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INVESTIGATIONS ON THE THERMOLUMINESCENCE OF LaOBr:Tb^{3+} PHOSPHORS

I. Experimental results

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Thermoluminescence measurements are thermoanalytical techniques that allow study of the thermally stimulated relaxation processes in solids, yielding qualitative information on the mechanism of energy storage and permitting calculation of quantitative trap-spectroscopic parameters, too.

The thermoluminescence of undoped and Tb^{3+}-activated LaOBr materials was investigated The experimental results are summarized and some factors influencing the thermoluminescence of this system are discussed.

The Tb^{3+}-doped lanthanum oxybromides are among the most efficient X-ray phosphors known [9]. They are increasingly used in X-ray intensifying screens for medical radiography, for example [2]. With steady-state luminescence, but also phosphorescence phenomena are important. On the one hand, the afterglow of X-ray phosphors has to be reduced in many cases, but on the other hand, the ability of such materials to store a high light sum may be used to provide new information storage systems [3].

In the course of our investigations on the luminescence properties of LaOBr:Tb^{3+} phosphors [4–6], it therefore seemed of interest to study the thermoluminescence (TSL) of undoped and Tb^{3+}-activated LaOBr. TSL measurements are usually classified as less-common thermoanalytical techniques [7]. However, TSL is an excellent method for the investigation of thermally stimulated relaxation in insulators and semiconductors. The occurrence of thermoluminescence phenomena during a thermal scan of an excited solid may be appreciated as direct evidence of the existence of electronic trap levels in such materials. Analysis of the TSL records ("glow curves") and the fitting of the resulting data to an appropriate kinetic model yields the corresponding trap-spectroscopic information [8] and may be used to study the radiative recombination processes, too.

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Experimental

Lanthanum oxybromide and Tb^{3+}-doped LaOBr phosphors were prepared by the reaction of a mixture of La_2O_3 with NH_4Br, followed by a recrystallization process from the molten $LaBr_3$ flux [9]. The LaOBr : Tb^{3+} phosphors thus obtained are well-crystallized and suitable for application as efficient X-ray converters. The minimum purity of the La_2O_3 starting materials (USSR import) was 99.99%. The average particle sizes of the prepared powders were 8–10 μm. Thermoluminescence measurements were carried out using an experimental arrangement of sample holder/heater system, photomultiplier, amplifier and recorder. Details of the experimental set-up have been described elsewhere [10]. The linear heating rate could be varied from 10 to 50 deg min^{-1}.

Results

Figure 1 presents the TSL records of LaOBr : Tb^{3+} phosphors with different activator concentrations. These glow curves were measured after 254 nm UV excitation, but there were no changes in the course of the glow curves if X-ray excitation was used. In the case of the blue-emitting LaOBr : $Tb^{3+}_{0.002}$, the TSL glow curve consists of two peaks in the 300–700 K temperature region. The maximum temperatures of the glow peaks depend on the heating rate q used in the TSL experiment. This dependence is well known from other thermoanalytical techniques, too. At q = 40 deg min^{-1}, the glow intensity maxima were found at 390 K and 550 K.

From the TSL emission spectra, it is clear that the first TSL peak is mainly due to Ce^{3+} impurity luminescence, whereas the second is produced by blue and/or green Tb^{3+} emission. With increasing Tb^{3+} content, concentration quenching of the 390 K TSL peak occurs. This can be seen from Fig. 1 and from the intensity values in Table 1. The TSL emission spectrum of the LaOBr: $Tb^{3+}_{0.05}$ phosphor shows the green $^5D_4$–$^7F_1$ emission linesof Tb^{3+} only. This should be referred to the concentration quenching of the steady-state luminescence of the $^5D_3$–$^7F_1$ transition of the Tb^{3+} ions in the LaOBr matrix [11].

Figure 2 shows that even undoped LaOBr exhibits relatively intense thermoluminescence. As illustrated previously [12], the glow intensities and the course of the TSL glow curves strongly depend on the content or rare earth impurities in the La_2O_3 starting material. Table 2 lists the results of instrumental neutron activation analysis (INAA) of several La_2O_3 samples from different producers. Obviously, the real connections between impurity content and TSL are rather complicated. Nevertheless, some general conclusions may be drawn, as follows.

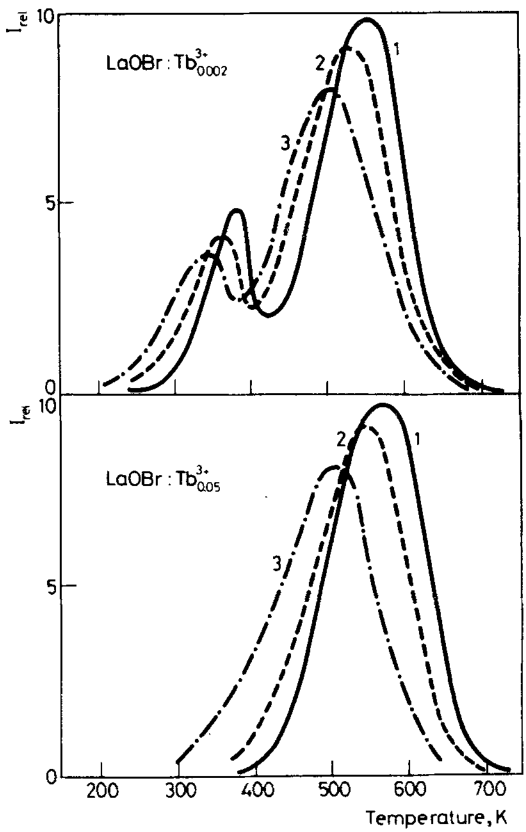

Fig. 1 TSL glow curves of different $La_{1-x}OBr:Tb_x^{3+}$ phosphors (1) $q = 37$ deg min^{-1}, (2) $q = 27$ deg min^{-1}, (3) $q = 20$ deg min^{-1}

