Functional Materials 11, No.3 (2004) 

# Calculations of the dipole electronic polarizability of ions in $LiNbO_3$ at temperature range (273 ÷ 873)K

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Using the modified well-known Lorenz-Lorentz equation, the dipole electron polarizabilities of ions in stoichiometric $LiNbO_3$ within a wide temperature range (273 to 873 K) have been calculated. The results obtained can be used in computer simulations of peculiarities of structure ordering and dynamics of ions in $LiNbO_3$.

С использованием модифицированного уравнения Лорентц-Лоренца проведены вычисления зависимости дипольной электронной поляризуемости ионов в стехиометрическом кристалле $LiNbO_3$ в диапазоне температур (273 ÷ 873)К. Полученные результаты могут быть использованы для проведения компьютерного моделирования особенностей структурного упорядочения и динамики ионов в $LiNbO_3$.

Today, lithium niobate ($LiNbO_3$) crystals are among the most important ferroelectric materials for practical applications due to its electrooptic, electroacoustic and photorefractive properties. Although this material is a very popular object of scientific investigation, some peculiarities of its structure dynamics at temperatures above 293 K are not explained yet. It is well known that the computer simulation is very informative when being applied to different dielectric materials [1]. For example, this method was used to study localization of $H^+$ ions in $LiNbO_3$ crystal at room temperature [2]. For the successful application of this method, it is necessary to know as completely as possible the electric characteristics of ions in the crystal, such as their effective charges and electron dipole polarizabilities (EP) as well as the short-range potential parameters of the pair ionic interaction [3].

The main aim of this work is to calculate the EPs of ions in stoichiometric $LiNbO_3$ within a wide temperature range (273 to 873 K). To that end, a method was used based on the application of modified well-known Lorenz-Lorentz equation :

$$\frac{n_k^2 - 1}{n_k^2 + 2} = \frac{1}{3\varepsilon_o}\sum_{i=1}^{S} N_i \cdot b_{ik} \cdot \alpha_i,$$

where $n_k$ is the crystal refractive index for electric component of light wave **E** directed along the **k** direction; $b_{ik}$, a correction for action of dipole moments of ions induced due to the light wave; $S$, the number of structurally non-equivalent ions in the crystal; $N_i$, the volume concentration of the $i$-th kind of ion [4]. This method was successfully applied before to stoichiometric $LiNbO_3$ [4] and to $\alpha$-$LiIO_3$ [5] crystals at room temperature.

To apply this method in the EP calculations in wide temperature range, it is necessary to know the data on the temperature dependences of the ion coordinates, lattice constants and on refractive indices of the crystal. To that end, known the structural data on temperature effect on $LiNbO_3$ structure [6], but there is no information on the temperature dependence of refractive indices for stoichiometric $LiNbO_3$ in far IR band. Similar data are known for $LiNbO_3$ crystals of nearly congruent composition

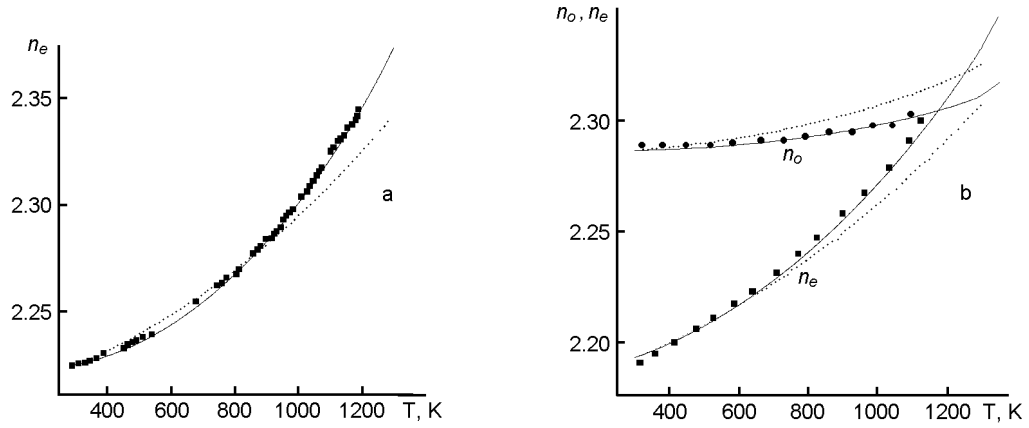


Fig. 1. Temperature dependences of refractive indices for (a) nearly congruent $LiNbO_3$ crystals at $\lambda = 546$ nm [7] and (b) nearly stoichiometric ones at $\lambda = 633$ nm [8]. Points are experimental data; dotted lines, approximations according to [9] data; solid lines, approximations according to recalculated parameters of Sellmeier equation.

