

Intrinsic Photorefractive Effect of LiNbO_3

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Abstract. The photorefractive effect of undoped LiNbO_3 crystals of high purity is studied by means of two-photon excitation of picosecond light pulses. We show that two-photon photorefractive recording is accompanied by characteristic changes of the optical absorption and electron spin resonance spectra due to the formation of color centers. The role of these centers for the photorefractive process is discussed.

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The photorefractive effect of pyroelectric crystals doped with transition metal impurities has been investigated in great detail [1]. This effect is generally believed to be based on photoionization of the impurities and subsequent transport of the electrical charges followed by trapping at different lattice sites. However, the details of the mechanisms are still not very clearly understood at the present time. In particular, the nature of the charge transport processes has been the subject of extensive discussions in the last few years. There is some experimental evidence for a new bulk photovoltaic effect [2] which is different from conventional photo-transport in non-pyroelectric materials, and appears to be characteristic of the polar crystal symmetry of pyroelectrics. It has also been suggested [3] that a bulk photovoltaic effect exists which can be attributed to a general intrinsic property of ideal pyroelectric crystals independent of crystal imperfections.

For a study of the intrinsic photorefractive and photovoltaic properties of undoped pyroelectric crystals photoexcitation via multi-photon band-to-band transitions provides an ideal tool. A large, uniform concentration of charge carriers can be generated in the bulk of the material at energies well above the band gap. In fact, photorefractive hologram recording by two-photon processes in high purity pyroelectrics was demonstrated a few years ago [4]. Here we report

results of a detailed study of the two-photon absorption induced photorefractive effect of LiNbO_3 single crystals. In particular we present measurements of the dynamics of the holographic diffraction efficiency, and of the concomitant changes of the optical absorption and electron spin resonance spectra.

In our experiments we used crystals grown from a congruent melt having a total transition metal concentration of less than 10 at ppm. For the optical measurements the crystals were mounted in a cryostat for continuous variation of the sample temperature down to liquid helium temperature. The crystals were photoexcited using trains of ultrashort light pulses from a mode-locked, frequency doubled Nd-YAG or Nd-glass laser ($\lambda=0.53\ \mu\text{m}$) [5]. The total exposure energy was typically $0.3\ \text{J}/\text{cm}^2$, corresponding to a peak intensity of about $10^9\ \text{W}/\text{cm}^2$. The diffraction efficiency of the hologram generated via two-photon excitation by the green picosecond pulses was monitored using cw HeNe and krypton lasers. The changes in the optical absorption spectrum caused by the two-photon excitations were measured with an iodine lamp and a monochromator. ESR spectra were recorded in situ by exposing a crystal mounted in a X-band cavity ($\nu=9.5\ \text{GHz}$) of an ESR spectrometer at 20 K.

We found that intense two-photon excitation of the crystal produced strong color changes. The solid curves

