

Research Article

Morphology and Luminescence of Nanocrystalline Nb₂O₅ Doped with Eu³⁺

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The synthesis of nanocrystalline Nb₂O₅:Eu³⁺ has been achieved by using a Pechini procedure. The obtained materials are single-phase niobia with the orthorhombic structure, average crystallite size around 25 nm and average lattice strain of about 0.002. TEM images show that the particles are rectangular and reasonably isolated. The luminescence of the Eu³⁺ ions in the niobia lattice is efficient and affected by a strong inhomogeneous broadening, due to an important disorder around the lanthanide ions.

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1. INTRODUCTION

Luminescent niobate crystals activated with trivalent lanthanide ions (Ln³⁺) have been the subject of considerable attention in the past decades. In particular, lithium niobate (LiNbO₃) has attracted huge interest as a valuable host for Ln³⁺ ions, with important applications in the field of optoelectronics and light emitting devices [1]. Moreover, other niobates such as strontium barium niobate (Sr_xBa_{1-x}Nb₂O₆) (SBN) and barium sodium niobate (BNN), activated with Ln³⁺ ions, are very promising materials in the field of photorefractive memories [2] and linear and self-frequency converter solid state laser materials [3, 4]. It is important to note that in all these crystals the location of the Ln³⁺ in the lattice is not obvious, as the trivalent lanthanide ions cannot easily replace the constitutional cations (Li⁺, Na⁺, Sr²⁺, Ba²⁺, Nb⁵⁺) due to clear size and/or charge mismatches. This location has been addressed by several studies where optical and/or structural techniques have been employed [5, 6]. Nevertheless, it is still a matter of debate whether the Ln³⁺ can substitute for the smaller and higher charged Nb⁵⁺ cation in a crystalline lattice [7]. One possible contribution to the solution of this problem is to verify if it is feasible to dope Ln³⁺ ions in a lattice in which *only* the formally pentavalent niobium cations can be replaced, that is, Nb₂O₅. For this reason, we found it in-

teresting to investigate the synthesis and the structural properties of crystalline niobia (Nb₂O₅), doped with Eu³⁺. Moreover, although nanocrystalline niobia has been shown to be a valuable material finding applications as catalyst and sensor [8, 9], very scarce information is available on the preparation and spectroscopic investigation of nanocrystalline Nb₂O₅ activated with lanthanide ions. For this reason, in this paper we report on the synthesis and characterization, and on the optical spectroscopy of Nb₂O₅:Eu³⁺ in nanocrystalline form.

2. EXPERIMENTAL PROCEDURE

Nanocrystalline powders of Eu³⁺ doped Nb₂O₅ were prepared by a Pechini approach [10]. The molar ratio between the niobium and the Eu³⁺ ions was 99:1. An appropriate amount of citric acid was first dissolved in hot water, then niobium ammonium oxalate (NAmOx), Eu(NO₃)₃, and polyethylene glycol (PEG) were added. The resulting solution was stirred for 10 minutes. The gel was obtained by drying the solution at 90°C for 2 days. The nanocrystalline powder was obtained by heat-treating the gel at 400°C for 2 hours and then at 600°C for 1 hour. The sample will be denoted as Nb₂O₅:Eu hereafter.

The powder X-ray diffraction (XRD) pattern of the Nb₂O₅:Eu sample was recorded overnight with a Bruker D8

diffractometer in the Bragg-Brentano geometry using Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$). The X-ray generator worked at a power of 40 kV and 40 mA and the goniometer was equipped with a graphite monochromator in the diffracted beam. The resolution of the instrument (divergent and antiscatter slits of 0.5°) was determined using $\alpha\text{-SiO}_2$ and $\alpha\text{-Al}_2\text{O}_3$ standards free from the effect of reduced crystallite size and lattice defects. The powder patterns were analyzed according to the Rietveld method [11] using the program MAUD [12] running on a personal computer. It is worth to recall that the MAUD program takes into account precisely the instrument broadening and, under the selected assumption of isotropic peak broadening as a function of reciprocal space, performs the separation of the lattice strain contribution to the broadening from the reduced crystallite size. Relative agreement factors R_{wp} and R_B are generally reported to determine the ability of the implemented structural model in accounting for the experimental data, which are unavoidably affected by statistical noise due to the limited time of pattern collection.

