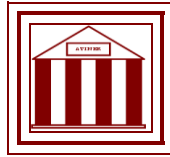


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## **Optical Properties of LiNbO<sub>3</sub>:Ru in the Near IR Spectral Region**

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### **Abstract**

The absorption spectra of LiNbO<sub>3</sub>:Ru single crystals are measured in the visible spectral region at room temperature. The absorption maximum around 3480 nm has complicated structure. The investigated samples are grown with four different concentrations of ruthenium. The energies of the electron transitions in Nb<sup>2+</sup> are calculated. The role of the spin-orbit interaction and Jahn-Teller effect is evaluated also.

**Keywords:** doped lithium niobate, absorption spectra, oxygen tetrahedra.

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## Introduction

Lithium niobate ( $\text{LiNbO}_3$ ) single crystal because of its good electro-optic, acousto-optic, and nonlinear properties has been widely used. The Czochralski (CZ) method is the most common technique for growing bulk lithium niobate single crystal from a congruent melt composition ( $[\text{Li}]/[\text{Nb}] = 48.6/51.4 \sim 0.945$ ) [1]. However, many intrinsic defects can appear in congruent  $\text{LiNbO}_3$  crystal due to the insufficient amounts of Li. The presence of these defects leads to some restrictions for several of the desired applications. The Ru ion doping of non-linear crystals, such as Ru:  $\text{BaTiO}_3$  [2], Ru:  $\text{Bi}_{12}\text{TiO}_{20}$  [3], Ru:  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  [4], Ru:  $\text{Bi}_{12}\text{SiO}_{20}$  [5], and Ru:  $\text{LiNbO}_3$  [6] has recently been investigated, and indeed Ru ions can be helpful to improve the photorefractive properties. Furthermore, although  $\text{LiNbO}_3$  is a good holographic recording material, it has a serious volatility problem when used for holographic data storage: the read-out process usually erases the stored information and amplifies the scattered light. Only a few of researchers have studied the optical properties of Ru:  $\text{LiNbO}_3$ . This is the basic reason for our investigations.

## Materials and Methods

We investigated doped  $\text{LiNbO}_3$  crystals with different concentration of Ru. All the crystals were grown using the Czochralski method to grow c-axis (the (001) orientation). During many years the best parameters for this growth procedure (temperature and its gradients, speed of the rotation, and pulling, etc.) have been clarified in detail. Such technique now allows obtaining conventional congruent crystals with a rather low concentration of macroscopic defects (bubbles, blocks, twins, mosaic structure, or disorientation of domain walls). The starting materials  $\text{Li}_2\text{CO}_3$  and  $\text{Nb}_2\text{O}_5$  are used with a high purity of 99.99% and 99.995%. The different amounts of  $\text{RuO}_2$  (99.95%) powders were added into the melt. The concentration of ruthenium in  $\text{LiNbO}_3$  is as follows: 0.03, 0.08, 0.12 and 0.2 mol%. According to the reference [5], Ru ions have three valences  $\text{Ru}^{3+}$ ,  $\text{Ru}^{4+}$ , and  $\text{Ru}^{5+}$ . The ruthenium ions are situated in the places of  $\text{Li}^+$  or  $\text{Nb}^{5+}$  ions in the distorted oxygen octahedrons [7]. The shearing cut of the samples is (100). The experimental set up for measurement of the absorption coefficient in the visible and near IR region consists of the following: a halogen lamp with a stabilized 3H-7 rectifier, a SPM-2 monochromator, a system of quartz lenses, a polarizer, a crystal sample holder, and a Hamamatsu S2281-01 detector.

## Results and Discussion

The absorption coefficient is calculated using the formula:  $\alpha = (1/d)\ln(I_0/I)$ , where  $I_0$  is the intensity of the incident light,  $I$  is the intensity of the passing light and  $d$  is the sample thickness (Figure 1). The first derivative

