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Reduction-induced polarons and optical response of Mg-doped LiNbO₃ crystals

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ABSTRACT We studied the visible and IR dispersion of absorption coefficient and refractive index for congruent LiNbO₃ and Mg : LiNbO₃ crystals before and after chemical reduction at different annealing temperatures. The concentration of Mg in Mg : LiNbO₃ samples was just below or above the photorefractive threshold. The reduction-induced changes in the absorption coefficient reveal the formation of polarons typical for doped LiNbO₃ crystals. It was shown that the polaron concentration is maximal when the Mg concentration is just below the photorefractive threshold and the annealing temperature is near 500 °C. This temperature is optimal for the most efficient polaron formation at all considered concentrations of Mg. The fitting of the experimental absorption dispersion curves indicates that intermediate polarons are formed in LiNbO₃ : Mg crystals preferably. The spectral dependence of transmission for samples of lithium niobate of various thicknesses was studied. The results indicate that there are spatial regions with much greater absorption than that of bulk crystals. We assume that, in general, polarons are localized in thin near-surface regions. The spectral dependence of the refractive index in the vicinity of the phonon absorption edge indicates some essential changes of the phonon subsystem taking place after reduction. The infrared contribution into the dispersion of the dielectric function real part increases considerably after reduction.

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1 Introduction

Lithium niobate crystals (LiNbO₃) are widely used in different areas of modern physics: electro–optics, solid state physics, non-linear optics, holographic storage of information, etc. At present, a new interest to LiNbO₃ is stimulated by the study of small polarons and bipolarons [1–3]. Besides of fundamental aspects, polarons are very perspective objects for practical purposes. Polaron states can be used in two-color holography as photoactive centers [4–8]. In two-color storage devices, recording is realized by using two pumps of the same frequency in the presence of the gating pump of a higher frequency. Readout is performed by an IR or a red pump. Since

photons of the readout pump have insufficient energies for the electronic transitions from deep levels, these techniques are non-volatile methods.

Apart from applications, there are important fundamental problems concerning the electron–phonon interaction and interaction of electromagnetic field with polaron states. For example, photorefractivity, which is caused by metastable polarons, is of considerable interest [9]. Another interesting and insufficiently explored problem is investigation of phonon spectra under excitation of polarons. Formation of polarons should lead to a change in the parameters of the phonon subsystem. Also, local lattice vibrations may appear [10] and variation of phonon anharmonicity can cause additional new effects.

There are a lot of methods to induce polarons in lithium niobate: one- and two-photon absorption [11], irradiation by high-energy pulsed electronic beams [12], chemical reduction [1, 13–15]. As a result, electrons appear in the conduction band and are localized on defect or regular ions due to electron–phonon interaction. In this paper, we consider reduced LiNbO₃ crystals, which were doped by magnesium. It is well known that doping of LiNbO₃ influences strongly its defect structure [17–20]. Consequently, doping also influences the type of polarons. For instance, Sweeney et al. [19] found a type of resonances in LiNbO₃ : Mg, which are missing in nominally pure congruent lithium niobate, but which are observed in nominally pure stoichiometric crystals. Up to now, there are a number of works devoted to the investigation of polarons in Mg-doped chemically reduced lithium niobate. Nevertheless, the influence of reduction conditions, as well as the influence of the doping concentration, was not studied systematically. Such investigation may be useful for fabrication of lithium niobate crystals with polaronic-type conductivity for other practical purposes. In this paper, we pursue the following aims:

1. To study the optical response (dispersion of the real part of permittivity and the absorption coefficient) of differently doped LiNbO₃ : Mg crystals after chemical reduction procedures at different temperatures.

2. To explore the parameters of polarons in reduced LiNbO₃ : Mg crystals at various Mg-concentrations and reduction temperatures.

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Section 2 contains a description of the experimental setups and characteristics of the used samples. Experimental results on absorption spectra and measurements of the real part of the permittivity are discussed in Sect. 3. The most important conclusions are formulated in Sect. 4.

