

Synthesis and Optical Study of The System $K_3Sr_2La_{1-x}Eu_xNb_{10}O_{30}$ with Tetragonal Tungsten Bronze Structure

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Abstract

A solid solution with the general formula $K_3Sr_2La_{1-x}Eu_xNb_{10}O_{30}$ has been isolated at 1250°C. X-ray crystallography has confirmed that the whole range of composition is of tetragonal tungsten bronze structural type. Intense red emission of Eu^{3+} ion was recorded under 466 nm argon ion laser excitation. The crystal-field levels originating from 5D_J ($J = 0,1,2$) \rightarrow 7F_J ($J = 0-4$) electronic transitions were separated using time resolved spectroscopy. The measured lifetimes for 5D_0 and 5D_1 levels were found to be of the order of 1 ms and 0.40 μ s, respectively.

Keywords: Lanthanide niobates, solid solution, Tungsten bronze structure, Europium (III) spectroscopy, Lifetime measurements.

Introduction

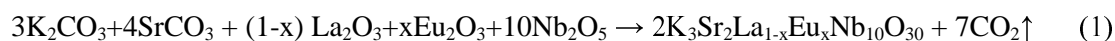
A large number of ferroelectric oxides crystallizing with the tetragonal tungsten bronze structural type (TTB) [1] has been studied and it was found that they are suitable for various industrial applications [2]. More specifically, the related niobate families have a great potential of applications due to many of their specific physical properties: ferroelectricity [2-5], ferroelasticity [6,7] electro-optics [8], non-linear optics [9], elasto-optics [10], acousto-optics [11], FRAM [16,17], etc. It has also been

observed that some rare earth cations embedded in niobate compounds, tend to enhance diffuse phase transitions [18-21] and the up-conversion emission in the green and blue laser light [22-25]. The purpose of the present work was to investigate the crystal chemistry and the optical properties of these TTB lanthanide niobate series in order to evaluate their change versus the nature and concentration of the rare earth ions.

Our study will concern more particularly the crystal chemistry of the solid solution $K_3Sr_2La_{1-x}Eu_xNb_{10}O_{30}$ ($0 \leq x \leq 0.2$) where Eu^{3+} was used as structural probe, due to its specific optical spectroscopy.

Experimental

Pulverulent samples with various compositions were synthesized within the system $K_3Sr_2La_{1-x}Eu_xNb_{10}O_{30}$, using the solid-state reaction at high temperatures, according to Eq.1:



with $0 \leq x \leq 0.2$.

The mixtures of appropriate amounts of the starting materials given in Eq.1 have been thoroughly ground before being submitted to various heat treatments within the temperature range of 300 - 1250°C. X-ray crystallography using $Cu_{(K\alpha)}$ radiation ($\lambda = 1.5418\text{\AA}$) has allowed to verify the phase purity and the completeness of the solid state reactions.

Luminescence of Eu^{3+} ion was recorded using an argon ion laser as exciting source. An intensified optical multichannel analyzer (OMA) was used for the detection of the luminescence. With this apparatus, it was also possible to record the emission at various times after the laser pulse and therefore to obtain the lifetime decay profiles of different emitting species.

Results and Discussion

Crystal Chemistry

X-ray crystallography has allowed the identification of a continuous solid solution with the general formula $K_3Sr_2La_{1-x}Eu_xNb_{10}O_{30}$. For optical purpose, we have investigated only the range $0 \leq x \leq 0.2$. All recorded diffraction lines were indexed with relation to the patterns of $K_4Ln_2Nb_{10}O_{30}$ (with Ln = Lanthanide), which was used as a structural reference [11, 26]. Therefore, the whole range of composition was found to crystallize with TTB structure.

It is also worth to notice that the crystal structures of the end members of the solid solution $K_3Sr_2LaNb_{10}O_{30}$ ($x=0$) and $K_3Sr_2EuNb_{10}O_{30}$ ($x=1$) have been recently resolved [12]. As expected, they both correspond to the tungsten bronze crystal structure type.

