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Luminescence properties of the layered niobate $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ doped with Eu^{3+} and La^{3+} ions

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Abstract

In the present work the layered perovskite phase $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ was doped with rare earth ions through a solid-state reaction, producing compounds of general formula $\text{K}_{1-x}\text{Ln}_x\text{Ca}_{2-x}\text{Nb}_3\text{O}_{10}$ (where $\text{Ln}=\text{La}^{3+}$ or Eu^{3+} and $x=0.02$). The photoluminescence properties of the layered oxide doped with rare earth ions in the perovskite-type layers were investigated based on the luminescence data. The $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ phase does not exhibit emission bands when excited in the UV region. On the other hand the matrices doped with Ln^{3+} ions show a blue emission ($\lambda_{\text{exc}}=270$ nm) at 298 and 77 K, indicating that the electronic properties of the layered materials are modified by the lanthanide insertion. In the case of $\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ the characteristic red emission of the trivalent europium ion is also observed under excitation at 270 and 394 nm. The luminescence spectra of the Eu^{3+} -compound show the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition split into two peaks, indicating that the Eu^{3+} ions are located in at least two distinct site symmetries. The results also suggest the occurrence of an energy transfer process between the niobate matrix and the Eu^{3+} ion. The luminescence decays exhibit biexponential curves corroborating the presence of Eu^{3+} ions in more than one chemical environment. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Layered perovskite; Layered niobate; Photoluminescence; Rare earth ions

1. Introduction

The layered niobate $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ belongs to the perovskite-like series described by the general formula $\text{M}_m[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$ [1], where B corresponds to Nb(V), M can be an alkali-metal ion (K^+ , Rb^+ , Cs^+) that neutralizes the negative layer charge, A represents an earth alkali ion (Ca^{2+} , Sr^{2+}), lead, bismuth, lanthanides (La^{3+} , Nd^{3+}), $m=1, 2$ and $2 \leq n \leq 7$ (n indicates the number of NbO_6 octahedra chains that form the perovskite-like layer). The structural characterization of the $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ matrix, made by Dion et al. [2], revealed that the layers consist of three corner-sharing chains of NbO_6 units and calcium ion occupying the 12-coordination sites in the perovskite-like structure. The layers are disposed in a stacking arrangement with the alkali-metal ion occupying a trigonal prismatic site in the region between the layers. A schematic representation of a perovskite-like layer can be seen in Fig. 1 (distortions in the NbO_6 octahedral units are not shown).

Some layered niobates have attracted attention due to their ion-exchange and intercalation properties. In this way, the potassium ion located at the $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ inter-layer region can be replaced by simple cation in aqueous solution [3], hydrogen ions [4] and organic cations [5] under mild conditions. The acidic form of this perovskite-like compound incorporates alkylamines [6,7] through an acid–base reaction, producing an increase in the basal spacing of the layered material. Some intercalated compounds derived from $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ have shown to be

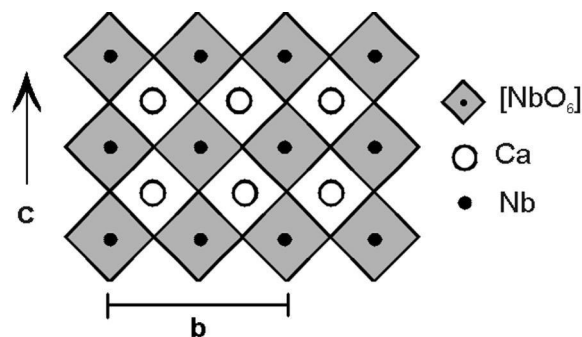


Fig. 1. Schematic representation of a perovskite-like layer of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ compound.

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photoactive. The matrix containing methylviologen between the layers can undergo a host–guest photoinduced electron transfer process [5,8]. The acidic form of $\text{MCa}_2\text{Nb}_3\text{O}_{10}$ has been explored as photocatalyst to molecular hydrogen generation in water/alcohol media [9,10]. Recently, some studies have been conducted with the aim of isolating microporous materials to be evaluated in the catalysis field. Hardin et al. [11] have tried pillaring the butylamine derivative of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ with $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ oligomers. A silica-pillared material has been isolated by Domen et al. [12,13], and its photoreactivity explored for the H_2 production.

Although some layered niobates exhibit photoluminescence properties when excited in the UV region [14–16], the $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ matrix does not present emission at room or liquid nitrogen temperatures. Wiegel et al. [17] reported the luminescence data of MLaNb_2O_7 layered perovskite ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$). These compounds show a band emission around 600 nm when excited in the range 330–340 nm at 4.2 K. Kudo [18] observed the luminescence quenching of the KLaNb_2O_7 when doped with some rare earth ions (for Eu^{3+} , Sm^{3+} , Tb^{3+} and Pr^{3+} -doped phases, the host emission is almost completely quenched while for Er^{3+} and Dy^{3+} phases the quenching is partial). For these materials of composition $\text{KLa}_{0.98}\text{Ln}_{0.02}\text{Nb}_2\text{O}_7$, the excitation at the host band produces a characteristic lanthanide luminescence, indicating a host–guest energy transfer process. According to the author, the lanthanide emission arising from the niobate doped with Eu^{3+} , Sm^{3+} , Tb^{3+} and Pr^{3+} can be due an electron- and hole-trapping mechanism taking into account that these ions can have the oxidation number changed more easily than other lanthanide ions. In the cases of Er^{3+} - and Dy^{3+} -doped niobates, the predominance of a resonant energy transfer was proposed.

Isostructural materials of composition $\text{K}_{1-x}\text{Ln}_x\text{Ca}_{2-x}\text{Nb}_3\text{O}_{10}$ ($0 < x \leq 1$) were prepared by Uma and Gopalakrishnan [19] and characterized by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS). These authors also conducted the proton ion-exchange reaction and the alkylamine intercalation for the compounds where $x = 0.25, 0.50$ and 0.75 . The Ca^{2+} replacement by La^{3+} decreases the niobate layer charge density, producing interesting materials for pillaring and, consequently, for catalytic purposes [13].

The spectroscopic properties of rare earth materials have been widely studied on the basis of the crystal field splitting of the $^{2S+1}L_J$ manifolds of the $4f^6$ configuration of the Eu^{3+} ion [20–22]. From the spectroscopic point of view this ion in general presents an intense red emission and also it has been considerably used as a probe due to the following facts [23–26]: (a) the excited states 5D_J ($J = 0, 1, 2$ and 3) are well separated ($\sim 12\,000\text{ cm}^{-1}$) from the ground terms 7F_J ($J' = 0, 1, 2, 3, 4, 5$ and 6); (b) the main emitting level, 5D_0 , and the ground state 7F_0 are non-degenerate, leading to a single $^5D_0 \rightarrow ^7F_0$ transition

when the Eu^{3+} ions occupy identical site symmetries of the type C_s , C_n or C_{nv} . This fact facilitates the interpretation of the spectral data and provides information on the eventual existence of more than one site symmetry being occupied by the Eu^{3+} ion; (c) the $^5D_0 \rightarrow ^7F_1$ transition is usually taken as a reference transition because it is allowed by magnetic dipole, and consequently the intensity of this transition is not considerably altered by the perturbing crystal field; (d) long luminescence decay time for the 5D_0 level (milliseconds) and (e) exceptionally large Stokes shift when the emission spectra are obtained through direct excitation of the 5L_6 level (around 394 nm) of the Eu^{3+} ion or through excited states, lying at higher energies, belonging to the host.