Transmission electronic microscopy (TEM) images were obtained with a JEM 200CX working at 200 kV; selected area diffraction images were obtained with a camera length of 82 cm.

The 488.0 nm line of a Spectra-Physics Stabilite 2017 argon Laser was used to excite the luminescence and Raman spectra. The emission radiation was collected by using an optical fiber and dispersed with a Jobin-Yvon HR460 0.46 m monochromator equipped with a 150 lines/mm (for low-resolution luminescence spectra) or a 1200 lines/mm (for high-resolution luminescence and Raman spectra) grating. A suitable notch filter was employed to measure the Raman spectrum, in order to suppress the 488.0 nm Rayleigh radiation. Due to the notch filter, the Raman spectrum can be collected for Raman shifts higher than 250 cm^{-1} . An air cooled Jobin-Yvon Spectrum One CCD device was employed to detect the emission radiation. The resolution of the luminescence spectra is $\pm 1 \text{ nm}$ for low-resolution luminescence spectra (560–730 nm range) and $\pm 0.2 \text{ nm}$ for high-resolution spectra (577–584 nm range). The spectral resolution of the Raman spectrum is $\pm 2 \text{ cm}^{-1}$. The emission decay curves were measured using as the excitation source the second harmonic (at 532 nm) of the fundamental radiation of a Quanta System pulsed Nd-YAG laser. The emission radiation was dispersed with the above mentioned monochromator and detected with a Hamamatsu GaAs photomultiplier connected to a Le Croy Waverunner 500 MHz digital oscilloscope. All the spectroscopic measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

The X-ray diffraction pattern of the $\text{Nb}_2\text{O}_5\text{:Eu}$ sample is reported in Figure 1 as data points, together with the result of the Rietveld fit (full lines). It is possible to assess that the sample is single phase. The pattern is typical of an orthorhombic Nb_2O_5 structure, reported with space group $Pbam$ by Kato and Tamura [13]. The values of lattice parameters refined from the pattern (see Table 1) are not too different from the

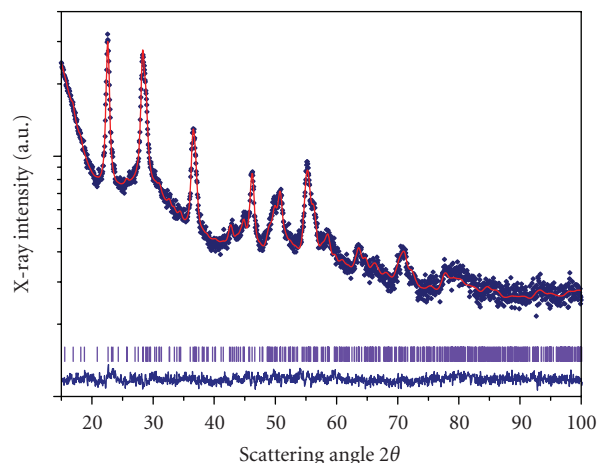


FIGURE 1: XRD patterns for the Eu^{3+} doped nanocrystalline Nb_2O_5 sample. Dots are experimental data points, full lines are the result of the Rietveld fit. The sequence of bars is calculated from the orthorhombic structure factor $Pbam$ with the lattice parameters reported in Table 1 and marks the positions expected for any peak. The band at the very bottom of the plot reports the residuals, that is, the difference between the square root of calculated and experimental intensities.

