Evidence for Two-Path Recombination of Photoinduced Small Polarons in Reduced $LiNbO_3$

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The recombination of photoinduced free Nb_{Nb}^{4+} and bound Nb_{Li}^{4+} small polarons to Nb_{Li}^{4+}:Nb_{Nb}^{4+} bipolarons is investigated in nominally pure, reduced $LiNbO_3$ single crystals by means of excited-state-absorption spectroscopy. We discovered a two-component decay of the light-induced absorption $\alpha_{li}(t)$ for probe light at $\lambda = 785$ nm and moderate pump beam intensities ($I_p \ll 670$ GW/m^2). These experimental results give strong evidence for the existence of a two-path recombination of the photoinduced polarons. A corresponding model taking into account hopping charge transport and trapping is presented.

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Introduction.—Polarons bound to defects are of general interest for the physical behavior of many optical materials, including oxide crystals. They are formed by charge carriers at certain shallow traps. Coulomb attraction and lattice distortion tend to localize the carrier at this site [1]. The population of these states under illumination is supposed to contribute to nonlinear optical effects, such as optical damage processes in $KTiOPO_4$ [2], LiB_3O_5 [3], $KNbO_3$ [4], $LiNbO_3$ and $LiTaO_3$ [5,6]. They further gained importance in the field of photorefraction. A famous example is the two-step recording of holograms with infrared light in Fe-doped $LiNbO_3$, using $Fe^{2+/3+}$ as deep and small Nb_{Li}^{4+} bound polarons as metastable shallow centers [7]. Even in undoped $LiNbO_3$ a two-step recording with large diffraction efficiency has been observed after thermal reduction of the samples. Here the deep center is the stable Nb_{Li}^{4+}:Nb_{Nb}^{4+} bipolaron [8], a strongly bound negative-U pair on neighboring cation sites. Because of this rich variety of stable and metastable polarons, $LiNbO_3$ is an ideal candidate for investigations of the properties of these intrinsic defects and the related charge transport processes.

This work focuses on the recombination kinetics of photoinduced metastable small bound and Nb_{Nb}^{4+} free polarons to bipolarons in nominally pure, reduced $LiNbO_3$. This congruently melting material shows a Li deficiency which is partly compensated by Nb ions on Li sites [9]. Thermal reduction leads to the formation of stable bipolarons with an optical absorption band at 2.5 eV (500 nm) [10,11]. Bipolarons are dissociated by light in the blue-green spectral range (''gating'' [12]). According to well established small-polaron theory [13] the gating process should excite one electron to an adjacent Nb_{Nb}^{5+} site, thus forming a metastable small free polaron with a binding energy of 0.5 eV. The corresponding optical absorption is centered at 1.0 eV (1250 nm) [14]. At the same time the second electron remains as small bound polaron with an optical absorption at 1.6 eV (760 nm) [11]. All polaronic absorption bands mentioned here show a large width of $\approx$1 eV [11,14]. Up to now, only the appearance of photoinduced bound polarons has been proven experimentally, either by exposure to cw or to pulsed laser light [15]. Information about the existence of photoinduced metastable free polarons is missing. Hence, the knowledge about the important charge transport and recombination processes is fragmentary.

We gained insight into this question by means of excited-state-absorption spectroscopy. We show measurements of the temporal development of the light-induced absorption $\alpha_{li}(t)$ detected in the blue, red, and infrared spectral range. A two-component decay of $\alpha_{li}(t)$ is discovered at $\lambda = 785$ nm for moderate pump beam intensities, which originates from the charge transport and recombination processes of small polarons. The signal amplitude and temporal behavior are investigated for different pump intensities and sample temperatures, also yielding activation energies. Based on our findings, a two-path model for hopping charge transport and recombination of metastable small polarons to bipolarons is developed.