Recently, we have reported on the luminescent behavior of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ and other layered niobates containing Eu^{3+} ions intercalated in the interlayer region [3]. In the present work, the layered niobate $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ was doped with rare earth ions, producing compounds of formula $\text{K}_{0.98}\text{Ln}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ ($\text{Ln} = \text{La}^{3+}$ or Eu^{3+}). The photoluminescence properties of the layered oxide doped with rare earth ions in the perovskite-type layers and the possibility of energy transfer from the matrix to the Eu^{3+} ions are investigated through the analysis of their excitation and emission spectra. The results show that the substitution of Ca^{2+} ions by Eu^{3+} ions induces structural modifications that lead to different chemical environments around the rare earth ion. Several transitions originating from the $^5D_{0,1,2,3}$ manifolds could be assigned, in particular the $^5D_3 \rightarrow ^7F_3$ one around 444 nm, which to our knowledge has not been assigned by previous authors.

2. Experimental details

The compounds $\text{K}_{0.98}\text{Ln}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ ($\text{Ln} = \text{La}^{3+}$, Eu^{3+}) were prepared based on the procedure described by Jacobson et al. [6] for $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ synthesis. A mixture of stoichiometric amounts of Nb_2O_5 (Companhia Brasileira de Metalurgia e Mineração, CBMM), K_2CO_3 , CaCO_3 and La_2O_3 or Eu_2O_3 (all reagents obtained from Merck) was heated at 1200°C for 5 h in a platinum crucible. All products were washed with deionized water and dried under vacuum in a desiccator with silica gel.

XRD patterns of oriented films were recorded on a Philips diffractometer mod. X'PERT-MPD using $\text{Cu K}\alpha$ radiation (30 kV and 30 mA), a scan speed of 1.2° in $2\theta/\text{min}$ and a step size of 0.020° .

A Shimadzu model UV-2401PC spectrophotometer equipped with an integration sphere was employed to record the diffuse reflectance spectra (BaSO_4 from Waco Pure Chemicals was used to dilute the solid samples). The Kubelka–Munk method was used to convert the diffuse reflectance spectra to the absorbance mode through the software supplied with the spectrophotometer.

The emission and excitation spectra of the powdered samples were performed in a SPEX Fluorolog-2 spectrofluorimeter, model FL212 system, double grating 0.22 m SPEX 1680 monochromators, 450-W xenon lamp as excitation source using the front face mode. This apparatus was fully controlled by a DM3000F spectroscopic computer. The lifetime measurements were recorded at room and nitrogen liquid temperature using the Phosphorimeter (SPEX 1934D) accessory coupled with the spectrofluorometer.

The scanning electron micrographs of carbon-coated

samples were recorded on a Leica microscope model Stereoscan 440 with Li detector (back-scattered electrons).

3. Results and discussion

According to Dion et al. [2], the unit cell of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ is tetragonal ($a=7.727 \text{ \AA}$ and $c=29.466 \text{ \AA}$) and accommodates two perovskite-like layers. Jacobson et al. [4] got a better fitting to the X-ray powder data

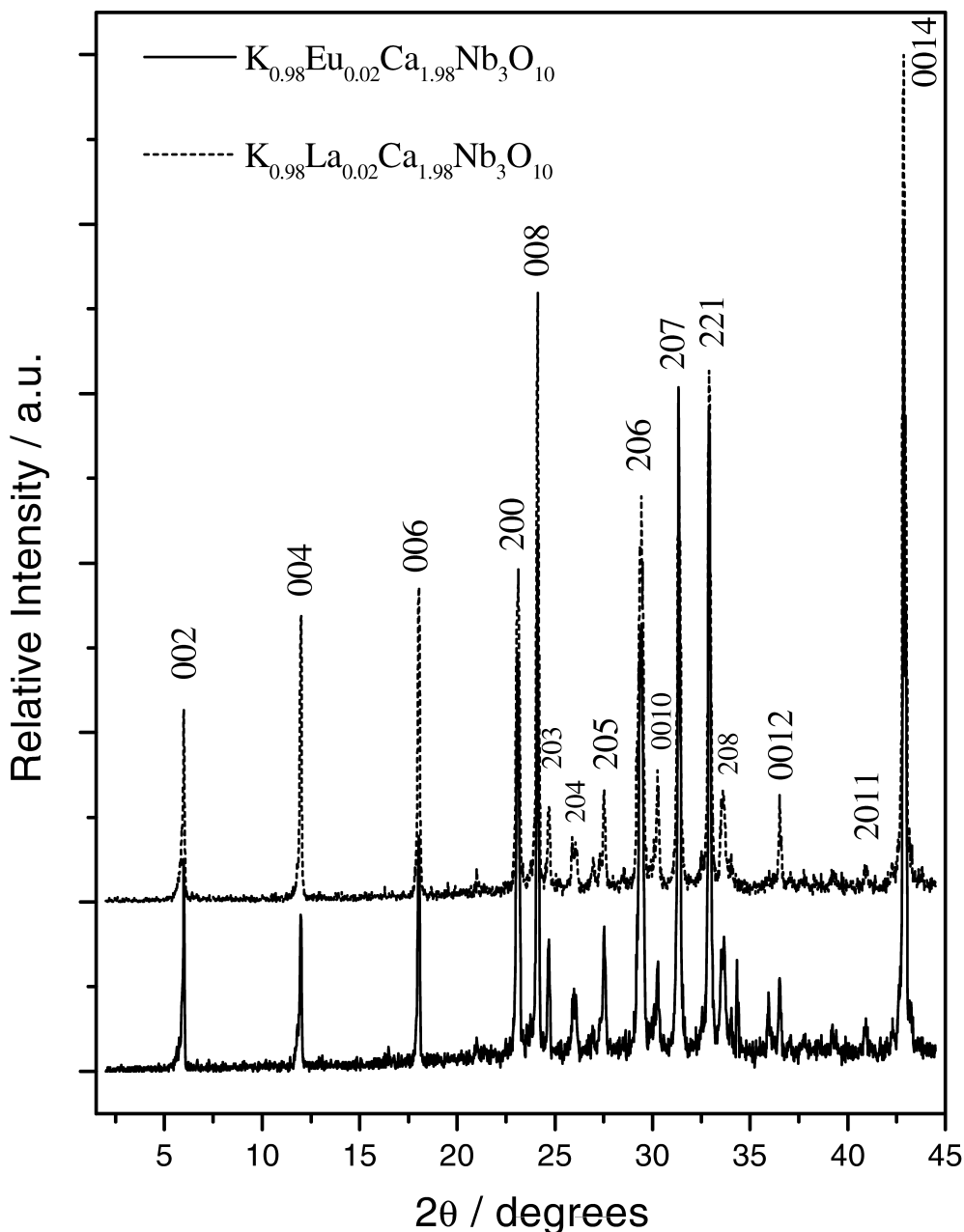


Fig. 2. XRD patterns of $\text{K}_{0.98}\text{La}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ (dashed line) and $\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ (solid line).

considering a distortion in the tetragonal unit cell of the layered niobate and proposed a orthorhombic structure ($a=3.870 \text{ \AA}$; $b=3.852 \text{ \AA}$ and $c=29.475 \text{ \AA}$). However, other cell parameters have been reported ($a=7.718 \text{ \AA}$, $b=7.753 \text{ \AA}$, $c=29.450 \text{ \AA}$; and $a=3.846 \text{ \AA}$; $b=3.864 \text{ \AA}$, $c=29.36 \text{ \AA}$) [1], demonstrating that the detailed structural analysis of the layered perovskites is difficult due to their structural complexity.

