ANALYTICAL ELECTRON MICROSCOPY OF Tm CLUSTERS IN CaF_2 MONOCRYSTALS

G. Drazic[1], A. C. Cefalas[2], S. Kobe[1], E. Sarantopoulou[2], Z. Kollia[2]
[1]Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia.
[2]National Hellenic Research Foundation, 48 Vas. Constantinou Avenue, Athens 11635 Greece

157 nm laser lithography enables achieving lithographic features with dimensions less than 50 nm [1]. However, there are problems related with the design of the projection system as the optical properties of materials are degrading constantly under prolonged irradiation at short laser wavelengths. Up to now, only CaF_2, doped with rare earth, seems to be promising to be used as optical material for 157 nm lithography, meeting the severe restrictions of refractive index stability for nanoscale imaging. From optical measurements it was suspected that rare-earth elements are forming very small clusters, degrading the properties of the material [2]. Using dedicated analytical electron microscope (J 2010 F FEG) we tried to image with atomic resolution sub-nano sized clusters of Tm atoms inside the CaF_2 matrix and thus confirming the assumption of their existence.

Detailed inspection of the samples with TEM did not reveal any secondary phase or precipitates with dimension of few nm or larger. To determine the presence of sub-nanometer sized agglomerates rich in Tm content the Energy Dispersive X-ray Spectroscopy (EDXS) technique was used in the first step. A series of quantitative EDXS measurements were performed using different beam diameter, from 2 to 50 nm. Basic idea was to perform sets of point analyses using different electron beam diameter and subsequently compare the spread of results. If Tm is evenly distributed in CaF_2 matrix (forming solid solution) the relative standard deviation of the results should be comparable, depending just on counting statistics, and not on the beam size. In the case that Tm is forming nano-sized clusters which are few nm apart, the relative standard deviation of measurements should be inversely reciprocal to the beam diameter. Analyses were performed on relatively thin parts of the sample to avoid extensive beam broadening and X-ray absorption. Results are summarized in Table 1, where also theoretical (calculated from counting statistics) relative standard deviations are tabulated. The spread of results was much higher for narrower beam diameter, the minimum concentration obtained using 2 nm beam diameter was 0.5 wt.% and the maximum around 1.5 wt. % (nominal concentration was 1 wt.%). Possible reason for large difference between theoretical and experimental deviations in the case of small beam diameters could be the degradation of the sample during the spectra acquisition. Smaller is the beam diameter, higher is the flux of electrons per unit area. Still, visual inspection of areas where analyses were performed showed no damages down to beam size less than 1nm. From those results it was suspected that Tm is not uniformly distributed in the crystal.

In the next step we tried to image the clusters using STEM/HAADF technique (Z-contrast). In Fig. 1 FFT filtered experimental high-resolution STEM/HAADF image of CaF_2 - 1% Tm in [110] zone is displayed. In micrograph, columns with higher contrast could be easily distinguished. From several micrographs (parts of the sample) it was estimated, that approximately 10% of columns have higher contrast. Ratio of intensities of brighter columns to normal columns was estimated to be around 1.4. To quantify the results we perform high-resolution image simulations. In Fig. 2 series of calculated HAADF images (for foil thickness of 20nm) for the model representing 4x4 unit cells is shown. One unit cell is displayed in Fig. 3. In this model CaF_2 is oriented in zone [110] and in each unit cell Ca atoms in the central Ca row were substituted with various amounts of Tm atoms. Calculations were made for 2, 5, 10, 50, 90 and 100 % substitution. Calculations were accomplished using computer code, developed by Yamazaki, Watanabe and Shiojiri. [3]. Columns that were completely substituted with Tm have very bright contrast compared to Ca columns (Fig 2, 100% Tm). In simulated images the ratio of intensities of Tm containing columns to pure Ca columns were calculated (Table 2). From these results it was estimated, that in experimental images around 5 % of Tm was present in brighter columns.