As can be seen in Fig.1, the title solid solution is part of the quaternary diagram $KNbO_3$ - $Sr_{1/2}NbO_3$ - $La_{1/3}NbO_3$ - $Eu_{1/3}NbO_3$. More precisely, the two limits of such solid solution $K_3Sr_2LaNb_{10}O_{30}$ ($x = 0$: $3KNbO_3.4Sr_{1/2}NbO_3.3La_{1/3}NbO_3$) and

$K_3Sr_2EuNb_{10}O_{30}$ ($x = 1$: $3KNbO_3 \cdot 4Sr_{1/2}NbO_3 \cdot 3Eu_{1/3}NbO_3$) belong to the ternary systems $KNbO_3 - Sr_{1/2}NbO_3 - La_{1/3}NbO_3$ and $KNbO_3 - Sr_{1/2}NbO_3 - Eu_{1/3}NbO_3$, respectively. Since the compounds $K_2Sr_4Nb_{10}O_{30}$ and $K_4Ln_2Nb_{10}O_{30}$ ($Ln = La, Eu$) are crystallising with TTB structural type [2, 6, 12, 26-28], it is therefore expected that all the compositions of the triangle $Sr_4K_2Nb_{10}O_{30} - K_4La_2Nb_{10}O_{30} - K_4Eu_2Nb_{10}O_{30}$, adopt the tetragonal tungsten bronze structural type (Fig.1b).