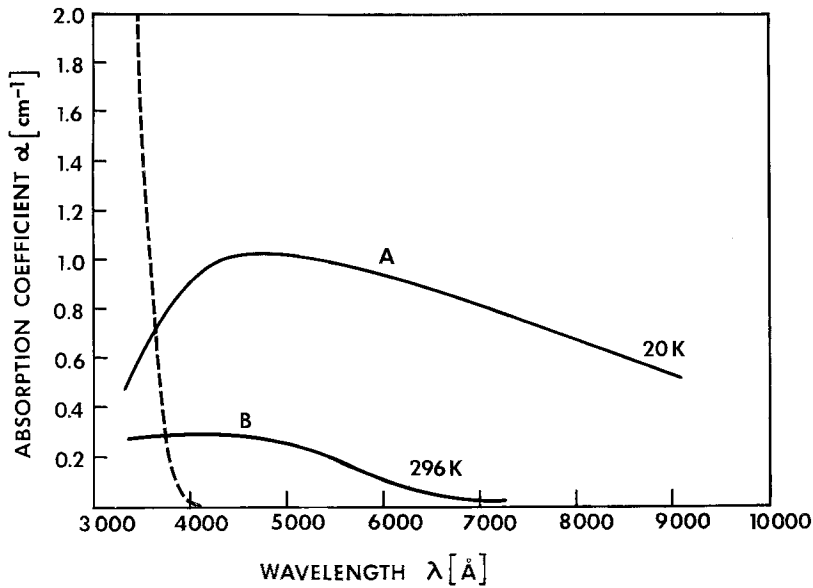


Fig. 1. Absorption spectrum of LiNbO_3 . (Dashed curve: Absorption edge before exposure, room temperature. Solid curves: Change of the absorption induced by two-photon excitation)

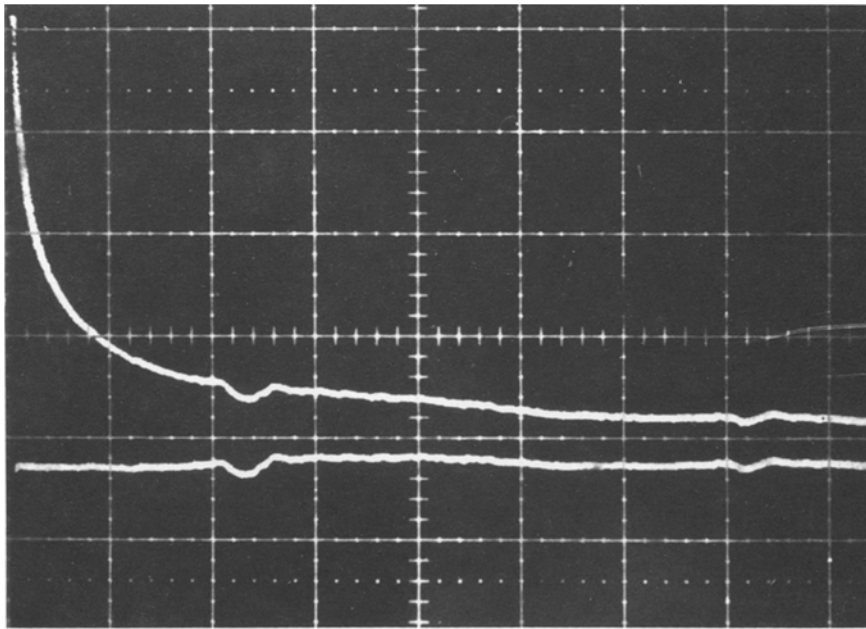


Fig. 2. Oscilloscope trace showing the decay of band A at room temperature (2 ms/div): The lower and the upper trace represent, respectively, the incident light as a reference, and the transmitted light. Light increases from top to bottom. The baselines are off scale. The difference between the two traces represents the induced absorption

of Fig. 1 depict the observed changes of the optical absorption spectrum resulting from an exposure of about 0.3 J/cm^2 at 20 K (spectrum A), and at room temperature (spectrum B). Assuming that each two-photon transition gives rise to one color center we estimate the peak absorption cross section at 20 K to be a few times 10^{-18} cm^2 .

Spectrum A transforms into a spectrum similar to B when the crystal is thermally bleached by heating to room temperature or flooded with red light from a HeNe laser.

The build up and decay of the induced absorption was studied at three different probe wavelength, 415 nm, 647 nm, and 799 nm, and the following observations were made.

A) The absorption bands A and B build up within less than 2 ns (time resolution of the experiment) after excitation of the crystal by a 30 ps light pulse at 532 nm.

B) Probing at 647 nm and 799 nm we find that band A decays nonexponentially with the same strongly temperature dependent time constant.

C) At 415 nm there is a permanent component which amounts to approximately 25% of the total initial induced absorption. The remaining 75% exhibit the same time dependence as seen at 647 nm and 799 nm.

