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Site-selective spectroscopy of Cr³⁺ in congruent co-doped LiNbO₃:Cr³⁺:ZnO crystals

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Abstract. This work reports the energy levels of chromium ions for different sites in congruent LiNbO₃ crystals doped with ZnO. Optical absorption and luminescence (fluorescence and excitation) experimental techniques were used. For crystals with Zn²⁺ concentration less than 4.7%, optical signals correspond to Cr³⁺ ions substituting for Li⁺ ions; for higher Zn²⁺ concentration, signals show two components coming from different sites for active Cr³⁺ ions. It is accepted that these two components can be assigned to Cr³⁺ ions substituting for Li⁺ ions and Cr³⁺ ions substituting for Nb⁵⁺ ions. The energy levels of the former site are reported for the first time in this work; the ⁴T₂ and ⁴T₁ levels lie 13 421 cm⁻¹ and 19 550 cm⁻¹ above the ⁴A₂ ground level, respectively. Analysis of the excitation spectra was the key result for achieving the resolution of the new site.

1. Introduction

LiNbO₃ is technologically important in view of its applications in electro-optic and integrated optical devices. Rare-earth and transition metal doping of LiNbO₃ has been developed in the search for new potential laser devices. Recently laser action in LiNbO₃:Nd³⁺:ZnO [1] and LiNbO₃:Yb³⁺:MgO has been demonstrated [2]. Crystals for laser applications are generally co-doped with relatively high concentrations of Mg (4.5%) [3] and Zn²⁺ (4.7%) [4] in order to increase the photorefractive threshold. The importance of the chromium-ion doping of LiNbO₃ arises from the combination of the widely tunable laser action of Cr³⁺ and the electro-optic properties of the LiNbO₃ host [5, 6], which can convert to multiple-wavelength emission via non-linear optical mixing.

The optical properties of any doped crystals are largely determined by the local symmetry of the optically active ions. Previous works using electron paramagnetic resonance (EPR) and ENDOR (electron–nuclear double-resonance) techniques at room and low temperature have found two different neighbourhood symmetries for Cr³⁺ ions in LiNbO₃ crystals when co-doping concentration was important [7, 8]. Likewise, by using optical techniques, Diaz-Caro *et al* [9] have shown that congruent LiNbO₃:Cr³⁺:MgO crystals present two Cr³⁺ sites with different crystal symmetries. Two centres for Cr³⁺ ions have been observed in congruent LiNbO₃:Cr³⁺:ZnO and stoichiometric LiNbO₃:Cr³⁺:MgO crystals [10, 11]. In the latter two

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cases the energy levels for Cr^{3+} ions substituting for Nb^{5+} ions could not be assigned due the small oscillator strength for absorption of this centre and the strong superposition of levels with those of the other centre.

In this work we show how the excitation spectra of Cr^{3+} in $\text{LiNbO}_3:\text{ZnO}$ for different co-doping concentrations can be used to find for the first time the energy levels corresponding to Cr^{3+} ions substituting for Nb^{5+} ions.

2. Experimental procedure

The congruent LiNbO_3 crystals used in this work were grown by the Czochralski method in the open atmosphere. Results for two crystals with different ZnO co-doping concentrations are presented. The Cr/Nb and Zn/Nb ratios were determined using the total-reflection x-ray fluorescence (TRXRF) technique, previously calibrated for these ions. The Cr/Nb ratio was constant in the samples: a ratio of 0.1%. The Zn/Nb doping ratio was 4.6% and 5.3% for the two crystals. The crystals are completely different visually: one is green and the other is violet. For the crystal with the high Zn^{2+} concentration, EPR experiments had been performed previously, and nearly 80% of the Cr^{3+} ions were found at perturbed sites, which can be assigned as Nb^{5+} sites. The lower concentration of zinc leads to only one centre position for Cr^{3+} —at Li^+ sites [10].

Optical absorption spectra at room temperature were taken by using a Hitachi U-3501 spectrophotometer. CW luminescence emission was achieved by using a multi-line argon laser as the excitation source. The luminescence excitation spectra were taken using a Ti:sapphire laser as the excitation source, from 728 nm to 900 nm. The spectra were corrected for excitation power variation. The emission was dispersed in a monochromator: ARC Spectra PRO 500-i, and the luminescence was detected with a silicon detector, amplified by an EG&G lock-in and register for each collection wavelength.