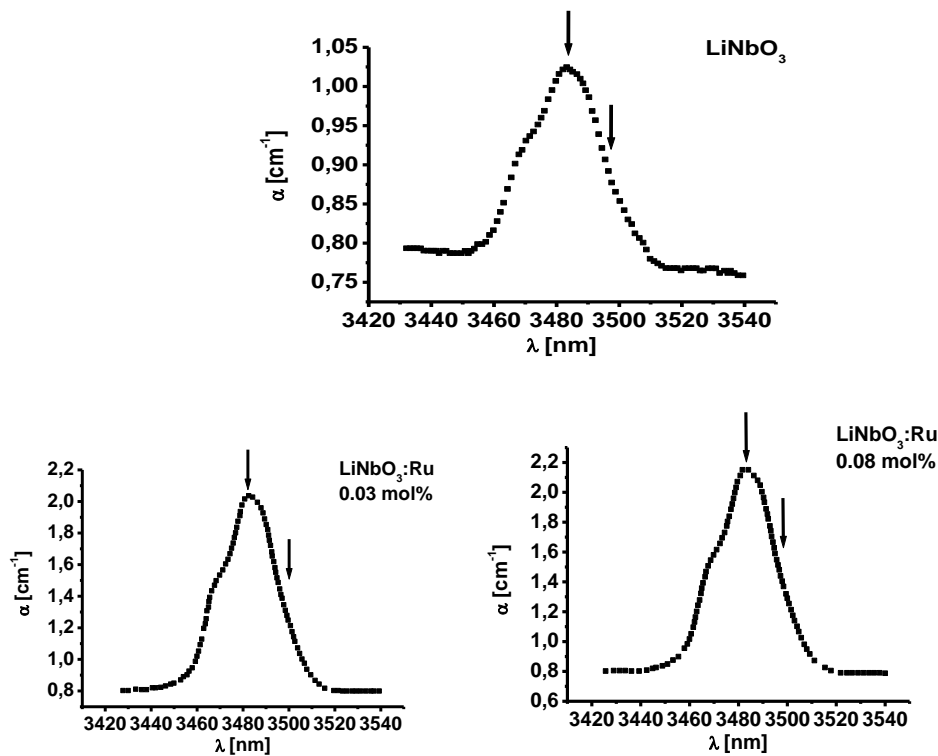
of the absorption coefficient at photon energy is calculated to be in the spectral region 3420 - 3540 nm (Figure 2). The  $[d\alpha/d(h\nu)]$  determines only the number of electron transitions in a  $\text{Nb}^{2+}$  ion and it does not give an exact information about the energy position of these transitions. This is the reason for the calculation of the second derivative of the absorption coefficient  $[d^2\alpha/d(h\nu)^2]$  (Figure 3). The components of the  $\text{Nb}^{2+}$  structure that are connected with the electron transitions are  ${}^4\text{A}_2({}^4\text{T}_1({}^4\text{F})) \rightarrow {}^2\text{E}({}^2\text{G})$  ( $3482 \text{ cm}^{-1}$ ),  ${}^4\text{A}_2({}^4\text{T}_1({}^4\text{F})) \rightarrow {}^4\text{A}_1({}^4\text{T}_2({}^4\text{F}))$  ( $3498 \text{ cm}^{-1}$ ) and  ${}^4\text{A}_2({}^4\text{T}_1({}^4\text{F})) \rightarrow {}^2\text{E}({}^2\text{T}_1({}^2\text{G}))$  ( $3512 \text{ cm}^{-1}$ ) (Figure 4). If the electron transitions are realized between the basic and the closest low energy excited states, then they are connected with the manifestation of the dynamical Jahn-Teller effect (Figure 4). This effect is manifested as the deformation of the niobium tetrahedron and the  $\text{T}_d$  symmetry transforms into the  $\text{C}_{3v}$  symmetry. The ionic radii of oxygen, niobium and ruthenium are different. Thus it can be observed the tetrahedral deformation. The final result is expressed by the great influence of the Jahn-Teller effect on the energy values of the observed impurity absorption bands (Figure 4) and the niobium complex becomes stable under the influence of the spin-orbit interaction.