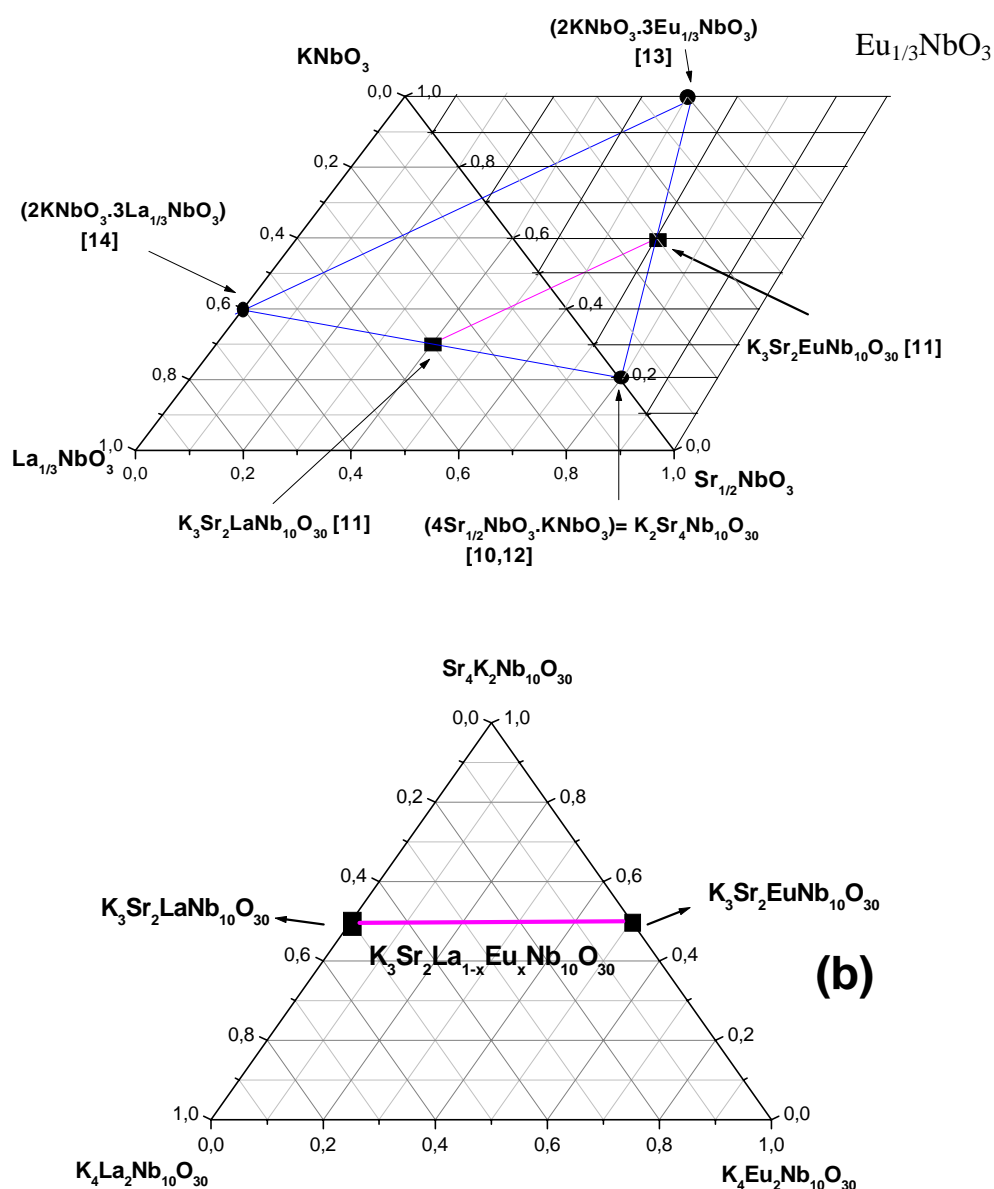


Figure 1: Domain of the solid solution $K_3Sr_2La_{1-x}Eu_xNb_{10}O_{30}$ within: the quaternary system $Sr_{1/2}NbO_3 - KNbO_3 - La_{1/3}NbO_3 - Eu_{1/3}NbO_3$ the ternary system $Sr_4K_2Nb_{10}O_{30} - K_4La_2Nb_{10}O_{30} - K_4Eu_2Nb_{10}O_{30}$,

Optical Spectroscopy

Emission spectra of Eu^{3+} ions, embedded at various concentrations in the host lattice $\text{K}_3\text{Sr}_2\text{LaNb}_{10}\text{O}_{30}$, were recorded at 300 and 77 K. All fluorescence spectra were found to be similar for all the samples investigated. Moreover, the temperature does not seem to have any significant effect on the luminescence of the europium ion in this host lattice. In addition, no obvious concentration effect was neither observed, within the limits investigated. The peaks are rather broad, alike in glasses or in disordered structures. Although X-ray diffraction patterns have evidenced a well-crystallised phase, no fine crystal field structure was obtained, as it would be normally expected for such ordered network. Under 466 nm argon ion laser excitation, and without time delay, $^5\text{D}_2$ and $^5\text{D}_1$ are the emitting levels. Fig.2a presents the emission spectrum from 400 to 750 nm for $x = 0.1$ as recorded at 77 K. It is known that within this spectral range, several electronic transitions are interfering, namely $^5\text{D}_2 \rightarrow ^7\text{F}_j$, $^5\text{D}_1 \rightarrow ^7\text{F}_j$ and $^5\text{D}_0 \rightarrow ^7\text{F}_j$. Such statement is confirmed by the time resolved spectra given in Fig.2b. As a matter of fact, 10^{-3}s after the excitation only the lowest $^5\text{D}_j$ ($J = 0$) is the emitting level and in that case, $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions can be assigned. On the spectra of Fig. 2(a) and 2(b), the first intense line corresponds to the laser excitation line at 466 nm.

The energy values of some intense $^5\text{D}_1 \rightarrow ^7\text{F}_j$ and $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions are given in Tables 1 and 2, respectively. Typical example of the decay curves is shown on Fig. 3 and the lifetime values are listed in Table 3. An exponential behaviour for the decay of $^5\text{D}_0$ level is observed confirming that no appreciable energy transfer from this europium site occurs. It was also found that the lifetime values are of the same order as the one encountered in oxide compounds [25].