3. Results and discussion

Figure 1 shows the room temperature (RT) absorption spectra corresponding to $\text{LiNbO}_3:\text{Cr}^{3+}$ samples doped with 4.6% (a) and 5.3% (b) ZnO in the crystal. The spectra show typical behaviour associated with Cr^{3+} ions in weak crystal fields [12]. Broad bands are associated with the vibronic transitions ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$, respectively. After adjustment using two Gaussian curves, the resulting bands peaked at $15\,252\text{ cm}^{-1}$ (655 nm) and $20\,725\text{ cm}^{-1}$ (482 nm) for the crystal with lower Zn^{2+} concentration, while for that with the higher Zn^{2+} concentration, a well known red-shift of the absorption bands—now situated at $15\,100\text{ cm}^{-1}$ (660 nm) and $19\,600\text{ cm}^{-1}$ (510 nm)—was observed. Also in this figure we present the cw luminescence emission for each crystal used in this work. For the crystal with lower Zn^{2+} concentration the broad luminescence band is centred at $11\,000\text{ cm}^{-1}$ (910 nm), with a FWHM of 2700 cm^{-1} , while for that with the high Zn^{2+} concentration, the emission spectrum is centred at $10\,526\text{ cm}^{-1}$ (950 nm) with a 2300 cm^{-1} FWHM.

Neither the absorption spectra nor the emission bands show conspicuous differences that would allow the characterization of the second centre present in the crystal with the higher concentration of Zn^{2+} . Even if the relative concentration of the two chromium centres is known, the optical absorption coefficients and the fluorescence quantum efficiencies of the two centres are still unknown; for that reason, spectra cannot be resolved by a subtraction weighted only with concentration. Despite the fact that there is visual evidence of the influence of Cr^{3+} at the Nb^{5+} site when the ZnO concentration is above a threshold of 4.7% (the crystal changes from

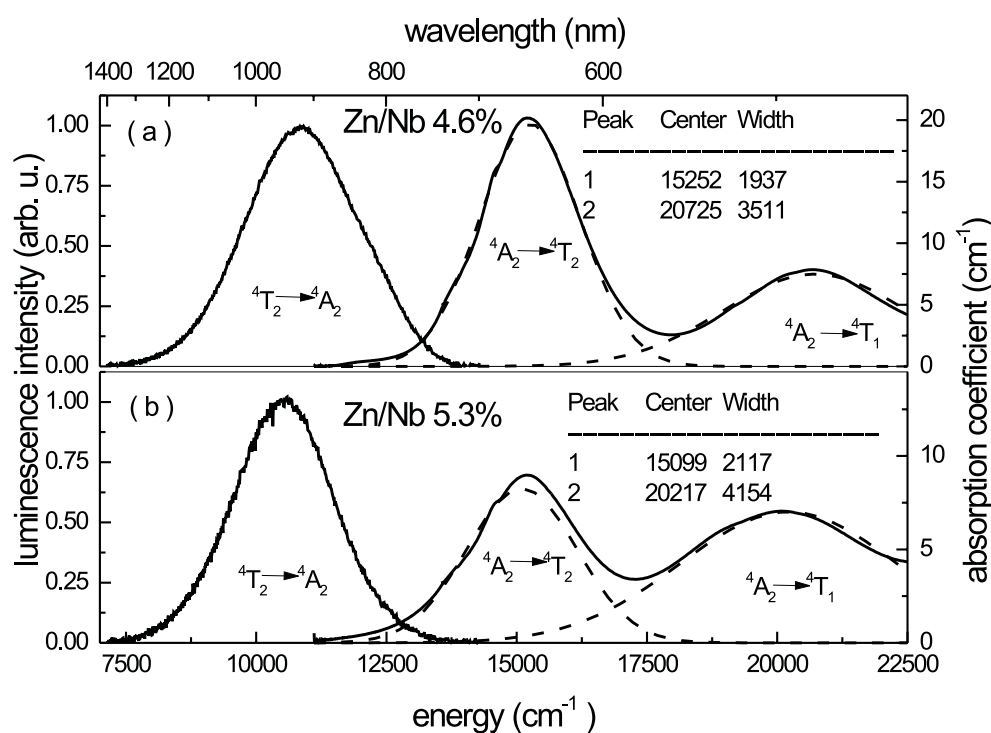


Figure 1. Absorption and emission spectra at RT corresponding to LiNbO₃:Cr³⁺:ZnO crystals with two different Zn²⁺ concentrations: (a) 4.6%; (b) 5.3%.

green to violet), more quantitative data are necessary to completely characterize the energy diagram of Cr³⁺ for both sites.

Figure 2 shows the excitation spectra for the two crystals for which the concentrations of ZnO were 5.3% and 4.6%. The spectra were normalized to unity at 728 nm. Unfortunately, we could only achieve a reduced excitation range because of experimental limitations as regards the power of the Ti:sapphire laser.

In this figure several excitation spectra taken at different fluorescence wavelengths are shown for the 5.3% crystal. For this crystal it can be seen that the long-wavelength tail of the fluorescence band is excited mainly at 13 330 cm⁻¹ (750 nm). Consecutive changes to shorter emission wavelengths result in the spectra corresponding to the lower-concentration crystal with only one centre.