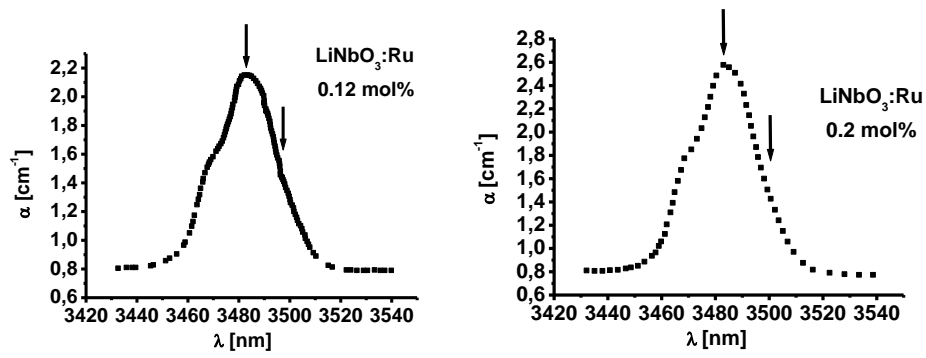
The d-orbital  $e_g$  is split of  $e_{\pm 2}(\delta)$  and the d-orbital  $t_{2g}$  is split of the two orbitals  $e_{\pm 1}(\pi)$  and  $a_1(\sigma)$ , when the symmetry changes from  $\text{T}_d$  to  $\text{C}_{3v}$  [8]. The Jahn-Teller effect leads to the transformation of symmetry. The radial parameters  $D_s$  and  $D_t$  are conditioned by the potential  $V_{\text{tet}}$ . [9]. In the case of  $\text{C}_{3v}$  symmetry the distance between  $e_{+2}(\delta)$  and  $e_{-1}(\pi)$  is  $\Delta_1 = 3D_s - 5D_t = 16 \text{ cm}^{-1}$ . This is the distance between the first and the second electronic transition in the  $\text{Nb}^{2+}$  ion (Figure 4). The distance between  $e_{+1}(\pi)$  and  $a_1(\sigma)$  is  $\Delta_2 = D_s + 10D_t = 14 \text{ cm}^{-1}$ . This is the distance between the second and the third 3d-electronic transition in the chromium (Figure 4). The values of these two parameters are calculated by our experiment. Thus the values of the parameters  $D_t$  and  $D_s$  are as follow 0.74 and 6.6. Racah defines the parameter  $B$  which includes the difference between the levels by the maximum multiplicity. The second parameter  $C$  stands for the energy difference between the different multiplicity terms. The value of  $B$  is  $825 \text{ cm}^{-1}$  [10]. The value of the parameter  $C$  is  $3820 \text{ cm}^{-1}$ . The value of the crystal field parameter  $D_q$  is  $350 \text{ cm}^{-1}$ . The literature [11] informs us of the Nephelauxetic parameter  $\beta = B(\text{complex})/B(\text{free ion})$ . If the value of  $\beta$  is in the interval 0.54-0.81, it manifests the metal ligand  $\sigma$  bond. The calculation of this parameter for  $\text{LiNbO}_3$  ( $\beta = 0.85$ ) shows that the metal ligand  $\pi$  bond is done. The spin-orbit interaction splits the state  ${}^4\text{T}_1({}^4\text{F})$  of one sextet ( $J = 5/2$ ), one quartet ( $J = 3/2$ ) and one doublet ( $J = 1/2$ ).

The symmetry of the complex  $[\text{NbO}_4]^{6-}$  is such that  $e_g$  and  $t_{2g}$  orbitals of the metal correspond only on  $\sigma$  – anti-connecting and only on  $\pi$  – anti-connecting orbitals [12]. The parameters  $\delta\sigma$  and  $\delta\pi$  are determined as follows:  $\delta\sigma = \sigma_z - \sigma_{xy} = -(12/8)D_s - (15/8)D_t$ ,  $\delta\pi = \pi_z - \pi_{xy} = -(3/2)D_s + (5/2)D_t$ . The parameters  $\sigma$  and  $\pi$  are indirect indicator for the  $\sigma$  – anti-connecting and  $\pi$  – anti-connecting properties of the ligands. Finally,  $\delta\sigma = -11.29 \text{ cm}^{-1}$  and  $\delta\pi = -8.05 \text{ cm}^{-1}$ . In this work, we have considered the Condon-Shortley parameters  $F_2$  и  $F_4$  for  $\text{LiNbO}_3$  [13]. These parameters are symbols which characterize the integrals of the electrons repulsion in the impurity ion. Each of the terms

