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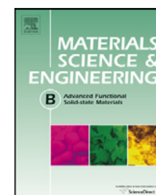

Observation of nanostructured cluster formation of Tm ions in CaF_2 crystals

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ABSTRACT

Transmission electron microscopy, energy dispersive X-ray spectroscopy, and high-resolution scanning-transmission electron microscopy, with electron beam sizes ranging from 2 to 50 nm, were used to investigate the spatial distribution and homogeneity of doped Tm^{3+} ions in CaF_2 host matrices with atomic resolution, in solid crystals grown from melts using the Bridgman–Stockbarger method. With the smallest size electron beam available of 2 nm, it was found that the Tm^{3+} ions were distributed inhomogeneously at the host sites. They took the form of sub-nm agglomerations of 3–5 atoms, rather than individual ions and the phase transition layer was 0.1 nm thick. The spatial extend of inhomogeneous Tm^{3+} concentration was 2.6–6 nm and originates from ionic density fluctuations in the liquid phase at the interface layer due to the local electrostatic field at the ionic sites.

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1. Introduction

For high image quality at shorter light wavelengths, defect free optical materials at nanoscale dimensions must be used. For example, lithography at 193 and 157 nm [1], besides posing problems of optical compactness, also places severe restrictions on the refractive index homogeneity of the optical elements (better than 10^{-7}), which in turn depends on crystal purity and spatial homogeneity.

Calcium fluoride (CaF_2) is considered to be the best optical material for short wavelength applications, and the growth of high-purity CaF_2 optical elements is essential not only for industrial but for space applications. Also, high purity wide bandgap fluoride dielectric crystals doped with trivalent rare-earth ions (RE) have been used as passive or active optical elements [2], such as optical filters in the vacuum ultraviolet (VUV) region of the spectrum, X and γ ray scintillators, and VUV emitters. All these optical properties are based on the interconfigurational $4f^n \leftrightarrow 4f^{n-1}5d$ strong, dipole allowed transitions. The homogeneity of the concentration of the RE ions determine the refractive index variation, and therefore set the limits of the optical performance of these materials. Thus, the efficiency of optical systems depends on several factors: the structure of the levels of the $4f^{n-1}5d$ electronic configuration of the RE ions [3,4], the homogeneous distribution of the RE ion concentration inside the crystal volume [5,6], and the possible agglomeration of the RE ions at the ionic sites of the host matrix, because the RE ion clustering have an effect on the refractive index of the material [7].

Several analytical techniques based on transmission electron microscopy (TEM) have been used in materials science to study the structure and chemistry of single crystals at atomic resolutions. The local structure is analyzed by high-resolution TEM (HRTEM) imaging, where various parameters such as defocus, thickness of the specimen, and aberrations are examined in the simulated images and compared with experimental results. Similarly, high-resolution scanning-transmission electron microscopy (STEM) and high-resolution high-angle annular dark-field detectors (HAADF–STEM) (*Z*-contrast methods) allow compositional structures to be resolved with atomic resolution [8].

Up until now, HRTEM has been used to study single crystal CaF_2 processed surfaces [9], the structure of CaF_2 films and interfaces [10], the formation of RE doped and undoped CaF_2 nanoparticles [11,12], and radiation-induced damages [13].

In this communication, we used HRTEM and HAADF–STEM, together with energy dispersive X-ray spectroscopy (EDXS), to investigate the homogeneity of the spatial distribution of Tm^{3+} ions in CaF_2 crystals grown from melts using the Bridgman–Stockbarger method. It was found that with a 2-nm electron beam, the concentration of Tm^{3+} ions was inhomogeneously distributed in the crystal bulk in the range of 2.6–6 nm and the ions occupied the host sites of the crystal as 3–5 atom agglomerations. The inhomogeneous Tm^{3+} concentration originates from ionic density fluctuations in the liquid phase at the interface layer due to the local electrostatic field at the ionic sites. From the analysis of the experimental data, it was found that the thickness of the phase transition layer was 0.1 nm.

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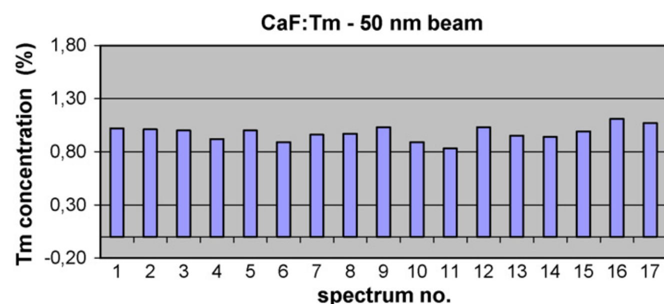

Fig. 1. Tm^{3+} concentration at various points using the EDXS technique with 50 nm beam diameter.

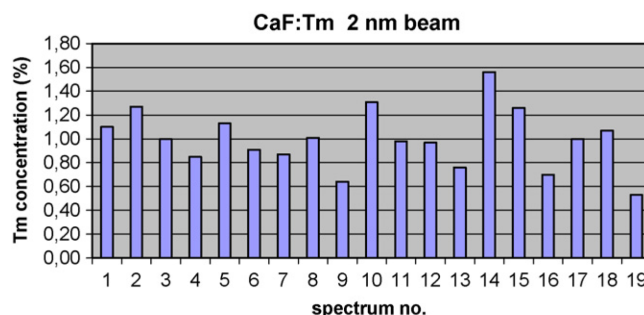

Fig. 2. Tm^{3+} concentration at various points using the EDXS technique with 2 nm beam diameter.

