Optical Materials 60 (2016) 94–100

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Photoluminescence study of $LiNbO_3:Cr^{3+}$; W^{4+} at high pressure. Pressure dependence of spectroscopic parameters and local structure of Cr^{3+}

M.A. Sánchez-Alejo [a,*], F. Rodríguez [b], J.A. Barreda-Argüeso [b], I. Camarillo [c], C. Flores J. [a], H. Murrieta S. [a], J.M. Hernández A. [a], F. Jaque [d], E. Camarillo [a]

[a] Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, México D.F., Mexico
[b] MALTA Consolider Team, DCITIMAC, Facultad de Ciencias, Universidad de Cantabria, 39005, Santander, Spain
[c] Departamento de Física, UAM-Iztapalapa, Apdo. Post. 55-534, México D. F. 09340, Mexico
[d] Facultad de Ciencias, Universidad Autónoma de Madrid, 28049, Madrid, Spain

ARTICLE INFO

Article history:
Received 30 March 2016
Received in revised form
10 June 2016
Accepted 12 July 2016

Keywords:
Lithium niobate
Chromium
High pressure
Photoluminescence

ABSTRACT

In this study, the photoluminescence properties of congruent codoped $LiNbO_3:Cr^{3+}$; W^{4+}, crystals have been systematically investigated by performing photoluminescence studies at room temperature in the 0−280 kbar pressure range. In particular, we focus on the influence that hydrostatic pressure has on the $^2E \rightarrow {}^4A_2$ (R-lines) transitions of Cr^{3+}. It has been observed that the pressure dependence of the spectral position of the R-lines associated with both Cr^{3+} centres β and γ shows a bilinear behaviour with an abrupt slope change near 210 kbar. This change is related to the existence of a pressure-induced structural phase transition in the $LiNbO_3$ host. The analysis of experimental results provides the Racah parameters *B* and *C* and the crystal field parameter 10*Dq* and their pressure and volume, through the crystal field theory and equation of state, dependences.

1. Introduction

Since the synthesis and growth of lithium niobate crystals ($LiNbO_3$, LN), a great interest arose due to their important technological applications as infrared tunable laser, frequency doubler, surface acoustic waves (SAW) devices, as well as in nonlinear optics, being an archetypical photorefractive material [1–4].

The LN crystals are grown using the Czochralski method, showing the so-called congruents (ratio [Li]/[Nb] = 0.945) a greater ease of growth. However, they present a high concentration of structural defects, for example: lithium vacancies, antisites, *i. e.* Nb^{5+} ions at lithium sites in different crystalline environments. It has been shown that the antisite concentration is 3.7% and vacancies, which can be decreased up to the point of almost getting 'stoichiometric-like' crystal through doping with metallic ions of valence 2+, 3+ and 4+ [2,5,6]. In particular, Cr^{3+} ions are incorporated in congruent LN crystals, either in distorted octahedra or antisites (γ centres), in distorted octahedra (α and β centres) or replacing Nb^{5+} (δ centre) in nearly stoichiometric crystals [7–9]. The congruent doped $LiNbO_3:Cr^{3+}$ have been intensively investigated for decades aiming to identify these centers by different experimental techniques such as electron paramagnetic resonance (EPR), electron-nuclear double resonance (ENDOR) and optical absorption/emission spectroscopies [7,10–13]. In particular, several octahedral Cr^{3+} centres having slightly different crystal surroundings have been identified, each centre exhibiting a different photoluminescent (PL) response depending on its crystal-field strength [14]. Emission spectroscopy reveals the crystal-field strength through the width and position of the PL band. A broad band emission occurs in weak field, and corresponds to the transition $^4T_2 \rightarrow {}^4A_2$, whereas in strong field a narrow PL peak appears due to the $^2E \rightarrow {}^4A_2$ transition, $^4A_2$ being the ground state. The application of hydrostatic pressure increases the crystal field strength at Cr^{3+} by shortening of the ion-ligand distance thus enabling an excited state spin crossover $^2E \leftrightarrow {}^4T_2$ on passing from a weak field to a strong field. This crossover modifies PL from a broad band to a narrow peak emission allowing a direct identification of Cr^{3+} centres in LN. Due to this, high pressure within optical spectroscopy constitutes a powerful tool to investigate Cr^{3+} optical centres formed in low symmetry crystals with multisite like LN.

