

Size-strain analysis in RE-doped KY₃F₁₀ fluorides using X-ray line profile analysis

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Abstract

Due to their optical properties and multitudinous applications in optoelectronic and laser devices, the interest in studying luminescent nanostructured materials is growing. In this work the crystallite size distribution of nanostructured rare-earth doped KY₃F₁₀ fluorides were determined as a first step to understand its microstructure behavior when different dopants are introduced. A pure and two RE-doped samples of KY₃F₁₀ were analyzed in order to verify the dopant influence in the size distribution of its crystallites. The Warren-Averbach method of X-ray line profile analysis was applied to obtain the area-weighted mean crystallite size. Alternatively, the volume-weighted mean crystallite size was calculated using a Full Profile Fitting method known as Pawley method without reference to a structural model. The results provided by the two methods were used to determine the crystallite size distribution, in order to obtain a more detailed study of the microstructure.

Keywords (Palavras chaves): X-ray line profile analysis, Warren-Averbach, Pawley method, crystallite size distribution.

1. Introduction

Nanostructured rare-earth doped KY₃F₁₀ (KY₃F) fluorides (KY₃F:TR, TR=Eu, Tb, Er, Nd, Yb e Tm) were studied through X-ray line profile analysis to determine microstrain, mean crystallite size and the crystallite size distribution. These materials are being increasingly studied due to its applications in random lasers, transparent ceramics, dosimeters and biological markers [1]. The understanding of microstructure behavior when different dopants are introduced plays a very important role as a first step to correlate physical and chemical properties of these fluorides to the mean crystallite size and its distribution.

In this work the mean crystallite size and the microstrain were determined using two methods: a Full Profile Fitting (first proposed by Pawley, also referred as Pawley method [2]) and the Warren-Averbach method [3]. In the Pawley method a fitting procedure is carried out in all the diffractogram. The Warren-Averbach (W-A) method on the other hand considers the Fourier coefficients of two parallel (at least two) peak reflections and no fit is considered *a priori*. The only limitation of the W-A method is that two parallel reflections need to be considered. In order to obtain a more detailed study

the results provided by the two methods were used to calculate the crystallite size distribution.

The size-strain analyses were performed on pure and RE-doped nanostructured KY₃F₁₀ fluorides mainly to verify the influence of the dopant in the microstructure.

2. Experimental

The nanostructured KY₃F₁₀ (KY₃F) fluorides were synthesized by the coprecipitation method using rare-earth oxides. Two samples were RE-doped with Er (0,3 mol %) and Yb:Nd:Tm (10 mol %: 1,3 mol %: 0,5 mol %), a detailed study of the synthesis and its optical properties were realized by Linhares [1]. It was also used Y₂O₃ produced at IPEN [4] as a standard reference material to correct the instrumental contribution in the measured X-ray profiles. Martinez et al. [5] using synchrotron diffraction analysis demonstrated that the Y₂O₃ reference material has large and homogeneous crystallites and negligible microstrain making it suitable to be used in microstructural analysis.

The X-ray diffraction data were collected at the Laboratory of Crystallography Applied to Materials Science (CristalMat) of the Nuclear and Energy

Research Institute (IPEN). A Rigaku Ultima IV diffractometer with Bragg-Brentano geometry was used. It is equipped with a diffracted-beam monochromator, and CuK α radiation and 0.02° steps was used. The divergence, antiscatter and slits were set to 1/2°, 1/2° and 0.3 mm, respectively.

3. Methods

In this work two XLP methods were applied: a Full Profile Fitting method and the Warren-Averbach method. The theory of the methods is briefly discussed in the next paragraphs.

3.1 Full Profile Fitting

The Full Profile Fitting also known as Whole Powder Pattern Decomposition was first proposed by Pawley [2] using neutron diffraction data (referred as Pawley method) and applied in X-ray diffraction data by Toraya [6]. This method is useful for unit cell refinement when peak overlap occurs, for space group determination and extracting intensities prior to structure solution [7]. It is useful since knowledge of the crystal structure is not required [2]. The method decomposes the diffractogram into individual Bragg components without reference to a structural model [8]. For the application of this method it was used the software Topas Academic Version 4.1 [9] that evaluates the volume-weighted crystallite size ($\langle L \rangle_V$) and microstrain of the analyzed material. In this work, for the fitting procedure, the modified Thompson-Cox-Hastings pseudo-Voigt profile function was used.