Experimental details and results.—Nominally pure samples of congruently melting $LiNbO_3$ (Crystal Technology, Inc.: $c_{Fe} < 5$ ppm) were thermally reduced by heating them up to approximately 920 K in vacuum ($p < 10^{-4}$ mbar) for six hours. The purity of the samples was controlled by instrumental neutron activation analysis. No detectable element was found with an impurity level above 1 ppm. The steady-state absorption at $\lambda = 500$ nm i.e., the maximum of the bipolaron absorption band, was $\alpha_{500\,nm} = 410$ m^{-1}. A Q-switched, frequency-doubled Nd:YAG pulse laser ($\lambda = 532$ nm, $\tau_{FWHM} = 8$ ns) served as the pump light source. The low-intensity probe light of an Ar^+ laser ($\lambda = 488$ nm) and of two diode lasers ($\lambda =$ 785 nm, 1310 nm) propagated through the crystal and were simultaneously detected by three PIN diodes. Ordinary light polarization was chosen for pump and probe beams ($\mathbf{e}_p \perp c$ axis). The signals of the diodes were recorded for 20 seconds after the laser pulse with a fast digital oscilloscope having a time resolution of 1 ns. After these 20 seconds any light-induced absorption vanished completely. From the transmitted probe intensity $I(t)$ the transient light-induced absorption was determined via

$\alpha_{li}(t) = (1/d)\ln[I(t \leq 0)/I(t)]$, with the sample thickness d and the intensity of the probe light prior to the laser pulse $I(t \leq 0)$. Figure 1 shows the temporal evolution of the light-induced absorption $\alpha_{li}(t)$ for the three probe wavelengths after a pump pulse of $I_p = 670$ GW/m^2 at $T = 315$ K. For $\lambda = 785$ nm and $\lambda = 1310$ nm the light-induced absorption has a positive sign, whereas for $\lambda = 488$ nm a light-induced transparency is observed. All transient absorption changes vanish within a few seconds. The $1/e$ lifetime is found in the range of 2 ms and the activation energy is around 0.53 eV for all probe wavelengths. In accordance with the data reported in Ref. [15], the light-induced transparency in the blue spectral region is assigned to the optical dissociation of bipolarons. The light-induced absorption in the red and infrared can be explained by the formation of Nb_{Li}^{4+} bound polarons and Nb_{Nb}^{4+} free polarons, leading to the respective absorption bands at $\lambda = 785$ nm and $\lambda = 1310$ nm [11,14]. Lowering of the pump intensity, however, leads to a drastic change of the temporal evolution of the light-induced absorption, as shown in Fig. 2(a) for $\lambda = 785$ nm. The particular spectra are normalized with respect to their maximum values. With decreasing intensity one observes the change from a single-shaped decay to a two-component decay. We will concentrate on this two-component decay in the following. A quantitative analysis of the light-induced absorption at $\lambda = 785$ nm for the lowest pump intensity (13.5 GW/m^2) is shown in Fig. 2(b). According to [16,17] and to the fact that fitting with single- or double-exponential functions fails, we describe our spectrum by a sum of two stretched exponential functions (solid gray line):

$$\alpha_{li}(t) = \alpha_1 \exp[-(t/\tau_1)^{\beta_1}] + \alpha_2 \exp[-(t/\tau_2)^{\beta_2}], \quad (1)$$

where $\alpha_{1,2}$ are the amplitudes, $\tau_{1,2}$ the characteristic lifetimes, and $\beta_{1,2}$ stretching factors of the fast and slow decay components. The fit parameters are shown in Table I. Two facts are remarkable: first, the lifetimes for the fast and slow components of the decay differ by more than 3 orders of magnitude; second, the lifetime of the slow decay is the same as that obtained for high pump intensities. It has to be emphasized that in the case of a two-component decay the initial amplitude of the light-induced absorption is directly proportional to the pump intensity, i.e., $\alpha_{li} \propto I_p$ for moderate pump intensities.