Fig. 2 shows the recorded XRD patterns and the Table 1 presents the diffraction peak assignments to $\text{K}_{0.98}\text{La}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ and $\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$. The XRD patterns obtained for the doped phases are very similar to some others reported in the literature to $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ [3,19,27].

As can be observed by XRD data (Table 1), there is minor modification in the $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ structure caused by the rare earth ions doping process. The XRD patterns of the isolated doped niobate phases do not show additional peaks when compared to the pattern recorded to $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ [3], corroborating the characterization of the doped solids as single phase materials. It is known that in mineral (as feldspars) and biological (as proteins) materials, the Ca^{2+} ions substitution by Ln^{3+} ions is observed due to their several similar properties [23]. In our view, this fact is also a strong evidence that the calcium isomorphous replacement by La^{3+} and Eu^{3+} in the doped layered niobates is more plausible than the hypothesis of the formation of undesirable phases contaminating the isolated material.

The SEM image of the $\text{K}_{0.98}\text{La}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ is shown in Fig. 3. As can be seen, the crystallites have a platelike shape and dimensions of about $4\text{--}8 \times 0.8\text{--}1 \mu\text{m}$. The sample crystals show the same brightness and also the same morphology which strongly suggests the isolation of a single phase. The images observed for $\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ compound are very similar to

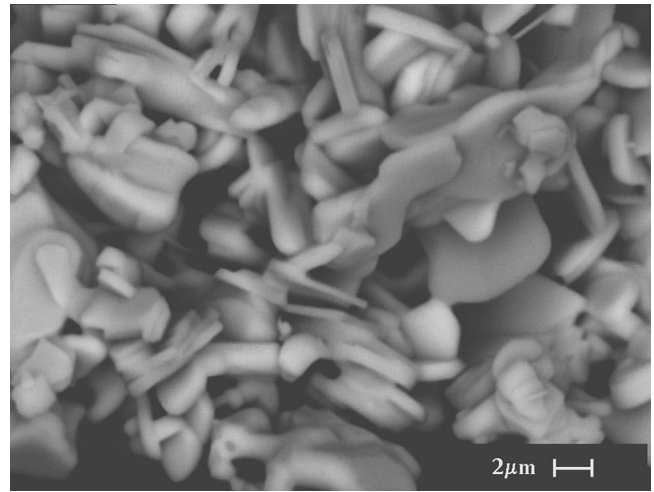


Fig. 3. SEM image of $\text{K}_{0.98}\text{La}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$.

that showed in Fig. 3. The SEM of the undoped layered niobate presents an image (not shown) similar to that of the doped compounds, indicating that the insertion of La^{3+} or Eu^{3+} in the niobate structure does not change the particles morphology.

The emission spectra of the lanthanide-doped compounds at room temperature showed a broad and structureless emission band in the region $375\text{--}550 \text{ nm}$ when excited at 270 nm (Fig. 4). It is important to emphasize that the undoped host material is not luminescent but that the lanthanide insertion in its structure produces a blue emitter compound at room temperature. Besides the fact that the nature of the ion in the 12-coordination site in the perovskite-like layers can change the photochemical behavior of niobates [9], it has been observed that other materials properties are dependent of the metal ion in the niobate layers. For example, it was reported that the calcium substitution for strontium ($\text{KSr}_2\text{Nb}_3\text{O}_{10}$) give rise

Table 1
Comparison of d_{hkl} values (\AA) of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ and the related materials doped with rare earth metal ions

$\text{KCa}_2\text{Nb}_3\text{O}_{10}^a$	$\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$	$\text{K}_{0.98}\text{La}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$	$(h k l)^a$
	14.76	14.74	0 0 2
7.36	7.39	7.38	0 0 4
4.91	4.92	4.92	0 0 6
3.85	3.86	3.85	2 0 0
3.68	3.69	3.69	0 0 8
3.60	3.61	3.61	2 0 3
3.43	3.43	3.44	2 0 4
3.23	3.24	3.24	2 0 5
3.03	3.03	3.04	2 0 6
2.95	2.95	2.95	0 0 10
2.85	2.86	2.86	2 0 7
2.72	2.73	2.72	2 2 1
2.66	2.66	2.67	2 0 8
2.46	2.46	2.46	0 0 12
2.20	2.20	2.20	2 0 11
2.11	2.11	2.11	0 0 14

^a Ref. [2].