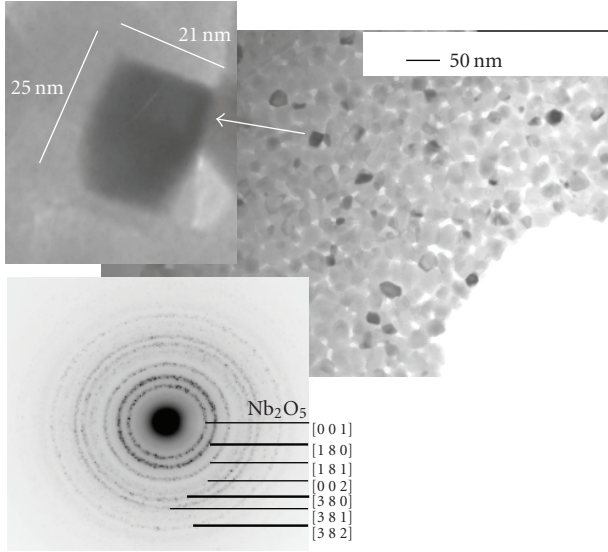
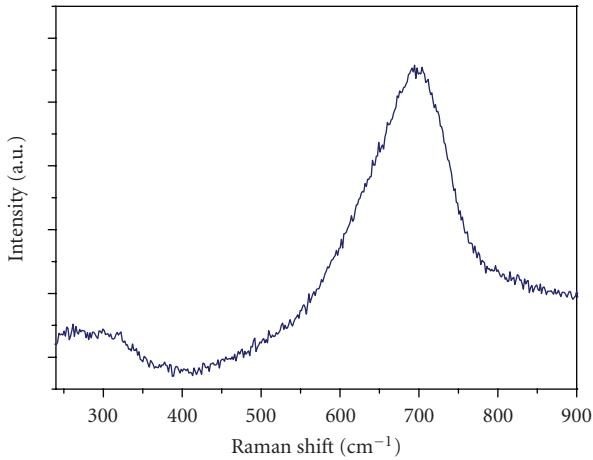
values reported by Kato and Tamura [13] from single crystal data and the small differences found may be ascribed to the insertion into the matrix of the doping agent here used. It should also be noted that various forms of the Nb(V) oxide are known from literature, namely tetragonal [14] and monoclinic [15]. Further, additional monoclinic forms exist, which are modified by pressure and temperature. The pattern of our orthorhombic $\text{Nb}_2\text{O}_5\text{:Eu}$ sample is in close agreement with that reported by Pinna et al. [16]. Direct evaluation of the line broadening by the Rietveld program MAUD, which includes the correction for the instrument function, gives an average crystallite size of about 25 nm with a sensible amount of lattice strain of 0.002.

The crystallography and morphology of the powder were also probed by selected Area electron Diffraction (SAD). In Figure 2(a), a TEM bright field image shows monodisperse rectangular nanoparticles with a narrow particle size distribution. The mean particle dimensions were determined by averaging over about one hundred particles. The average length and width were observed to be 26 and 19 nm, respectively. This result agrees with the size obtained from XRD with the Rietveld method and with the observations by Pinna et al. [16].

The Raman spectrum of the niobia sample under investigation is shown in Figure 3. A strong broad band peaking at about 700 cm^{-1} dominates the Raman spectrum although some weaker features around 300 cm^{-1} can be observed. The spectrum is very similar to the one found by Brayner and Bozon-Verduraz for a nanocrystalline orthorhombic Nb_2O_5 sample prepared by a soft chemical route [17]. The broad band around 700 cm^{-1} can be attributed to the stretching modes of the NbO_6 polyhedra typical of the orthorhombic

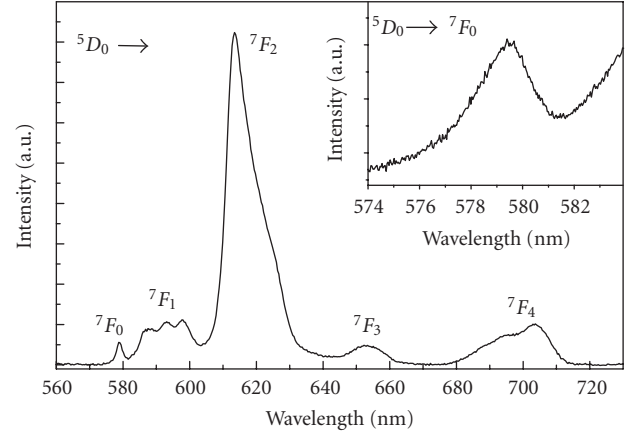
TABLE 1: The main crystallographic and microstructure parameters for the $\text{Nb}_2\text{O}_5:\text{Eu}$ sample from the best-fit data of Figure 1.

