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Experimental and theoretical studies of polaron optical properties in KNbO$_3$ perovskite

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Abstract

Time-resolved absorption and luminescence spectra have been measured in KNbO$_3$ perovskite crystals after pulsed band-gap excitation by 200 fs laser pulses and 10 ns electron pulses. Quantum chemical calculations using the large unit cell periodic model support the interpretation of the observed transient absorption bands at 0.8 and 1.1 eV as the self-trapped electron polarons and bound hole polarons, respectively. The activation energy for the 2.2 eV green luminescence quenching is 0.05 eV. We suggest that the short lifetime (< 15 ns) of the luminescence at RT is caused by the radiative recombination of nearest electron and hole polarons.
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1. Introduction

Although the idea of small-radius *polarons* in ionic solids was theoretically suggested by Landau in 1933, an explicit experimental proof of self-trapped *holes* (intrinsic molecular polarons) was obtained only a quarter of century later by means of ESR in alkali halides [1–3]. A family of free and bound hole polarons (O$^-$) was observed since then in ABO$_3$ ferroelectric perovskites [4,5]. For a long time it was believed that electron self-trapping is not energetically favorable in ionic solids due to a large energy loss necessary for electron localization on a single cation at the first stage of the polaron trapping process, which is not compensated by sufficient energy gain due to a crystal polarization at the second stage of the self-trapping. However, in 1993 the first

ESR evidence appeared for the *electron* self-trapping in PbCl$_2$ [6], and one year later for LiNbO$_3$ perovskite crystals [7], accompanied by an IR absorption band around 1 eV. Recently self-trapped electrons were detected also in BaTiO$_3$ [8]. The electron polarons in oxide perovskites reveal the optical absorption in the IR region, typically around 0.5–0.9 eV, whereas the hole polaron absorption lies at higher energies. On the other hand, the *bound* polarons absorb light at higher energies than similar free polarons. As to KNbO$_3$, existence of the hole and electron polarons was discussed in Refs. [9,10]. The photo-induced absorption in KNbO$_3$ harmonic generation crystals suppresses the second harmonic generation efficiency and is an undesirable effect [11]. For the first time the *transient absorption* spectra in KNbO$_3$ crystals were measured in Ref. [12] (see also [13]). In this paper, we present a detailed experimental study of the transient optical absorption of electron and hole polarons in the IR region, accompanied by theoretical calculations.

Measurements of intrinsic luminescence of $KNbO_3$ perovskite crystals are also presented.

2. Experimental

The measurements have been made using two experimental set-ups. In the first case an electron accelerator has been used, with pulse duration of 10 ns, electron energy ~ 270 keV, average density of electron beam 10^{12} el/cm^2, and overall time resolution of 20 ns. The probe light from a Xe flash lamp was directed into the sample at such an angle that it undergoes total internal reflection from the surface which is irradiated by the electron beam. It is subsequently focused on the entrance slit of the monochromator. A storage oscilloscope recorded the data. The absorption spectra were measured in the energy range of 0.75–3.3 eV (see details in Ref. [10]). The experimental error bars in the optical density measurements depend on the detector used. Thus, in the region of 1.1–3 eV errors are 0.025 whereas in the region 0.75–1.1 eV they are twice larger, 0.05.

The electron energy threshold for displacing the O ion from its regular lattice site in $KNbO_3$ is about 350 keV [14]. That is, under our experimental conditions the electron beam energy was below the threshold energy, and therefore, only the electronic excitations and the ionization of pre-existing defects take place. The penetration depth of 270 keV electrons into the crystal is sufficiently large, ~ 0.2 mm, so that we deal mainly with the bulk effects.

In the second experimental set-up, a mode-locked Ti: sapphire laser beam was used to generate 200 fs pulses in the 820–855 nm spectral region. The electron-hole pairs were generated by the two-photon absorption of the laser second harmonic (2×2.9 eV) [15].

We present here results for two undoped, non-poled colourless $KNbO_3$ crystals grown by Virgo Optics (hereafter samples S1N4 and S3N5). The domain structure of our samples was not studied. As known from the literature, most non-poled ferroelectrics have a multidomain structure. The IR InGaAs photodiode was used in both types of experiment for an extension of the spectral range towards the IR region. The transient absorption spectra and the relaxation kinetics were measured only at room temperature (RT) where the orthorhombic $KNbO_3$ phase is stable.

