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TRANSIENT OPTICAL ABSORPTION IN KNbO_3 CRYSTALS IRRADIATED WITH PULSED ELECTRON BEAML. Grigorjeva,^a D. Millers,^a E.A. Kotomin^a and E.S. Polzik^b^aInstitute of Solid State Physics, University of Latvia, Kengaraga 8, LV-1063, Riga, Latvia^bInstitute of Physics and Astronomy, University of Aarhus, DK-8000, Aarhus C, Denmark

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Transient optical absorption spectra as well as absorption decay kinetics in pure, Mg- and Rb-doped KNbO_3 have been measured at RT after pulsed (10 ns, 0.27 MeV) electron beam irradiation. Three types of short-lived radiation defects are observed with bands peaking at ~ 460 nm, ~ 780 nm and >1000 nm. The relevant radiation-induced decay processes are discussed. © 1997 Published by Elsevier Science Ltd

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1. INTRODUCTION

Radiation-induced short-lived absorption has been observed in many ABO_3 perovskite crystals, including BaTiO_3 [1], LiNbO_3 [2, 3], KNbO_3 [4, 5], widely used in non-linear optics and holography. A particular manifestation of this effect in KNbO_3 called *blue-light-induced-IR-absorption* (BLIIRA) considerably suppresses the second-harmonic generation (SHG) efficiency [4] and its mechanism remains to be unclear so far. Usually, this effect is observed at room temperature (RT) after/under an excitation pulse. The transient absorption in near-IR spectral region 800–1060 nm can be induced by γ - and X-rays [2], or by the laser with photon energy less than the optical gap [1–5]. Opposite opinions exist on a role of two-photon absorption: ref. [6] claims that defects are created in a two-photon process due to absorption in wide spectral region whereas [3] rejects this idea. In both studies LiNbO_3 crystals were investigated, but at different temperatures: at 20 K [5] and at 300 K [6]. It is not clear whether the transient IR absorption observed arises due to a charge transfer between pre-existing defects (impurities or intrinsic defects – vacancies, etc.) absorbing in the spectral region of 400–550 nm, or due to the band-to-band (electron–hole) processes. It is very important to understand the nature of defects causing absorption in the 400–550 nm spectral region for the BLIIRA explanation. According to O.F. Schirmer [6–8], in LiNbO_3 and KNbO_3 crystals the strong, wide optical absorption band in the 410–820 nm region is due to a

hole trapped as O^- ion and stabilised by the lattice distortion (*bound small polaron*). This defect is unstable at RT. Another defect, very common in many oxide crystals, is the oxygen vacancy occupied by either two (F-centre) or one (F^+ -centre) electron. F-type defects are stable at RT and can be introduced either by reduction treatment [9, 10] or under the electron beam irradiation [11], provided the electron energy exceeds the threshold energy for oxygen displacement (0.35 MeV in KNbO_3). Moreover, the absorption magnitude in the spectral region 410–600 nm increases in perovskite crystals doped with Fe, Mn, Ni and Cu [12].

The spectra of short-lived absorption induced by an Ar-laser excitation (514 nm, 1.2 W cm^{-2}) and Xe-lamp as a source of the probe beam in the spectral region of 430–690 nm have been measured in $\text{KNbO}_3 : \text{Fe}$ [5]; absorption maximum in the blue spectral region (≈ 465 nm) was detected. The similar short-lived induced absorption spectra have also been observed in $\text{LiNbO}_3 : \text{Zn}$ and $\text{LiNbO}_3 : \text{Mg}$ immediately after 1200 shots of 18 MW cm^{-2} Nd : YAG second-harmonic (532 nm) irradiation [13]. In both experiments an induced absorption was observed after excitation with photon energies from the optical transparency region. Two-photon excitation mechanism cannot be excluded since an excitation density was very high.

We do not know of any investigations of the *time-resolved* induced absorption spectra in niobates. In fact, only few papers [2, 4, 5, 14] deal with the absorption decay kinetics. This kinetics is not exponential, the

half-life time (during which the induced absorption coefficient decays by 50%) depends on the excitation pulse duration and its intensity. The decay kinetics was explained in terms of the two- and three-center charge transfer models [4, 5]. However, the nature of defects responsible for induced absorption remains unclear.

In this paper, we study for the first time the short-lived induced absorption spectra and the decay kinetics observed in KNbO_3 (pure, Mg- and Rb-doped) at RT after pulsed electron beam irradiation. The SHG efficiency and the BLIIRA effect for the same crystals were measured earlier [4] where an attempt to explain the nature of induced absorption was made.