The excitation spectra for the crystal with the lower concentration of Zn²⁺ were similar for all luminescence wavelengths; in the figure only one spectrum, corresponding to a luminescence wavelength of 950 nm, is shown.

After an appropriate normalization using the Ti:sapphire excitation power, the energy levels for Cr³⁺ ions at the pure Nb⁵⁺ sites were found. The levels are centred at 13 200 cm⁻¹ (757 nm). We have assumed that the luminescence contribution from Cr³⁺ ions at Li⁺ sites can be ignored at long wavelengths.

In order to complete the energy diagram of Cr³⁺ ions at Nb⁵⁺ sites and reach the values for the ⁴T₁ levels, we used the method developed by Diaz-Caro *et al* which was used for the congruent compound LiNbO₃:Cr³⁺:MgO [9]. By this method, the absorption spectrum of Cr³⁺ ions at Nb⁵⁺ sites is obtained through subtracting the spectrum corresponding to Cr³⁺ ions at

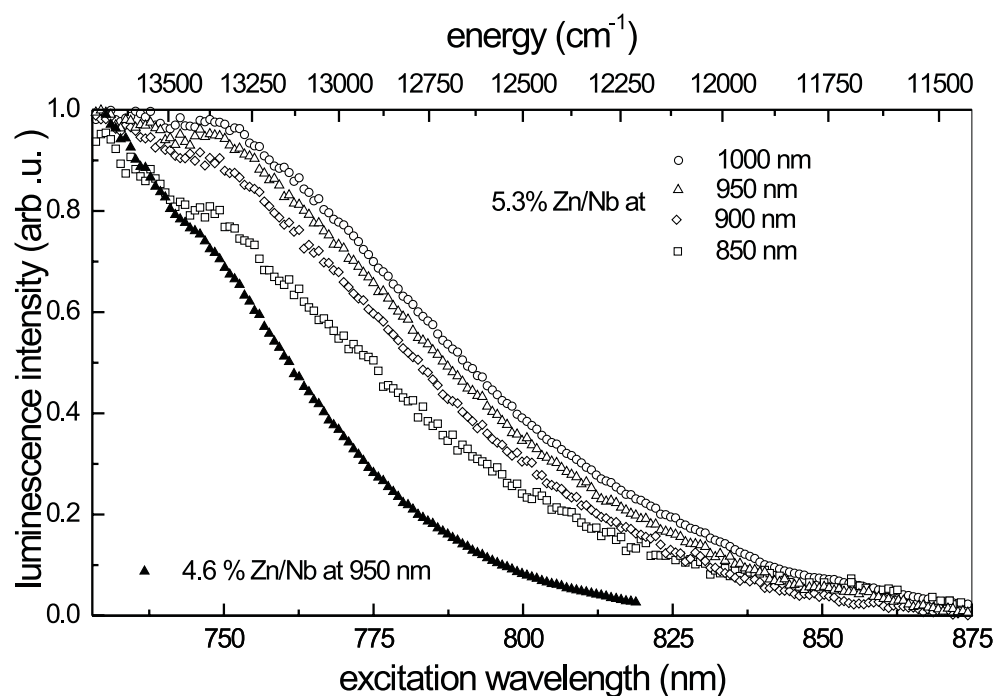


Figure 2. Excitation spectra of $\text{LiNbO}_3:\text{Cr}^{3+}:\text{ZnO}$ crystals for the two Zn^{2+} doping concentrations achieved in this study. Four spectra for different emission wavelengths for the crystal with two Cr^{3+} centres are shown, but only one for the crystal with the lower concentration of Zn^{2+} .

Li^+ sites from the absorption spectrum corresponding to the two-centre crystal. In our case we scale the subtracted spectrum in order to fit the values for the wavelength range accessed by the excitation spectra.

Figure 3 shows the calculated absorption spectrum (solid line) corresponding to Cr^{3+} ions at Nb^{5+} sites for the range from $11\,000\text{ cm}^{-1}$ (910 nm) to $22\,500\text{ cm}^{-1}$ (440 nm) obtained by using the method mentioned above. By means of a Gaussian fit (dashed lines) performed on the calculated absorption spectrum, new positions of the bands centred at $19\,550\text{ cm}^{-1}$ (511 nm) and $13\,421\text{ cm}^{-1}$ (745 nm) were found. The same figure shows the experimental results from excitation spectra experiments (open circles). The inset in figure 3 shows the calculated energy diagram for the chromium at the two different sites available in the co-doped $\text{LiNbO}_3:\text{Cr}^{3+}:\text{ZnO}$ crystals.