3.2 Warren-Averbach method

The Bragg reflections in X-ray diffraction profiles can be considered as the convolution of crystallite size, microstrain [2] (related to the sample) and also instrumental contributions. After the correction of the instrumental contribution the Fourier transform can be applied to the profile. This procedure permits to separate the crystallite size and microstrain contributions. This method is known as the Bertaut-Warren-Averbach Method or simply Warren-Averbach Method:

$$\ln A \left(L, \frac{1}{d} \right) = \ln A^S(L) - 2\pi^2 \langle \varepsilon_L^2 \rangle L^2 / d^2 \quad (5)$$

Where L is the Fourier Length, defined as $L = n \cdot a_3$, where $a_3 = \lambda / 2(\sin \theta_2 - \sin \theta_1)$, n is the harmonic number, θ_1 is the initial angle of the peak, θ_2 is the final angle of the peak, d is the interplanar spacing and $\langle \varepsilon_L^2 \rangle$ stand for mean squared strain (MSS) [2]. Therefore, MSS can be determined from the coefficients of Eq. (5). With MSS it is possible to calculate the root mean square strain ($\sqrt{\langle \varepsilon_L^2 \rangle}$, RMSS) which is more used.

To calculate the mean crystallite sizes, $A^S(L)$ was plotted against L , where the intercept of the initial slope on the L -axis gives the area-weighted crystallite size $\langle L \rangle_A$ [2].

3.3 Lognormal size distribution

The crystallite size distribution in this work was calculated using an approximation for the size distribution. Krill and Birringer [10] showed that a widely function used to describe the distribution of volumetric entities is the lognormal function:

$$g(D) = \frac{1}{\sqrt{2\pi D \ln \sigma}} \exp \left\{ -\frac{1}{2} \left[\frac{\ln(D/D_0)}{\ln \sigma} \right]^2 \right\} \quad (6)$$

As presented by Eq. 6 the lognormal function $g(D)$ can be calculated determining the parameters D_0 and σ , also known as median and lognormal variance respectively [11]. To perform the determination of these parameters it is necessary to assume that the crystallite has a specific form of a convex solid. In this work it was assumed that the crystallites can be approximated by spheres with diameters D . The determination of the parameters D_0 and σ can then be performed using the area-weighted mean crystallite size and the volume-weighted crystallite size.

Armstrong et al. [11] showed that D_0 and σ are related to the average diameter (D_S) and the variance (σ_V) of the distribution.

4. Results

Pure KY₃F₁₀ (termed as KY3F10 PURE), and KY₃F₁₀ RE-doped with Er and Yb:Nd:Tm (termed as KY₃F₁₀ Er and KY₃F₁₀ Yb:Nd:Tm, respectively) were analyzed by the Warren-Averbach method. For these samples it was chosen the (220) and (440) reflections for the application of the method. The reflections (211) and (422) of Y₂O₃ were used to perform the instrumental contribution correction on the KY₃F₁₀ X-ray diffraction profiles. Fig. 1 shows the (220) reflections for the KY₃F₁₀ samples and the (211) reflection for the Y₂O₃. The Y₂O₃ reflection was slightly shifted in its Bragg angle in order to facilitate the comparison.

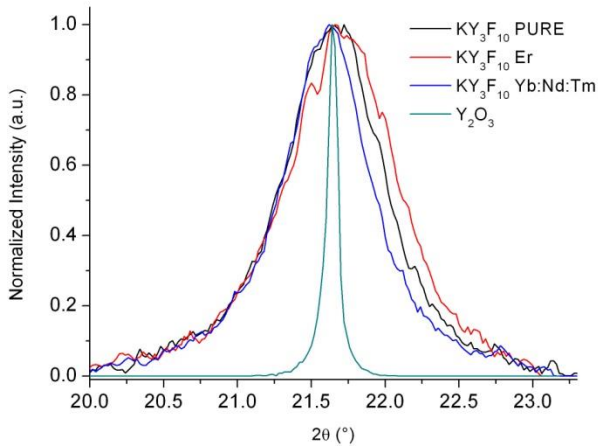


Figure 1 – (220) reflections for the KY_3F_{10} samples and the (211) reflection for the Y_2O_3 .

The Warren-Averbach method was applied according to the guideline discussed by Martinez [12] and Ichikawa [12].

Figure 2 shows the determination of the area-weighted mean crystallite by means of the Warren-Averbach method.