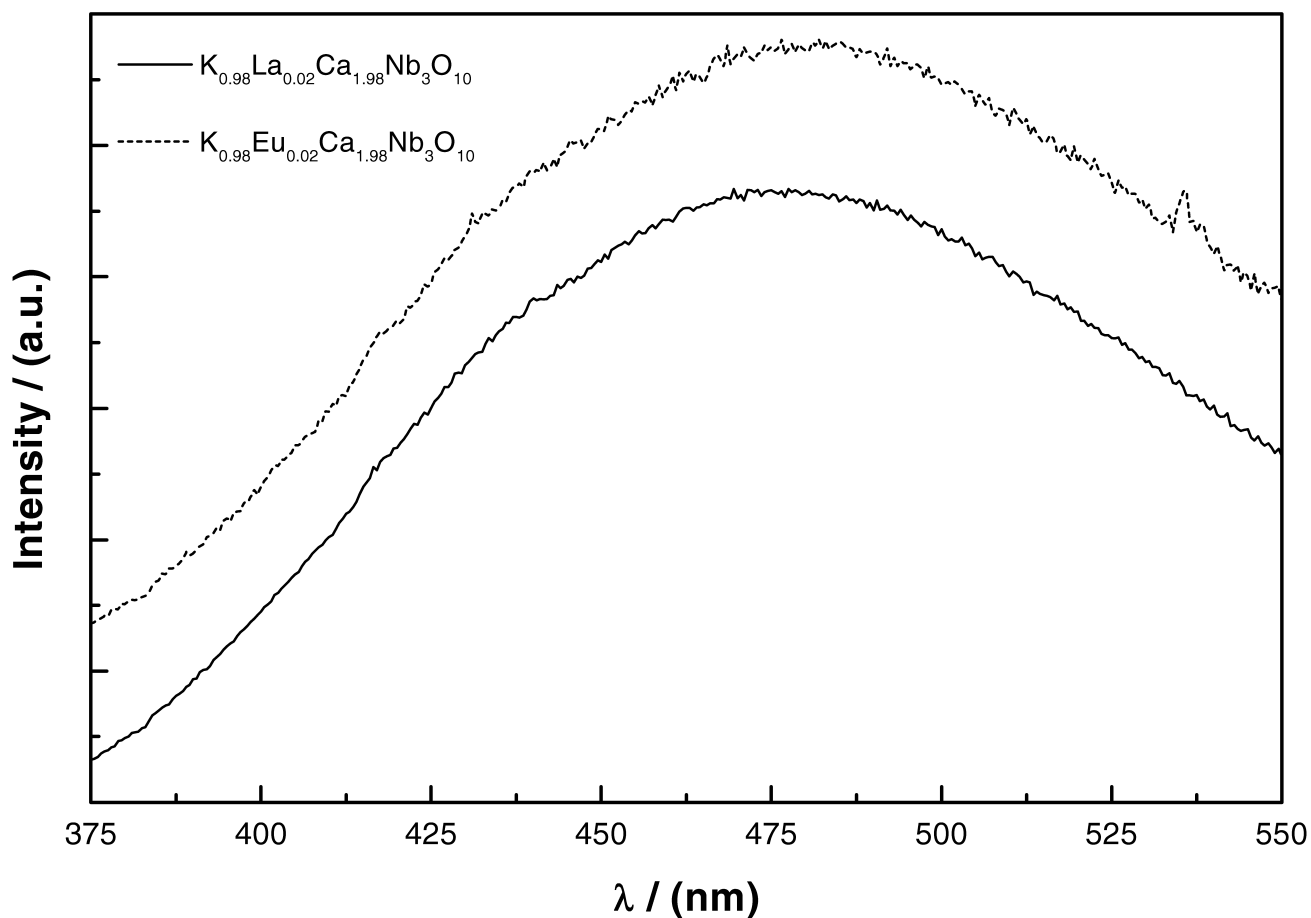


Fig. 4. Emission spectra of $K_{0.98}La_{0.02}Ca_{1.98}Nb_3O_{10}$ (solid line) and $K_{0.98}Eu_{0.02}Ca_{1.98}Nb_3O_{10}$ (dashed line) at room temperature ($\lambda_{exc.} = 270$ nm).

a luminescent material (maximum emission at 580 nm) at 77 K [28].

The excitation spectra of the doped compounds (Fig. 5a,b) show a band with maximum at 265 nm when the emission is monitored at 480 nm at room temperature. The observed Stokes shift is around $16\,200\text{ cm}^{-1}$.

For comparison purposes, Fig. 5 also shows the diffuse reflectance spectra of the Ln^{3+} -doped materials (curves c and d) and of the undoped one (curve e). An absorption edge of 300 nm is observed for all samples. For niobates, the absorption in this spectral region has been attributed to a ligand metal charge transfer transition (LMCT) from O^{2-} to Nb(V) [22]. It is possible to observe in Fig. 5 that the excitation maximum (265 nm) does not agree with the absorption edge, pointing out that not all Nb(V) sites are contributing to emission. It is known that the luminescence properties of niobates are strongly dependent of their structure. Niobates built up from corner-sharing octahedra as the perovskite-like ones, show weak or do not show luminescence. For such systems, the spectral profile is characterized by a small Stokes shift ($\sim 13\,000\text{ cm}^{-1}$), low quenching temperature ($< 298\text{ K}$) and absorption bands at high energies ($\sim 330\text{ nm}$) which have been related to the existence of delocalized excited states [17]. In the case of

$K_{0.98}Ln_{0.02}Ca_{1.98}Nb_3O_{10}$ compounds, the high quenching temperature ($> 298\text{ K}$) and the observed Stokes shift ($16\,200\text{ cm}^{-1}$) may exclude an explanation in terms of delocalized excited states. It is possible to assigned that Nb–O–Nb angle between corner-sharing NbO_6 does not approach to 180° , owing to the fact that this arrangement can favor a π -bonding interaction and the electronic delocalization [17].

According to Blasse [29], NbO_6 octahedron is the luminescent center in the perovskite-like compounds. We can suppose that electronically isolated NbO_6 units are the luminescent center in the $K_{0.98}Ln_{0.02}Ca_{1.98}Nb_3O_{10}$ compounds. A possible explanation for the matrix luminescence arises in the fact that the insertion of the lanthanide in the intralamellar region could cause some crystallographic disorder or structure defects. As a consequence the energy levels of niobate groups around the lanthanide ion site could change, originating some Nb(V) octahedra with lower excited state levels than others. These octahedra could act as traps to electrons and, consequently, the luminescence would occur from these sites [17].

The absorption spectrum of the $K_{0.98}Eu_{0.02}Ca_{1.98}Nb_3O_{10}$ compound (Fig. 5d) does not show the 4f–4f transitions that corresponds to the charac-

