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Thermoluminescent Properties of Calcium Fluoride Doped with Lanthanum and Aluminum

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Abstract

In the present paper we studied the TL emission of CaF_2 doped with Al^{3+} and La^{3+} in the nominal concentration range from 0.01 to 1 mol %. The sample doped with Al^{3+} showed the best sensitivity to γ-rays while the pure sample displayed the best sensitivity to UV and visible light. The TL signal of the Al^{3+} doped sample has a maximum intensity for a nominal concentration of 0.2 mol% of the dopant while in the La^{3+} sample, the TL emission increases with the concentration of the dopant. The tridimensional TL plot revealed that the emission at 480 nm, observed in all samples, can be due to a luminescence center of intrinsic origin while the emission at 570 nm of the Al^{3+} doped sample is due to a transition of the Al^{3+} ion.

INTRODUCTION

Calcium Fluoride is one of the most widely studied materials concerning the Thermoluminescence (TL) emission mainly in the applications in TL dosimetry. Commercial TL dosimeters are available based on natural or artificial CaF_2 doped with Dy (TLD-200), Tm (TLD-300) or Mn (TLD-400).

The main features of the TL emission of CaF_2 were tabulated by Sunta [1]. He found three main groups of TL peaks in the range from room temperature to 300°C whose emission spectra were characteristic of the dopant ion. Sunta proposed the following model for the TL of CaF_2: during the irradiation, the rare earth ions (RE^{3+}) transfers a hole to two F- ions thus forming RE^{2+} and a V_k center, respectively. During the heating, the V_k center releases the hole that recombines with the RE^{2+} forming an RE^{3+} in an excited state that relaxes back to the ground state giving rise to a light emission which is characteristic of the particular RE^{3+} ion. A model similar to this one was proposed by the same author to explain the TL of the CaF_2 doped with Mn. This model has been confirmed with only minor modifications by recent works either in natural or in artificial CaF_2 samples doped with different rare-earths [2,3].

However, some few comments should be made related with this model. Firstly, this model does not explain the microscopic mechanism of the recombination of charges. Secondly, the model does not clearly explain the multitude of peaks in CaF_2 below and above room temperature. Since the important part of the model is the presence of the rare-earth, this model does not hold for the emission of highly pure samples. This model was not tested yet for samples of CaF_2 doped with ions different from the rare-earth or Mn ones.

In the present work we studied, for the first time, the TL emission of CaF_2 samples doped with Al^{3+}. We also investigated the CaF_2 doped with La^{3+} and pure samples.

EXPERIMENTAL

Artificial CaF_2 samples were grown by a standard Stockbarger technique in a graphite crucible and in an argon atmosphere. The nominal concentration of Al^{3+} or La^{3+} ranged from 0.01 to 1 mol % and some of the obtained samples were analyzed by the neutron activation method followed by a high resolution gamma spectrometry. The results are summarized in table 1.

Sample	dopant	X_n (mol %)	X_a (mol%)
653	(pure)	-	(traces of Eu)
666	La^{3+}	1	-
668	La^{3+}	0.5	-
670	La^{3+}	0.01	-
768	La^{3+}	0.1	0.065
731	Al^{3+}	0.1	0.093
732	Al^{3+}	0.2	-
734	Al^{3+}	0.5	0.15

Table 1: Samples used in the present work. X_n - nominal molar fraction of the dopant and X_a - results from the neutron activation analyses.

Group	Thermal treatment	Irradiation
1	no	no
2	no	200Gy - γ-rays from ^{60}Co source
3	600°C/10 min. + fast quenching	200Gy - γ-rays from ^{60}Co source
4	600°C/10 min. + fast quenching	1h exposure to artificial visible light
5	600°C/10 min. + fast quenching	1 h of UV light from Hg lamp

Table 2: Groups of the samples divided according to the thermal, irradiation or illumination treatments

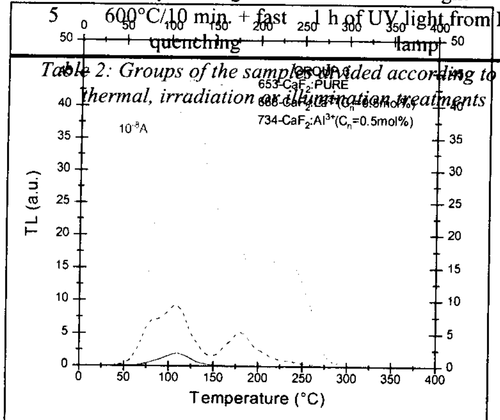


Figure 1: TL emission of the pure samples and the A^{l3+} and La^{3+} doped samples from group 3.

The samples were then powdered and only the grains between 0.075 and 0.149 mm were used for the TL measurements. The samples were then divided in 5 groups according to specific combinations of thermal treatment (TT), irradiation with γ-rays, UV or visible light (Table 2).

The thermal treatments were done in an open air oven followed by a subsequent fast quenching back to room temperature obtained by dropping the sample on a cold metal plate. All this process was done inside a dark room in order to prevent the effect of the natural light. UV illumination was done with a Hg lamp without the glass bulb for 1 hour and in order to prevent the warming up of the sample during the UV illumination, the sample were kept inside of a metal pot floating on cold water. The visible light illumination were done with fluorescence lamps.

