Materials Research, Vol. 1, No. 1, 1-4, 1998. © 1998

Synthesis and Luminescence Spectroscopy of $YNbO_4$ Doped with Eu(III)

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Received: December 18, 1997; Revised: July 21, 1998

The solid compound $YNbO_4:Eu^{3+}$ was synthesized by an usual solid state reaction and a non-conventional method of thermal decomposition of precursors. X-ray diffraction data of the monoclinic $YNbO_4$ were used to identify the crystalline M-fergusonite phase. The symmetry of the luminescent Eu^{3+} site is very close to the D_2 point symmetry. Spectroscopic quantities, namely, the $^5D_0$-$^7F_0$/$^5D_0$-$^7F_2$ intensity ratio, the $^5D_0$-$^7F_1$ transition splitting ($\Delta E_{0\text{-}1}$) and the intensity parameters Ω_λ (λ = 2, 4) were obtained from the emission spectrum at 77 K. In this sequence their values are 4.0 10^{-3}, 103 cm^{-1}, 18.0 10^{-20} cm^2 and 3.2 10^{-20} cm^2. Theoretical predictions are discussed in terms of the simple overlap model (SOM). The yttrium niobate structural data were taken as basis to obtain the spherical coordinates of the ligand oxygen atoms. The Eu-O distances being corrected in the frame of rare earth niobate series *vs.* atomic number. Their predicted values are 3.9 10^{-3}, 85 cm^{-1}, 14.9 10^{-20} cm^2 and 3.0 10^{-20} cm^2, assuming 0.9 as the effective charge of the ligand ions and their polarizabilities relative to the metal-ligand (M-L) distance as follows [R(Å)/ α(Å^3)]: 2.443/0.6, 2.427/1.2, 2.370/2.3, 2.349/3.5.

Keywords: *yttrium niobate, europium, luminescence, intensity parameters* r_λ

1. Introduction

Luminescent properties of niobium-containing systems are known since the fifties and several theoretical models were proposed to explain them. The interest in understanding such properties is due to the possibility of using niobates in solid state lasers. A great deal of work was reported in the literature[1-14] mainly focusing the niobate group. In the yttrium niobate, the niobium atom can be considered tetrahedrically coordinated to the oxygen atoms, although in a highly distorted site. Two crystalline forms are known for the rare earth niobates, the high temperature T-phase corresponding to the scheelite structure ($I4_{1/a}$) and the low temperature monoclinically distorted M-phase (M-fergusonite, C_2). The transition between the two phases occurs reversibly in the range 500-800 °C, depending on the rare earth ion[15-17]. When $YNbO_4$ is excited at 260 nm a broad emission band at 405 nm is observed[18]. Total or partial quenching of the NbO_4 emission occurs in $Y_{1-x}Eu_xNbO_4$ due to an energy transfer mechanism, resulting in the characteristic emission of the Eu^{3+}.

In the present work a new way of preparing $YNbO_4$ doped with Eu is described. Excitation and emission measurements were performed at room and nitrogen temperature. The simple overlap model (SOM) was applied in order to predict the $^5D_0$-$^7F_0$/$^5D_0$-$^7F_2$ intensity ratio ($I_{0\text{-}0}/I_{0\text{-}2}$), the $^5D_0$-$^7F_1$ transition splitting ($\Delta E_{0\text{-}1}$) and the intensity parameters Ω_λ (λ = 2, 4)[19,20] with the aim of comparing to the experimental values.

2. Experimental

The powdered samples of rare earth niobates were obtained by a method developed by Donegá (1990)[21]. The yttrium niobate doped with 15% of Eu^{3+} was prepared starting with a solution 0.1 mol/L of the rare earth nitrates in the suitable proportion in N,N-dimethylformamide (DMF) as solvent. A solution of the ammonium oxalate-niobate complex[22] - $Nb_2C_{10}N_2O_{32}H_{30}$ - in DMF was added

to the nitrate solution regarding the molar ratio (Y+Eu)/Nb equal to 1.04. A precipitate was formed by addition of a volume of anhydrous acetone (v/v = 2.5, acetone/DMF). The precipitate was isolated and calcinated in order to obtain the desired product. The calcination was repeated twice at 1000 °C for four hours, with slow heating and cooling (5-7 °C/min). The $YNbO_4$:Eu presented tetragonal and monoclinic crystalline mixed phases. The monoclinic compound was synthesized from the mixture of europium, niobium and yttrium oxides by a solid state reaction at 1300 °C for 10 h. Excitation and emission spectra were obtained in a Fluorolog SPEX 212 I spectrofluorometer at liquid nitrogen and room temperature.