2   Experimental

2.1   *Samples*

We carried out experiments for four samples of lithium niobate, three of them doped by magnesium ($LiNbO_3$: Mg). Bulk $LiNbO_3$: Mg single crystals were grown by the Czochralski technique. The starting material was close to the congruent melting composition [21] with the ratio $Li/Nb = 0.942$. The specimens were doped by magnesium at molar concentrations 0, 4.4, 5.1, and 7.1 mol %. The spatial variation of Mg concentration in the samples was within ± 0.01–0.03 mol %. Measurements of the impurity concentration distribution within each crystal were made by X-ray microanalysis using Camebax SX-50 with a high relative accuracy. However, the absolute error of the average Mg-concentration was sufficiently larger and sometimes exceeded 0.2 mol %. The typical overall dimensions of starting samples were about 1 cm^3. A number of plates were cut from the samples. The typical thickness of the plates was about 1 mm. Then, every three places cut from crystals with different Mg-content were chemically reduced together. The reduction procedure consisted of the following: plates were loaded into a furnace and annealed in vacuum at $P = 10^{-5}$ Torr. The samples were heated to the temperature T_{RED} during the first three hours, kept at constant temperature for more than three hours and, finally, cooled down to the room temperature for three hours. Reduction temperatures T_{RED} were chosen equal to 400, 500, and 600 °C, the undoped sample was reduced at 500 °C (see Table 1). Also, we had one plate of thickness 80 μm, placed on BaF_2 substrate. This plate was cut from a doped sample ($C_{Mg} = 4.4$ mol %), which was reduced at 500 °C.

2.2   *Experimental equipment*

In order to measure refractive indices in the visible range, we applied the well-known prism method (PM) using goniometer. The total absolute error of the data obtained by PM was equal to ± 0.0002. Measurements in the IR range were performed using nonlinear optical methods, namely, second-harmonic generation (SH) at 1.06–1.26 μm and spontaneous parametric down-conversion (SPDC) at 2–5 μm [22, 23]. Both methods are based on the strong dependencies of signal intensities on the phase matching conditions. It enables one to determine the wave vectors $k_i = 2\pi n_i \nu_i$ (ν_i-wavenumber in cm^{-1}) and refractive indices n_i of idle waves in the crystal transparency region if the corresponding values in the visible range are known and the position of maximum of the angular distribution of the visible signal intensity is measured. To be precise, these methods give the values of $\sqrt{\varepsilon'}$, where ε' is the real part of the dielectric constant [36]. In the transparency range, $\varepsilon'' \ll \varepsilon'$, so $\sqrt{\varepsilon'} \simeq n$. The absolute error of n_o values obtained by these methods grows with wavelength, being near 0.0005 at 1–2 μm and approaching 0.002 at 5 μm.

To obtain the absorption coefficient, we have measured transmission in the visible and IR ranges at room temperature for all our samples of reduced $LiNbO_3$: Mg. Measurements in the spectral interval 2–8 μm were made by means of Fourier spectroscopy with the spectral resolution of 1.5–2 cm^{-1}. A standard spectrophotometer was used for the measurements in the visible range. In the near-infrared range (0.8–2.4 μm), measurements were done by the use of a special spectrophotometer with a monochromatic selection of incident radiation. Using the obtained data on transmission, we calculated the dispersion of the absorption coefficient for all of our samples. Anisotropy was not taken into account. It can be shown that the account of birefringence is insignificant [23]. To calculate and avoid the reflection-induced losses, we used our data on the refractive index.

