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Photoionization energies of Cr^{3+}-doped $LiNbO_3$

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Abstract

We report on a study of intra-ion and electron transfer transitions in Cr^{3+}-doped $LiNbO_3$. The energies of the meta-stable emitting levels of Cr^{3+} on both Li and the Nb sites are determined by standard optical spectroscopy techniques. Photoconductive measurements are used to determine the ionization energies of both species of Cr^{3+} ions. From these results, energy level diagrams are created which give the energies of the optically active levels with respect to the host valence and conduction bands. The emitting $^4T_2$ level of Cr^{3+} on a Li site and on a Nb site is found to lie 1.5 and 1.2 eV below the conduction band bottom, respectively. These results lead to the suggestion that the lack of laser action found in $LiNbO_3$:Cr^{3+} may be due to strong excited state absorption transitions from the meta-stable $^4T_2$ level to the host conduction band.

Keywords: Ferroelectrics; Spectroscopy; Chromium

Continuously tunable solid-state lasers over large wavelength ranges, such as the Ti:Sapphire laser, are of great importance in the optical community. They are used in a variety of fields from fundamental research to industrial applications due to their ease of use, high light yields, durability, and long-term stability. Cr^{3+}-doped $LiNbO_3$ has been proposed as a tunable laser system owing to its broad luminescence in the near infrared, high quantum efficiencies and its inherent nonlinear properties, with the corresponding potential for self-frequency doubling of the near-infrared luminescence to visible luminescence [1–5]. The emission in the near infrared spectral region alone makes this material potentially competitive with the well-established Ti:Sapphire laser. An added incentive originates from reports which demonstrate self-frequency doubling $LiNbO_3$ crystals doped with rare earths [3]. Since the laser material is nonlinear there is no need for extra doubling optics. However, no efficient lasing, so far, has been demonstrated from this system despite the numerous lasers based on Cr^{3+} luminescence in other host. In this paper we consider the possibility of an excited state absorption (ESA) that leads to transition from the meta-stable emitting level of the Cr^{3+} on both Li and Nb sites to the host conduction band as being detrimental to efficient lasing.

For our study two crystals were grown by the Chrochalski technique from congruent melts. The first sample was doped with 0.25% Cr and has green color. The second sample was co-doped with 6% Mg and exhibits a deep red color. The sample dimensions are $4 \times 6 \times 1$ mm with the *c*-axis parallel to the short side. Cooling of the samples was achieved by an Oxford flow through cryostat for absorption and luminescence measurements and a Kel-Tran cold finger cryostat for photoconductivity measurements.

A Bruker FTIR spectrometer with a Ge detector was used to measure the broad $^4T_2$ emission while exciting the sample with an argon laser. The photoexcitation spectra were measured using a modified Cary-14 spectrophotometer with a tungsten excitation source while monitoring the broad-band emission using a liquid nitrogen cooled InGaAs detector with a 900 nm low-pass filter. A Xe lamp coupled through a McPherson double monochromator was used for the photoconductivity measurements. The sample was pressed between two nickel meshes with up to 10 kV/cm applied along the *c*-axis. All conductivity measurements were performed under vacuum to stabilize the crystal and

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prevent electrical breakdown. The photocurrent was recorded using a Keithley electrometer with 1 fA resolution and a built in high voltage supply. For the photoconductivity measurements two sets of opposite polarity electrodes were used while only one pair of electrodes was illuminated. Any currents generated by thermal effects are cancelled by these compensating electrodes. Without these special considerations the spectrum of the photocurrent could be dominated by the pyroelectric effect and in general would simply follow the absorption spectrum of the crystal.

It has been well established that Cr^{3+} is located on a Li site, Cr^{3+}_{Li}, in $LiNbO_3$:Cr [6–8]. The introduction of Mg, which was first done for practical reasons, led to the discovery that Cr^{3+} will also replace both Li and Nb, Cr^{3+}_{Nb}, when Mg concentrations are greater than Nb 4.5% [9–11]. In this report we investigate both types of crystals.

The absorption and luminescence spectra for Cr^{3+} in the singly doped and co-doped crystals are presented in Figs. 1(a) and (b), respectively. The dashed data plot the $^4T_2 \rightarrow {}^4A_2$ broad band luminescence. The decay rate of this luminescence is similar for (a) and (b), yielding a lifetime of the $^4T_2$ level around 9 μs. The full-width at half-maxiumum luminescence in both (a) and (b) is 0.25 eV with a peak at 1.4 and 1.3 eV, respectively.

The zero-phonon transition of the $^4T_2 \rightarrow {}^4A_2$ transition was first assigned by our group at an energy of 13540 cm^{-1}, or 1.7 eV. The $^4T_2$ level is lower in energy than the ^2E levels, or R lines, at 13810 and 13772 cm^{-1}, and gives rise to the fast, broad band luminescence [8]. Cr^{3+}_{Nb} is also located on a low-field site where the $^4T_2$ level has been observed by our group at 12408 cm^{-1}, 1.5 eV, and the R lines are estimated to be around 13350 cm^{-1} [12,13].

