Synthesis, Fabrication, and Photoluminescence of CaF_2 Doped with Rare Earth Ions

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Ambient condition wet synthetic techniques were used to synthesize CaF_2 doped with europium and erbium. Photoluminescence spectroscopy and energy-dispersive x-ray analyses were used to study the electronic states of rare earth (RE) ions and the degree of heterogeneity/homogeneity in the matrix. Raman spectroscopy was used to study the degree of crystallinity of CaF_2. Effects on the photoluminescence spectra were studied as a function of the thermal treatment of CaF_2 samples.

INTRODUCTION

Calcium difluoride, CaF_2, has been the focus of many studies related to both its chemistry and related applications in both physics and chemical physics. Investigations of F-, M-, and R-centers have been studied in single crystals of CaF_2 [1], thin films on CaF_2 plates [2], Raman and scanning electron microscopic properties of CaF_2 on enamel [3], and cubes of CaF_2 using hyper-Raman scattering techniques [4]. Additionally, CaF_2 has been used as a sequestering host for uranium in the development of laser techniques for detecting trace quantities of uranium [5]. Chemical and spectroscopic properties, which previously have been shown to vary as a function of heating for these materials, are important for using the materials as probes for various chemical species in conjunction with different complementary experimental types of techniques such as infrared, Raman,

and fluorescence spectroscopy as well as spectromicroscopic approaches.

The present work was undertaken for a twofold purpose. First, it is important to devise a reliable synthetic method for the preparation of both heterogeneous and homogeneous CaF_2 matrices. By studying both types of matrices, one can use the two in conjunction with one another both to employ the spectroscopic approaches mentioned above and to use lateral spectromicroscopic imaging studies as a function of the different chemical compositions in the heterogeneous matrix. Second, in order to use the CaF_2 matrix in chemical and spectroscopic analyses, it is necessary to determine the variations in the chemical and spectroscopic properties of the europium and erbium ions in CaF_2 matrices. Variations of the metal ion in these matrices must be documented in order to establish their baseline prior to reaction with desired chemical analytes; accordingly, CaF_2:RE systems must be studied both as totally homogeneous and well as heterogeneous systems. Accordingly, a synthetic approach for making CaF_2 matrices in which erbium and europium ions have been heterogeneously dispersed is described here for making such studies. Energy-dispersive x-ray analyses, along with Raman and photoluminescence spectroscopy, have been used to characterize the samples.

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Table I. Heat Treatment of the Samples in the
Present Work

CaF₂:Eu	
Sample 1	
800°C	15 h
Cooling to RT	
Sample 2	
200°C	1 h
400°C	1 h
600°C	1 h
800°C	3 h
Cooling to RT	10 times = 5 days
CaF₂:Er	
Sample 3	
200°C	1 h
400°C	1 h
600°C	1 h
800°C	3 h
Cooling to RT	

EXPERIMENTAL

Chemicals and Materials

All chemicals in the work were purchased commercially and used as received without further purification, including reagent-grade NaF (purchased from MCB Reagents), $Ca(NO_3)_2 \cdot 4H_2O$ (Mallincrodt Reagents), $Eu(NO_3)_2 \cdot 6H_2O$ (99.99%; Alfa Products), and $Er(NO_3)_3 \cdot 5H_2O$ (99.99%; Alfa Products). All glassware was washed with dilute nitric acid, followed by a final rinse of distilled, deionized water. All solutions of chemicals were made using distilled, deionized water.

Procedure

A modified procedure of the one previously reported by Perry et al. [5] for the synthesis of CaF_2 with uranium homogeneously distributed in the matrix was used to prepare the europium and erbium ion-containing samples of CaF_2. A volume of 5 ml of 1.0 M $Ca(NO_3)_2 \cdot 4H_2O$ was diluted with 14 ml of distilled, deionized water. Individual lanthanides (0.05 g) were added to this solution, followed by stirring. A volume of 30 ml of 0.3 M NaF was added with stirring over a 1- to 2-min period, with each solution covered with Parafilm, and then allowed to stand for 24 h. Additionally, 2.5 ml of 1 M $Ca(NO_3)_2 \cdot 4H_2O$ and 15 ml of 0.3 M NaF

were added with stirring and allowed to settle for an additional 24-h period. After settling, most of the water supernatant was pipeted off, and the remaining CaF_2/water mixture was placed in a centrifuge tube and centrifuged for 20 min. After the centrifugation, the final water supernatant was removed. The wet CaF_2 precipitate was then evenly spread into a petri dish and placed in a drying oven at 110°C for several hours to dry. Portions of the milky compounds were then heated in air in 200°C steps up to 800°C or for times of 3 h, 15 h, and 5 days (see Table I) to redistribute the rare earth metal ions in the CaF_2 matrix for taking spectra as described below.