3   Results and discussion

3.1   *Absorption spectra*

Examples of absorption spectra are shown in Fig. 1 for samples reduced at 500 °C. Here one can see three peaks, located near 0.5, 1.2, and 5.7 μm [16]. The peak marked by one arrow was attributed by Schirmer et al. to bipolarons localized at neighboring sites: defect Nb ion occupying Li-vacancy (Nb_{Li}) and Nb ion at its regular site (Nb_{Nb}) [1]. It is well known that defects Nb_{Li} disappear under doping by Mg or other impurities [18, 24] if the dopant concentration is large enough. Commonly, it is supposed that this threshold concentration for Mg is equal to 5 mol % (photorefractive threshold) in the case of congruent $LiNbO_3$ [18]. So, at concentrations above the threshold, there can not exist bipolarons, but new polarons can appear. Intraband hopping of these polarons is responsible for the peak marked by two arrows in Fig. 1. Different assignments of this band have been made [19, 20]. Faust et al. [20] gave a conclusive proof that this band arises due to the hopping of polarons localized at regular Nb_{Nb}. The peak near 5.7 μm is not caused by polaron transitions, since its half-width is too narrow. From the first work by Barker and
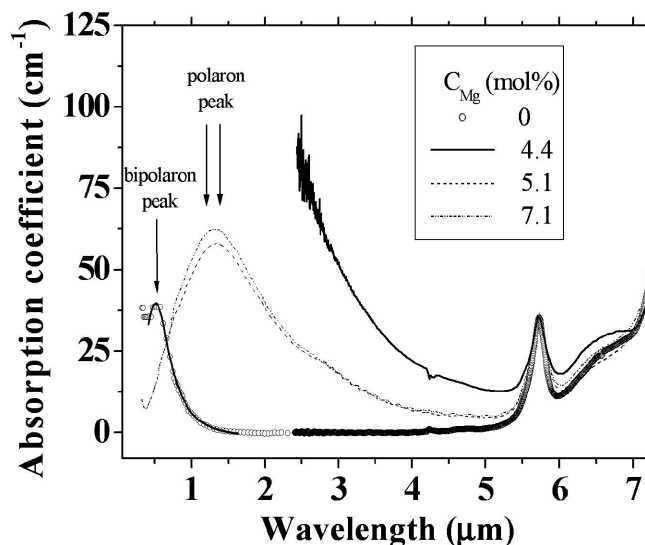

FIGURE 1   Absorption spectra of $LiNbO_3$ and $LiNbO_3$: Mg crystals reduced at 500 °C

Loudon [25], it is usually attributed to a bound two-phonon state. Nevertheless, we found that there are quasi-periodical phonon iterations near this peak with typical periods of the order of lowest LO-phonon frequencies [23]. This fact points at possible electron–phonon origin of this peak. It is important to note that the observed modulation is quite analogous to the results by Brebner et al. [26]. They found a similar narrow peak with phonon iterations in SrTiO₃ and supposed that it was caused by electrons localized within the bounds of one unit cell. Apparently, analogous scenario is realized in LiNbO₃, and it is necessary to make a further testing of this hypothesis.

To obtain the parameters that characterize polarons, we made a fit of our absorption curves by analytical expressions. We supposed that the considered absorption band occurs due to intraband polaron hopping. The form of contribution to absorption due to such polaronic transitions was studied theoretically in [27–30]. Reik [27, 28] considered the photon-assisted hopping of small polarons between next-to-neighbor sites. Firsov [30] expanded the theory of small polaron absorption to the cases when the conduction band $\Delta\varepsilon$ is rather wide and the hopping to second and higher neighbors can also occur. Firsov's theory is based on three parameters: $\eta_1 = J/E_a$, $\eta_2 = J^2/\hbar\omega_0\sqrt{kTE_a}$, and $\eta_3 = J^2/kTE_a$, where J is a two-center overlap integral, which is proportional to $\Delta\varepsilon$; E_a is a thermal activation energy of hopping; T is the temperature. If $\eta_1 < 1$, then small polarons can exist. The second parameter, η_2, is a measure the polaronic system adiabaticity. If $\eta_2 > 1$, then the electron follows the nuclei adiabatically. Also, under the condition $\eta_3 < 1$, polarons hop between neighboring lattice sites. Polaron hopping can occur at quite large distances if the theory parameter η_3 is sufficiently large: $\eta_3 > 1$. This regime is called hopping under "relay-race" mechanism.