2. Experimental study

The experimental apparatus for crystal growth has been described in detail previously [2]. CaF_2:Tm^{3+} crystals were grown from liquid melts in carbon crucibles. The concentration of the Tm^{3+} ions in the doped crystals varied from 1.0% to 0.01%.

A JEOL2010F STEM/TEM analytical electron microscope operating at 200 keV was used for HAADF and high-resolution electron microscopy (HREM) imaging. The microscope was equipped with an EDXS detector. A series of quantitative EDXS measurements were performed using beam diameters ranging from 2 to 50 nm to determine the chemical composition of the samples.

Samples for the TEM investigation could not be prepared from bulk, since the monocrystal was very prone to cleaving during the preparation. The crystals were therefore crushed in a mortar, and the resulting powder was subsequently embedded in phenol-formaldehyde resin. Phenol-formaldehyde powder (3–5 wt.%) was added to the CaF_2:Tm^{3+} powder and thoroughly mixed. The mixture was placed in a dye with a suitable diameter, subjected to a pressure ranging from 0.5 to 1 MPa, and cured at 180 °C for few minutes. The resulting pellet was mechanically strong, and there was no difficulty with the subsequent grinding, dimpling, and ion erosion. Due to the high number of powder particles, liquid nitrogen cooling during the ion erosion process was unnecessary, and no charging effects were observed in the TEM.

3. Results and discussion

When the electron beam diameter in the EDXS analysis was larger than the cluster size, the relative standard deviation (R.S.D.) of the Tm ion concentration was dependent only on instrumental factors such as the sensitivity of the counting rate. With long sampling periods, appropriate counting rates, and corrections for the absorption of the electron beam from the sample, the R.S.D. at different points was as low as 5–10%. However, when the electron beam diameter was comparable to the cluster size, or when the average distance between different clusters was larger than the beam size, the repeatability of the measurements was poor and the R.S.D. was inversely proportional to the beam diameter.

Furthermore, the 200-keV electron-beam's broadening for a 30-nm thick CaF_2 matrix was calculated to be 0.8 nm, and for a 50 nm sample thickness was 1.8 nm. The measurements were performed for sample thicknesses between 30 and 50 nm.

The concentration (%) of the Tm^{3+} ions at different points, using 50 and 2 nm electron beams, is shown in Figs. 1 and 2, respectively. The R.S.D. is higher for the narrower beam (Fig. 2). The experimental and theoretical values of the R.S.D. of the Tm^{3+} concentration for 2, 5, 20, and 50 nm electron beams, respectively, are tabulated in Table 1. The spread of the experimental values of the Tm ion concentrations was higher for narrower beam diameters. The spread between the minimum and maximum concentration of Tm ions, obtained using a 2-nm beam, was 0.5–1.5 wt.% (the stochiometric Tm concentration was 1 wt.%).

There is a large deviation between the theoretical and experimental values in the case of small beam diameters (Table 1). This is attributed to the non-uniform distribution of Tm ions in the form of clusters rather than ions, at beam sizes smaller than 2 nm. Inspection of the areas where analyses were performed showed no damage, down to beam sizes less than 1 nm.

Besides using an EDXS analysis, the appearance of Tm clustering in CaF_2 matrices is verified with HRTEM imaging, which in these experiments provides structural information with a spatial resolution better than 0.2 nm. In most crystalline inorganic materials, including ceramics, semiconductors, and metals, the positions of individual atomic columns can be resolved, at least for the low-index zones. When recorded under optimum conditions, electron micrographs can be directly interpreted in terms of projected crystal potentials. In other cases, simulated images are matched to the experimental imaging features.

HRTEM imaging of CaF_2:Tm^{3+} crystals was performed at different orientations, with different defocus amounts for the electron beam, and with different foil thicknesses. The experimentally obtained images were compared with the simulated images of pure CaF_2 matrices and doped CaF_2 with Tm^{3+} clusters. The simulated images were generated using the "EMS software package", which allows for modelling and a comparison with experimental images [14]. A through-focus series of simulated images for pure CaF_2 for the [1 1 0] zone is shown in Fig. 3, for 10 nm foil thickness, 21 nm aperture diameter, 8 nm spread of focus, 0.48 cs, and 0.5 mrad beam semi-convergence. The image simulation when one or more columns of Ca atoms were substituted with Tm atoms is shown in Fig. 4. The corresponding crystal structure for this case is shown in Fig. 5. For those calculations, no charge compensation (such as anion vacancies) was taken into consideration. The effect of column substitution by Tm ions on the simulated image is clearly seen in a comparison of Figs. 3 and 4.

The CaF_2: Tm^{3+} HRTEM images were recorded at different areas with non-uniform contrast. A typical image recorded with 10 nm foil thickness and 20 nm defocus is shown in Fig. 6. The foil thickness for EDXS measurements was estimated using the convergent

Table 1
Measured and calculated R.S.D. values of EDXS measurements at different beam diameters

Beam diameter (nm)	Measured R.S.D. (%)	Theoretical R.S.D. (%)
2	22	12
5	19	7
20	9	7
50	4	6

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