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Investigations of $4f \leftrightarrow 5d$ Transitions of Ce^{+3} in CaF_2†

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The $4f \leftrightarrow 5d$ transitions of Ce^{+3} in CaF_2 crystals are investigated, using thermoluminescence and other optical techniques. The effect of heat treatment on the thermoluminescence, luminescence, and absorption spectra is shown. The differences in spectra between as-received and heat-treated specimens arise from the variation in abundance of rare-earth ion sites of various point symmetries. This variation is caused by oxygen diffusing into the crystals during heat treatment. On cooling to liquid-nitrogen temperature, structure develops on most of these spectra. This structure is discussed and a tentative explanation is suggested.

1. INTRODUCTION

THE $CaF_2:Ce^{+3}$ system is one of the least promising members of the rare-earth-doped CaF_2 series for developing solid-state lasing materials. This may be the reason that relatively few researchers have studied this system in detail, and then only as part of a research program pertaining to other systems. Kaplyanskii *et al.*[1] have studied the absorption and luminescence of Ce^{+3} in alkaline earth fluorides, pointing out the influence of the conditions under which the crystals were grown. Loh[2] has studied the absorption spectrum of the trivalent rare-earth ions in CaF_2, attributing the ≈3050 Å absorption band in $CaF_2:Ce^{+3}$ to a $4f \rightarrow 5d$ transition in the Ce^{+3} ion. Merz and Pershan[3] have studied the thermoluminescence of rare-earth-doped CaF_2, but mention only $CaF_2:Ce^{+3}$ as having broad emission bands in the uv.

In a recent publication[4] from this laboratory, thermoluminescence was used to study the emission centers in $CaF_2:Gd^{+3}$. It was shown that the thermoluminescent emission even at temperatures close to 77°K may originate from rare-earth ions in sites of symmetries other than cubic. While this observation seemed to conflict with conclusions of Kiss and Stabler[5] and more recently of Merz and Pershan,[3] it seemed to be in agreement with those of Makovsky.[6] Our conclusions were further substantiated by subsequent theoretical calculations.[7]

The present work is concerned with $CaF_2:Ce^{+3}$. Here again, it will be evident that the thermoluminescent emission of glow peaks between 77 and 300°K, believed to be due to $5d \rightarrow 4f$ transitions of the Ce^{+3}, is due to rare-earth ions in sites of at least two kinds of symmetry, one of which is trigonal. The relative abundance of these is influenced and can be changed by heat treatment in an oxygen environment. A study of the thermoluminescent emission, constant-temperature luminescence, and absorption spectra shows that structure develops in these spectra at temperatures close to 77°K. While an exact analysis is difficult at present, a tentative explanation is proposed and discussed.

2. EXPERIMENTAL

The crystals used in the present work were supplied by the Harshaw Chemical Co., with a concentration of cerium of about 0.01%. For the thermoluminescence measurements, cleaved crystals of about 5×5×1 mm were cooled to 77°K in a vacuum cryostat and x irradiated for various periods of time with a tube having a copper target, operated at 20 kVP and 10 mA. The general glow curve and its spectral distribution were recorded simultaneously by placing the tail of the cryostat between a 9558Q EMI photomultiplier and the entrance slit of a Hilger and Watts quartz spectrograph, the latter having a resolution of about 3 Å at the wavelength region of 3100 Å. The photographic plate in the spectrograph was moved between peaks (in some cases in the middle of a peak) so as to record the individual spectra of each glow peak (or part of a peak).

Luminescence measurements were carried out by allowing the light from a continuous source, a Hanovia 100-W xenon arc lamp, to pass first through a Leiss double monochromator and then to fall on the crystal in the cryostat, which was placed in front of the entrance slit of the spectrograph.

Absorption measurements were carried out either (a) by using a Cary Model No. 14 spectrophotometer, or (b) by placing the cryostat close to the entrance slit of the spectrograph, and illuminating the crystal from behind with the continuous light source.

Heat treatment was carried out in vacuum (10^{-6} Torr) dry nitrogen or dry oxygen atmospheres. In all cases the crystal was placed in a silica tube which was either evacuated or flushed continuously with the appropriate gas. The furnace surrounding the tube was heated to about 1000°C in 90 min, kept at this temperature for various periods of time, and then cooled gradually to room temperature in 3 h.