To calculate the absorption curve in this case, we used the expression

$$\mathrm{Re}\,\sigma(\omega) = n_\mathrm{p}eu_0\frac{\omega_1}{2\omega_2}\int\limits_0^\pi\frac{\mathrm{d}k_y}{\pi}\int\limits_0^\pi\frac{\mathrm{d}k_z}{\pi}$$
$$\times\left\{1-\left[\frac{\omega-\omega_2}{\omega_1}+\cos k_y+\cos k_z\right]^2\right\}^{1/2}, \qquad (1)$$

obtained in [30] for the real part of the electric conductivity $\sigma(\omega)$ in cubic crystals. Here, $\omega_1 \equiv 2J/\hbar$ is responsible for the linewidth of the spectral maximum, $\hbar\omega_2 \equiv 2E_\mathrm{p}$ is the energy position of the peak of $\mathrm{Re}\,\sigma(\omega)$. The energy E_p determines the polaron shift between the narrow ground polaron band and the wide electron conductivity band, $E_a = E_\mathrm{p}/2$, n_p is polaron concentration, e is the electron charge, and the coefficient $u_0 = ea^2/\hbar$ is of the same dimension as the charge mobility. The real part of the electric conductivity is directly connected with the polaron contribution to the absorption coefficient:

$$\alpha(\omega)_\mathrm{pol} = \frac{4\pi}{nc}\mathrm{Re}\,\sigma(\omega), \qquad (2)$$

where n is the refractive index. We used (1) and (2) to fit the reduction-induced absorption obtained in experiments. One of the fitting curves is cited as an example in Fig. 2 (dot-

ted line). We obtained the polaron shift $E_\mathrm{p} = 0.47\,\mathrm{eV}$ and the electronic transfer integral $J = 0.145\,\mathrm{eV}$. We found that the normalized experimental and calculated absorption curves coincide very well in the low-frequency range. Next, we conclude that the obtained parameters E_p and J are the same for all Mg-doped reduced samples and the parameters of Nb_Nb-polarons do not depend on the temperature conditions of reduction. The calculated parameters η_j ($j = 1, 2, 3$) are $\eta_1 = 0.6$, $\eta_2 = 11$, and $\eta_3 = 3.5$. Therefore, one can conclude that small polarons are responsible for the absorption peak, the adiabatic approach is valid, and the relay-race mechanism of hopping is realized. As is obvious from Fig. 2, there is no agreement between the fitting and experimental curves at high wavenumbers; experimental curves are asymmetric. Apparently, it is a typical situation for small polarons. There are a lot of works noting this. For example, the very high asymmetry of polaronic lineshape was found in $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{NiO}_{4+\Delta}$ [31, 32]. Schirmer et al. [1] found an asymmetry of the polaronic peak near $0.76\,\mu\mathrm{m}$ in LiNbO₃. In [1], it was pointed out that this effect is due to disorder in the distribution of Nb_Li-defects. Bryksin et al. proved theoretically [33] that disorder may influence the shape of the absorption curve. It is not unlikely that disorder in the distribution of Nb_Nb ions causes this asymmetry. Another possible reason of this asymmetry is the existence of Nb_Li-polarons in our samples due to the formation of Nb_Li-defects in Mg-doped crystals after reduction [23].

Nevertheless, there can exist another reason of this discrepancy between theory and experiment, which seems to be more probable. As it was proved by Emin [34], frequency dispersion of polaronic absorption has an asymmetric lineshape in the case of large or intermediate polarons. In this case, dispersion of absorption coefficient is described by the following expression (three-dimensional polarons):

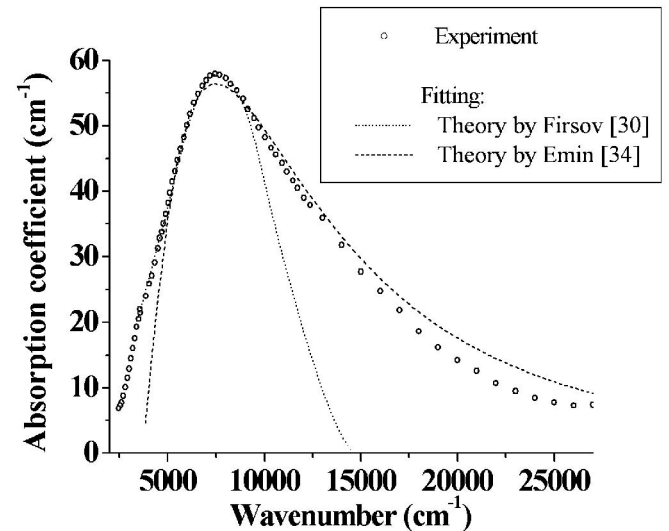$$\alpha(\omega) = \frac{128n_\mathrm{p}\pi e^2}{3m\omega c} \times \frac{(kR)^3}{\left(1+(kR)^2\right)^4}, \qquad (3)$$