3. Experimental results

3.1. Transient absorption

The transient absorption spectra for two different $KNbO_3$ samples are shown in Figs. 1 and 2.

The spectra in Fig. 1 show the results of the two types of excitations: (1) with ns electron beam, and (2) with ps laser. In Fig. 2 the IR part of the electron beam-induced absorption
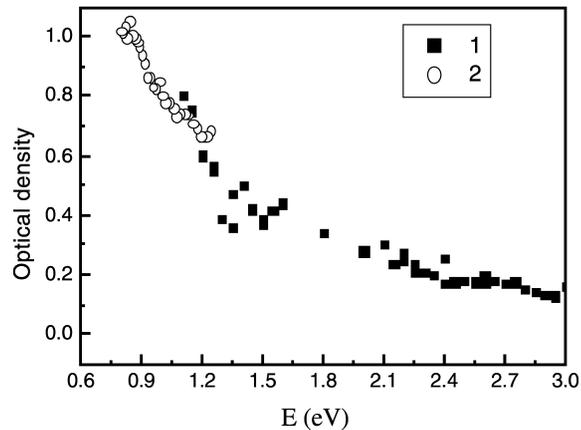

Fig. 1. The transient absorption spectrum for sample S3N5 at the end of the excitation pulse; 1 ps laser, 2 ns electron beam.

is shown. The rise-time of the IR transient absorption is very fast (≤ 0.8 ps).

The transient absorption in the spectral range of 1.3–3.3 eV (Fig. 1) is always observed in $KNbO_3$ crystals under pulsed electron beam excitation [10]. The absorption bands are poorly resolved in this energy range and they are believed to arise due to several different defects including the F-type centers (O vacancies with trapped electrons). The decay kinetics of the transient absorption considerably depend on the impurities and defects present in samples, and never obey a simple exponential or algebraic decay law. After high-density electron beam excitation, the transient absorption completely decays on the ms time scale. We suggest that under irradiation, electrons and holes form bound polarons or recharge lattice imperfections and these centers are responsible for the transient absorption in the range 1.3–3.3 eV. These complementary defects recombine in pairs, which is supported by the similar decay kinetics
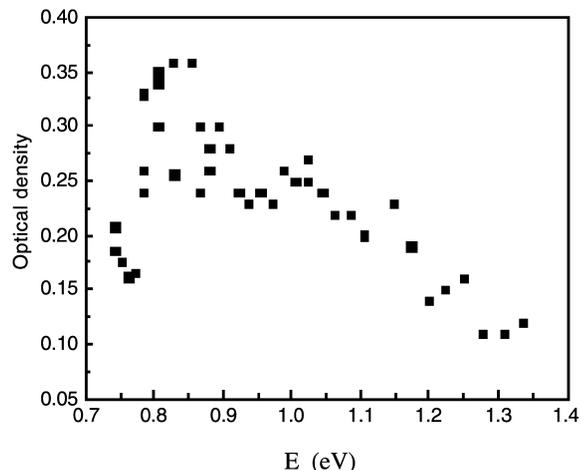

Fig. 2. The IR part of the transient absorption spectrum for sample S1N4 at the end of ns electron excitation.

over this part of the spectra. Note that similar complex non-exponential transient absorption decay kinetics due to polaron recombination were observed also in $LiNbO_3$ [15], $SrTiO_3$ [16], and $Sr_{0.6}Ba_{0.39}Nb_2O_6$ [17].

In this study, we were able to measure the optical absorption at smaller energies. The main effect was observed in the range of 0.8–1.3 eV. The band peaking at ~0.8 eV was observed in both experiments—under ns electron beam and ps laser excitations. [Probably, the low-energy side of the spectra in Figs. 1 and 2 is not perfectly correct due to the spectral limit of the IR detector (0.75 eV)]. Since the energy absorption is observed in both samples, we believe this is due to some intrinsic defect. The similar IR absorption was observed earlier in Mg-doped, thermochemically reduced $LiNbO_3$ crystal and interpreted by means of EPR as the electron polaron [5,7].