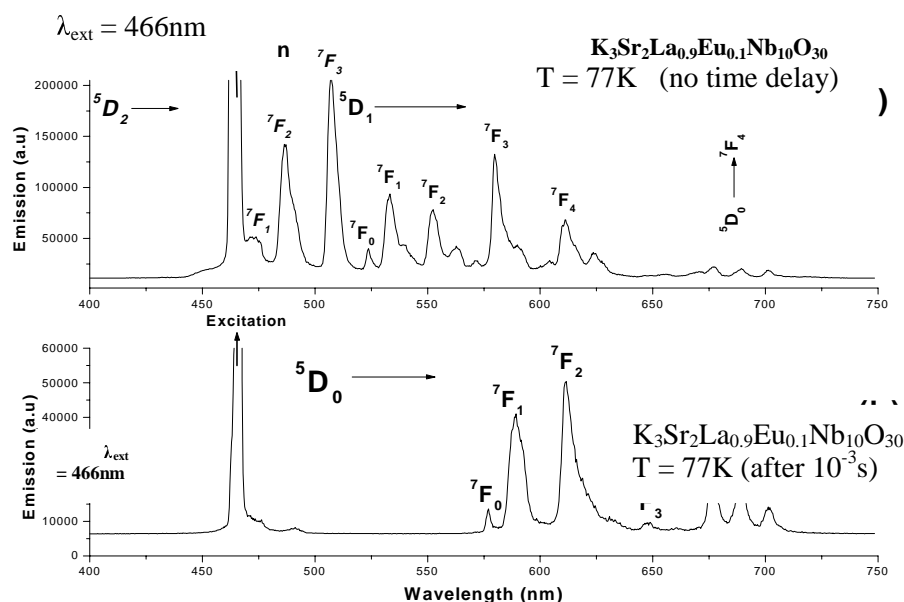


Figure 2: Fluorescence spectra of Eu^{3+} in $\text{K}_3\text{Sr}_2\text{La}_{0.9}\text{Eu}_{0.1}\text{Nb}_{10}\text{O}_{30}$
 (a) Without time delay
 (b) Time resolved (10^{-3}s after the pulse)

Table 1: Characteristics of Eu^{3+} emission lines in $\text{K}_3\text{Sr}_2\text{La}_{0.9}\text{Eu}_{0.1}\text{Nb}_{10}\text{O}_{30}$ corresponding to ${}^5\text{D}_1 \rightarrow {}^7\text{F}_J$ ($J = 0-4$) transitions.

Emitting level ${}^5\text{D}_1$ to:	Emission lines	
	wavelength λ (nm)	Energy (cm^{-1})
${}^7\text{F}_0$	523.75	19093
${}^7\text{F}_1$	533.67	18738
${}^7\text{F}_2$	553.23	18076
${}^7\text{F}_3$	580.14	17237
${}^7\text{F}_4$	604.83	16533
	611.46	16354
	624.41	16015

Table 2: Characteristics of Eu^{3+} emission lines in $\text{K}_3\text{Sr}_2\text{La}_{0.9}\text{Eu}_{0.1}\text{Nb}_{10}\text{O}_{30}$ corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J = 0-4$) transitions.