FIGURE 2   *Points*: dispersion of the absorption coefficient for LiNbO₃ : Mg crystal ($C_\mathrm{Mg} = 5.1\,\mathrm{mol\,\%}$, $T_\mathrm{RED} = 500\,°\mathrm{C}$). *Dotted line*: approximation by the theory for small polarons [30]. *Dashed line*: approximation by the theory for large polarons [34]

where n_p is polaron concentration, e is the electron charge, m is the effective mass of a photoinduced electron, R is the polaron radius, $k \equiv \sqrt{2m(\hbar\omega - 3E_{Lp})}/\hbar$ is the polaron wave vector, E_{Lp} is the lowering of the electronic energy. One can see a good agreement between the numerical fit and the experimental results. It should be noted that the theory by Firsov describes very well the low-frequency wing of the absorption curve while Emin's theory is worse in this wavenumber region. The effective mass of photoinduced carriers was taken equal to the electron mass in vacuum. We obtained the $n_p \approx 1.28 \times 10^{18}$ cm^{-3}, $E_{Lp} \approx 0.568$ eV, and $R \approx 1.5$ Å. Since the distances between the ions of the crystal lattice are of the order of several ängströms, one can conclude that most likely intermediate polarons are formed in LiNbO$_3$ crystals. Also it should be pointed, that Faust et al. [20] have found an essential temperature dependence of absorption spectra, but theory of large polarons doesn't predict that. Probably, this fact may point to intermediate size of polarons in lithium niobate.

Another interesting conclusion follows from the comparison between the absorption curves obtained for differently reduced Mg-doped samples. Although they have the same shape, their amplitudes are dependent on the Mg-concentration and reduction temperatures. For the same reduction conditions, the maximum absorption occurs for the doping concentration of 4.4 mol %, which is just below the photorefractive threshold. For the same Mg-content, the maximum absorption is achieved at reduction temperatures near 500 °C. This feature has not been mentioned previously. Bordui et al. [15] studied the optical absorption of nominally pure LiNbO$_3$ crystals being reduced under nitrogen/hydrogen atmospheres at temperatures 350–750 °C. They found that absorption increases monotonously when the temperature rises. Nevertheless, one can see from Table 1 that the temperature dependence of the absorption coefficient at fixed wavelengths has a non-monotonous character for each Mg-doped lithium niobate. Probably, it is due to doping by magnesium. Maximum absorption coefficients are observed at 500 °C for all LiNbO$_3$: Mg crystals. Concentration of polarons is directly proportional to the absorption coefficient: $n_p \propto \alpha$. It is known that under reduction, oxygen ions leave crystal and free electrons appear in the conduction band being localized at displaced ions [1]. So, we can conclude that there is an optimal temperature T_{opt} between 400–600 °C, at which chemical reduction, resulting in the release of elec-

trons, is most effective. The non-monotonous temperature dependence may point to the existence of two processes that influence the polaron concentration differently. For instance, after T_{opt}, the activation mechanism of an electron departure from a crystal can predominate. At high temperatures, $T > 500$ °C, this process can become more important than the process of polaron localization. Electrons would be emitted from the crystal surface into vacuum, and the resulting polaronic concentration in a crystal would decrease.