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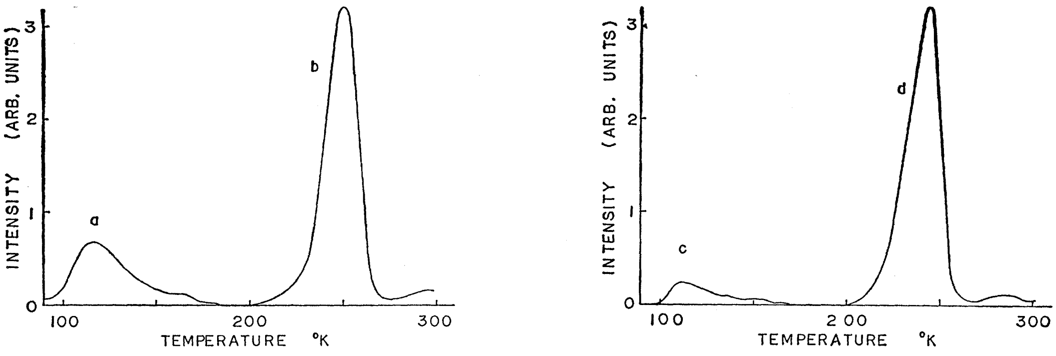


(a) (b)

FIG. 1. General glow curve of $CaF_2:Ce^{+3}$ recorded after x irradiation for 30 min at LNT. (a) Crystal as-received; (b) Crystal heat treated in oxygen at atmospheric pressure for 2 h at 1000°C.

3. RESULTS

A. Thermoluminescent Glow Curves

Figure 1(a) is the general glow curve of an as-received $CaF_2:Ce^{+3}$ crystal, recorded after x irradiation for 30 min at liquid-nitrogen temperature (LNT). Two main peaks at about 115 and 250°K can be seen. It is evident from the shape of the first peak that it consists of more than one component. Figure 1(b) is the general glow curve of a $CaF_2:Ce^{+3}$ crystal heat treated in oxygen at atmospheric pressure for about 2 h at 1000°C, recorded after x irradiation at LNT for 30 min. Thermal activation energies for the traps associated with the two main peaks were estimated by the method used previously[4] and the values are given in Table I. The heat treatment introduces no changes in these values.

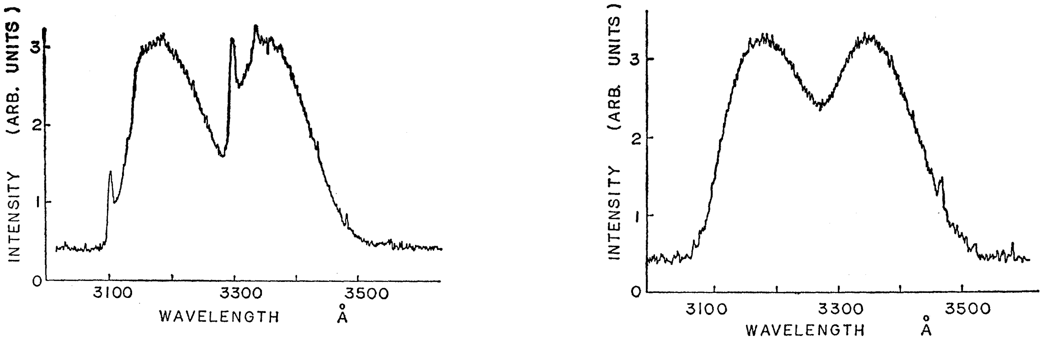
B. Spectral Distribution of Thermoluminescence

Figure 2 shows the microdensitometer traces of the spectral distribution of the thermoluminescent emission in the as-received crystal. In Fig. 2(a) the spectrum of the low-temperature peak (peak a in Fig. 1) and in Fig. 2(b) that of the higher-temperature peak (peak b in Fig. 1) are given. The main difference between Figs. 2(a) and 2(b) is the structure that appears on the high-energy sides of the two emission bands in Fig. 2(a).

Figure 3 shows the microdensitometer trace of the spectral distribution of the high-temperature peak (peak d in Fig. 1) in the heat-treated crystal. Upon comparison with Fig. 2, the appearance of an additional emission band toward longer wavelengths, and some changes in the relative intensities of the emission bands, is evident. Structure has been observed in the spectral distribution of the low-temperature peak (peak c in Fig. 1); however, its intensity is too low to allow satisfactory reproduction. In a series of measurements it has been established that heat treatment either in vacuum or in a nitrogen atmosphere is ineffective in producing the changes observed between Figs. 2 and 3. Thus our conclusion, discussed in detail in Sec. 4, is that diffusion of oxygen into the crystal causes these changes.

C. Absorption Spectra

In Fig. 4, curve a is the absorption spectrum taken at room temperature, in the 3000–4500 Å range, of the as-received $CaF_2:Ce^{+3}$ crystal. Curve b is the same for a crystal heated to 800°C for 2 h in an oxygen atmosphere at 5×10^{-3} torr. Heat treatment is seen to have introduced two additional absorption bands, at 3280 and 3750 Å.



