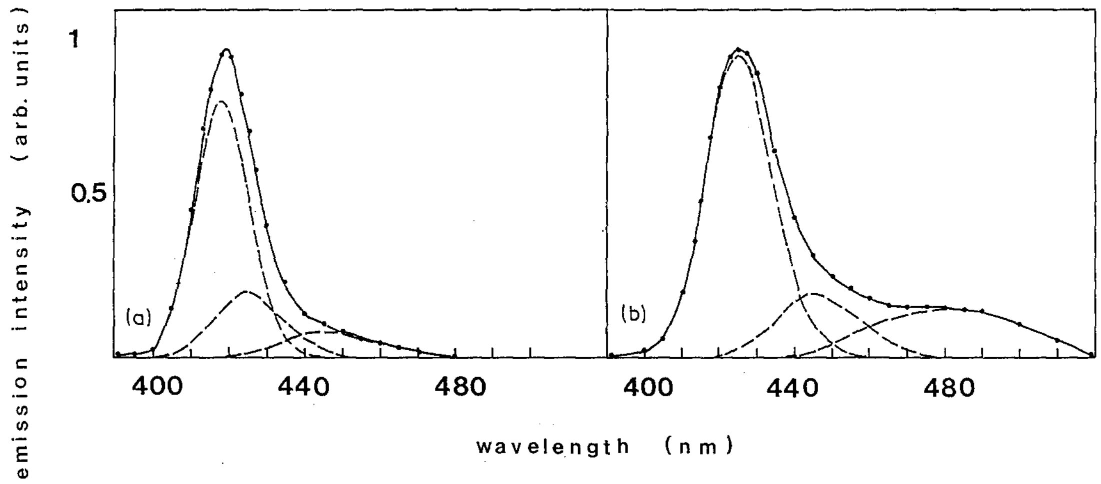

Figure 1 Emission spectra of samples S_1 and S_2 after (a) γ-irradiation and (b) optical bleaching respectively. The measurements were performed at LNT.

and particularly for sample S_1 (20 times lower than that found in freshly quenched samples). For this reason the coloured S_1 and S_2 samples were optically bleached to suppress the F centre concentration. Owing to this treatment, the luminescence intensity of Eu^{2+} ions increased about four times, which resulted in an easier detection of the weak band located at longer wavelengths (Figs 1a and b).

It has been ascertained previously [1, 3] that optical bleaching does not change the radiation-induced aggregation state of europium ions. It should be emphasized that the same component bands have been detected in samples S_1 and S_2 whether γ-irradiated or bleached. As shown in Fig. 1, the spectrum of sample S_1 (irradiated at 200 K) consists of three component bands peaking at 418, 425 and 446 nm. It may be noticed that the intensity of the 425 and 446 nm bands is very low with respect to the 418 nm band. In freshly quenched crystals the 418 nm band is related to the isolated dipoles present in the crystal [13].

As the irradiation at 200 K significantly reduces the dipole concentration [3] this strong band cannot be ascribed solely to the isolated dipoles present in the sample. However, the peak position of the emission band of small aggregates like dimers and trimers, produced during the initial aggregation stages in uncoloured crystals, does not change [9] if compared with the emission of the dipoles. Hence it can be supposed that the 418 nm band of sample S_1 corresponds to the emission of the remaining europium dipoles and to the small aggregates induced by irradiation at 200 K, both emitting in the same spectral region.

The weak 425 and 446 nm bands found in sample S_1 seem to be similar to those detected in sample S_2. In sample S_2 irradiated at RT, the 418 nm band is practically absent, due to lack of dipoles as well as to some small aggregates like dimers and trimers in agreement with ITC data [1]. Most of the emission detected in this sample is related to the 425 nm band

TABLE I Peak positions and half-widths (hw) of component bands of the emission spectrum of γ-irradiated or thermally annealed KCl:Eu^{2+} samples; T_{meas} = LNT

Sample	Component			
	I	II	III	IV
S_1	λ = 416 nm hw = 0.112 eV			
S_1(OB)	λ = 418 nm hw = 0.114 eV	λ = 425 nm hw = 0.14 eV	λ = 446 nm hw = 0.17 eV	
S_2		λ = 423 nm hw = 0.14 eV	λ = 446 nm hw = 0.16 eV	λ = 480 nm hw = 0.24 eV
S_2(OB)		λ = 425 nm hw = 0.14 eV	λ = 446 nm hw = 0.16 eV	λ = 480 nm hw = 0.24 eV
Quenched	λ = 418 nm hw = 0.10 eV			
RT-aged		λ = 425 nm hw = 0.13 eV		
Thermally annealed (200 h, 220° C)			λ = 443 nm* hw = 0.16 eV	λ = 480 nm hw = 0.20 eV

OB = optically bleached.