Also, we found interesting features in the dependence of absorption on the sample thickness. Dispersions dependencies of absorption coefficients obtained from the transmission spectra are shown in Fig. 3. Absorption in a thin reduced sample ($d_1 = 80$ μm) is much greater than that in thicker crystals. It is important to note that dispersion dependencies of absorption in the reduced sample ($d_1 = 80$ μm) and non-reduced sample ($d_4 = 8$ μm) coincide very well in the region 1200–1800 cm^{-1} (see the inset in the right-hand part of Fig. 3). Also, dispersion curves of absorption for reduced samples (thicknesses $d_2 = 600$ μm and $d_3 = 1300$ μm) coincide in the same range. We suppose that the origin of such behavior is the existence of specific spatial near-surface regions. Apparently, these regions are characterized by much greater lattice absorption than that in the bulk crystal. In the insets, one can see a fine structure in the range 1000–2000 cm^{-1} in crystals of various thicknesses. Probably, this is a LO-phonon iteration of the main peak at 1740 cm^{-1} [23]. It is obvious that this modulation is more pronounced in the sample with the thickness 80 μm. Also, it seems that absorption of light by polarons is greater in the thinnest sample. We could not measure the whole dispersion curve for a thicker reduced sample due to very low transmission in the region 4000–12 000 cm^{-1}, but the results in the range 2000–4000 cm^{-1} justify the previous statement. In the left-hand inset, we cite the difference between the absorption values of the reduced crystals with

Mg-content C_{Mg}, (mol.%)	Thickness d, (cm)	Reduction temperature T_{RED}, (°C)	Wavelength λ, (μm)	Absorption coefficient $\alpha(\lambda)$, (cm^{-1})
0	0.1	500	0.52	38
4.4 ± 0.1	0.008	500	2.4	147
	0.008	500	1.3	277
	0.06	500	2.4	86
	0.48	600	1.3	21
5.1 ± 0.1	0.1	500	1.3	58
	0.1	600	1.3	21
7.1 ± 0.2	0.1	400	1.3	13
	0.1	500	1.3	63
	0.16	600	1.3	18

TABLE 1 Parameters of chemically reduced LiNbO$_3$: Mg crystals
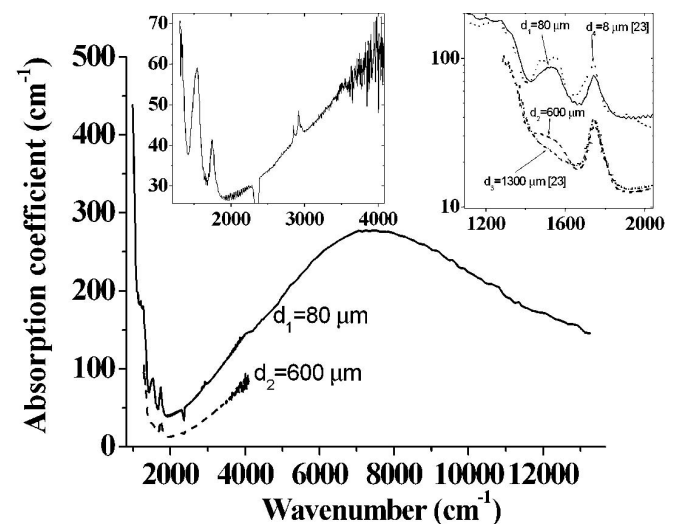
FIGURE 3 Absorption spectra of LiNbO$_3$: Mg crystals of various thickness d_j reduced at 500 °C. *Right inset:* absorption spectra of LiNbO$_3$: Mg crystals ($C_{Mg} = 4.4$ mol %): $j = 1$–3 – for the samples reduced at 500 °C, $d_1 = 80$ μm, $d_2 = 600$ μm, $d_3 = 1300$ μm. $j = 4$ – for the non-reduced undoped congruent sample, $d_4 = 8$ μm. *Left inset:* the difference between the absorption coefficients for samples No. $j = 1, 2$

$d_1 = 80\,\mu m$ and $d_2 = 600\,\mu m$. It seems that decreasing the thickness results in the increase of both lattice and polaronic contributions. It is likely that an increase of polaronic intraband absorption is caused by accumulation of polarons in the near-surface region. It seems that distributions of polarons have a non-homogeneous character in bulk of reduced samples.