An example of the decay of band A at room temperature is given in Fig. 2. The incident and the transmitted probe light is shown by the lower and the upper oscilloscope trace, respectively. The traces are adjusted

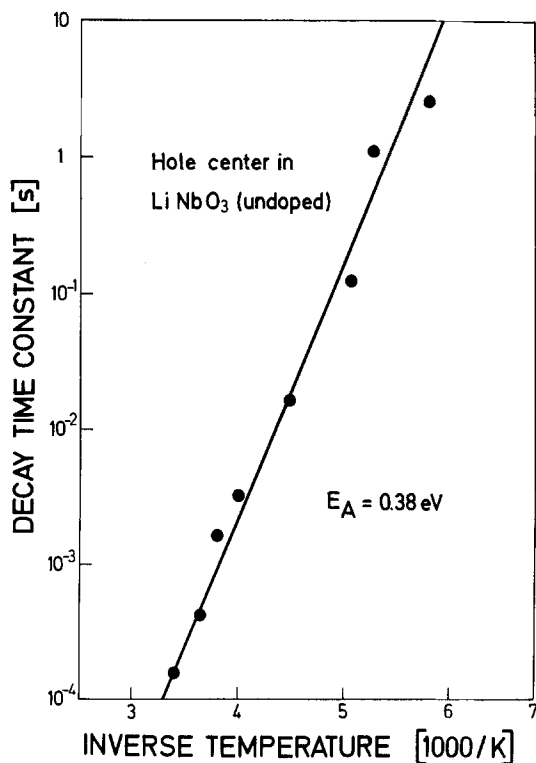


Fig. 3. Decay time constant of band A as a function of inverse temperature

such that they coincided before exposure. The maximum induced absorption $\Delta\alpha$ at the start of the traces corresponds to about 30% decrease of the sample transmission. A distinctly nonexponential decay is obvious from the oscilloscope trace of Fig. 2.

It is interesting to note that for the temperature range studied here the decay curves could be well described by assuming that the rate of change of $\Delta\alpha$ is given by

$$d\Delta\alpha/dt = -\gamma(\Delta\alpha)^3$$

with a strongly temperature dependent time constant γ . As shown in Fig. 3, γ increases by four orders of magnitude when going from room temperature to 173 K. From the slope of the exponential curve in Fig. 3 we obtain an activation energy of $E_A = 0.38$ eV.

The time dependence of the two-photon induced refractive index changes was studied by recording elementary holograms with two interfering picosecond pulses [4]. The essential features of the time variation of the diffraction efficiency can be summarized as follows.

- 1) The holograms build up within less than 2 ns after two-photon recording by a pair of 30 ps light pulses.
- 2) The initial hologram consists of a transient and a permanent component of approximately the same diffraction efficiency.
- 3) The time dependence of the transient component mirrors that of the induced A-band absorption.