Instrumentation

The Raman spectra were obtained with a Brucker Fourier-transform spectrometer at room temperature and 4-cm⁻¹ resolution and excited with the 1064-nm line of a Nd:YAG laser set at a power of 200 mW.

The photoluminescence spectra were recorded using the single monochromator of a Jobin–Yvon T64000 spectrophotometer, using a 600-groove/mm grating and a slit width of 20 μm. The systems were excited with the 457.9-nm line of an Ar⁺ laser. The laser power at the sample was set at 50 mW for the erbium system and between 0.5 and 5 mW for the europium system. Experiments were made in a nitrogen gas flowing cryostat under a 50× microscope objective at room temperature and 78 K.

Energy-dispersive x-ray (EDX) analyses were performed using a Princeton Gamma Tech spectrometer coupled with a Jeol Model JSM 5800 LV scanning electron microscope.

RESULTS AND DISCUSSION

Analytical Data

EDX analyses of several places in the CaF₂:Eu and CaF₂:Er samples before heat treatment showed the samples to be inhomogeneous, with the rare earth compositions ranging from 0.09 to 0.85% for the europium system and 0.25 to 0.67% for the erbium system. Thermal treatment of the two samples resulted in more homogeneous compositions, from 0.76 to 0.92% (with one analysis at 1.55%) for CaF₂:Eu and from 0.52 to 0.58% in CaF₂:Er.

Raman Data

The laser excitation at 1064 nm was chosen to avoid fluorescence in the Raman spectra, which could hide the vibrational lines. First, it is important to notice that the Fourier-transform Raman spectra were taken un-
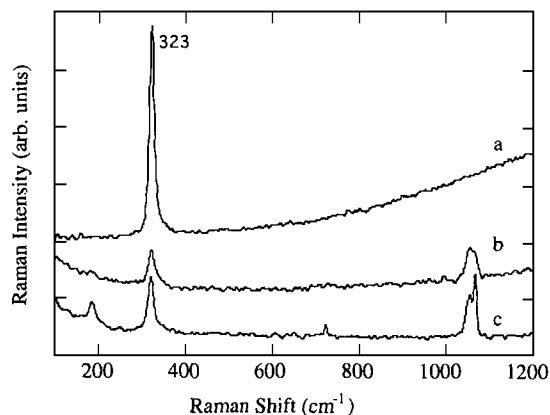
Fig. 1. Fourier-transform Raman spectra of (a) CaF_2 crystal, (b) CaF_2:
Er, and (c) CaF_2:Eu.

der the same stable conditions of laser power density with the same geometry. Under these conditions the Fourier-transform Raman spectrum of a synthetic CaF_2 crystal shows an intense line at 323 cm⁻¹. Second, we find this characteristic 323-cm⁻¹ line of CaF_2 in all the rare earth-doped samples, in addition to other features. Fluorescence does not interfere significantly in the 1064- to 1220-nm spectral region where the Raman spectra are recorded (Fig. 1). Neglecting the asymmetry of the bands, we then assume that the full width at half-maximum (FWHM) and the height $I(\omega_{max})$ of this line are related to the crystallinity of the samples. The 323-cm⁻¹ lineshape may thus be considered as a reference for evaluating the relative crystallinity, τ, or the amorphization of the material given by the integrated intensity of the lineshape normalized to the integrated intensity of the CaF_2 crystal,

$$\tau = \frac{\int I(\omega)\, d\omega}{\int I_0(\omega)\, d\omega} \approx \frac{I(\omega_{max})\, \Gamma}{I_0(\omega_{max})\, \Gamma_0}$$

where Γ is the FWHM of the line. The τ ratio may not be affected if the deformation of the bands is approximated to be similar for both the reference and the doped compound spectra.

We find $\tau = 21\%$ for CaF_2:Er and 33% for CaF_2: Eu. These materials therefore have some crystalline character which should strongly influence their luminescence properties and the arrangement of rare earth ions in the matrix.

However, if the bandshape asymmetry is taken into account, one can evaluate an asymmetry parameter, $q = \Gamma_a/\Gamma_b$, from the lineshape, where Γ_a and Γ_b are the widths at half-maximum from the center of the peak and $\Gamma_a +$

$\Gamma_b = \Gamma$. The shift of the peak position and the asymmetry parameter are caused by local strains and microcrystalline effects in the samples [6]. The q values determined for CaF_2, CaF_2:Eu, and CaF_2:Er are 0.85, 0.88, and 0.81, respectively. The maximum intensity frequency of the CaF_2:Er sample does not shift significantly from that of the crystal, whereas it is shifted by 1 cm⁻¹ in the CaF_2:Eu compound; however, their respective q parameters are quite at variance. This means that the average microcrystallite size differs in the two doped compounds.