4. Conclusions

This work presents for first time the energy diagram corresponding to both sites accessed by chromium ions in congruent $\text{LiNbO}_3:\text{Cr}^{3+}:\text{ZnO}$ crystals. Optical absorption and luminescence (fluorescence and excitation) results were used to get the energy values corresponding to Cr^{3+} ions substituting for Nb^{5+} ions. Excitation spectroscopy was of great value as regards getting the energy levels corresponding to this centre. Energy levels were found after subtracting the appropriate scaled absorption spectra of the two crystals in such a way that the calculated absorption spectrum for $\text{Cr}^{3+}_{(\text{Nb}^{5+})}$ fits the tail reached by the excitation spectra. By this method, the ${}^4\text{T}_2$ levels associated with $\text{Cr}^{3+}_{(\text{Nb}^{5+})}$ were found, peaked at $13\,200\text{ cm}^{-1}$ (757 nm), and the

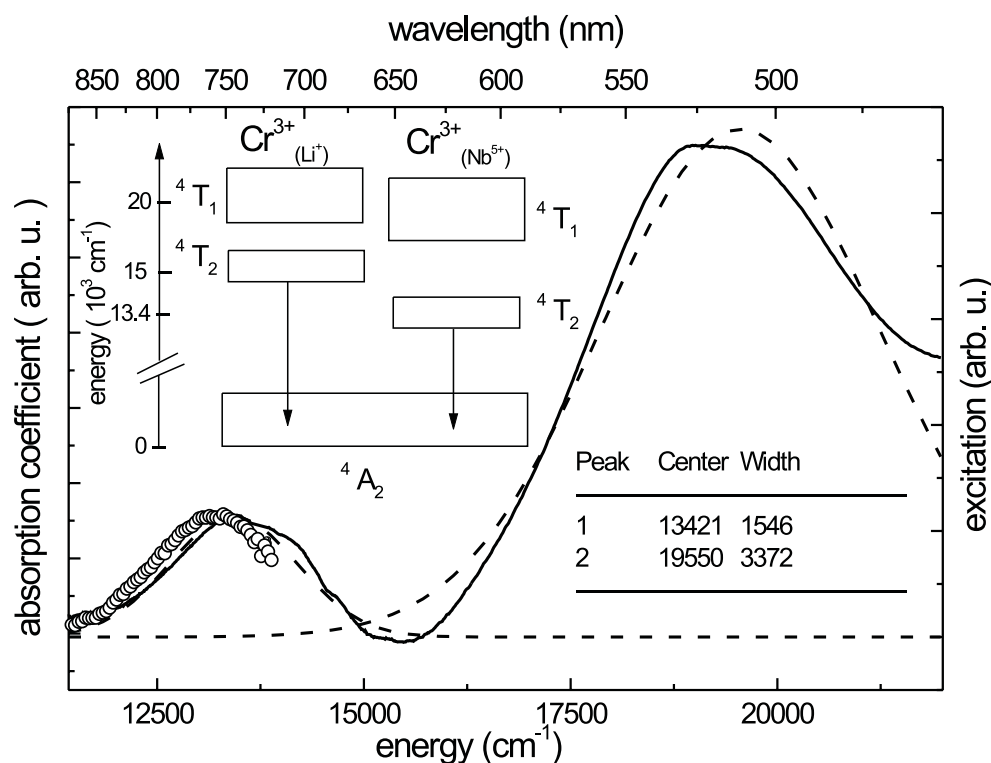


Figure 3. Calculated absorption spectra for Cr³⁺ ions at Nb⁵⁺ sites (solid line) and the adjusted Gaussian fit (dashed lines). Experimental excitation spectra normalized for the laser power (circles) are also shown. The inset shows the energy levels corresponding to the two different centres occupied by Cr³⁺ ions in doped LiNbO₃:Cr³⁺:ZnO crystals for high concentrations of Zn²⁺.

high-energy level (⁴T₁) for Cr³⁺ ions at Nb⁵⁺ sites was found, centred at 19 550 cm⁻¹ (511 nm). Differences between the positions of the ⁴T₂ levels determined by excitation and from the corrected absorption spectrum can be attributed to the assumption that the luminescence contribution from Cr³⁺ ions at Li⁺ sites can be ignored at long emission wavelengths as compared with the more important contribution of Cr³⁺ ions at Nb⁵⁺ sites.

The results of this work are in good agreement with those from the work performed on congruent LiNbO₃:Cr³⁺:MgO crystals [9]. For such material, centres of Cr³⁺ ions at Nb⁵⁺ sites are shifted to lower energies relative to centres at Li⁺ sites. The energy shifts are similar to those obtained in the present work.

The cubic-field splitting parameters Dq/B were calculated for both centres: the values obtained were 2.9 and 2.1 for Cr³⁺ ions at Li⁺ sites and Cr³⁺ ions at Nb⁵⁺ sites, respectively. This can be attributed to the smaller distance between Cr³⁺ and oxygen ligands for Li⁺ sites than for Nb⁵⁺ sites. Similar results have been found for Cr³⁺ doped into other oxides [13] and fluorides [14, 15].

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