3.2 *Refractive indices*

The real part of the dielectric function $\varepsilon'(\nu)$ should also be changed after chemical reduction. It is obvious to expect these changes to be small, since concentration of polarons is not high. To obtain these small variations of $\varepsilon'(\nu)$, we made use of the difference method, which has a higher sensitivity. The difference between the squares of refractive indices $\Delta\varepsilon'_{o,e}(\nu) \equiv n^2_{o,e}(\nu)_{REDUCED} - n^2_{o,e}(\nu)_{UNREDUCED}$ in the transparency region of the crystals (or in the region of small absorption) characterizes the variation of dielectric function after a chemical reduction. Using this method, one can obtain the contribution of polarons to $\varepsilon'(\nu)$, as well as the contribution of other reduction-induced changes in crystals. Because of probable non-homogeneous distribution of polarons in crystals, we measure certain effective changes of average dielectric function of reduced crystals only. Apparently, it should lead to spreading of angular SPDC spectra.

We considered the results of PM and SPDC-measurements of two samples of LiNbO$_3$: Mg with the same Mg-content 7.1 mol %. The reduced sample was annealed at 600 °C. Further, we determined the spectral dependence of $\Delta\varepsilon'_o(\nu)$ (for ordinarily polarized waves) under fixed Mg-concentration. Figure 4 shows the spectral dependence $\Delta\varepsilon'_o(\nu)$. One can see that $\Delta\varepsilon'_o(\nu)$ looks like a horizontal line in the visible range for $\nu > 15\,000\,\text{cm}^{-1}$ ($\lambda < 0.7\,\mu m$). Deviations of the experimental points from zero are very small. Apparently, this range is far from electron and phonon resonances, the reduction-induced changes are very small and do not depend on frequency strongly. The reduction-induced contribution should increase in the vicinity of lattice resonances. Indeed, one can see that $\Delta\varepsilon'_o(\nu)$ departs strongly from zero in the range $\nu < 8000\,\text{cm}^{-1}$ ($\lambda > 1.3\,\mu m$). This is not a contribution of polaronic intraband transitions (hopping). To prove this, we calculated the hopping contribution of polarons $\Delta\varepsilon'_{high} = 4\pi\,\text{Im}\,\sigma(\omega)/\omega$, taking into account high-frequency conductivity only. We made a numerical Kramers–Kronig transform,

$$\text{Im}\,\sigma(\omega) = \frac{2\omega}{\pi}\int_0^\infty \frac{\text{Re}\,\sigma(z)\,dz}{z^2 - \omega^2}\,, \qquad (4)$$

where $\text{Re}\,\sigma(\omega)$ is described by (1), which is applicable for the case of small polarons. Also, we calculate $\Delta\varepsilon'_{high}$ for the case of intermediate polarons, using (2), (3), and (4). These contributions are shown in the inset of Fig. 4. In any case, it is clear that high-frequency contributions are very small in comparison with the observed changes both for small polarons and for intermediate polarons. Also, $\Delta\varepsilon'_{high}$ is so small in comparison with our experimental error that we can not resolve this kind of contribution in our measurements of ε'.
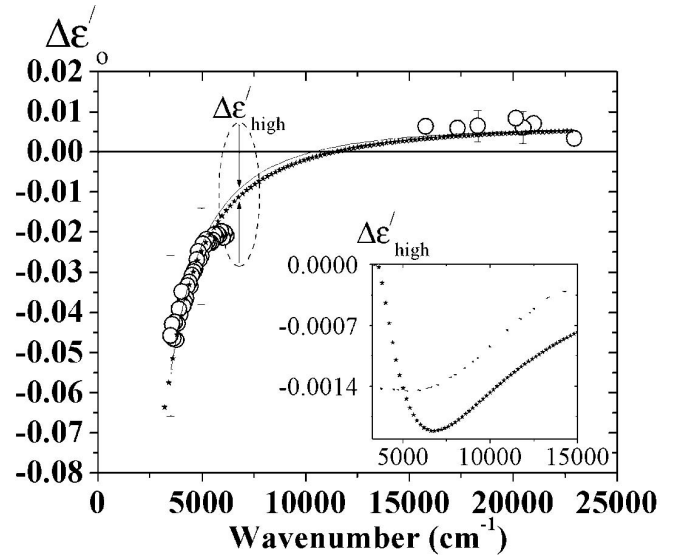