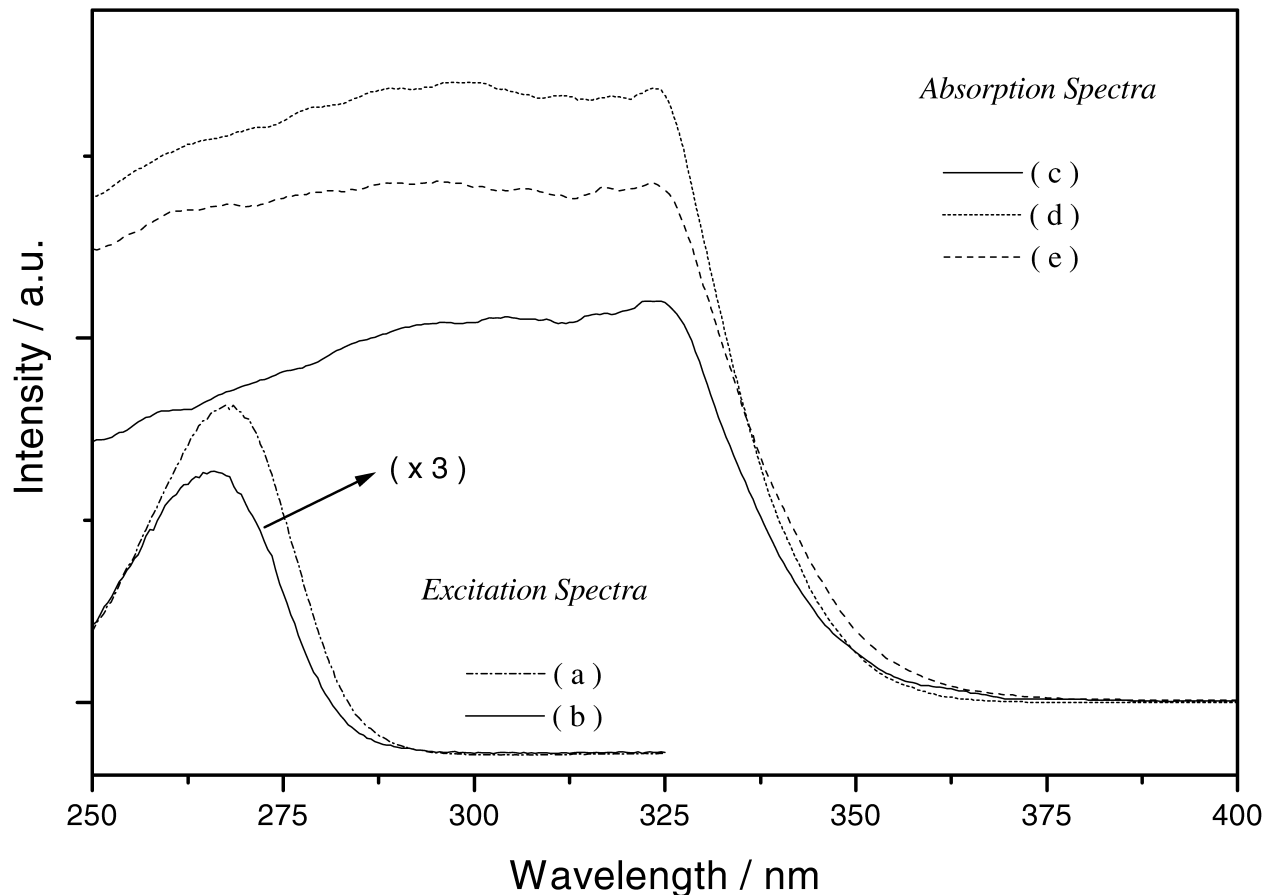


Fig. 5. Excitation spectra ($\lambda_{\text{em.}} = 480$ nm, at 298 K) of (a) $\text{K}_{0.98}\text{La}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ and (b) $\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$. Electronic absorption spectra of (c) $\text{K}_{0.98}\text{La}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$, (d) $\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ and (e) $\text{KCa}_2\text{Nb}_3\text{O}_{10}$.

teristic energy levels of the Eu^{3+} ion possibly due to the rare earth ion low concentration in the host material.

Fig. 6 shows the emission spectrum of the $\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ compound recorded at 77 K temperature which presents the characteristic bands attributed to the ${}^5\text{D}_J \rightarrow {}^7\text{F}_{J'}$ transitions (where $J=0-3$ and $J'=0-4$) in the 440–720-nm range. The emission spectrum at room temperature shows the same spectral profile but lower resolution compared to that obtained at 77 K. These data indicate that structural changes are not occurring in the niobate when the temperature is lowered to 77 K.

It is possible to observe two emission peaks around 577.8 and 580.0 nm corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition (Fig. 6). This is taken as an evidence that the Eu^{3+} ions are in at least two site symmetries since the energy level with $J=0$ is not split by any chemical environment. This result corroborates with the existence of more than the maximum number of the $(2J+1)$ components that contains 6, 10, 10 and 15 peaks related to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transitions (see Table 2), respectively. The transitions that arise from the ${}^5\text{D}_0$ emitting level are more intense than those originating from the ${}^5\text{D}_{1,2,3}$ levels.

Single-crystals XRD studies of a $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ related phase containing cesium in the interlayer region were performed by Dion et al. [30]. The authors identified four types of $[\text{NbO}_6]$ octahedra (site symmetries almost D_{4h} and C_{4v}) and four types of 12-coordination sites occupied by Ca^{2+} . A detailed structural resolution is not reported to $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, but the emission spectrum recorded for the Eu^{3+} -doped compound (Fig. 6) also evidences the distorted structural nature of the perovskite-like layers since more than one site symmetry can be assigned for the metal ion in the 12-coordination interstice.

The luminescence spectrum of $\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ at 77 K (Fig. 6) also shows the transitions corresponding to the ${}^5\text{D}_{1-3} \rightarrow {}^7\text{F}_{0-4}$ in the range 440–720 nm (see Table 2). As a consequence of the crystal field effect on the $4f^6$ configuration, it is observed that these transitions split in a number of components higher than expected, indicating the presence of more than one site symmetry occupied by the Eu^{3+} ions.

As can be seen in Table 3, for the $\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ the lifetimes of the excited state (${}^5\text{D}_0$) at liquid nitrogen are 1.47 and 6.04 ms for τ_1 and τ_2 , respectively. The luminescence decay curves (not shown)

