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LETTER TO THE EDITOR

Determination of the absorption cross section of dopants in lithium niobate crystals

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Abstract

A method is presented to acquire the absorption cross sections of dopants in photorefractive lithium niobate crystals utilizing doubly doped samples. The absorption cross section of one dopant must be well known. By illumination with ultraviolet light, electrons are transferred from one centre to the other. From the changes of the absorption spectra, the absorption cross section of the centre under investigation is deduced. For a wavelength of $\lambda = 577$ nm the absorption cross section of Mn^{3+} is determined by this method to be $\sigma_{\text{Mn}^{3+}, 577 \text{ nm}}^0 = (9.2 \pm 1.3) \times 10^{-19} \text{ cm}^2$ for ordinarily polarized light. The described method can be adapted to other dopants and host materials.

1. Introduction

Doping of lithium niobate crystals can be used to tailor the properties of this important optical material [1]. For example, doping with iron or copper makes the material photorefractive: such dopants can occur in LiNbO_3 in various valence states. Therefore they enable a light-induced build-up of space-charge fields that modulate the refractive index through the electro-optic effect [1].

Dopant ions occurring in two valence states act as electron sources D^- and electron traps D . The oxidation state is defined as the ratio of the concentrations of filled and empty traps. In lithium niobate doped with iron ($\text{LiNbO}_3:\text{Fe}$), the absorption cross section of iron in the valence state 2+ (Fe^{2+}) is well known: for a light wavelength of $\lambda = 477$ nm, the cross section for ordinarily polarized light is $\sigma_{477 \text{ nm}}^0 = 4.63 \times 10^{-18} \text{ cm}^2$. The cross section is found by relating the concentration of Fe^{2+} centres measured with Mößbauer spectroscopy to the absorption spectrum [2]. Absorption cross sections are very useful: once they are known, simple absorption measurements are sufficient to determine ion concentrations that are needed, e.g., to predict the photorefractive performance for one-colour and for two-colour holography [1].

However, the Mößbauer spectroscopy is limited to iron. For other paramagnetic ions electron parametric resonance (EPR) analysis would be possible. Here a reference material

Table 1. The total iron and the total manganese concentrations of the samples used in the experiments.

Sample	c_{Fe} (10^{18} cm^{-3})	c_{Mn} (10^{18} cm^{-3})
LNF _e	30.3	—
LNM _n	—	120
LNF _e M _n	17.6	12.2

is needed to calibrate the detected amplitude of the resonance signals. For diamagnetic dopants even EPR is not applicable.

In this letter an optical method is presented to obtain the absorption cross section of a dopant ion. For this purpose a doubly doped crystal is needed for which the absorption cross section of one dopant ion is already known. The method is demonstrated here for lithium niobate doped with iron and manganese, to determine the absorption cross section of manganese in the valence state 3+ (Mn^{3+}).

2. Experiments

For the investigations three different lithium niobate crystals are used: an iron-doped, a manganese-doped, and a crystal doubly doped with iron and manganese. As is the case for iron, that only occurs as Fe^{2+} and Fe^{3+} in LiNbO_3 [2], manganese also occurs in LiNbO_3 only in two valence states: Mn^{2+} and Mn^{3+} [3]. Some properties of these crystals are listed in table 1. The total concentrations of iron and manganese are known from the crystal growth process and x-ray fluorescence analysis. The absorption coefficients are calculated from light transmission measurements with a Varian Cary 500 spectrometer.

The absorption bands of Fe^{2+} and Mn^{3+} are needed. They are measured with the help of singly doped crystals. For this purpose the samples LNF_e and LNM_n are first oxidized for 8 h in an oxygen atmosphere at 1000 °C to receive high Fe^{3+} and Mn^{3+} ion concentrations respectively. Afterwards they are reduced for 8 h in an argon atmosphere at 1000 °C to increase the Fe^{2+} and Mn^{2+} ion concentrations, respectively. By subtracting the absorption spectra of the samples in the different oxidation states, the Fe^{2+} and the Mn^{3+} absorption is obtained: it is known that Fe^{2+} shows in LiNbO_3 an absorption shoulder with a maximum at a wavelength of about $\lambda = 477 \text{ nm}$ [2]. The Mn^{3+} absorption has a clearly discriminable absorption shoulder with a maximum at about $\lambda = 577 \text{ nm}$ [4]. Also the absorption of the doubly doped crystal LNF_eM_n is measured after moderate heating (200 °C for 30 min). Then this crystal is illuminated at room temperature by unpolarized ultraviolet (UV) light from a Hg lamp. The illumination transfers electrons from the Mn^{2+} centres to the Fe^{3+} centres [5, 6]. After this treatment the absorption is measured again. The thick dashed line in figure 1 shows the absorption changes of the sample LNF_eM_n which are induced by the illumination.