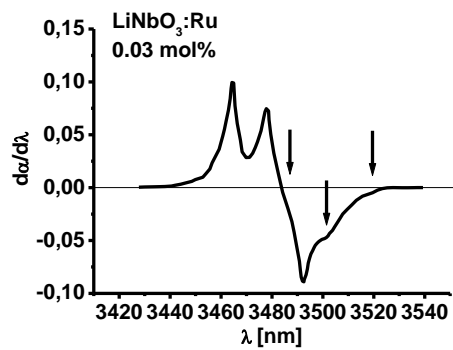
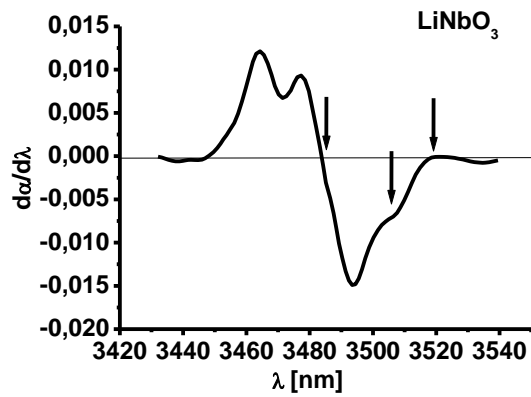
expressions which determines the energy dependence of these parameters, doesn't depend on the metals ion. The magnitude of the Condon-Shortley parameters changes according to the type of the impurity ion. Racah determines additionally the empirical Condon-Shortley parameters and they have the following values  $F_4 = C/35 = 109 \text{ cm}^{-1}$  and  $F_2 = B + 5F_4 = 1370 \text{ cm}^{-1}$  in our case. The next equations are fulfilled for the investigated  $\text{LiNbO}_3$ :  $F^2 = 49F_2 = 67\,130 \text{ cm}^{-1}$  and  $F^4 = 441F_4 = 48\,069 \text{ cm}^{-1}$ . It is convenient to introduce the exchange interaction  $J(\text{dd})$  here, describing the intrashell exchange attraction between parallel spins [6]:  $J(\text{dd}) = 1/14(F^2 + F^4)$  and the additional parameter describing the angular part of the multiplet splitting is  $C(\text{dd}) = 1/14(9/7F^2 - 5/7F^4)$ . The  $J$  and  $C$  are especially useful when describing the lowest state of an  $l^n$  multiplet ( $l = 2$  for d-electrons). According to Hund's rule this is always the state with the highest possible spin quantum number. In our case, the values of  $J(\text{dd})$  and  $C(\text{dd})$  are as follows:  $8229 \text{ cm}^{-1}$  and  $3713 \text{ cm}^{-1}$ . The integral of the exchange interaction  $K(z^2, xy) = 4B + C = 7120 \text{ cm}^{-1}$ . This exchange interaction is realized between the orbitals  $d_z^2$  and  $d_{xy}$ . The orbital  $d_{xy}$  has very important role, because when the crystal is illuminated one electron is situated on this orbital. In the opposite when the sample is untreated the  $d_{xy}$  orbital is empty.

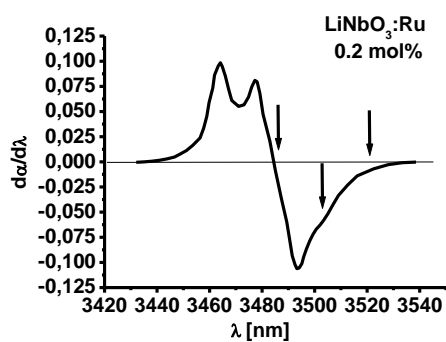
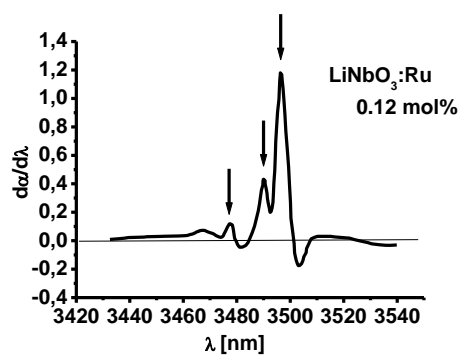
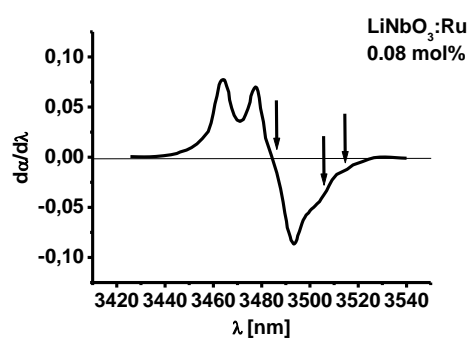
**Figure 1.** Absorption spectrum of undoped and doped  $\text{LiNbO}_3:\text{Ru}$  in the spectral region 3420 – 3540 nm