Emitting level ${}^5\text{D}_0$ to:	Emission lines	
	wavelength λ (nm)	Energy (cm^{-1})
${}^7\text{F}_0$	577.10	17328
${}^7\text{F}_1$	589.14	16973
${}^7\text{F}_2$	612.07	16338
${}^7\text{F}_3$	648.26	15426
${}^7\text{F}_4$	676.67	14778
	689.93	14494
	701.97	14246

As formerly mentioned, the emission spectra of Eu^{3+} ion in the title solid solution consist of broad bands. Such feature can be also attributed to the mixing of different electronic transitions from several ${}^5\text{D}_J$ emitting levels. Furthermore, the observation of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition (only possible for C_s , C_n , and C_{nv} local symmetry sites), indicates that the europium local coordination sphere in the present TTb typical materials can have the highest symmetry corresponding to C_{4v} . Therefore, no clear data can be extracted from the optical analysis for this statement. The magnetic dipolar ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and the electric dipolar ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions are of comparable intensity, which could be considered as an indication that the Eu local symmetry is higher than C_{2v} .

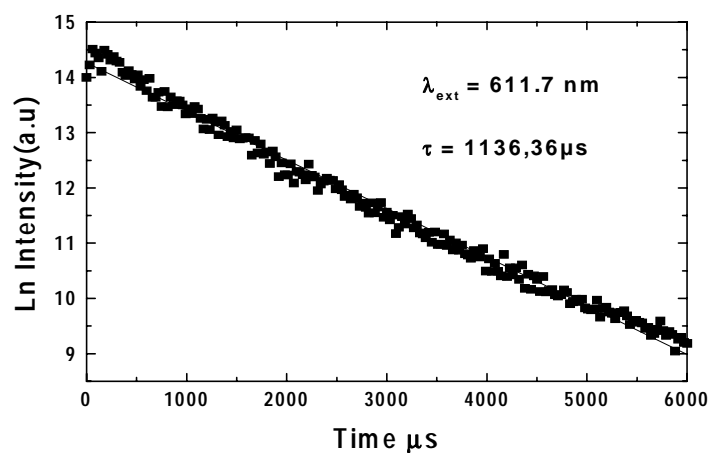


Figure 3: Typical decay curve of 5D_0 at 77 K for the composition $K_3Sr_2La_{0.9}Eu_{0.1}Nb_{10}O_{30}$.

Table 3: Variation of the lifetime values for different compositions along the series $K_3Sr_2La_{1-x}Eu_xNb_{10}O_{30}$, with $0 \leq x \leq 0.2$.

Composition	Temperature	Emitting level 5D_0	Emitting level 5D_1
x = 0.05	300 K	$\tau = 1031 \mu s$	$\tau = 36 \mu s$
	77 K	$\tau = 1123 \mu s$	$\tau = 48 \mu s$
x = 0.1	300 K	$\tau = 926 \mu s$	$\tau = 36 \mu s$
	77 K	$\tau = 1136 \mu s$	$\tau = 47 \mu s$
x = 0.2	300 K	$\tau = 877 \mu s$	$\tau = 36 \mu s$
	77 K	$\tau = 1101 \mu s$	$\tau = 46 \mu s$

The large peaks of the luminescence spectra (shown in Fig.2), caused by the interference of different electronic transitions, could be attributed to some structural disorder and the compositional fluctuation in the title niobate family. Such a disorder is also compatible with the diffuse character of the phase transitions, evidenced by dielectric measurements on equivalent compounds as reported in references [18-21].

The distribution of Eu^{3+} cations over 12- and 15-fold coordination spheres corroborates the idea of a cationic disorder, which is consistent with the preliminary structural results obtained for some members of the series of rare earth niobates $K_3Sr_2LnNb_{10}O_{30}$, with $Ln = La, Nd, Eu, Gd$ and Ho [12,27].

Conclusion

Tetragonal tungsten bronze solid solution with the general formula $K_3Sr_2La_{1-x}Eu_xNb_{10}O_{30}$ ($0 \leq x \leq 0.2$) was isolated at 1250°C. The first spectroscopic study of trivalent europium ion in this family shows a broadening of peak emission, which was found compatible with a structural disorder causing the interference of different electronic transitions. However, a rigorous interpretation of fluorescence transition was found to be more difficult to correlate to the local environment around the Eu^{3+} ion. The results of such optical structural study will be discussed elsewhere [27].

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