To see whether this two-component decay is a characteristic feature of small-polaron recombination, the measurements presented above were performed for different sample temperatures. For thermally activated processes the lifetime depends on the temperature obeying Arrhenius' law:

$$\tau(T) = (1/Z)\exp[E_a/(k_B T)], \quad (2)$$

where E_a is the activation energy and Z is a frequency factor. Figure 3 shows the temperature dependence of the lifetimes for the fast and slow decay components of the light-induced absorption at $\lambda = 785$ nm. Fits of Eq. (2) to the measured data yield the activation energies and frequency factors shown also in Fig. 3. These activation

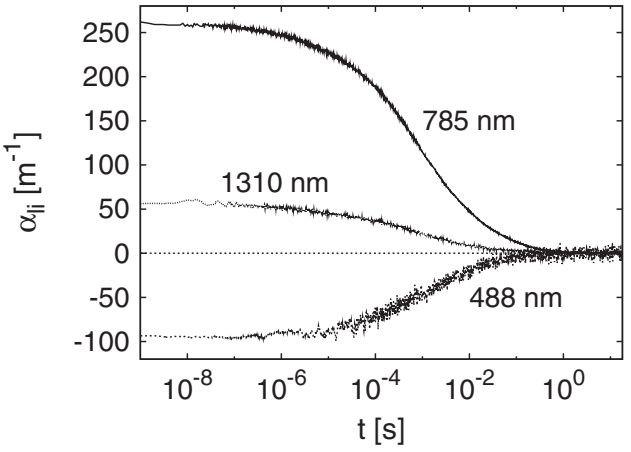

FIG. 1. Temporal development of the light-induced absorption for the three probe wavelengths at $T = 315$ K and maximum pump intensity of $I_p = 670$ GW/m^2.

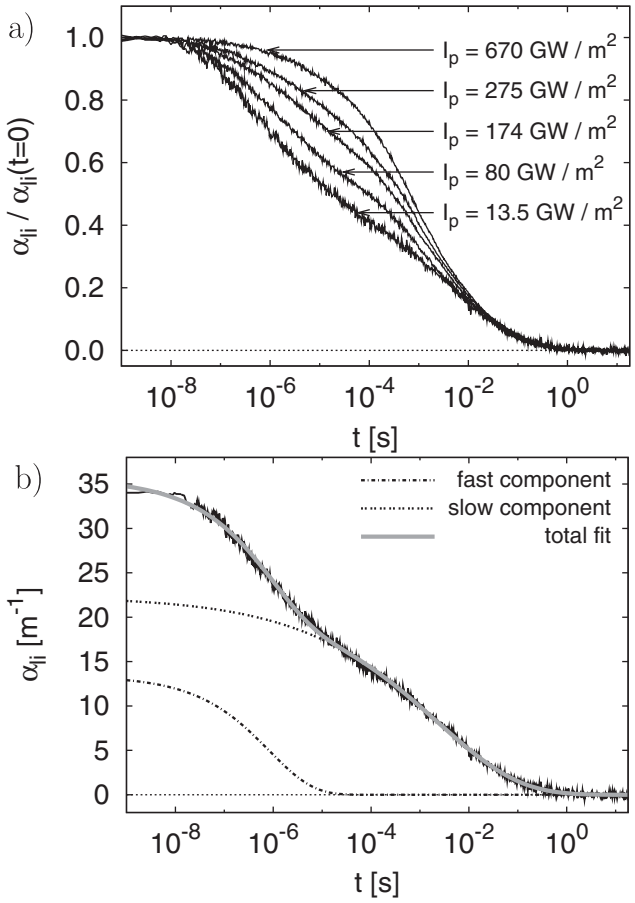

FIG. 2. (a) Temporal development of the light-induced absorption for a probe wavelength $\lambda = 785$ nm for different pump intensities at $T = 315$ K. The spectra are normalized to their maxima for reasons of comparability. (b) $\alpha_{li}(t)$ for $I_p = 13.5$ GW/m^2. The lines are fits of stretched exponential functions [see Eq. (1)] to the experimental data.

TABLE I. Parameters for the fast and slow component of the decay of $\alpha_{li}(t)$ at $\lambda = 785$ nm as obtained from fits of Eq. (1) (see Fig. 2) to the measured data.

	α [m^{-1}]	τ [μs]	β
fast	13 ± 3	0.8 ± 0.4	0.49 ± 0.05
slow	22 ± 5	2000 ± 1000	0.26 ± 0.05

energies have to be compared with those proposed by small-polaron theory [1,18], being 0.25 eV for free polarons (half the binding energy of $E_{FP} = 0.5$ eV). Faust *et al.* have determined the activation energy for small free polarons in $LiNbO_3$:Zn and $LiNbO_3$:Mg to be in the range of 0.20 eV to 0.30 eV [14]. For bound polarons this energy is enhanced by the Coulomb interaction. Schirmer *et al.* have obtained a value of 0.62 eV from conductivity measurements [19].