(a) (b)

FIG. 2. Microdensitometer traces of thermoluminescent emission. (a) Peak a in Fig. 1; (b) Peak b in Fig. 1

TABLE I. Activation energies (±15%) of some glow peaks in $CaF_2:Ce^{+3}$.

Crystal	Peak (see Fig. 1)	T_g(°K)	Activation energy (eV)
As-received	a	117	0.13
	b	251	0.60
Heat-treated	c	112	0.13
	d	244	0.57

Figure 5 is the microdensitometer trace of the absorption spectrum in the region 3000–3150 Å, recorded by method b—see Sec. 2—at LNT, for an as-received crystal. Essentially the same result is obtained in this spectral region from a heat-treated crystal.

D. Luminescence Spectra

Luminescence spectra, excited by illumination in the ≈3050 Å band, were taken at LNT or room temperature from both the as-received and the heat-treated crystals. The results at LNT were identical with the thermoluminescence spectrum obtained from the corresponding low-temperature peaks (peaks a and c in Fig. 1); at room temperature they were identical with the corresponding higher-temperature peaks (peaks b and d in Fig. 1).

4. DISCUSSION

A. Mechanism for Thermoluminescence

The rare-earth ion, believed to enter the CaF_2 lattice substitutionally for Ca^{+2}, seems to be more stable in the +3 state.[4,8] This results in some charge compensation; a number of such mechanisms can occur which may differ from each other in their type of symmetry[4,6,9,10] (see Table II). We believe[4] that the thermoluminescence takes place in the following way: X irradiation reduces the rare-earth ion to the +2 state, while the hole is trapped in a nearby site. Different kinds of trapping sites, corresponding to the different glow peaks, can exist in the crystal. Upon heating the crystal the trapped hole is released and recombines with the extra electron on the rare earth, reoxidizing it to an excited +3 state. The rare earth +3 relaxes to its ground state, emitting its characteristic radiation. Therefore, one expects the thermoluminescent emission to be characteristic of transitions within the rare-earth +3 ion.

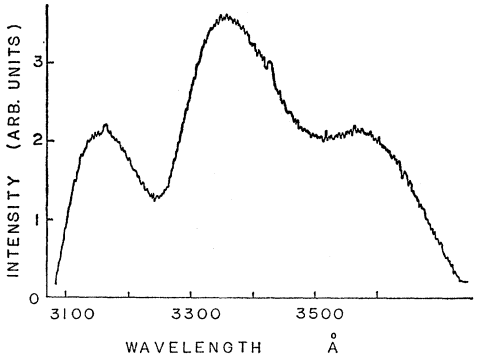


FIG. 3. Microdensitometer trace of thermoluminescent emission. Peak d in Fig. 1.

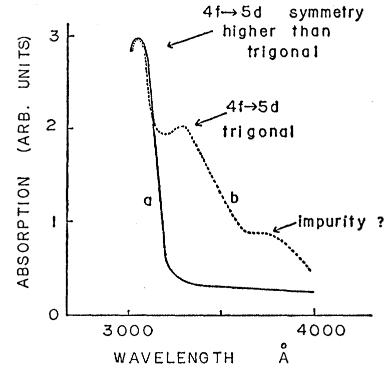


FIG. 4. Absorption spectrum of $CaF_2:Ce^{+3}$ at 295°K. Curve a: crystal as-received. Curve b: crystal heated to 800°C in oxygen for 2 h at 5×10^{-3} Torr.

B. Emission Spectra

The Ce^{+3} ion has a configuration of $4f^1$, which has only a doublet F level; spin-orbit coupling splits this level by about 2100 cm^{-1}. The emission bands in Figs. 2(a) and 2(b), and the corresponding luminescent spectra, are probably due to $5d\rightarrow4f$ transitions into the two F levels ($^2F_{5/2}$, $^2F_{7/2}$). The bands are indeed separated by 2100 cm^{-1}, which corresponds to the separation between these two levels. These measurements are in agreement with the luminescence results obtained by

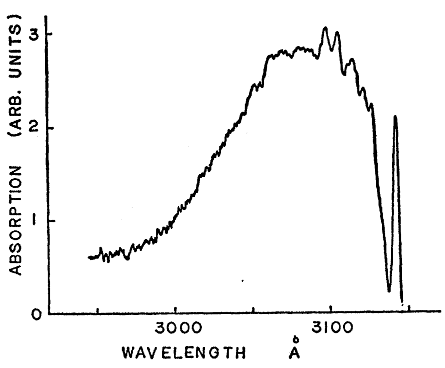


FIG. 5. Absorption spectrum of $CaF_2:Ce^{+3}$ at 77°K. Crystal as-received.