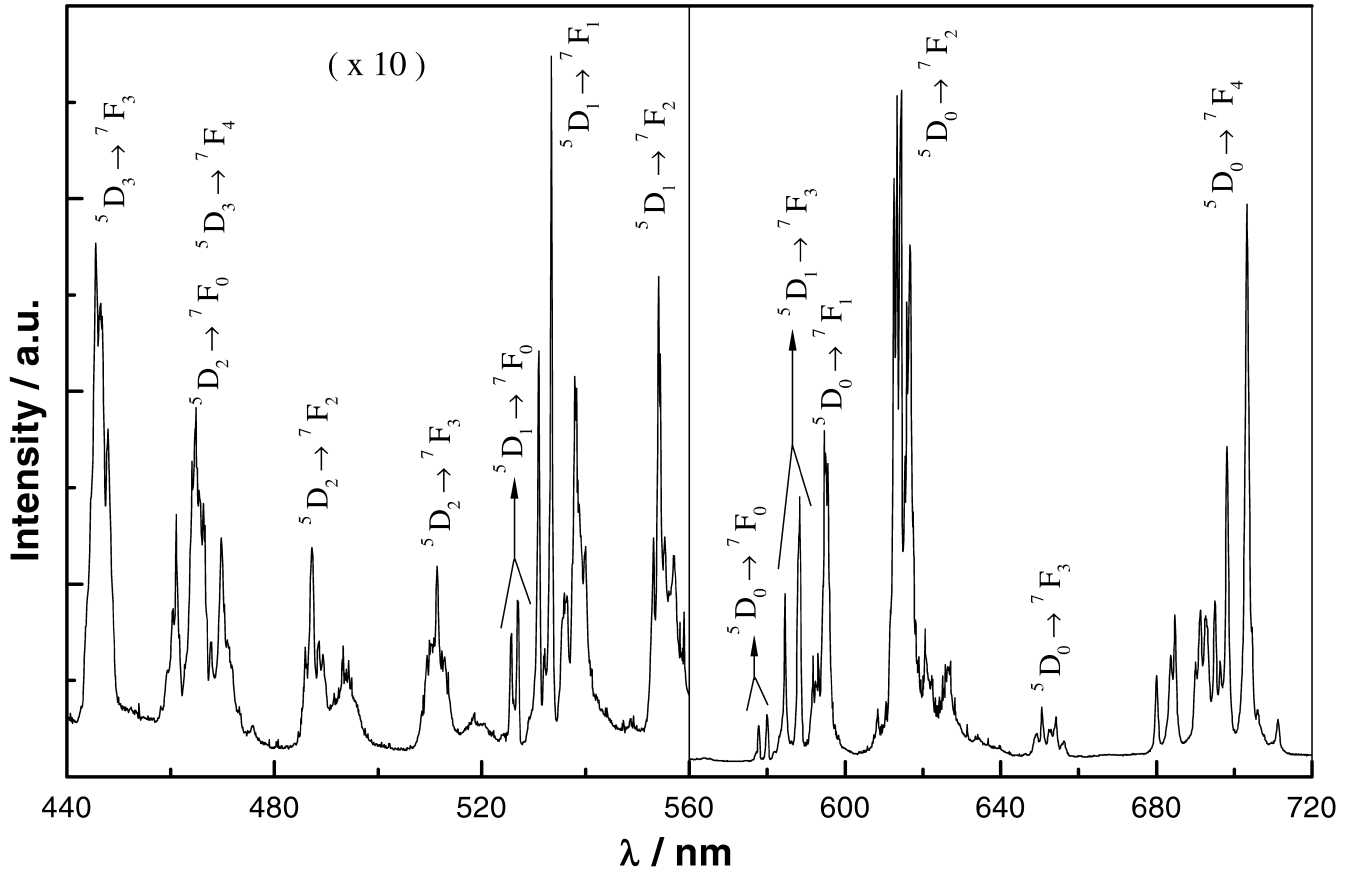


Fig. 6. Emission spectrum of $K_{0.98}Eu_{0.02}Ca_{1.98}Nb_3O_{10}$ at liquid nitrogen temperature ($\lambda_{exc.} = 394$ nm).

exhibit a biexponential feature for the 5D_0 emitting level also indicating the presence of Eu^{3+} ions in more than one chemical environment.

Considering the ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_4$ transitions for the Eu^{3+} ion in the perovskite-like layers (Fig. 6), we have determined the Ω_λ ($\lambda=2$ and 4) experimental intensity parameters, by taking the magnetic dipole allowed ${}^5D_0 \rightarrow {}^7F_1$ transition as the reference and by expressing the emission intensity, $I = \hbar\omega AN$, in terms of the surface under the emission curve. In this equation, $\hbar\omega$ is the transition energy, N is the population of the emitting level (5D_0) and Einstein's coefficient of spontaneous emission [26], A , in this case may be given by

$$A_{0-\lambda} = \frac{4e^2\omega^3}{3\hbar c^3} \chi \sum_{\lambda} \Omega_{\lambda} \langle {}^5D_0 \| U^{(\lambda)} \| {}^7F_{\lambda} \rangle^2 \quad (1)$$

where $\chi = n_0(n_0^2 + 2)^2/9$ is a Lorentz local field correction, n_0 being the index of refraction of the medium. The magnetic dipole allowed ${}^5D_0 \rightarrow {}^7F_1$ transition was taken as the reference. The reduced matrix elements $\langle {}^5D_0 \| U^{(2)} \| {}^7F_2 \rangle^2 = 0.0032$ and $\langle {}^5D_0 \| U^{(4)} \| {}^7F_4 \rangle^2 = 0.0023$ in Eq. (1) were taken from Ref. [31] and an average index of refraction equal to 1.5 was used. In this case the $A_{0-\lambda}$ values are obtained by using the relation

$$\frac{A_{0-\lambda}}{A_{0-1}} = \frac{S_{0-\lambda}}{S_{0-1}} \frac{\sigma_{\lambda}}{\sigma_1} \quad (2)$$

where $S_{0-\lambda}$ is the area under the curve related to the ${}^5D_0 \rightarrow {}^7F_{\lambda}$ transition obtained from the spectral data, σ_{λ} is the barycenter of the $0-\lambda$ transition and A_{0-1} is Einstein's coefficient for the $0-1$ magnetic dipole transition that is given by $A_{0-1} = 0.31 \times 10^{-11} n_0^3 \sigma_1^3$. The Ω_6 intensity parameter was not included in this study since the ${}^5D_0 \rightarrow {}^7F_6$ transition could not be observed.

Table 3 shows that the experimental intensity parameters, Ω_{λ} ($\lambda=2$ and 4), for the $K_{0.98}Eu_{0.02}Ca_{1.98}Nb_3O_{10}$ are smaller than those calculated for the compound containing the rare earth ion intercalated between the layers [3]. When a comparison is made between the Ω_2 parameters for the doped ($\Omega_2 = 4.5 \times 10^{-20} \text{ cm}^2$) and the intercalated ($\Omega_2 = 11 \times 10^{-20} \text{ cm}^2$) compounds, we can observe a smaller character of the hypersensitive behavior related to the ${}^5D_0 \rightarrow {}^7F_2$ transition for the $K_{0.98}Eu_{0.02}Ca_{1.98}Nb_3O_{10}$ compound. This fact suggests that the Eu^{3+} ion is not in a highly polarizable environment as have been observed in β -TTA (thenoyltrifluoroacetate) complexes ($\Omega_2 = 30 \times 10^{-20} \text{ cm}^2$) [26]. In this work, the Ω_4 value ($8.7 \times 10^{-20} \text{ cm}^2$) is higher than the Ω_2 value. On the basis of the theory of 4f intensities [32–35] the Ω_2 parameter depends

Table 2

Energy levels of the $^5D_J \rightarrow ^7F_J$ manifolds (in cm^{-1}) observed in the emission spectra of the $\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ at 77 K

Transition	Energy	Transition	Energy	Transition	Energy
	22492.1		19022.3		16347.9
	22446.7	$^5D_1 \rightarrow ^7F_0$	19007.8		16323.9
$^5D_3 \rightarrow ^7F_3$	22396.4		18978.9		16307.9
	22381.4				16302.6
	22326.4		18832.4	$^5D_0 \rightarrow ^7F_2$	16273.4
			18793.5		16247.0
			18747.7		16236.4
	21762.8		18670.6		16215.3
	21720.2	$^5D_1 \rightarrow ^7F_1$	18660.2		16194.3
	21687.3		18642.8		16113.4
	21659.1		18608.1		
	21547.1		18590.8		
$^5D_2 \rightarrow ^7F_0$	21510.0		18570.1		15410.7
+	21482.3		18518.5		15401.2
$^5D_3 \rightarrow ^7F_4$	21445.4				15370.4
	21431.6		18079.9		15328.0
	21372.1		18047.3	$^5D_0 \rightarrow ^7F_3$	15313.9
	21285.7		18037.5		15292.9
	21258.5		18018.0		15285.8
	21231.4	$^5D_1 \rightarrow ^7F_2$	18008.3		15271.8
	21199.9		17985.6		15248.6
			17950.1		15236.9
			17914.7		
	20576.1		17889.1		
	20563.4		17841.2		14705.9
	20521.2				14626.3
$^5D_2 \rightarrow ^7F_2$	20470.8	$^5D_0 \rightarrow ^7F_0$	17307.0		14622.0
	20433.2		17241.4		14602.8
	20279.9				14490.7
	20271.6		17126.2		14463.4
	20230.6	$^5D_1 \rightarrow ^7F_3$	17105.7	$^5D_0 \rightarrow ^7F_4$	14444.6
			17003.9		14436.3
			16995.2		14386.4
	19600.2				14359.6
	19554.2		16897.6		14322.5
$^5D_2 \rightarrow ^7F_3$	19519.8		16880.5		14218.7
	19500.8	$^5D_0 \rightarrow ^7F_1$	16860.6		14192.4
	19474.2		16815.2		14162.3
			16809.5		14058.8
			16772.9		

rather on the lower rank components of the crystal field and dynamic coupling interactions, while the Ω_4 and Ω_6 parameters depend rather on the corresponding higher components. Thus, $\Omega_4 > \Omega_2$ suggests that in the present case the coordination geometry is such that the higher rank components of these interactions have higher values than

the lower rank ones. As a consequence, this might suggest that the site symmetries occupied by the Eu^{3+} ions are not very low, probably a C_{nv} type.