*For thermally annealed samples, component III peaks at 443 nm, whilst for irradiated samples a shift to 446 nm is observed. This is probably due to the fact that, by choosing suitable annealing temperatures, it is possible to obtain only two components in the emission spectrum. A more accurate decomposition in gaussian bands is obtained than for more complex emission spectra of irradiated samples.

TABLE II Lifetime values, τ, of component bands of the emission spectrum for samples S_1 and S_2 before and after optical bleaching (OB) taken at LNT. The last columns give some lifetime values obtained for non-irradiated KCl : Eu^{2+} samples annealed at RT or 493 K

Wavelength (nm)	τ, sample S_1 (nsec)		τ, sample S_2 (nsec)		τ, Non-irradiated sample (nsec)		
	γ-irradiated	OB	γ-irradiated	OB	quenched	RT-aged	220° C annealed
420	1000	1000			1100		
425	1100* 500†	1050* 600†	1000* 450†	1000* 500†		1200	
446	860	900	830	830			550
480				640			550

*τ_1.
†τ_2.

not present in quenched samples before irradiation. The Eu^{2+}-rich precipitates of the Suzuki-like phase found in non-irradiated samples that have been annealed in the range RT to 100° C, emit at the same wavelengths (see Table I). This fact suggests that RT irradation induces Eu^{2+} dipole precipitation. The remaining two weak bands, peaking at 446 and 480 nm, seem to be similar to that produced by thermal annealing above 473 K (see Table I) which suggests the beginning of the formation of Eu^{2+} precipitates of $EuCl_2$ structure [7, 8].

Further information on radiation-induced aggregation products has been obtained from the luminescence decay measurements. It should be noted that for a given emission band, independent of the irradiation temperature and optical bleaching, identical decay curves have been found. The emission decay taken for the 425 nm band is composed of two components with the lifetime value equal to 500 and 1000 nsec (see Table II). A single exponential decay has been obtained for the other bands. It has been shown in a previous paper [9] that the lifetime value of dipoles, when measured at LNT, is 1000 nsec. For thermally annealed samples, the precipitates related to the 425 nm emission band are characterized by a lifetime value similar to that measured for dipoles. For the precipitates emitting at 443 and 480 nm the lifetime value decreases continuously from 1000 nsec (early aggregation stages) to 500 nsec (late aggregation stages) [13]. For irradiated samples, the two components detected for the 425 nm band can be explained as arising from the Suzuki-phase contributing to the 425 nm band (1000 nsec) and from the tail of 446 nm band (500 nsec) that overlaps the 425 nm band (see Fig. 1).

For the emission bands peaking at 446 and 480 nm the lifetime values are in agreement with those detected for thermally annealed samples that is between 1000 and 500 nsec depending on the aggregation stage [13].

4. Conclusions

Irradiation induces the appearance of additional Eu^{2+}-related emission bands in quenched KCl crystals. Similar bands, corresponding to Eu^{2+} ions in various aggregation states, have been observed in thermally annealed crystals of the same origin. On the basis of this similarity one may conclude that the γ-irradiation results in the formation of Eu^{2+} aggregates, the structure of which depends on the irradiation temperature. In samples irradiated at 200 K, small dipole aggregates such as dimers or trimers, seem to be the main aggregation product although the presence of weak 425 and 446 nm bands indicates the appearance of Eu^{2+} ions in the form of some precipitates. The RT irradiation, at the same dose, induces the precipitation of dipoles originally present, resulting in the formation of Eu^{2+}-rich phase characteristics of non-irradiated, well-aged (for several years) crystals.

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