Luminescence of Eu^{3+}

In the as-grown CaF_2:Eu system, the clump of bands centered at 590 nm comes from the $^5D_0 \rightarrow {}^7F_1$ Eu^{3+} electronic transitions [7]. The other, weaker features near 608, 613, and 627 nm are attributed to the $^5D_0 \rightarrow {}^7F_2$ transitions of the Eu^{3+} ion (Fig. 2). The strong intensity of the $^5D_0 \rightarrow {}^7F_1$ emission lines with respect to the weak $^5D_0 \rightarrow {}^7F_2$ features shows that Eu^{3+} occupies a site with a center of symmetry [7]. Lowering the temperature to 78 K results in an increase in the luminescence yield.

The five peaks of the $^5D_0 \rightarrow {}^7F_1$ emission (Fig. 2, inset) at 585.8, 589, 590, 591.5, and 593 nm may be ascribed to octahedral O sites. The O site at 590 nm is occupied by a single Eu^{3+}, and charge compensation is made by F^- ions at distant locations. The other sites have emission lines lying very close but split about the O site emission. The $O1$ site at 589 nm emits at an energy very close to that of O; the other sites $O2...O4$ are more perturbed, since they have larger energy shifts and weaker intensities. These results are similar to those obtained from doped CaF_2 crystals [8].

The annealing of this system with the procedure described in Table I for 15 h (Sample 1) or 5 days (Sample 2) up to 800°C considerably modifies the luminescence but does not improve it (Fig. 3). After 15 h of annealing, the luminescence yield decreases strongly, although the major components of the untreated sample spectrum are still present. However, the $^5D_0 \rightarrow {}^7F_2$ transitions gain in intensity. This trend is enhanced in the sample treated for 5 days: the $^5D_0 \rightarrow {}^7F_1$ emission vanishes almost completely to the gain in intensity for the $^5D_0 \rightarrow {}^7F_2$ emission, which now dominates the spectrum. One possible explanation of this effect is the site migration of the Eu^{3+} ion in the matrix, which loses the center of inversion symmetry, therefore progressively depopulating the octahedral centers [5,9–11].
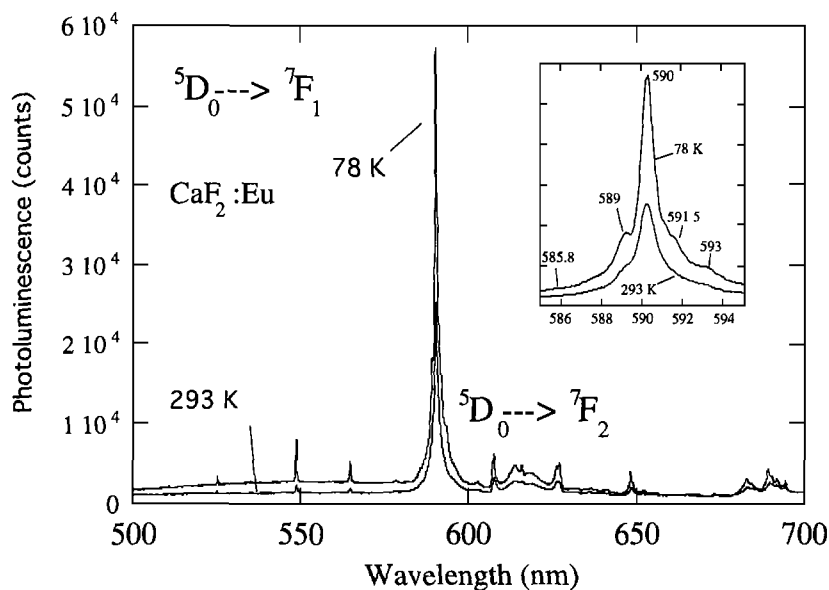
Fig. 2. Photoluminescence spectrum of the as-synthesized CaF_2:Eu material taken at 78 K and room temperature.

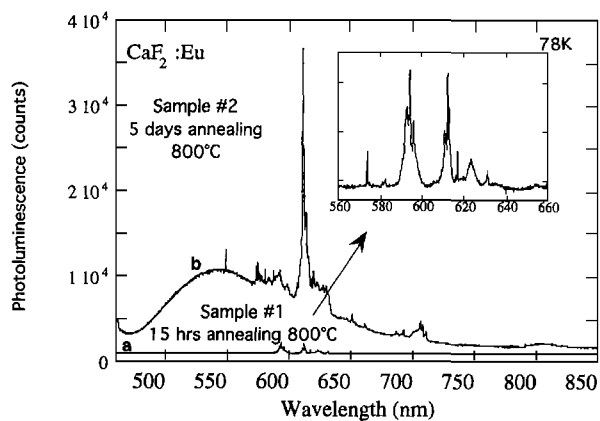Fig. 3. Photoluminescence spectra of CaF_2:Eu annealed for (a) 15 h up to 800°C and (b) 5 days up to 800°C recorded at 78 K.