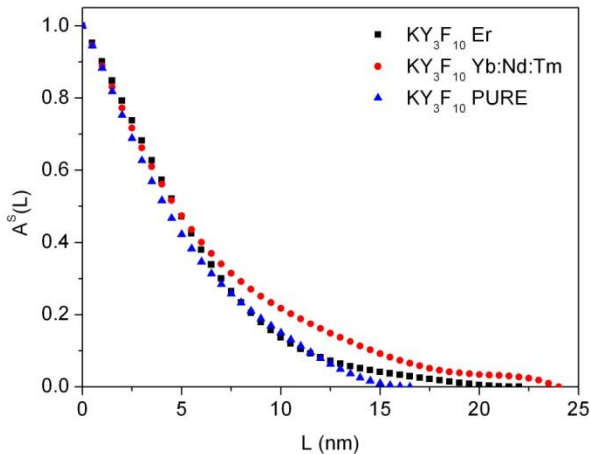


Figure 2 – Plot of $A^S(L)$ vs L for the determination of $\langle L \rangle_A$.

Tab. 1 presents the values for the area-weighted crystallite size ($\langle L \rangle_A$) and RMSS.

Table 1. Area-weighted mean crystallite sizes ($\langle L \rangle_A$) and root mean squares strains (RMSS) for the KY_3F_{10} samples.

KY_3F_{10}	$\langle L \rangle_A$ (nm)	RMSS (10^{-4})
Er	7.6	16
Yb:Nd:Tm	8.4	15
PURE	7.4	12

From the results presented in Tab. 1 it is possible to conclude that the dopant increases the mean crystallite size and RMSS values, since higher values were obtained for KY_3F_{10} Yb:Nd:Tm when comparing with PURE and Er doped samples. For KY_3F_{10} Er the values for $\langle L \rangle_A$ and RMSS were higher than the values obtained for the PURE samples.

The values for volume-weighted crystallite size and RMSS calculated using the Pawley method is presented in Table 2.

Table 2. Area-weighted mean crystallite sizes ($\langle L \rangle_A$) and root mean squares strains (RMSS) for the KY_3F_{10} samples.

KY_3F_{10}	$\langle L \rangle_V$ (nm)	RMSS (10^{-4})
Er	10.3	58
Yb:Nd:Tm	11.4	55
PURE	10.0	35

The values presented in Tab. 2 are higher than the ones presented in Tab. 1 since these values are volume-weighted. As for the results obtained when the Warren-Averbach method was applied, the KY_3F_{10} PURE presents lowest values for mean crystallite sizes and RMSS.

Considering $\langle L \rangle_A$ and $\langle L \rangle_V$ values it is possible to calculate the crystallite size distributions considering the lognormal distribution and spherical shaped crystallites with diameter (D). In a work by Linhares [1], TEM images confirmed the spherical shape for the crystallites of the three samples analyzed in this work. Fig. 3 shows the distributions for the three samples.

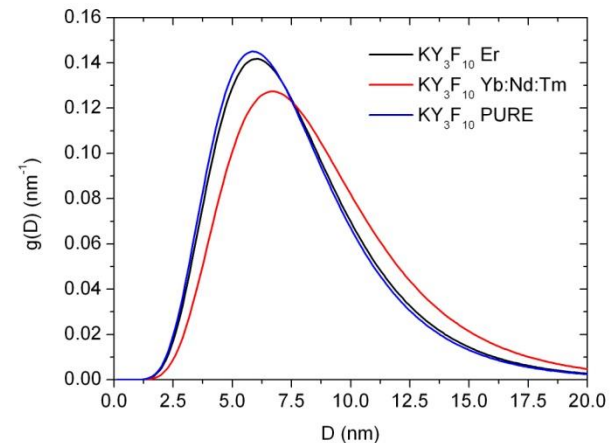


Figure 3 – Crystallite size distribution for the three KY_3F_{10} samples.

The broader distribution was obtained for the KY_3F_{10} Yb:Nd:Tm sample. The distribution for the KY_3F_{10} Er sample was a little broader than the PURE sample, but both results also suggests an influence of the doping process on the crystallite size distribution, as for the application of the Warren-Averbach and Pawley methods, the higher mean value of the distribution was obtained for the KY_3F_{10} Yb:Nd:Tm sample.

Table 3. Mean crystallite size diameters (D) and standard deviation (σ) of the distribution.

KY_3F_{10}	$\langle D \rangle$ (nm)	σ (nm)
Er	7.9	3.5
Yb:Nd:Tm	8.8	3.9
PURE	7.7	3.4

5. Conclusions

It is possible to conclude that the microstructure of KY_3F_{10} is affected by the dopant. It can be seen that the values for the mean crystallite sizes and RMSS increases when the material is doped with Er or Yb:Nd:Tm, considering the results provided by the Warren-Averbach and Pawley method. Additionally, the crystallite size distribution was successfully calculated considering the lognormal distribution and spherical shaped crystallites. The results for the distribution also are agreement with the ones provided by the Warren-Averbach and Pawley methods, confirming the influence of the doping process in the microstructure of KY_3F_{10} .

6. Acknowledgments

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7. References

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