3. Discussion

By the moderate heating of the doubly doped crystal, electrons are redistributed from the shallower Fe^{2+} traps to the deeper Mn^{3+} traps, whereas the electrons are transferred from the Mn^{2+} centres to the Fe^{3+} centres by illumination with UV light [7]. This becomes clear when looking at the simplified band model in figure 2. As a result of the illumination, the concentrations of Fe^{2+} and Mn^{3+} ions increase. The overall absorption changes of the doubly doped crystal can be treated as a linear superposition of the individual absorption changes of the Fe^{2+} and Mn^{3+} centres (see figure 1).

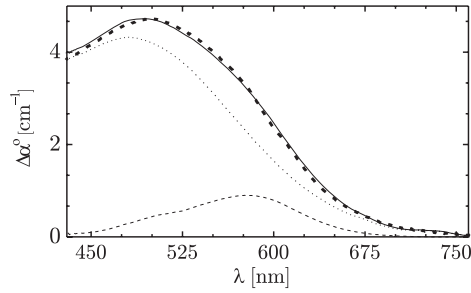


Figure 1. Absorption changes $\Delta\alpha^0$ induced by illumination of the sample LNFemn with UV light versus the wavelength λ . The thick dashed line shows the absorption changes. The thin solid line is a fit of a linear combination of absorption changes resulting from Fe^{2+} (dotted line) and Mn^{3+} (dashed line).

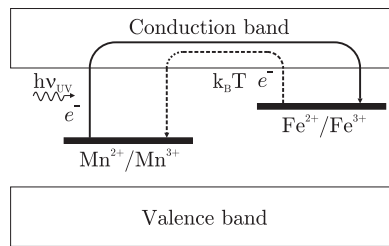


Figure 2. Simplified band structure of a doubly doped lithium niobate crystal. Heating transfers electrons from the shallower Fe^{2+} traps to the deeper Mn^{3+} traps, and the UV illumination has the reverse effect.

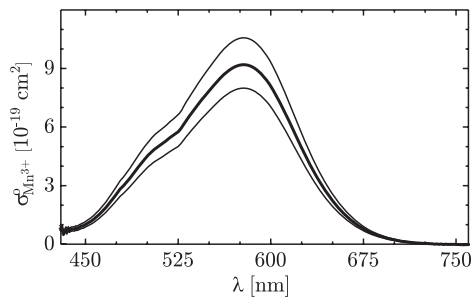


Figure 3. Absorption cross section of Mn^{2+} centres versus the wavelength λ . The thin lines mark the uncertainties of the determined values.

The concentration change which is needed for the best fit in figure 1 is $\Delta c_{\text{Fe}^{2+}} = (9.8 \pm 1.0) \times 10^{17} \text{ cm}^{-3}$. The given error of about 10% is estimated by the significance of the performed fit. The contribution of Mn^{3+} centres to the absorption changes that is obtained from the fit originates from an identical concentration change $\Delta c_{\text{Mn}^{3+}} = \Delta c_{\text{Fe}^{2+}}$ because of charge conservation. This gives us the absorption cross section of the Mn^{3+} centres. In figure 3 its spectral characteristics is presented; the thin lines in the graph mark the uncertainties. For a wavelength of $\lambda = 577 \text{ nm}$ the absorption cross section is $\sigma_{\text{Mn}^{3+}, 577 \text{ nm}}^0 = (9.2 \pm 1.3) \times 10^{-19} \text{ cm}^2$. The uncertainty of the value is again estimated based on the quality of the fit.

Knowledge of the photon absorption cross section of Mn^{3+} is useful in many respects. The main advantage is that simple absorption measurements provide together with the photon absorption cross section the absolute concentration, which is the basis of a deeper understanding of dopant-induced effects in lithium niobate crystals. Furthermore, the method described in this letter is quite general. It can also be applied to other host materials and doping elements. An obvious requirement is that the absorption bands of the two absorbing centres are spectrally separated.

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