Geometry and space group	Lattice parameters (Å)	Crystallite size (Å)	Lattice strain ($\times 10^{-3}$)	Agreement index R_{wp}
Orthorhombic $Pbam$	a = 6.191 (± 2) b = 29.244 (± 5) c = 3.926 (± 2)	230 \pm 30	2.0 (± 0.2)	4.7 %

FIGURE 2: TEM and SAD images for the Eu^{3+} doped nanocrystalline Nb_2O_5 sample.FIGURE 3: Room temperature Raman spectrum of the Eu^{3+} doped nanocrystalline Nb_2O_5 sample.

Nb_2O_5 crystalline structure. The remarkable broadening of this band suggests the presence of distorted niobia polyhedra. Besides, the weaker bands around 300 cm^{-1} are characteristic of the bending modes of the Nb–O–Nb linkages [17].

The room temperature laser excited luminescence spectrum in the 560–730 nm region is shown in Figure 4. The spectrum is characterised by emission bands ascribed to

FIGURE 4: Room temperature luminescence spectrum of the Eu^{3+} doped nanocrystalline Nb_2O_5 sample ($\lambda_{\text{exc}} = 488.0\text{ nm}$). Inset: ${}^5D_0 \rightarrow {}^7F_0$ emission band.

${}^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3, 4$) transitions. These bands appear to be significantly broadened, a behaviour typical of lanthanide impurities in disordered environments. It should be noted that the ${}^5D_0 \rightarrow {}^7F_0$ emission band of the Eu^{3+} ion (shown in the inset of Figure 4) is characterised by a full width at half maximum (FWHM) of $32 \pm 2\text{ cm}^{-1}$, which is much higher than for ordered crystalline materials, in agreement with the presence of a high degree of disorder for the Eu^{3+} sites in the Nb_2O_5 host. This FWHM value results to be even higher than the one observed for Eu^{3+} doped strontium barium niobate (SBN) single crystals (FWHM = 24 cm^{-1}) [6], which are among the crystals affected by a high degree of intrinsic disorder. Moreover, the FWHM for the $\text{Nb}_2\text{O}_5:\text{Eu}$ sample is very similar to that found for Eu^{3+} doped SBN nanocrystalline powders (FWHM of about 30 cm^{-1}) [18]. The presence of such disorder is attributed to the difference in the ionic radii in octahedral coordination for Nb^{5+} (78 pm) and for Eu^{3+} (108.7 pm) [19], so that the substitution of the dopant ion cannot easily occur without distortions, which are likely to be affected by a site-to-site variation. Moreover, the necessary charge compensation could also occur in a variety of different ways, giving rise to a distribution of possible sites for the Eu^{3+} ions.

The asymmetry ratio

$$R = \frac{I({}^5D_0 \rightarrow {}^7F_2)}{I({}^5D_0 \rightarrow {}^7F_1)} \quad (1)$$

of the integrated intensities of the hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ and the magnetic dipole ${}^5D_0 \rightarrow {}^7F_1$ transitions can be considered indicative of the asymmetry of the coordination

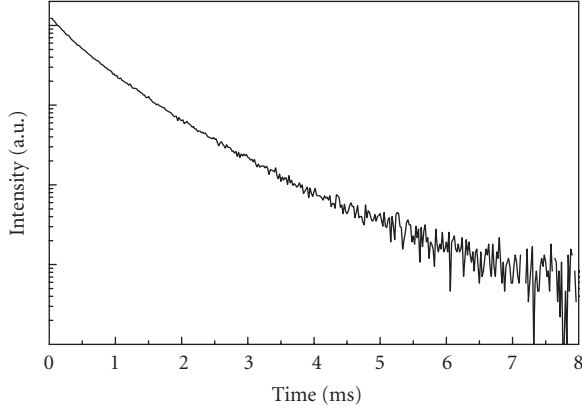


FIGURE 5: Room temperature luminescence decay curve of the Eu^{3+} doped nanocrystalline Nb_2O_5 sample ($\lambda_{\text{exc}} = 532 \text{ nm}$, $\lambda_{\text{em}} = 610 \text{ nm}$).

polyhedron of the Eu^{3+} ion [20]. In particular, the lower the R value is, the higher is the site symmetry at the Eu^{3+} ion. The value of the asymmetry parameter for the $\text{Nb}_2\text{O}_5:\text{Eu}$ sample, obtained from the measured emission spectra (see Figure 4), results to be 6.0 ± 0.1 . This value indicates that the Eu^{3+} ions are accommodated in noncentrosymmetric sites [20], in agreement with the fact that the forbidden transition is clearly detectable. This value appears to be on the upper side of the R range commonly found for Eu^{3+} doped glass hosts ($R = 3 - 6$) [20].