TL measurements were taken from room temperature to 350°C following a linear heating program (heating rate = 2°C/min.). The TL equipment is a home made TL reader with an EMI 9789QB photomultiplier tube. A microcomputer is connected to the equipment via a HP3852A data acquisition unit. For the measurements of the emission spectra , an UNICRON monochromator was attached between the photomultiplier and the sample holder and a TL emission were taken every 10-20 nm. The data obtained for different wavelength were then corrected considering the spectral response of the photomultiplier and the monochromator.

RESULTS AND DISCUSSION

CaF_2 is known to be very sensible to visible light. Due to this high sensitivity samples in groups 1 and 2 were not used because we could not control the total intensity and time of exposure to visible light of each sample since when they were grown. This effect induces a poor reproducibility of the TL measurements of the samples in these two groups.

In Figure 1 we show typical TL glow curves of the doped samples and the pure one in group 3. Three main groups of peaks can be seen close to 100, 180 and 230°C. An interesting feature revealed by this figure is the high sensitivity to γ-rays of the sample doped with Al^{3+} compared with the other samples. On the other hand, when the samples are illuminated with UV or visible light (groups 4 and 5), it was observed that the pure samples displayed the highest sensitivity.

The increase in the nominal concentration of Al^{3+} from 0.1 mol% to 0.2 mol%, enhanced the intensity of the TL glow curve. When the nominal concentration of Al^{3+} increased to 0.5 mol %, the peak around 120°C decreased by a factor of 0.3 while the other peaks almost do not vary. In the La^{3+} doped samples, all the observed peaks in the glow curves increased when the nominal concentration of the dopant increased from 0.01 to 1 mol%.

These results can explain the high sensitivity of the natural CaF_2 observed by many authors. Natural fluorite samples, mainly the green and blue species, always have some few hundreds of ppm of Al^{3+}, a concentration in the same range of our samples #731 or #732 where we found to be the best sensitivity to γ-rays. The natural crystal of other coloration have smaller concentrations of Al^{3+} thus inducing a less intense TL signal [2].

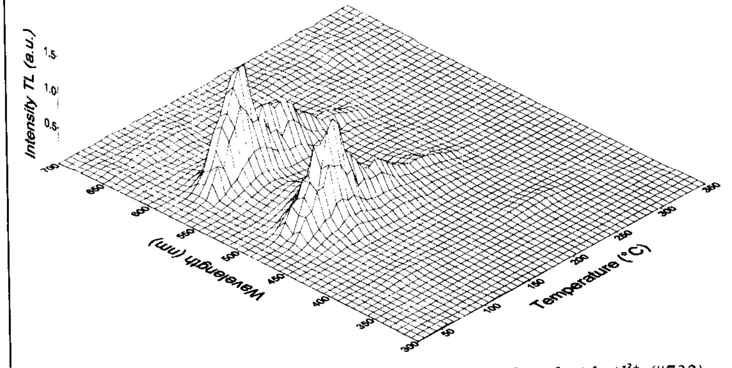
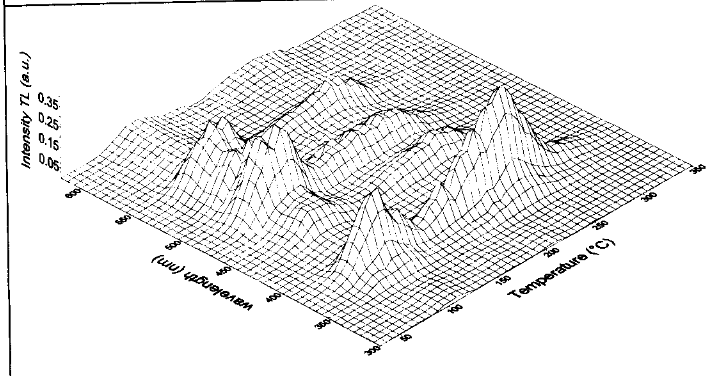


Figure 2: Tridimensional TL plot of the CaF_2 sample doped with Al^{3+} (#732).



In Figures 2 and 3 we present the tridimensional TL emission of the samples doped with Al^{3+} and La^{3+}. It can be seen that the emission of the Al^{3+} doped sample is composed by two sharp lines around 480 and 570 nm. The emission of the La^{3+} doped sample is composed by several lines, broader than the Al^{3+} doped sample, with main emission at 375, 480 and 530 nm and secondary emissions at 430 and 510 nm. The 480 nm emission was also observed in tridimensional TL plot of the pure sample. This result suggests that the 480 nm emission is due to a recombination center of intrinsic origin. The emission at 570 nm is known to be due to the Al^{3+} ion.

It is possible to conclude that for the CaF_2 doped with Al^{3+}, the model of the TL emission proposed by Sunta can account for one of the TL emissions (at 570 nm) observed. The emission at 480 nm detected in all samples, however, remains to be identified.

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