3. Results and Discussion

The structure of $YNbO_4$ is well known. The unit cell parameters of the monoclinic and tetragonal phases are very similar[17,23]. Using the M-fergusonite cell parameters of the $YNbO_4$, the diffraction lines of the $Y_{0.85}Eu_{0.15}NbO_4$ were identified. A very good correspondence between them was obtained. The excitation spectra at room temperature was monitored at 410 nm, which is the maximum of the niobate group emission band (Fig. 1) and, at 612 nm (Fig. 2), which is the more intense line of the $^5D_0$-$^7F_2$ transition of the Eu^{3+}. The emission spectrum of the Eu^{3+} ion was recorded at liquid nitrogen temperature (Fig. 3). The excitation at 344 nm is to emphasize the energy transfer mechanism between the niobate group and the luminescent site even at a weak excitation band of the niobate group. Emission spectrum with similar structure is obtained when the excitation is positioned at 270 nm.

The experimental values of $I_{0\text{-}0}/I_{0\text{-}2}$, $\Delta E_{0\text{-}1}$, Ω_2 and Ω_4 are obtained from the emission spectrum. The low $^5D_0$-$^7F_0$ transition intensity (inset of Fig. 3) and the number of 0-J split lines indicate that the Eu^{3+} site symmetry is approximately D_2. The same features are observed for the compounds prepared by both methods.

The simple overlap model (SOM) has made good theoretical predictions when applied to several systems[19,20,24-26]. Recently, this model was modified to introduce a factor in the dynamic coupling (DC) mechanism, called the SOM factor, $\rho(2\beta)^{\lambda+1}$, to take into account the shielding effect in a self-consistent way[20,27,28]. This means that the SOM itself has a factor to consider the $5s^25p^6$ screening. Moreover, the value of the $\langle r^8 \rangle$ radial integral is now extrapolated through the function

$$\langle r^k \rangle = 0.884\, e^{0.02425\, k^{2.5454}}$$

This function reproduces the Freeman-Desclaux $\langle r^k \rangle$ integrals[29] (k = 2, 4, 6) within an average relative deviation less than 6%.

Instead of describing the SOM here, we stimulate the reader to investigate the Refs. 19, 20 and 28 for a detailed discussion.

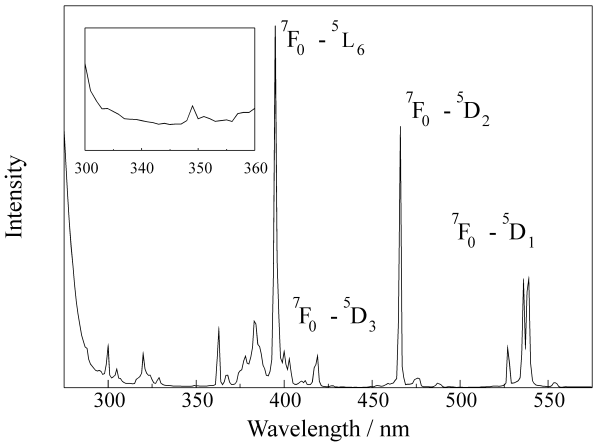

Figure 2. Excitation spectrum of the $Y_{0.85}Eu_{0.15}NbO_4$ at room temperature (λ_{emis} = 612 nm).

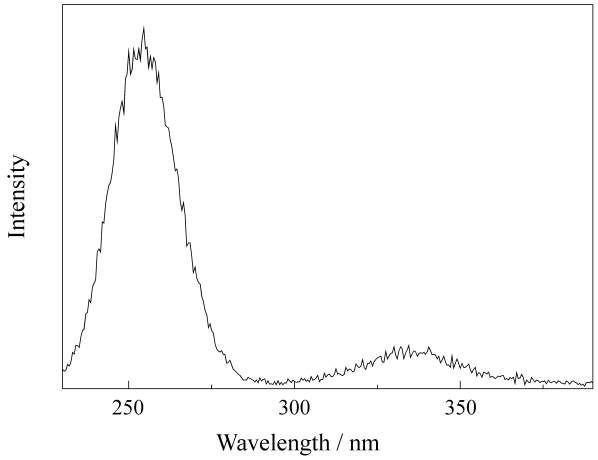

Figure 1. Excitation spectrum of the $YNbO_4$ at room temperature (λ_{emis} = 410 nm).