The IR spectrum in Fig. 2 (sample S1N4) clearly shows the absorption band at ~1.1 eV (within error bars mentioned above). However, this band is hardly resolved in another sample, S3N5. Very likely, the band amplitude and shape are affected by defects and thus this band could be attributed to the *bound hole polarons* (see discussion below). The slight difference in the absorption peak around 1.1 eV observed under the electron beam and the laser excitation arises due to: (a) the difference in the time resolution of the relevant set-ups and in the decay time after the excitation pulses. Under the laser excitation the time resolution exceeds by four orders of magnitude that for the electron beam; (b) the different pulse duration means also different distributions in the relative distances of close defects. That is, some polarons are observed under the ps excitation but no longer detected under ns excitation. Note that the Ti-bound hole polaron in $KNbO_3$ reveals much larger absorption energy, around 2 eV [18], thus demonstrating how strongly point defects can shift the free polaron absorption energies. It was observed in the literature [13] that the free-carrier lifetime could be as short as 4 ns. This agrees with our observations of the fast decay of the polaron absorption (≤ 0.8 ns). This lifetime depends strongly on defect concentration in a crystal, both the polaron lifetime reduction and enhancements are possible due to the polaron-defect interaction. Trapping at deep levels can reduce the polaron lifetime due to bound polaron formation. On the other hand, shallow traps can reduce the polaron mobility and thus enhance their lifetime.

3.2. Luminescence

Since the transient luminescence spectra and their decay kinetics were discussed earlier [9], we focus here only on the so-called *green* luminescence band peaking at ~2.2 eV. This band has been observed under the pulsed electron beam excitation in a wide temperature range of 80–300 K. This luminescence has been earlier observed in all samples—both pure and doped. Probably, this is a non-elementary band. The luminescence decay is exponential. However, its

decay time (and the activation energy estimated from its temperature dependence) strongly depend on sample stoichiometry and on the impurity concentration. This can explain a large variation in reported quenching energies (cf. 0.03 and 0.012 eV [19,20] respectively). Based on our measurements, we estimate this quenching energy in pure $KNbO_3$ to be 0.05 eV.

The transient absorption relaxation (1) and the luminescence decay kinetics (2) are shown together in Fig. 3. It is important to note that both kinetics were measured under the same experimental conditions (10 ns electron beam excitation at RT). The luminescence decay is very short, <15 ns. However, we do not observe a similar decay constant in the absorption kinetics. Probably, only electron-hole pairs created in a single ionization event recombine radiatively, which is a monomolecular (first-order) process with the exponential kinetics. On the other hand, well-separated and thus longer-lived electron and hole polarons are probably responsible for the transient absorption observed. These polarons recombine, very likely non-radiatively, as a result of a diffusion-controlled tunnelling process. A similar situation takes place for the primary radiation defects in alkali halides [1].

4. Computational

4.1. Method

We have used the semi-empirical quantum chemical method of Intermediate Neglect of Differential Overlap (INDO) [21]. The modification of the standard INDO method for ionic solids is described in detail in Refs. [22, 23]. This method is based on the Hartree–Fock formalism and allows self-consistent calculations of the atomic and electronic structure of pure and defective crystals. In the last decade the INDO method has been used for the study of bulk solids and defects in many oxides [24] and semiconductors
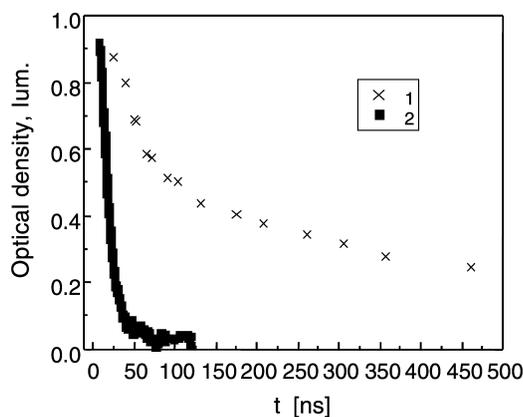

Fig. 3. (1) The kinetics of the optical density relaxation at 1.15 eV, and (2) 2.2 eV luminescence decay (sample S1N4).

[25,26]. This method has been applied to the study of phase transitions and frozen phonons in pure $KNbO_3$ [27], pure and Li-doped $KTaO_3$, point defects in $KNbO_3$ [28], and solid perovskite solutions $KNb_xTa_{1-x}O_3$. More details about the INDO method and relevant computer code are given in Ref. [22,23]. We use a periodic, so-called *large unit cell* (LUC) model [30].

In ABO_3 crystals under study with the unit cell containing five atoms, the $2 \times 2 \times 2$ extended LUC used mostly in our calculations consists of 40 atoms. We performed the calculations for the lattice constant $a_o = 3.997$ Å. The detailed analysis of the development of the INDO parameterization for a pure $KNbO_3$ is given in Ref. [27].