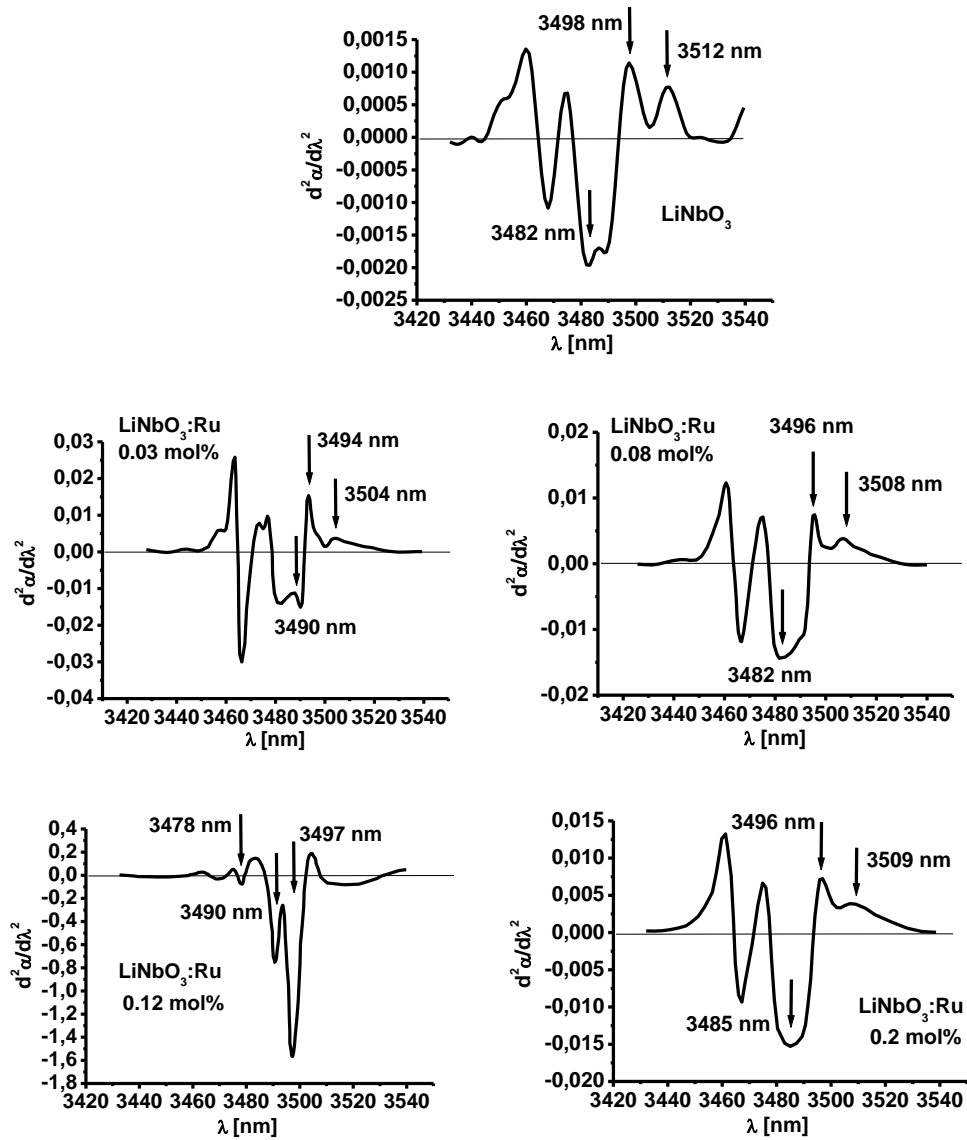
**Figure 2.** Calculated first derivative of absorption coefficient to the wavelength in the spectral region 3420 – 3540 nm

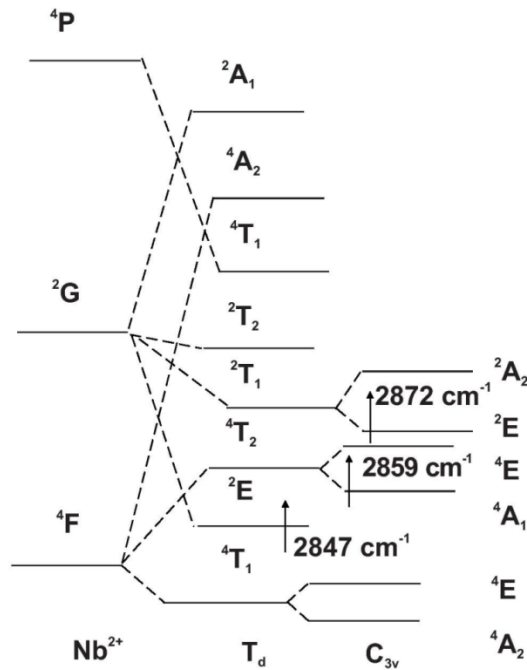






**Figure 3.** Calculated second derivative of absorption coefficient to the wavelength in the spectral region 3420 – 3540 nm



**Figure 4.** Energetic diagram of  $Nb^{2+}$  ion in  $T_d$  symmetry


## Conclusion

The ruthenium shifts the wavelength position of the energy levels of  $Nb^{2+}$  and the absorption coefficient increases with increasing of ruthenium concentration.

The  $Nb^{2+}$  ions have stronger influence in comparison with ruthenium dopant on the optical properties of  $LiNbO_3:Ru$  in the near IR spectral region.

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