Fig. 4. Photoluminescence of the as-synthesized CaF_2:Er material at 294 and 78 K.

Luminescence of Er^{3+}

Although the luminescence intensity of the as-grown CaF_2:Er system increases at 78 K (Fig. 4), the emission band is extremely broad between 500 to 750 nm, with two maxima, at 558 and 580 nm. The absence of distinct features indicates that the rare earth ions lie at no preferential site of the matrix. Broad emission arises from the different configurational–coordinate curves of the Er^{3+} levels. At 78 K and room temperature, the spectrum of the CaF_2:Er Sample 3 annealed for 3 h at 800°C with the procedure described in Table I

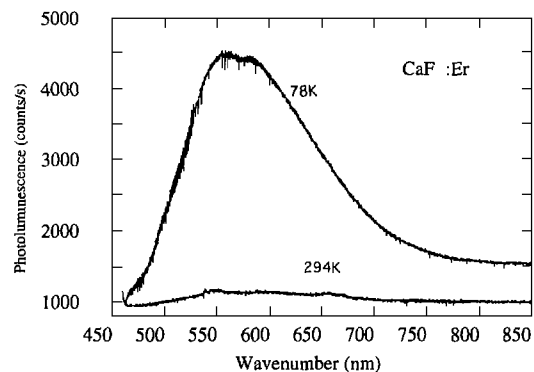changes dramatically. Extremely well-resolved features appear, contrary to the experiment carried out on the as-grown sample (Fig. 5). The emission may be attributed unambiguously to the transitions of the Er^{3+} ion, for instance, at 546 ($^2S_{3/2} \rightarrow {}^1I_{15/2}$), 549 ($^2S_{3/2} \rightarrow {}^4I_{15/2}$), 552 ($^1S_{3/2} \rightarrow {}^4I_{15/2}$), 556.6 ($^1S_{3/2} \rightarrow {}^6I_{15/2}$), 557 ($^2S_{3/2} \rightarrow {}^7I_{15/2}$), and (not shown in the spectra) 657 ($^4F_{9/2} \rightarrow {}^4I_{15/2}$) nm. These assignments are in excellent agreement with those published in the literature [12,13]. This obviously corresponds to a rearrangement of the Er^{3+} ions in the CaF_2 matrix, which acquire preferential site locations, likely at inversion centers. Attempts to record spectra on longer-annealed samples such as described in the pro-
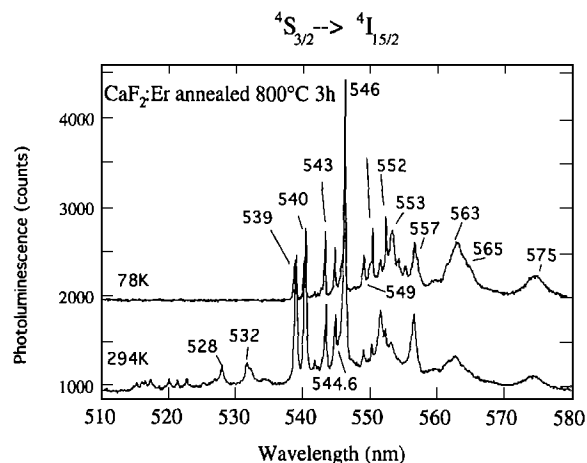
$^4S_{3/2} \longrightarrow {}^4I_{15/2}$

Fig. 5. Photoluminescence spectra of CaF$_2$:Er annealed for only 3 h at 800°C recorded at 78 K and 294 K.

cedure for europium-doped Samples 1 and 2 resulted in a loss of photoluminescence and a strong degradation of the sample. The spectral differences between Eu^{3+}- and Er^{3+}-doped samples may come from different microstructures of the starting nonannealed samples, CaF$_2$:Er being more amorphous than CaF$_2$:Eu. Er^{3+} does not lie in a very well-crystallized matrix before treatment, but slight annealing seems to improve the crystallinity-therefore enhancing ion migration and trapping at higher symmetry sites favoring sharp luminescence emission.

CONCLUSIONS

Samples of europium and erbium ions heterogeneously distributed in CaF$_2$ were prepared using an ambient condition wet synthetic technique. Energy-dispersive x-ray analyses and photoluminescence spectroscopy were used successfully to study both the degree of segregation of the europium and erbium ions and their elec-

tronic states, while Raman spectroscopy was used to study the degree of crystallinity of the phases. The degree of heterogeneity/homogeneity of the europium and erbium ions in the CaF$_2$ was studied as a function of the thermal treatment of the fluoride matrix.

ACKNOWLEDGMENTS

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