---

* Corresponding author.
E-mail address: marco@fisica.unam.mx (M.A. Sánchez-Alejo).

http://dx.doi.org/10.1016/j.optmat.2016.07.013

Interestingly, solid-state reactivity yielding multisite formation in LN can be studied by codoping with different valence state ions such as Mg^{2+} [15] or, as in the present case, W^{4+}, and Cr^{3+}. The formers influencing the LN multisite structure and the latter being a useful probe to unveil which multisite-related Cr^{3+} centres are formed. In this work we focus on the effect of coping LN with W^{4+} and Cr^{3+} through the formation of Cr^{3+} centres. The results will be compared with those previously obtained in LN doped with Mg^{2+} and Cr^{3+} [15] aiming to unveil the role played by W^{4+} upon Mg^{2+} replacement. On the other hand, it must be noted that, according to Shannon ionic radii [16], W^{4+} and Cr^{3+} are similar, 0.65 Å and 0.62 Å, respectively; making it suitable for these ions to get into the Li^{+} site (ionic radius, 0.74 Å) of LN, from the melt, during the crystal growth.

This work investigates the room-temperature PL and its dependence with hydrostatic pressure on a codoped $LiNbO_3$:Cr^{3+} (0.05%); W^{4+} (0.5%) crystal. In this study, pressure was applied in the 0–280 kbar range. The idea is twofold: 1) codoping with W^{4+} modifies the Cr^{3+} centre formation with respect to Mg^{2+} codoping, thus favouring Cr^{3+} centre formation which can be minority, or even not formed, in congruent LN, or LN doped with Mg^{2+} and Cr^{3+}; 2) high hydrostatic pressure induces excited state crossover in most Cr^{3+} ions making easy the identification of new Cr^{3+} centres through their narrow $^2E \rightarrow {}^4A_2$ emissions, and/or to study their pressure behaviour.

A relevant feature is to explore the PL behaviour of the surviving Cr^{3+} PL centres above the first-order structural phase transition of the host crystal LN, which is known to occur at about 210 kbar [17,18]. We are also interested in correlating the spectroscopic data with structural parameters by means of Crystal Field Theory and the Murnaghan equation of state. We aim to explore the crystal volume and interatomic Cr–O dependences of the crystal field 10*Dq* and Racah *B* and *C* parameters obtained as a function of pressure.

2. Materials and experimental methods

Single crystals of $LiNbO_3$ doped with Cr^{3+}; W^{4+} were grown by Czochralski method in the Crystal Growth Laboratory at the Institute of Physics in UNAM. The crystal was prepared using 99.99% Sigma-Aldrich Lithium Niobate; in the melt, doped with WO_2 (0.5 mol %) and CrO_2 (0.05 mol %). A Cary 6000i spectrophotometer was used to obtain the absorption spectra. Absorption spectra as a function of temperature were done in a spectrophotometer Cary 6000i and a helium closed cycle cryostat Advance Research Systems (ARS), model DE-204 AE, with a temperature controller Lake Shore, model CS202 AI-DMX-4, allowing temperature variations in the 7–300 K with stability of ±0.01 K. Several single crystal plates from the as-grown rod were cut and polished with 1 μm alumina powder for optical absorption studies. Experiments were done on a plate of 2.030 ± 0.010 mm thickness. High-pressure experiments were performed at the University of Cantabria, Spain, using a Diamond Anvil Cell (DAC) – Böehler-Almax – with 300 μm culet diamond anvils. A 200 μm hole was drilled in a 40 μm thickness preindented gasket, and silicon oil was used as pressure transmitter. The sample was polished to 80 μm width and the pressure was calibrated using the R line shift of a 20-μm ruby balls. PL measurements at high pressure were performed in the 0–260 kbar range using a Triax 330 spectrometer equipped with a fast ICCD. The optical signal was collected with a Newfocus 9092-M and guided with optical fibre coupling to the spectrometer entrance slit. Optical absorption measurements under high-pressure conditions were done in a specially designed micro-spectrophotometer for working with DAC [19]. All pressure measurements were done at room temperature.