Discussion.—The recombination of small polarons after optical dissociation of bipolarons with a single-shaped decay of the light-induced absorption has been reported earlier for high pump intensities [15]. Based on these findings, the transient light-induced transparency observed in our experiments at $\lambda = 488$ nm (see Fig. 1) is clearly assigned to the dissociation of bipolarons, causing the respective absorption band to decrease. The light-induced absorption at $\lambda = 785$ nm is consequently assigned to the formation of small bound polarons [11]. To our knowledge the light-induced absorption at $\lambda = 1310$ nm was not reported before and is most likely due to a superposition of the absorption band of the small bound with that of the small free polaron. Hence, and due to low signal-to-noise ratio, intensity-dependent spectra are not analyzed at $\lambda =$ 488 and 1310 nm. The second new observation is an intensity dependence of the decay shape at $\lambda = 785$ nm. At low pump intensities the recombination of the bound polarons has two components with different time constants: a fast one in the range of microseconds and a slow one in the range of milliseconds. Temperature-dependent measurements yield activation energies for these two components resembling those reported for the small free and small bound polarons. The open question is how to describe these findings by an appropriate charge transport model, taking the recombination of the polarons involved into account.

There are two points important for our model illustrated in Fig. 4, which we have to mention in advance. First, all charge transport processes are thermally activated and are thus of the hopping type, which is characteristic for small polarons [13,18]. Second, as bipolarons consist of two electrons of which one is localized at a Nb_{Li} antisite ion, it is clear that every recombined bipolaron leads to a decrease of the absorption band of the bound polaron. This is why one can deduce the entire recombination process of bound *and* free polarons to bipolarons from the decay of $\alpha_{li}(t)$ at $\lambda = 785$ nm.

We propose the following two different recombination paths after optical dissociation of bipolarons. In the fast process [Fig. 4(a)] we consider only the energy levels of the free polaron and the bipolaron, denoted as $Nb_{Nb}^{4+/5+}$ and

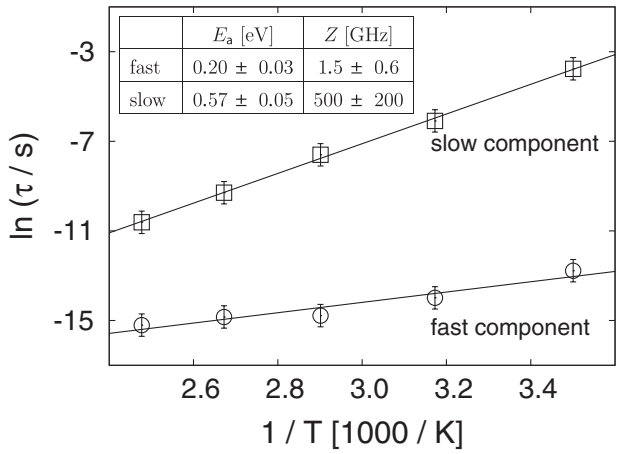

FIG. 3. Arrhenius plot of the characteristic lifetimes for the fast and slow component of the decay of the light-induced absorption at $\lambda = 785$ nm ($I_p = 13.5$ GW/m^2).