Table 1 Influence of the Tb^{3+} activator concentration on the glow intensities of $LaOBr:Tb^{3+}$ TSL peaks (254 nm excitation)

TB^{3+} content, %	Relative TSL intensity	
	peak I (T_{max} = 390 K)	peak II (T_{max} = 550 K)
0.05	75	210
0.1	33	230
0.2	21	222
0.3	9	252
0.5	1	248
0.75	—	230
2	—	230
2.5	—	82
5	—	46

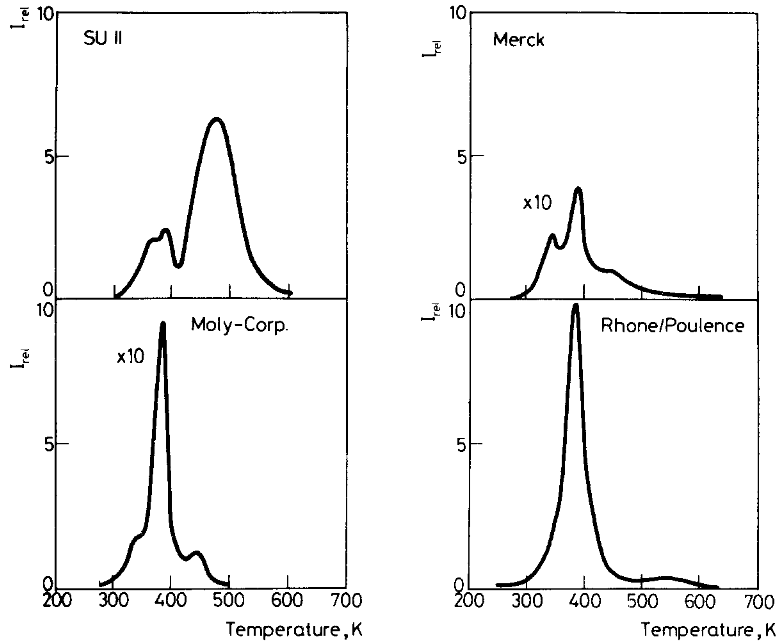

Fig. 2 Influence of the starting material (La_2O_3 of different origins, impurities listed in Table 2) on the TSL glow curves of undoped LaOBr

Table 2 Results of the instrumental neutron activation analysis (INAA) on different La_2O_3 samples

La_2O_3 sample	Ce (ppm)	Nd (ppm)	Eu (ppb)	Gd (ppm)	Tb (ppb)	Yb (ppb)	Th (ppm)
SU I	72	5.7	194	0.7	95	93	5.4
SU II	75	4.9	67	0.7	192	93	7.6
SU III	44	10.5	53	1.9	348	90	0.04
Moly-Corp.	36	2.8	7	0.2	61	335	0.01
Merck	37	0.5	1	0.1	3	29	0.08
Rhone/Poulence	39	26	46	0.1	498	1305	0.08

RE^{3+} impurity ions forming hole-attractive centres in the LaOBr matrix (cf. Ce^{3+}, Tb^{3+}) mostly enhance the glow intensity in the visible spectral range. RE^{3+} ions giving rise to electron-attractive impurity centres (cf. Yb^{3+}), however, diminish the TSL intensities. The same tendency was found for the isothermal decay of thermoluminescence at room temperature (phosphorescence, afterglow).

Interestingly, the TSL of LaOBr:Tb^{3+} phosphors may even be excited by

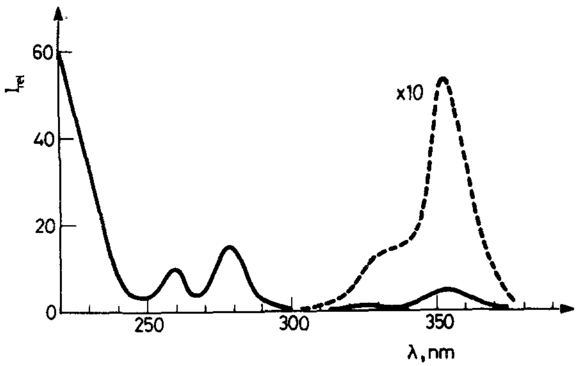

Fig. 3 TSL excitation spectrum of a LaOBr: $Tb^{3+}_{0.002}$ phosphor

365 nm UV radiation (cf. Fig. 3). The band gap energy of LaOBr has been measured as 5.8 eV. As reported earlier [4], the results obtained may be interpreted by suggesting a two-photon excitation mechanism.

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Zusammenfassung — Thermolumineszenzmessungen gehören zu den thermoanalytischen Methoden und dienen der Untersuchung thermisch stimulierter Relaxationsvorgänge in Festkörpern, der Erlangung qualitativer Informationen über den Mechanismus der Energiespeicherung und zur Berechnung quantitativer spektroskopischer Parameter der Haftstellen. Die Thermolumineszenz von undotierten und Tb^{3+}-aktivierten LaOBr-Materialien wurde untersucht. Die experimentellen

Ergebnisse eigener Arbeiten werden zusammengestellt und einige Faktoren von Einfluss auf die Thermolumineszenz des Systems werden diskutiert.

Резюме — Метод термолюминесценции является одним из термосналитических методов, позволяющий изучать термически стимулированные релаксационные процессы в твердых телах и дает качественную информацию о механизме накопления энергии, а также подволяет проводит вычисления количественных параметров спектроскопических ловушек. Изучена термолюминесценция чистого LaOBr и его образца, активированного трехвалентным тербием. Обобщены экспериментальные результаты и обсуждены некоторые факторы, затрагивающие термолюминесценцию этой системы.