3. Theoretical considerations

First, making the most of some theoretical relationships of the crystal field and the Murnaghan equation of state, it is possible to correlate the exponent *n* of the power law relating the crystal field with the interatomic distance, *i.e.* the ion-ligand distance, the value of which is important for the knowledge of the singularities of Cr^{3+} in LN. Second, using the Tanabe-Sugano diagrams [20], the crystal field parameter 10*Dq* derived from the first $^4A_2 \rightarrow {}^4T_2$ band of the absorption spectrum, and the Racah parameters, *B* and *C*, from the $^2E \rightarrow {}^4A_2$ emission, we can obtain the pressure dependence of these parameters from the high pressure measurements and thus their volume dependence with the LN Equation of State.

It should be noticed that there is no detailed knowledge about the parameters involved in the description of the different LN centers, except for their symmetry and on the other hand the Tanabe-Sugano crystal field approximation describes very well the Cr^{3+} optical spectra by which the octahedral crystal site approximation would be followed in this work.

Within the Crystal Field Theory, 10*Dq* is related to the ion-ligand distance *R* as $10Dq \sim R^{-n}$. With the modification of the ion-ligand distance *R*, the crystal field strength is given by: $Dq/Dq_0 = (R_0/R)^{n}$. For small variations of *R* this equation can be written as:

$$\frac{\Delta Dq}{\Delta R} = -n\frac{Dq_0}{R_0} \tag{1}$$

On the other hand, the equation relating the increase 10*Dq* with pressure is given by Ref. [21]:

$$\frac{dDq}{dP} = -nDq\frac{1}{R}\frac{dR}{dP} = Dq\frac{nk}{3K_0} \tag{2}$$

Where K_0 is the bulk modulus at ambient pressure and $nk \sim 3$–5 is an effective parameter scaling the pressure variation of *R* to the lattice interatomic distance, *i.e.* the volume cubic root, $L = V^{1/3}$. Parameter *k* is less than, equal to or greater than the unit, when the pressure on the ion site is respectively less than, equal to or greater than the pressure on the bulk, *i.e.* the local bulk modulus of the CrO_6 octahedron is K_0/k.

The Murnaghan equation of state is [22,23]:

$$L = L_0\left(1 + P\frac{K'}{K_0}\right)^{-1/3K'} \tag{3}$$

where L_0 and *L* are the LN lattice interatomic distances at ambient, and *P* pressure, respectively, $K_0 = 1340 \pm 30$ kbar is the bulk modulus for LN, and $K' = 2.9 \pm 0.5$ its pressure derivative [17].

The local equation of state relates the ion-ligand (Cr-O) distance R_0 at ambient pressure P_0, and the ion-ligand distance *R* at a pressure *P*, which is modified as the shift per ion-ligand distance unit:

$$\frac{\Delta R}{R_0} = \left(1 - \left(1 + P\frac{kK'}{K_0}\right)^{-1/3K'}\right) \tag{4}$$

where $\Delta R = R_0 - R$.

Furthermore, in addition to *Dq*, the Racah parameters *B* and *C* are required when describing the interelectronic interaction. All these parameters are determined from the absorption spectrum taking into account the following relations [24,25]:

$$E(^4T_2) = 10Dq \tag{5.1}$$