The RT emission decay curve of the 5D_0 level (see Figure 5) show a nonexponential behaviour. The nonexponential shape of the luminescence decay curve is mainly ascribed to the disorder affecting the sites in which the Eu^{3+} ions are accommodated, as also evidenced by the significant inhomogeneous broadening of the emission bands. We evaluate the effective average emission decay time τ_{avg} using the equation (see [21])

$$\tau_{\text{avg}} = \frac{\int tI(t)dt}{\int I(t)dt}, \quad (2)$$

where $I(t)$ represents the luminescence intensity at time t corrected for the background and the integrals are evaluated on a range $0 < t < t^{\text{max}}$, where $t^{\text{max}} \gg \tau_{\text{avg}}$. The obtained τ_{avg} value for the $\text{Nb}_2\text{O}_5:\text{Eu}$ sample is 0.78 ± 0.01 millisecond. This value of the effective decay time is similar to that found for SBN nanopowders (about 0.70 millisecond) [18]. The radiative lifetime τ_R of the 5D_0 level of the Eu^{3+} ion can be estimated using the formula (see [22])

$$\frac{1}{\tau_R} = A_{\text{MD},0} n^3 \left(\frac{I_{\text{tot}}}{I({}^5D_0 \rightarrow {}^7F_1)} \right), \quad (3)$$

where n is the refractive index of the medium, $A_{\text{MD},0}$ is the spontaneous emission probability for the ${}^5D_0 \rightarrow {}^7F_1$ transition in vacuo, and $I_{\text{tot}}/I({}^5D_0 \rightarrow {}^7F_1)$ is the ratio of the total area of the Eu^{3+} emission spectrum to the area of the ${}^5D_0 \rightarrow {}^7F_1$ band. The refractive index of the Nb_2O_5 host is taken as 2.4, as reported for Nb_2O_5 thin films [23, 24]. The

$A_{\text{MD},0}$ value is estimated to be 14.65 s^{-1} [22]. The radiative lifetime τ_R of the 5D_0 level of the Eu^{3+} ion, obtained from (3) and the measured emission spectrum (see Figure 4), results to be 0.56 millisecond. It is worth noting that the experimental effective lifetime τ_{avg} results to be longer than the radiative lifetime obtained from (3). The lengthening of the emission decay time of the 5D_0 level was also observed for some Eu^{3+} doped nanosized materials, such as Eu^{3+} doped Y_2O_3 nanopowders [25] and Eu^{3+} doped nanocrystalline zirconia [26]. This behavior can be due to a lower refractive index (n_{eff}) surrounding the Eu^{3+} ion in the nanocrystalline material with respect to the bulk size host, due to the fact that the filling factor (the fraction of the volume of the host occupied by the nanoparticles) is lower than one [25].

4. CONCLUSIONS

This work has shown that the synthesis of nanocrystalline niobia activated with Eu^{3+} ions is successfully achieved with the Pechini method. The obtained materials are single phase, with rectangular cross section nanoparticles of crystallite average length and width of 26 and 19 nm. Among the possible niobia polymorphs, the orthorhombic one with space group *Pbam* is observed. The luminescence features are affected by sizeable inhomogeneous broadening due to disorder around the dopant ions. The strongest emission band of the Eu^{3+} doped nanocrystalline Nb_2O_5 sample peaks at about 610 nm, suggesting a possible use of the present material as a red phosphor for lighting devices. In fact, the emission is quite efficient with reasonably long decay times, also due to the relatively low phonon cutoff of the niobia lattice (about 700 cm^{-1}), making nonradiative relaxation inefficient. Therefore, it appears justified concluding that nanocrystalline Nb_2O_5 activated with Eu^{3+} ions can be considered as an interesting and promising luminescent and multifunctional material. The present study shows that pentavalent niobium ions can be substituted by trivalent lanthanide ions in crystalline niobates. This substitution is accompanied by a strong disorder around the Ln^{3+} ions.

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