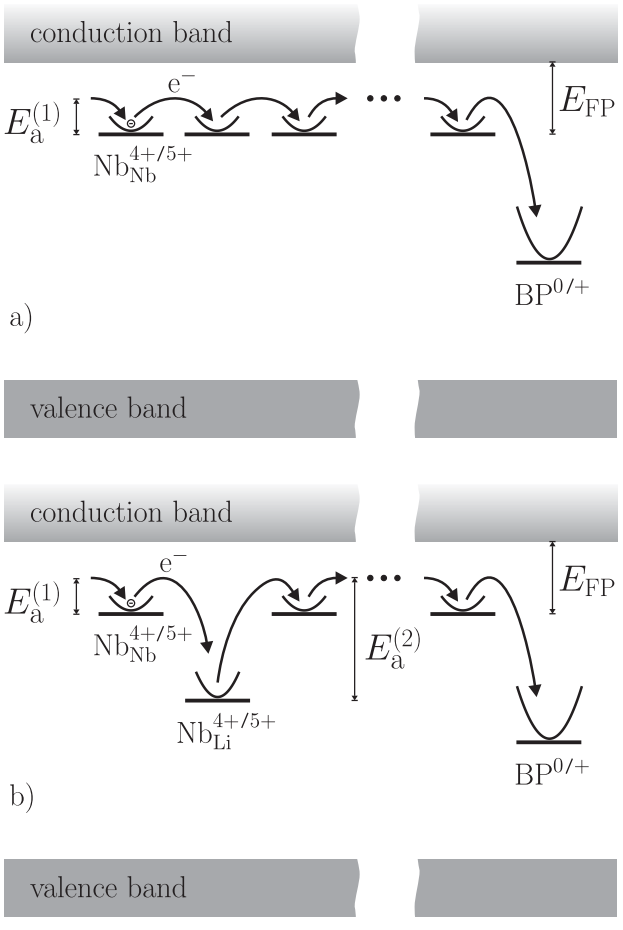

FIG. 4. (a) Fast hopping transport of excited electrons via small free polarons with final trapping at bipolarons. (b) Trapping of electrons at bound polarons during the transport.

$BP^{0/+}$, respectively. The transport of electrons occurs via free polarons to the final trapping at ionized bipolarons (Nb_{Li}^{4+}:Nb_{Nb}^{5+}). The activation energy $E_a^{(1)}$ required for each jump is that of the free polaron. This corresponds to the fast component of the decay of the light-induced absorption.

In the second path [Fig. 4(b)] we consider in addition the energy level of the small bound polaron, denoted as $Nb_{Li}^{4+/5+}$. In this case, some electrons may be trapped during the transport at unoccupied Nb_{Li}^{5+} ions, thus forming bound polarons. The activation energy $E_a^{(2)}$ needed to liberate the electron from this deeper trap is larger, leading to much longer lifetimes. Hence, after most of the free polarons have recombined, some bound polarons still remain. Consequently one expects a slower decay of the residual light-induced absorption at $\lambda = 785$ nm, which is observed in our experiments.

The superposition of the two recombination paths presented above allows us to describe the overall shape of the decay of the light-induced absorption for moderate pump intensities, in particular, the appearance of a two-component decay. Here, the fast component mirrors the charge transport solely by free polarons while the slow component results from the contribution of bound polarons. Because of hopping charge transport, both decay components should resemble a stretched exponential behavior according to [16,17,20,21]. Here, the parameter β is related to the distribution of relaxation times, while τ is the characteristic lifetime [16,20,21]. For high pump intensities the experimental data indicate a dominating contribution of the second recombination path, which is consistent with previous results [15]. This predominance explains why the first path has not been discovered so far.

The validity of our model is strongly supported by the consistence of the predicted and experimentally determined activation energies: 0.25 eV compared with 0.20 eV for the fast component, and 0.62 eV compared with 0.57 eV for the slow component, respectively. We stress that this result also contains strong evidence for the existence of metastable small free polarons after optical dissociation of bipolarons at room temperature.

Summarizing our results, the recombination paths of photoinduced free and bound small polarons have successfully been investigated by means of excited-state-absorption spectroscopy in nominally pure, reduced $LiNbO_3$. The temporal and thermal behavior of the light-induced absorption at $\lambda = 785$ nm gives very strong evidence for the simultaneous presence of small free polarons and small bound polarons at room temperature. A model describing the discovered two-component decay of the light-induced absorption on the basis of a two-path recombination is presented. In conclusion, an important and valuable insight into the charge transport and recombination properties of polarons has been gained in the large band gap material $LiNbO_3$. We are sure that our model can be adapted to other large band gap insulators as well, and that the results definitely are of importance for a broad range of optical applications of $LiNbO_3$. For instance, the metastable free polaron could also be used as a shallow trap for dynamic holographic recording with light in the infrared spectral range.

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