In the case of an ideal solid solution, where Tm are evenly distributed in the crystal, the concentration in columns should be around 0.6 % (for 1 wt. % nominal composition). This means that in brighter columns in Fig. 1 around 10 times more Tm is present than it would be in the case of solid solution.

The distribution of brighter columns (enriched in Tm) is relatively nonuniform, as could be seen from fig 4 where another area of the sample is shown and brighter columns are designated with stars. The radius of electron beam used during the EDXS analysis is also shown. We can estimate that during the EDXS analysis using 2 nm beam size (during analyses CaF_2 monocrystal was of course not in one of the low-index zone) none or up to 5 – 10 enriched columns were irradiated. Such a distribution of enriched columns could explain the spread of Tm concentrations during EDXS analyses.

From these results we can state quite convincible that Tm is forming clusters, few tenth of nanometer in size, consisting of some 3 - 5 atoms. These findings are in agreement with measurements of optical properties of the material [2].

Beam diameter (nm)	Measured Rel. st. dev.(%)	Theoretical Rel. st. dev (%)
2	22	12
5	19	7
20	9	7
50	4	6

Table 1: Measured and calculated (statistical) relative standard deviation of EDXS measurements vs beam diameter

Composition of columns (% of Tm)	Ratio of intensities (Ca+Tm/Ca)
0	1.0
2	1.1
5	1.5
10	2.0
50	2.4
90	3.4
100	3.5

Table 2: Ratio of intensities in mixed (Ca+Tm) and pure Ca columns vs column composition in simulated HAADF images.

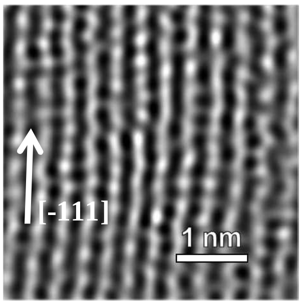

Fig1. FFT filtered experimental high-resolution STEM - HAADF image of CaF_2 - 1% Tm in [110] zone

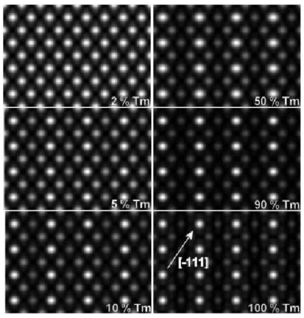

Fig 2. Calculated images, using computer simulation

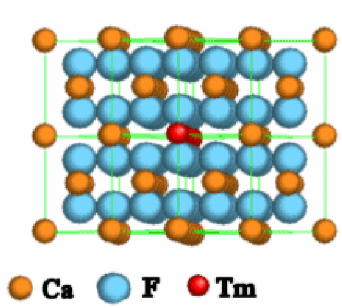

Fig 3. CaF_2:Tm unit cell in [110] zone

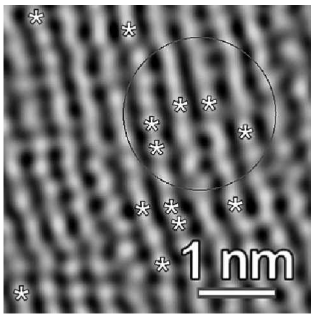

Fig 4. Experimental image where columns enriched in Tm are labelled with stars.

References

[1]. V. Bellas, E. Tegou, E. Gogolides, P. Argitis, H. Iatrou, N. Hatzichristides, E. Sarantopoulou and A. C. Cefalas, Journ. Vac. Soc. Am. B20(6), 2909 (2002).

[2]. A. C. Cefalas, E. Sarantopoulou, P. Argitis and E. Gogolides, Appl. Phys. A. 69 929 (1999).

[3]. T. Yamazaki, K. Watanabe, A. Recnik, M. Ceh, M. Kawasaki, M. Shiojiri, *J. Electron Microsc.*, vol. 49, 753-759, 2000