The absorption spectrum displayed in Fig. 1(a) resembles the typical Cr^{3+} absorption such as those found in ruby [14]. The intra-ion transitions are easily assigned with the strong spin-allowed $^4A_2 \rightarrow {}^4T_2$ transition dominating the spectrum [15]. At higher energies, approximately 3.2 eV, the onset of strong absorption is observed. This onset is discussed later and assigned to the photoionization (PI) of Cr^{3+}_{Li}.

In Fig. 1(b) the absorption spectrum is broader, making straight forward assignments difficult. However, it is evident that the two lowest well separated energy bands consist of $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1$ transitions for both Cr^{3+}_{Li} and Cr^{3+}_{Nb}, since both species are incorporated in this crystal. Similar to Fig. 1(a) a strong absorption edge is observed in Fig. 1(b) but lower in energy, approximately 2.7 eV. This will later be assigned to the PI energy of Cr^{3+}_{Nb}. Excitation into any of these absorption bands leads to the near-infrared luminescence plotted in Figs. 1(a) and (b) for all temperatures between 4 and 300 K.

Considering the spectroscopic results, it is not difficult to realize the attractiveness of producing laser action from Cr^{3+} in $LiNbO_3$. The NIR luminescence spans the wavelength range from 700 to 1000 nm. In the self-frequency doubling mode this laser would be continuously tunable from 350 to 500 nm. No such solid-state laser has yet been realized, and all attempts to produce laser action with these materials have produced weak results, if any.

As mentioned in the introduction, ESA leading to PI might be the reason for the poor laser performance of Cr^{3+}-doped $LiNbO_3$. To investigate this possibility, we performed photoconductivity measurements in order to determine the location of the Cr^{3+} ground state relative to the host conduction band.

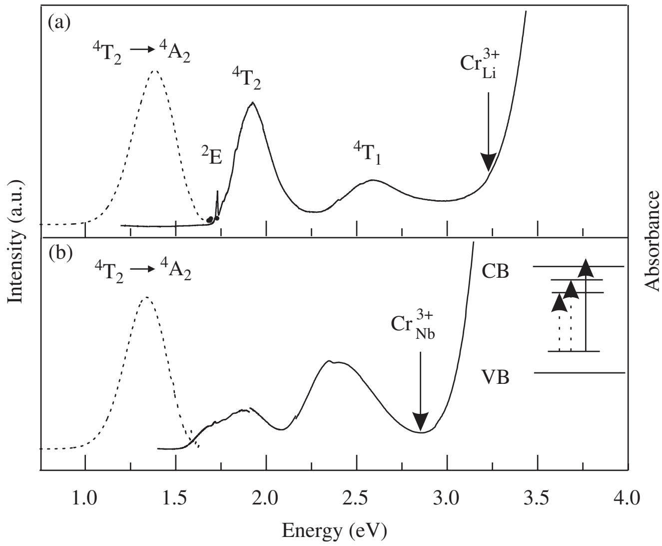

Fig. 1. 4 K absorption (solid) and luminescence (dotted) spectra of $LiNbO_3$:Cr^{3+} and $LiNbO_3$:Cr^{3+}, Mg are plotted in (a) and (b), respectively. Intra-ion transitions are labeled and arrows mark the onset of photoionization of the Cr^{3+} ion at each site. The dotted arrows in the diagram represent intra-ion transitions and the solid arrows represent inter-ion transitions.

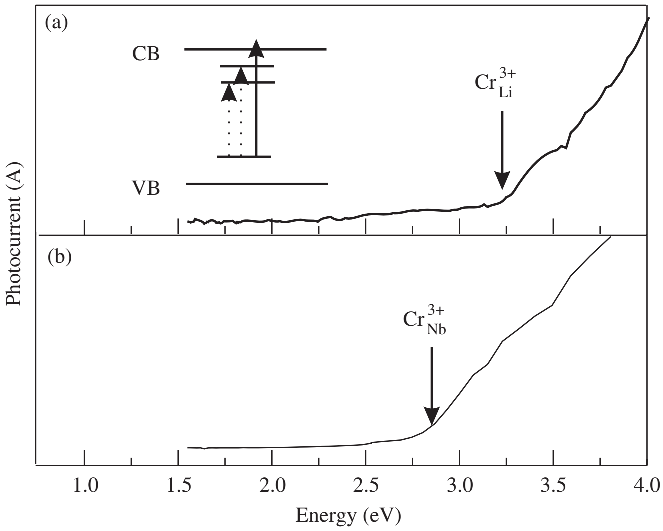

Fig. 2. Photoconductivity spectra at room temperature for $LiNbO_3$:Cr^{3+} and $LiNbO_3$:Cr^{3+}, Mg are plotted in (a) and (b), respectively. The rise of the photocurrent at 3.2 and 2.7 eV for (a) and (b), respectively, are marked with arrows. The dotted arrows in the diagram represent intra-ion transitions which are not present and the solid arrows represent inter-ion transitions.