Recently [29,31] we performed the INDO calculations for the hole polarons bound to a K vacancy in $KNbO_3$. We found that both the one-site (atomic) and two site (molecular) polarons bound to a K vacancy have close formation energies and thus could co-exist. A hole is either localized by a single O ion displaced toward the vacancy, or it is shared by a pair of nearest O ions. Both polarons reveal similar thermal stability (the energy gain due to a lattice relaxation), and the optical absorption ≈ 1 eV (Table 1). High accuracy of the INDO results is confirmed by good agreement of our INDO lattice relaxation around the F center and hole polarons with the *ab initio* LMTO calculations [28,29].

4.2. Self-trapped electron polaron

As an extension of the hole polaron study, we have modelled the *self-trapped electron* polaron in a cubic phase (see also [32]). To preserve the supercell (LUC) neutrality, we have replaced one of the K^+ ions by an Mg^{2+} ion which was maximally separated from the polaron. As before, we used the $2 \times 2 \times 2$ extended cubic cell with the LUC containing 40 atoms. We allowed six nearest oxygen atoms in the octahedron around a central Nb atom in $KNbO_3$ to relax, in order to find the total energy minimum. All other Nb and K atoms, as well as the rest of O atoms in most cases were kept fixed at their perfect lattice sites (see below).

As a test of how use of the experimental lattice constant could affect our results for polarons, we made a simple calculation, allowing 6 nearest neighbor O ions surrounding

Table 1
The INDO calculated absorption energies for the electron and hole polarons in $KNbO_3$

Type of a polaron	Absorption energy (eV)
Self-trapped electron polaron	0.78
Bound electron polaron (Mg impurity)	0.88
Bound one-site hole polaron (K vacancy) [29]	0.90
Bound two-site hole polaron (K vacancy) [29]	0.95

the Nb ion in the perfect lattice to relax to the minimum of the total energy. As a result, we found negligibly small atomic displacements from the perfect lattice sites. This demonstrates that our polaron geometry optimization is reliable.

According to our INDO calculations, initially the polaron ground state is three-fold degenerate (t_{2g}). This degeneracy is lifted as a result of the combination of the breathing mode and the Jahn–Teller effect: 1.4% a_o *outward* displacement of four equatorial O atoms nearest to Nb (with the energy gain of 0.12 eV) and *inwards* 1% a_o relaxation of the two oxygens along the z direction (the additional gain of 0.09 eV). That is, the total lattice energy gain is 0.21 eV. A similar Jahn–Teller electron polaron was recently observed by means of the ESR in $BaTiO_3$ [8]. Equal atomic displacements found for all four O equatorial ions surrounding the polaron mean that the charge-compensating Mg^{2+} ion does not affect the results.

Calculations show that a considerable (0.5e) electron density is localized on the central Nb atom producing three closely spaced energy levels in the band gap (Fig. 4(c)). They consist mainly of the xy, xz and yz Nb $4d$ atomic orbitals (splitted t_{2g} energy level in an isolated ion) whereas two empty levels are located close to the conduction band bottom. The electron polaron absorption energy was calculated as the difference of the total, self-consistent energies for the ground and excited states (ΔSCF) to be 0.78 eV. The relevant absorption process corresponds to an electron transfer to the nearest Nb atom. As to the energy balance for the self-trapped electron formation, previous *ab initio* LMTO calculations [27] have demonstrated that the bottom of the $KNbO_3$ conduction band has a narrow sub-band which probably permits the electron localization energy to be small enough, thus giving a positive total self-trapping energy balance.

We have studied additionally the effect of other atom relaxations: first of all, 8 K atoms which are nearest to Nb. Results are shown qualitatively in Fig. 4(a). Briefly, the additional lattice energy gain is only 0.02 eV, considerably smaller than the contribution from the asymmetrical relaxation of the 6 nearest O atoms. Our experience with the F-center calculations for the cubic and orthorhombic phases [28,31] clearly demonstrated that the defect optical absorption energies depend very weakly on the particular *para*/ferroelectric phase, because the lattice relaxation energy around point defects is an order of magnitude larger than that for the tiny deformation due to the phase transition. We believe this is also the case for the polarons under study.