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TABLE II. Rare-earth-site symmetries observed in CaF_2. [See Refs. 4, 6, 9, and 10.]

Rare-earth-site symmetry	Probable compensation mechanism
Cubic	Nonlocalized compensation
Tetragonal	Intersitial F^- in center of nearest cube
Trigonal	(a) Intersitial F^- in center of next-nearest empty cube
	(b) Substitutional O^{-2} in nearest-neighbor F^- lattice site

Kaplyanskii *et al.*[1] from crystals grown under reducing conditions, i.e., their type-II crystals. Heating our crystals in an oxygen environment results in relatively minor changes in the general glow curve (Fig. 1). In the emission spectrum, however, a new band towards longer wavelengths appears (Fig. 3). We interpret the spectrum exhibited by the oxygen-treated crystals as being the superposition of two pairs of emission bands with the low-energy band of one pair coinciding with the high-energy band of the other. The high-energy pair of bands is identical to the bands shown in Fig. 2, and also corresponds to Kaplyanskii's type-II luminescence spectrum, obtained from crystals grown under reducing conditions. The low-energy pair of bands, however, corresponds to Kaplyanskii's type-I luminescence spectrum, obtained from crystals grown under oxidizing conditions. We suggest that oxygen diffuses into the crystal during heating, replaces F^- ions, and takes the charge state of O^{-2}. This would imply that part of the rare-earth sites would, after heat treatment in oxygen, assume trigonal symmetry[4,6] (see Table II), while some of the sites still retain their original point symmetry.

C. Crystal Field

The effect of the crystal field on the ground state of the $4f^05d$ configuration of the free ion is to lower it by 18 000 cm^{-1}.[2,11] One may reasonably expect that the amount of this shift will vary with the symmetries of the rare-earth ion sites, as the different compensating mechanisms give rise to different field strengths. In particular, the compensating mechanism of an O^{-2} at a nearest-neighbor F^- lattice site will have a crystal field that should exceed that of the cubic nonlocalized compensation. Thus the shift in energy by about 2200 cm^{-1} between the two pairs of emission bands (Fig. 3) is an indication that the corresponding rare-earth ion sites have different symmetries. Further, since the energy of the original bands (Fig. 2) is the higher, one may speculate that the symmetry associated with them is higher than that of the oxygen compensated sites, i.e., perhaps cubic.

D. Absorption Spectra

We apply a similar argument to the absorption bands at 3050[12] and 3280 Å,[13] attributing the latter, introduced by heat treatment (see Fig. 4), to the $4f \rightarrow 5d$ transition in the Ce^{+3} ion at trigonal sites while the former is due presumably to ions in higher-symmetry sites. The shift between the two absorption bands is about 2200 cm^{-1}, which is very close to the shift observed in the emission bands in Fig. 3, in agreement with our proposed interpretation. At LNT the bands shift by about 300 cm^{-1} towards lower wave numbers, due probably to increasing crystal field in the contracted lattice. The band at 3750 Å (Fig. 4) is probably due to impurities other than oxygen which diffuse into the crystal during heat treatment.

E. Phonon Structure

Figures 2(a) and 5 show the structure on corresponding emission and absorption bands. The absorption line at 3142 Å is thought to be a zero phonon line while the structure towards shorter wavelengths imposed on the continuous band is referred[2] to as vibrational structure. We propose a similar identification for the structure in the emission. In this case, the zero phonon lines appear on the short-wavelength side of the bands at 3095 and 3323 Å. Note, however, that there is a shift of 47 Å between the absorption zero phonon line and the corresponding emission zero phonon line (3095 Å as compared to 3142 Å). This shift is much more than one would expect on grounds of the temperature difference between the measurements: absorption at 77°K, and emission at 110°K. Our suggestion is that they belong to different Stark components in the Stark split spectrum of this $4f \leftrightarrow 5d$ transition. Accordingly, one should not expect the absorption and emission to be mirror images of each other, since they represent a mixture of different vibrational structures of various Stark components emphasized to different extents in the absorption and emission spectra.

5. CONCLUSION

It has been shown that in $CaF_2:Ce^{+3}$, as in $CaF_2:Gd^{+3}$,[4] even close to LNT, emission takes place from rare-earth ions in sites whose symmetry is lower than cubic. It seems that heat treatment allows oxygen to diffuse into the crystal. This result is in agreement with previous suggestions,[4,14] pertaining to heat treatment of CaF_2 and alkali-halide crystals in air.

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