The excitation spectra of the $\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ at room and a nitrogen liquid temperatures with emission monitored at 614 nm in the range 350–500 nm are presented in the Fig. 7. These spectral data show narrow bands referent to the $^7F_0 \rightarrow ^5H_4$, $^7F_0 \rightarrow ^5G_6$, $^7F_0 \rightarrow ^5L_6$ and $^7F_0 \rightarrow ^5D_2$ transitions characteristic of the Eu^{3+} ion corroborating with the insertion of the rare earth ion in the matrix.

The $\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ also shows the characteristic lanthanide red emission when excited at 270 nm (spectrum not shown), the region of the niobate absorption (see Fig. 5). The doped host emission (see Fig. 4) overlaps the region of Eu^{3+} absorption (for example, $^7F_0 \rightarrow ^5H_4$, $^7F_0 \rightarrow ^5G_6$, $^7F_0 \rightarrow ^5L_6$ and $^7F_0 \rightarrow ^5D_2$ transitions observed in Fig. 7). At a first glance, these data can suggest a resonant energy transfer process between the niobate matrix and the Eu^{3+} ion. However, an electron trapping mechanism such as that proposed for $\text{KLa}_{0.98}\text{Eu}_{0.02}\text{Nb}_2\text{O}_7$ [18] cannot be discounted. The proposition of a mechanism to explain the Eu^{3+} emission by the host excitation is out of the scope of the present work but will be considered in future investigations.

4. Conclusions

The emission and excitation spectra obtained for $\text{K}_{0.98}\text{Ln}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ ($\text{Ln} = \text{La}^{3+}$ or Eu^{3+}) phases suggest that the matrix blue luminescence can probably occur from electronically isolated $[\text{NbO}_6]$ units of low energy next to the lanthanide ion site in the intralamellar region. The blue luminescence of the doped materials reported in the present work can be taken as one more evidence that optical and chemical properties of perovskite-like niobates are dependent of the metal ion in the 12-coordination site.

The luminescence data of $\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ also show that the rare earth ion is present in at least two distinct sites in the perovskite-type layers indicated by the $^5D_0 \rightarrow ^7F_0$ transition split in two peaks and the more than $2J+1$ components for the all other transitions. Although detailed XRD characterization is not available for $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, as can be found for the cesium-related

Table 3

Experimental intensity parameters, Ω_2 , Ω_4 and R_{0-2} and lifetimes (τ) for $\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$ at 77 K

	Ω_2 (10^{-20} cm^{-1})	Ω_4 (10^{-20} cm^{-1})	R_{0-2}	τ_1 (ms)	τ_2 (ms)	Ref.
$\text{K}_{0.98}\text{Eu}_{0.02}\text{Ca}_{1.98}\text{Nb}_3\text{O}_{10}$	4.5	8.7	0.009	1.47	6.04	^a
$\text{Eu}_{0.07}\text{K}_{0.79}\text{Ca}_2\text{Nb}_3\text{O}_{10}$	11.0	10.5	0.010	–	–	[3]

^a This work.

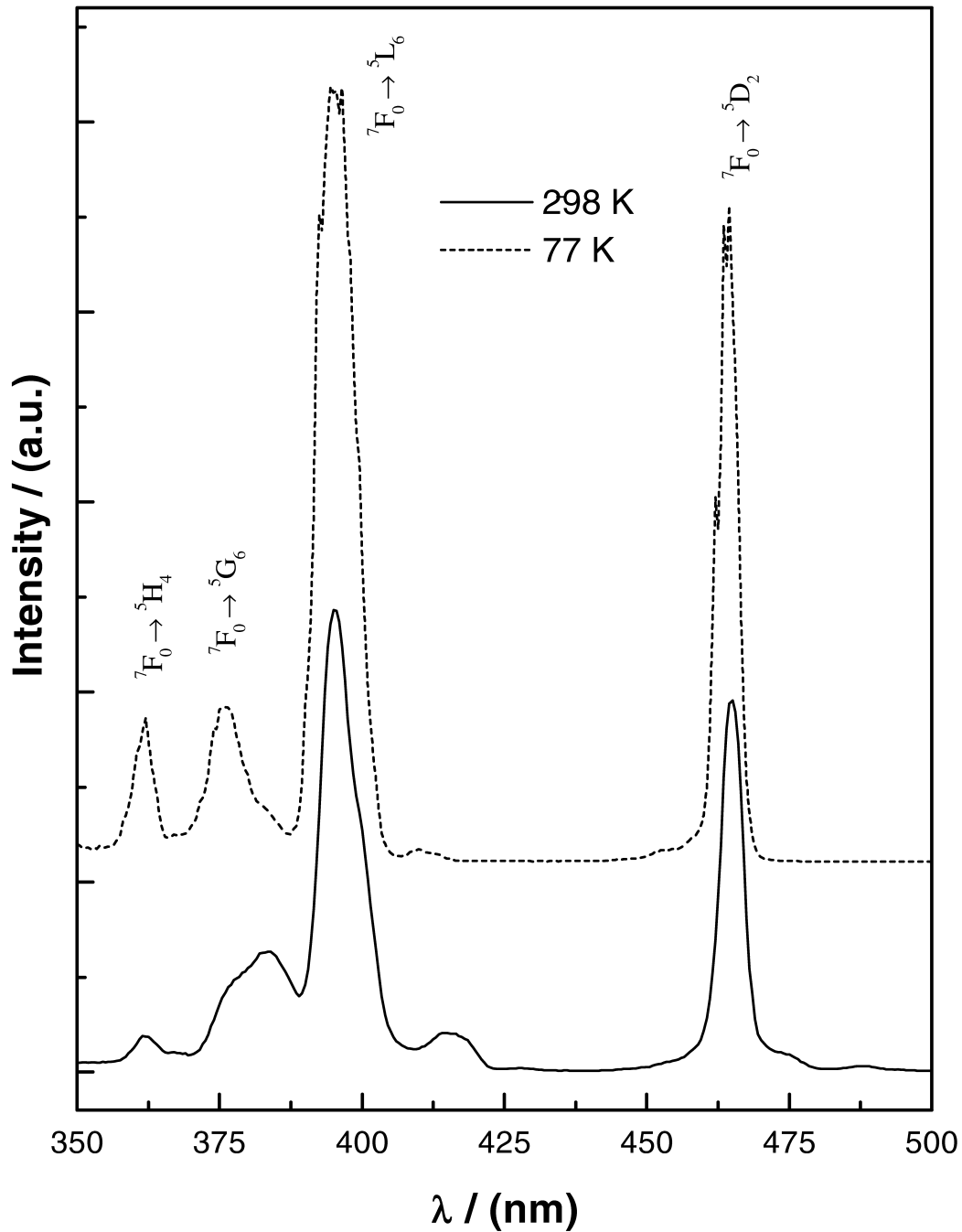


Fig. 7. Excitation spectra of $K_{0.98}Eu_{0.02}Ca_{1.98}Nb_3O_{10}$ at liquid nitrogen (dashed line) and room temperatures (solid line) ($\lambda_{em.} = 614$ nm).