FIGURE 4 Dispersion dependence of the variation in dielectric function for ordinary polarized waves after chemical reduction for LiNbO$_3$: Mg crystal ($C_{Mg} = 7.1$ mol %, $T_{RED} = 600$ °C). Calculated high-frequency polaronic contributions $\Delta\varepsilon'_{high}$ are shown in the inset. *Dotted line*: the case of small polarons. *Asterisks*: the case of intermediate polarons

The observed changes at $\nu < 8000\,\text{cm}^{-1}$ can not be explained by the heating of crystal by laser irradiation under exposure either. A direct measurement of the crystal temperatures shows only a weak heating approximately up to 1 °C. Using the data of Schlarb et al. [18], we estimated the variation of refractive indices for all frequencies of the interacting pumps. These variations turn out to be insufficient to explain the observed reduction induced variation of $\varepsilon'(\nu)$ at the long-wave edge. Apparently, this effect takes place due to a contribution of polar phonons, as $\Delta\varepsilon'_o(\nu)$ decreases in the vicinity of phonon frequencies. The dependence $\Delta\varepsilon'_o(\nu)$ looks like a typical oscillator contribution. It can be interpreted as a result of effective enhancement of phonon oscillator strengths or new local phonon modes due to the formation of polarons. Also, we should point at another probable reason of this oscillator-type behavior for the dielectric function, measured by SPDC-technique. In [23], in the difference SPDC spectra, we have found a small resonance near 3.5 μm for all unreduced Mg-doped samples. It is not unlikely that the same resonance but with smaller amplitude has been observed in the previous work. It is interesting that this resonance is absent in the absorption spectra. The physical origin of this peak remains unclear.

We estimated the observed enhancement using the Sellmeyer formulas. The refractive index for the unreduced sample was calculated according to the relation

$$n^2_{UNREDUCED} = A - \frac{B}{C - 1/\nu^2} - D/\nu^2\,, \qquad (5)$$

where the term A is the plasmon contribution, the second term describes the contribution from electronic interband transitions and the third term is the contribution from dipole-active phonons. We obtained $A = 4.889$, $B = 1.03 \times 10^{-9}$, $C = 5.7 \times 10^{-10}$, $D = 3.37 \times 10^6$. To fit $\Delta\varepsilon'_o(\nu)$ dependence,

we applied the expression neglecting the contribution from interband electronic transitions:

$$\Delta\varepsilon'_o(\nu) = \Delta A - \Delta D/\nu^2 , \qquad (6)$$

where $\Delta A = 7 \times 10^{-3}$, $\Delta D = 7.5 \times 10^5$.

To explore this problem in detail, a further study of Raman scattering seems to be a very attractive way. At present, there are experimental works concerning this problem relative to other crystals [35] but there are no works concerning reduced lithium niobate with polaronic conductivity.

4   Conclusion

We have measured absorption coefficients and refractive indices for chemically reduced $LiNbO_3$: Mg crystals containing polarons. Samples were reduced at various temperatures from $400\,^\circ\mathrm{C}$ to $600\,^\circ\mathrm{C}$ and differed in the Mg-content. The influence of the reduction procedure as well as the influence of Mg-doping on the absorption spectra of lithium niobate was studied. It was shown that the main parameters of Nb_{Nb}-polarons do not change under the variation of reduction temperature T_{RED} and the Mg-content. Numerical fitting indicates that intermediate polarons are formed preferably. Also, we have proved that the concentration of polarons depends considerably on the reduction temperature. It was shown that the concentration of polarons has a maximum value at $T_{RED} = 500\,^\circ\mathrm{C}$ for all Mg-doped crystals. Investigation of transmission for samples with various thicknesses shows the existence of spatial areas characterized by higher absorption. We analyzed the changes in the real part of the dielectric function, $\Delta\varepsilon'_o(\nu)$, arising due to the formation of polarons. An oscillator-type contribution to $\Delta\varepsilon'_o(\nu)$, which increases in the vicinity of phonon modes, was found. The obtained behavior of $\Delta\varepsilon'_o(\nu)$ was interpreted as a modification of phonon spectra under reduction and formation of polarons.

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