In order to check whether our supercell is large enough for neglecting the interaction of periodically repeated polarons and $Mg^{2+}–Nb^{4+}$ dipoles, we performed additional simulations for the 135 atom supercell ($3 \times 3 \times 3$ extended unit cell). After geometry optimization around the self-trapped electron, we have found that the four equatorial O atoms nearest to the Nb ions are relaxed outwards, now by 1.34% a_o, whereas the two O atoms along the z-axis relax
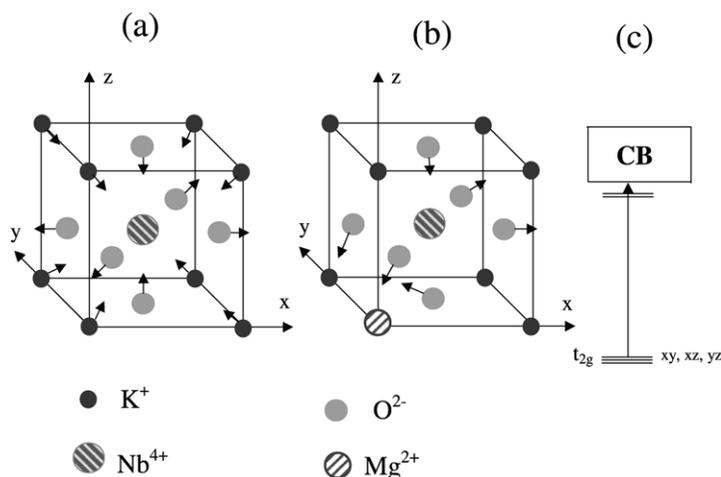
Fig. 4. (a) Sketch of the asymmetric relaxation of 14 atoms around the central Nb atom with the self-trapped electron, (b) the same for a bound electron polaron, (c) the local energy levels within the optical gap.

inwards by 0.97% a_o. The total energy gain is 0.205 eV, i.e. practically the same as that obtained for the 40 atom supercell, and the absorption energy is 0.80 eV. That is, the 40-atom supercell is large enough for the semi-quantitative polaron modelling.

4.3. Bound electron polaron

Along with the self-trapped (intrinsic) electron polaron discussed above, we have also modelled the electron polaron (Nb^{4+}) bound to the *nearest* neighbor Mg^{2+} impurity (Fig. 4(b)). As an initial guess, we used the atomic configuration for the self-trapped electron polaron described above. However, the Coulomb field of Mg impurity results in a considerable additional relaxation of three O atoms nearest to both Nb and Mg ions. The optimized displacements of these three O atoms directed towards the Mg atom along the relevant cubic faces are 1.84% a_o which gives the additional energy gain of 0.15 eV. It means that the total relaxation energy turns out to be 0.36 eV, i.e. the bound electron polaron is much more stable than the self-trapped electron polaron.

As a result of the asymmetric O relaxation, similarly to the self-trapped electron polaron, $\approx 0.5e$ is localized on the central Nb atom. In the bound electron polaron the degeneracy of Nb 4d atomic orbitals, having t_{2g} symmetry and consisting mainly of Nb $4d_{xy}$, d_{xz} and d_{yz} atomic orbitals (where an electron polaron is localized), is lifted (Fig. 4(c)). According to our calculations, the absorption energy of the bound electron polaron exceeds by 0.1 eV that for the self-trapped electron polaron and thus equals 0.88 eV (Table 1).

5. Conclusions

Based on both the similarity of our optical absorption

measurements in the IR region to the 1 eV band observed in $LiNbO_3$ [5] and the results of our INDO calculations, we ascribe the optical absorption around 0.8 eV to the intrinsic self-trapped electron polarons localized on the regular Nb atoms. We estimate the rise time of the relevant infrared transient absorption to be very fast (≤ 0.8 ps). Our INDO calculations predicted the absorption bands due to bound hole polarons at $\approx$ 1 eV. We have observed, indeed, the relevant transient absorption at 1.1 eV. (The slight difference of optical absorption in different samples is likely due to trapping of electron and hole polarons at different impurities and/or lattice defects.) Our predictions for polarons could be checked by means of the ESR measurements. We estimate the activation energy for the electron polaron migration to be quite small, about 0.1 eV (half the polarization energy). That is, the electron polarons should be much much less stable compared to the hole polarons. The luminescence energy of $KNbO_3$ (and other ABO_3 perovskites) were calculated by us in Ref. [32]. We have demonstrated there that the 2.2 eV luminescence band very likely arises as a result of the radiative recombination of the nearest electron-hole polarons forming the triplet exciton. In this study we estimated its quenching energy as 0.05 eV.

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