phase, for example, our study showed spectroscopic evidence of the number of distinct coordination sites in the $KCa_2Nb_3O_{10}$ structure (to our knowledge, these data have not been reported in the literature).

The small value of the Ω_2 intensity parameter calculated for $K_{0.98}Eu_{0.02}Ca_{1.98}Nb_3O_{10}$ indicates that the Eu^{3+} ion is not in a highly polarizable environment when compared with this ion located in the interlayer region or in the β -dicetonate complexes. The Eu^{3+} -doped compound pre-

sents a Ω_4 value higher than the Ω_2 value suggesting that the Eu^{3+} ions are found probably in different C_{nv} site symmetries ($n > 2$).

When the $K_{0.98}Eu_{0.02}Ca_{1.98}Nb_3O_{10}$ phase is excited at 270 nm (host absorption band), besides the blue emission attributed to the niobate structure, it is also observed the characteristic red emission of the trivalent europium ion. These data indicate that an energy transfer process is occurring between the host and the Eu^{3+} ion.

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References

- [1] A.J. Jacobson, Synthesis and reaction chemistry of layered oxides with perovskite related structure, in: P. Bernier, J.E. Fischer, S. Roth, S.A. Solin (Eds.), *Chemical Physics of Intercalation II*, NATO ASI Series, Series B: Physics, Vol. 305, Plenum, New York, 1993, pp. 117–139.
- [2] M. Dion, M. Ganne, M. Tournoux, *Mater. Res. Bull.* 16 (1981) 1429.
- [3] V.R. L Constantino, M.A. Bizeto, H.F. Brito, *J. Alloys Comp.* 278 (1998) 142.
- [4] A.J. Jacobson, J.T. Lewandowski, J.W. Johnson, *J. Less-Common Met.* 116 (1986) 137.
- [5] T. Nakato, K. Kuroda, *Eur. J. Solid State Inorg. Chem.* 32 (1995) 809.
- [6] A.J. Jacobson, J.W. Johnson, J.T. Lewandowski, *Inorg. Chem.* 24 (1985) 3727.
- [7] A.J. Jacobson, J.W. Johnson, J.T. Lewandowski, *Mater. Res. Bull.* 22 (1987) 45.
- [8] T. Nakato, K. Ito, K. Kuroda, C. Kato, *Microp. Mater.* 1 (1993) 283.
- [9] A. Tanaka, J.N. Kondo, K. Domen, *Critical Rev. Surf. Chem.* 5 (4) (1995) 305.
- [10] K. Domen, J. Yoshimura, T. Sekine, A. Tanaka, T. Onishi, *Catal. Lett.* 4 (1990) 339.
- [11] S. Hardin, D. Hay, M. Millikan, J.V. Sanders, T. W. Turney, *Chem. Mater.* 3 (1991) 977.
- [12] K. Domen, Y. Ebina, T. Sekine, A. Tanaka, J. Kondo, C. Hirose, *Catal. Today* 16 (1993) 479.
- [13] K. Domen, Y. Ebina, S. Ikeda, A. Tanaka, J.N. Kondo, K. Maruya, *Catal. Today* 28 (1996) 167.
- [14] J.A. Sanz-Garcia, E. Dieguez, C. Zaldo, *Phys. Stat. Sol. (a)* 108 (1988) K145.
- [15] A. Kudo, T. Sakata, *Chem. Lett.* 11 (1994) 2179.
- [16] A. Kudo, T. Sakata, *J. Phys. Chem.* 100 (1996) 17323.
- [17] M. Wiegel, M. Hamoumi, G. Blasse, *Mater. Chem. Phys.* 36 (1994) 289.
- [18] A. Kudo, *Chem. Mater.* 9 (1997) 664.
- [19] S. Uma, J. Gopalakrishnan, *J. Solid State Chem.* 102 (1993) 332.
- [20] W.T. Carnall, G.L. Goodman, K. Rajank, R.S. Rana, *J. Chem. Phys.* 90 (1989) 3443.
- [21] J. Hölsä, P. Porcher, *J. Chem. Phys.* 75 (5) (1981) 2108.
- [22] G. Blasse, B.C. Grabmaier, in: *Luminescence Materials*, Springer, Heidelberg, 1994.
- [23] J.-C.G. Bünzli, G.R. Choppin (Eds.), *Lanthanide Probes in Life, Chemical and Earth Sciences: Theory and Practice*, Elsevier, Amsterdam, 1989, Ch. 7.
- [24] W.DeW. Horrocks Jr., M. Albin, *Prog. Inorg. Chem.* 31 (1984) 9.
- [25] G.F. Buono-Core, H. Li, B. Marciniak, *Coord. Chem. Rev.* 99 (1990) 55.
- [26] O.L. Malta, H.F. Brito, J.F.S. Menezes, F.R. Gonçalves e Silva, S. Alves Jr., F.S. Farias Jr., A.V.M. de Andrade, *J. Luminesc.* 75 (3) (1997) 255.
- [27] H. Fukuoka, T. Isami, S. Yamanaka, *Chem. Lett.* 8 (1997) 703.
- [28] A. Kudo, E. Kaneko, *J. Mater. Sci. Lett.* 16 (1997) 224.
- [29] G. Blasse, *Phys. State Sol.(a)* 20 (1973) K99.
- [30] M. Dion, M. Ganne, M. Tournoux, J. Ravez, *Rev. Chim. Minér.* 21 (1984) 92.
- [31] W.T. Carnall, H. Crosswhite, H.M. Crosswhite, *Energy Structure and Transition Probabilities of the Trivalent Lanthanides in LaF₃*, Argonne National Laboratory Report, unnumbered, 1977.
- [32] B.R. Judd, *Phys. Rev.* 1237 (1962) 750.
- [33] G.S. Ofelt, *J. Chem. Phys.* 37 (1962) 511.
- [34] R.D. Peacock, *Structure Bonding* 22 (1975) 83.
- [35] O.L. Malta, S.J.L. Ribeiro, M. Faucher, P. Porcher, *J. Chem. Phys. Solids* 52 (1991) 587.