2. SAMPLES AND EXPERIMENTAL METHODS

KNbO_3 crystals, both pure (#2 and #5), 0.1% Mg (#4) and 0.1% Rb (#6) doped were grown, polished and antireflection coated by Virgo Optics. All measurements were carried out at RT. The BLIIRA effect caused by the blue light with the density of 30 kW cm^{-2} is at the level of $\sim 1\text{--}2\%$ for the investigated crystals, which leads to significant SHG efficiency dropping [4].

The induced absorption spectra were measured after crystal excitation with pulsed electron beam. Figure 1 shows the experimental setup for absorption measurements. The electron beam energy is 270 keV with the excitation density $\sim 15 \text{ mW cm}^{-2}$ and a pulse duration 10 ns. The system's time resolution is 30 ns. As the probing light (PL), the pulsed Xe-lamp is used. Absorption spectra were measured in the spectral region of 420–1100 nm. The probe light passes through a sample and then through a monochromator (M), the light intensity is monitored by the photomultiplier (PMP) and an output signal is displayed on the oscilloscope.

3. RESULTS

The induced absorption spectra measured under an excitation pulse for different KNbO_3 samples are presented in Fig. 2. Three types of defects are observed, with absorption peaks at $\sim 460 \text{ nm}$, $\sim 780 \text{ nm}$ and $> 1000 \text{ nm}$, respectively. We could not measure precisely the peak position for the latter band due to the fact that our

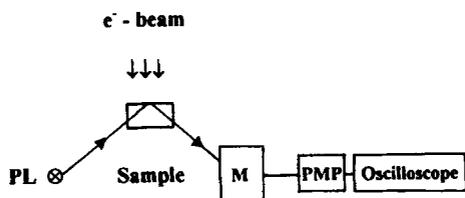


Fig. 1. Experimental setup for the measurements of induced absorption relaxation kinetics (PL, probing light; M, monochromator; PMP, photomultiplier).

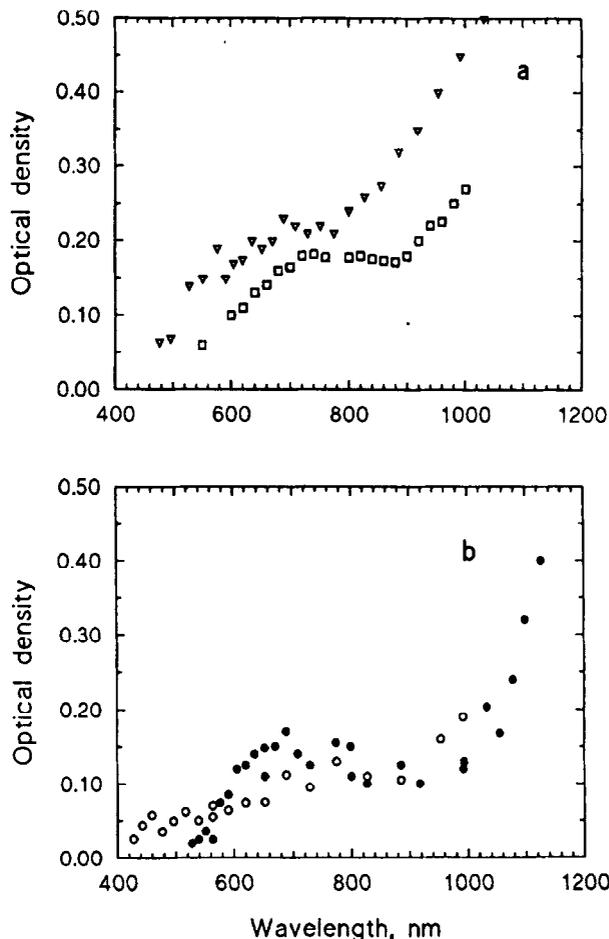


Fig. 2. Induced absorption spectra measured under an excitation pulse. (a) \square sample #2 and ∇ sample #5. (b) \bullet sample #4 and \circ sample #6.

equipment is not suited for this spectral region. The spectra measured with a certain time delay after the excitation pulse show that absorption bands at 460 nm and 780 nm have approximately the same half-life time whereas the long wavelength band has an *additional* long-time ($\tau \sim 1 \mu\text{s}$) component (may be, the long-time component is not observed at 500 nm band because its relevant optical density is small). In Fig. 3 the decay kinetics for the three bands are shown. The total kinetics are not exponential, and their decomposition into several elementary exponents is quite difficult. Usually, in such cases the temperature dependencies of the decay time help to determine the decay law. However, in KNbO_3 crystals the induced absorption spectra and the relaxation kinetics can not practically be measured at temperatures below RT in view of the fact that at 210 K the phase transition occurs in these materials and crystals become turbid.