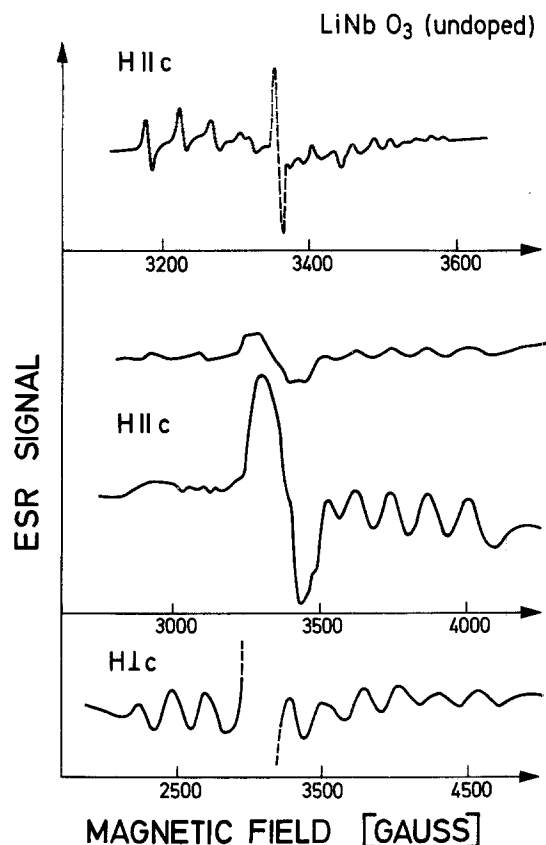


Fig. 4. ESR spectra. (Top trace: low microwave power. The dashed resonance is due to the sample holder. Second trace: High microwave power. Third and bottom trace: ESR spectra of an x-irradiated crystals)

Valuable information about the physical processes produced by two-photon excitation was inferred from ESR measurements [6]. No ESR signals were detected before optical exposure. Typical spectra observed after exposure are shown in Fig. 4. The top trace depicts the spectrum measured at low microwave power. These resonances persisted even when the crystal was heated to room temperature after exposure. At higher microwave power a different spectrum composed of a broad central band superimposed on a weaker multilined structure was observed (second trace). Both features disappeared when the sample was heated to room temperature or when the sample was flooded with HeNe laser light. It is interesting that an almost identical but much stronger spectrum was measured when the crystal was exposed to x-rays for about 30 min (third trace). For $H \perp c$ the x-irradiated sample exhibits ten well resolved components superimposed on a very strong single resonance (bottom trace of Fig. 4).

We suggest the following interpretation of the optical and ESR observations. The broad ESR resonance having a g value near 2 (second trace of Fig. 4) is due to holes self-trapped at O^{2-} ions near lattice defects.

Similar hole centers are observed in many oxide materials after suitable irradiation [6].

The pattern of ten lines, on the other hand, is attributed to electrons self-trapped at Nb sites forming Nb^{4+} centers. The tenfold splitting is caused by hyperfine interaction with ^{93}Nb nuclei with $I=9/2$. The ESR pattern observed at low microwave power (top trace of Fig. 4) is believed to be due to an increase of the Mn^{2+} concentration as a result of electron capture by residual Mn^{3+} impurities. The broad optical absorption (band A) is attributed to the hole centers. Broad intense absorption bands with peaks in the visible are characteristic features of such trapped holes in oxide materials [7]. These bands arise from optically induced small polaron hole transfer between equivalent sites [7, 8]. Consistent with this interpretation is the fact that the absorption bands A and the ESR resonances due to the hole centers exhibit the same thermal and optical quenching behavior.

With this interpretation in mind we propose the following picture for the two-photon induced photorefractive effect of LiNbO_3 . As a first step mobile electrons and holes are generated by two-photon band-to-band transitions. The holes are subsequently trapped at O^{2-} ions near defects forming small polaron hole centers, while the electrons are trapped at niobium sites forming Nb^{4+} centers, but part of the electrons may also be captured by residual impurities. Because the trapped holes and the electrons trapped by niobiums are unstable at room temperature, these centers are responsible only for the transient component of the hologram. The nature of the charges constituting the permanent hologram is not known at the present time, but it is very likely that extrinsic deep traps such as residual transition metal impurities play an important

role. The stable weak absorption band B of Fig. 1 may be due to these still unidentified traps.

The presence of intermediate color centers may have important consequences in regard to the existence of a truly intrinsic photovoltaic effect. We have performed an experiment [9] showing that the self-trapped holes generated by two-photon excitation act as photorefractive centers. When a LiNbO_3 crystal is colored by exposure to a uniform beam of picosecond pulses at 532 nm a permanent hologram can be recorded subsequently by two interfering infrared pulses at 1.06 μm during the lifetime of the hole centers. From the presently known experimental facts it is not possible to rule out that the formation of color centers is actually a necessary precondition for the observation of photorefractivity in undoped pyroelectric crystals.

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