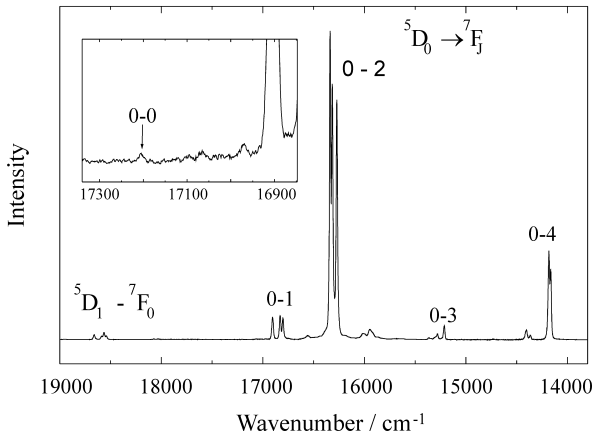

Figure 3. Emission spectrum of the $Y_{0.85}Eu_{0.15}NbO_4$ at liquid nitrogen temperature (λ_{exc} = 344 nm).

In order to apply the SOM, the coordinates of the ligand oxygen atoms were taken from the yttrium niobate structural data[16] and the Eu-O distances were corrected (Table 1) by an average factor which was obtained through the metal-ligand distance of the rare earth niobate series *vs.* atomic number (Fig. 4)[30-33]. The effective charge of the oxygen atoms was g = 0.9 and their polarizabilities are shown in Table 1. The experimental results and theoretical predictions are in Table 2.

$\Delta E_{0\text{-}1}$ does not depend on the polarizability. Thus, the only reason for a good fit of this quantity using g=0.9, which is a reasonable charge factor that one would expect for the Eu-O single bond, is the introduction of the interpolated average value of the Eu-O distances (Fig. 4).

4. Conclusions

A new way to prepare $YNbO_4$ doped with Eu^{3+} was presented. This method produces a mixture of phases caused by a low annealing temperature. Experimental values of the $^5D_0$-$^7F_0$/$^5D_0$-$^7F_2$ intensity ratio, $^5D_0$-$^7F_1$ transition splitting ($\Delta E_{0\text{-}1}$) and intensity parameters Ω_λ ($\lambda = 2, 4$) were obtained. By inputting very reasonable values of effective charge and polarizability of the ligands the theoretical predictions of the SOM are in good agreement with the experimental results.

Table 1. Ligand coordinates (R in units of 10^{-8} cm and angles in degrees) and their polarizabilities (α in units of 10^{-24} cm^3).

R	θ	ϕ	α
2.443	85.763	132.94	0.6
2.443	94.237	47.057	0.6
2.427	131.004	261.08	1.2
2.427	48.976	-81.112	1.2
2.370	152.97	92.105	2.3
2.370	27.019	87.895	2.3
2.349	81.737	202.27	3.5
2.349	98.238	-22.27	3.5

Table 2. Experimental and theoretical values of $I_{0\text{-}0}/I_{0\text{-}2}$, $\Delta E_{0\text{-}1}$ (cm^{-1}), Ω_2 and Ω_4. (10^{20} cm^2).

Parameters	Experimental	SOM
$I_{0\text{-}0}/I_{0\text{-}2}$	0.004	0.0039
$\Delta E_{0\text{-}1}$	103	85
Ω_2	18.0	14.9
Ω_4	3.2	3.0

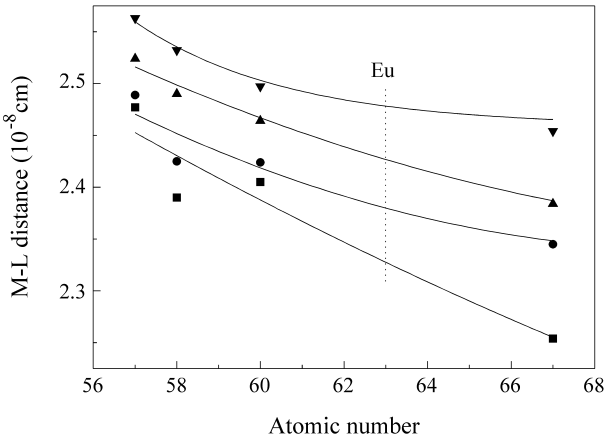

Figure 4. Metal-ligand (M-L) distance of $LnNbO_4$ (Ln = La^{3+}, Ce^{3+}, Nd^{3+}, Ho^{3+}) *vs.* atomic number.

Acknowledgments

The authors are grateful for FAPESP and CNPq (Brazilian agencies) for financial support and also for Dr. P. Melnikov for helping the determination of the crystalline phases.

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