The induced absorption spectra for all samples studied were quite similar with small peculiarities. The

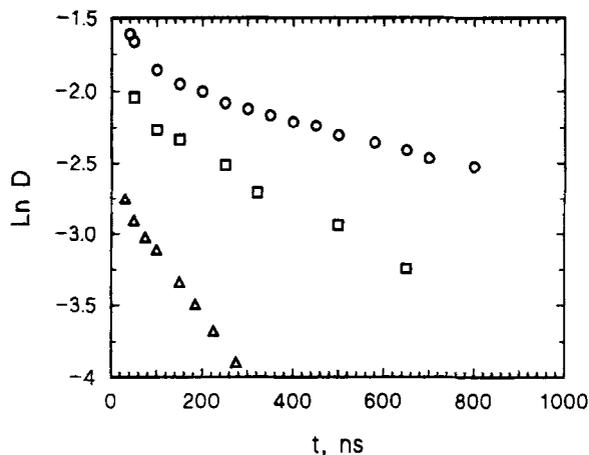


Fig. 3. The decay kinetics for different absorption bands for sample #6. (○, 990 nm; □, 775 nm; △, 515 nm).

most interesting is the absorption in the long-wavelength side of spectral region (> 1000 nm) which is observed in all samples, irrespectively on the crystal doping.

4. DISCUSSION

The electron beam energy used in our experiments is not sufficient for defect creation by a direct oxygen displacement mechanism. Thus we suppose only electron-hole pairs were created under our electron excitation. It means that new defects were not created and all effects observed are due to charge capture, transfer and recombination processes related to pre-existing defects. As a result of our excitation, free-electrons and hole were created in equal concentrations which is similar to two-photon excitation or X-ray irradiation.

According to the literature, in KNbO_3 and LiNbO_3 the absorption band peaking at ~ 500 nm may be due to impurity centres (for example, Fe^{2+}) [9] or bound hole polarons (O^- centres) [6–8]. It is also suggested that in KNbO_3 F-type centres could be responsible for the 460 nm absorption band [11]. Our study can not give the direct evidence for the nature of this absorption. In LiNbO_3 the band at 760 nm is quite certainly attributed to the F^+ -centre and that at 500 nm to the F centre [10, 14]. However, the nature of the defect which gives the absorption in this spectral region in KNbO_3 is under question.

The long-wavelength absorption is the most significant effect of our experiments. The short-lived absorption at 1060 nm in LiNbO_3 (pure, MgO and TiO_2 doped) was observed earlier under γ -ray excitation [2] but the time-resolved spectra were not measured. This absorption band is considerably higher in pure LiNbO_3 than in MgO and TiO_2 doped samples. Despite the fact that long-lived induced absorption peaked at 1200 nm was observed only in LiNbO_3 : MgO crystals [14] we suggest

that the *short-lived* absorption in the same spectral region of 1000–1200 nm is *not* Mg^{2+} (or Mg^+ complex) centre absorption, but is due to an intrinsic defect or unknown technological impurity present in *all* samples in considerable concentration. Earlier, the long-wavelength induced absorption was observed under X- and γ -rays excitation as well as under the electron and laser beam excitations. Exactly, this absorption is directly related to the BLIRA effect. Similar to the present study, *two* components of the absorption relaxation kinetics were observed at 990 nm in [4]. The slow component in the latter study has life-time ≈ 0.6 ms. Note that under prolonged excitation (60 s) the life-time becomes respectively much longer, ≈ 90 s [5]. Respectively, in our study done under n.s. excitation pulses this life-time is much shorter, ≈ 1 μs (Fig. 3). This demonstrates a strong effect of the excitation pulse duration.

Nonexponential decay kinetics, coexistence of the fast and slow decay components in accumulation and relaxation processes [4], the decay half-life time dependence on the excitation pulse duration – all this shows that defect creation and recombination processes are quite complicated. Alternatively, these effects could be explained in terms of two- or three-center models [4, 5] or by the tunneling mechanism of donor-acceptor defect recombination [15]. In the latter mechanism the relaxation kinetics is usually well described by the Becquerel's law, $n(t) \propto t^{-\alpha+1}$, $\alpha > 1$ is constant. This type of kinetics arises from the mutual *spatial distribution* of donors and acceptors rather than from the defect level distribution in thermal ionization energies. Analysis of this model is in progress now.

5. CONCLUSIONS

(1) Short-lived absorption observed in a wide spectral region (450–1100 nm) occurs after electron beam excitation in *all* studied samples, both pure and Mg-, Rb-doped KNbO_3 . Absorption at $\lambda > 1000$ nm arises due to either intrinsic defects or unidentified impurity present in all the samples studied.

(2) The relaxation kinetics of the induced absorption is not exponential which, very likely, is related to the tunnelling charge transfer between several kinds of defects.

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