($\lambda = 546$ nm) [7] and nearly stoichiometric one ($\lambda = 633$ nm) [8]. To describe the ordinary ($n_o$) and extraordinary ($n_e$) refractive indices of $LiNbO_3$ as functions of temperature, wavelength, and crystal composition, the generalized Sellmeier equation was proposed before [9]. In final form, this equation can be written as:

$$n_i = \frac{50 + c_{Li}}{100} \frac{A_{0,i}}{(\lambda_{0,i} + \mu_{0,i}F)^{-2} - \lambda^{-2}} + \frac{50 - c_{Li}}{100} \frac{A_{1,i}}{(\lambda_{1,i} + \mu_{1,i}F)^{-2} - \lambda^{-2}} - A_{IR,i}\lambda^2 + A_{UV},$$

where $c_{Li}$ is the $Li_2O$ content in the crystal (in mole %); $\lambda$, the wavelength; $A_{0,i}$, $A_{1,i}$, $A_{IRi}$, $A_{UV}$, $\lambda_{0,i}$, $\lambda_{1,i}$, $\mu_{0,i}$, $\mu_{1,i}$, the fitting parameters presented in the Table; $F$, a function of temperature defined as $F = f(T) - f(T_0)$, where $T_0 = 297.5$ K and

$$f(T) = T^2 + 4.0238 \times 10^5 [\coth\left(\frac{261.6}{T}\right) - 1]. \quad (1)$$

Unfortunately, this equation is valid only in the 50 to 600 K temperature range [8]. So, the former results of EP calculations in $LiNbO_3$ were obtained only for the same temperature range [9].

Nevertheless, the testing of the Sellmeier equation applicability (under modification of some its parameters) to the experimental data reported in [7, 8] has shown that a successful approximation can be obtained up to 1000 K (Fig. 1). The recalculated parameters of Sellmeier equation are presented in the Table, too. According to the new set of these parameters, the temperature dependences of refractive indices for stoichiometric $LiNbO_3$ crystal at $\lambda = 1200$ nm were calculated (Fig. 2). These data allowed us to calculate the possible sets of the EPs of ions in stoichiometric $LiNbO_3$ crystal in the wide temperature range 273 to 873 K. In what follows, the EP of $Li^+$ ion is assumed to be isotropic and temperature-independent: $\alpha_{Li} = 0.032 \cdot 10^{-24}$ cm$^3$ [4]. The EP of $Nb^{5+}$ ion ($\alpha_{Nb}$) is taken to be isotropic as

Table. Parameters of the generalized Sellmeier equation according to [9] and values thereof recalculated in this work (indicated by atrerisks)

| $n_o$ | $n_e$ | $n_o$ | $n_e$ |
|---|---|---|---|
| $A_{0,o} = 4.5312 \cdot 10^{-5}$ | $A_{0,e} = 3.9466 \cdot 10^{-5}$ | $A_{IR,o} = 3.6340 \cdot 10^{-8}$ | $A_{IR,e} = 3.0998 \cdot 10^{-8}$ |
| $\lambda_{0,o} = 223.219$ | $\lambda_{0,e} = 218.203$ | $A_{UV} = 2.6613$ | $A_{UV} = 2.6613$ |
| $A_{1,o} = 2.7322 \cdot 10^{-5}$ | $A_{1,e} = 8.3140 \cdot 10^{-5}$ | $\mu_{0,o} = 2.1203 \cdot 10^{-6}$ | $\mu_{0,e} = 7.5187 \cdot 10^{-6}$ |
| | | $\mu_{0,o} = 1.320 \cdot 10^{-6}$ * | $\mu_{0,e} = 8.80 \cdot 10^{-6}$ * |
| $\lambda_{1,o} = 260.26$ | $\lambda_{1,e} = 250.847$ | $\mu_{1,o} = -1.8275 \cdot 10^{-4}$ | $\mu_{1,e} = -3.80432 \cdot 10^{-5}$ |
| | | | $\mu_{1,e} = -1.480 \cdot 10^{-4}$ * |

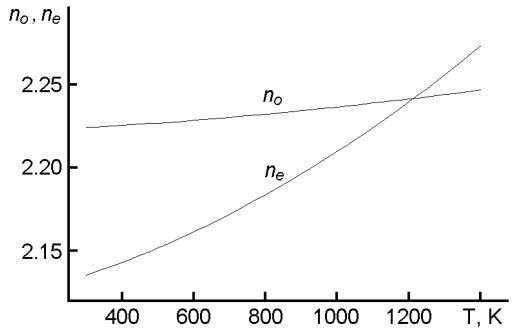


Fig. 2. Calculated temperature dependences of refractive indices for stoichiometric $LiNbO_3$ crystal at $\lambda = 1200$ nm.

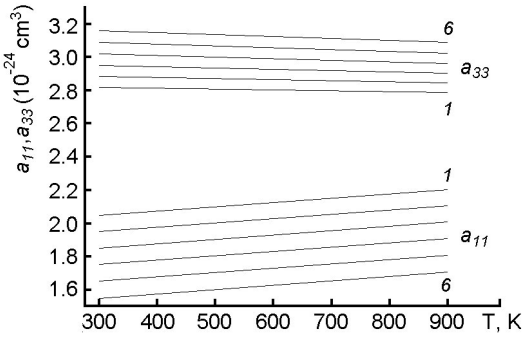


Fig. 3. Temperature dependences of main components $\alpha_{11}$ and $\alpha_{33}$ of the $O^{2-}$ ion EP tensor in stoichiometric $LiNbO_3$ for some $\alpha_{Nb}$ values ($\times 10^{-24}$ cm$^3$): 0 (*1*); 0.1 (*2*); 0.2 (*3*); 0.3 (*4*); 0.4 (*5*); 0.5 (*6*).

well but varied within a reasonable range with respect to the classical value $\alpha_{Nb} = 0.22 \cdot 10^{-24}$ cm$^3$ at room temperature. The EP were calculated under so-called "bond polarizability" approximation [4], when the electric dipole-dipole interaction in the shortest (Nb–O) bonds is excluded when $\alpha_{eff}$ values for oxygen and niobium ions are determined. From symmetry considerations, we believed that the principal axes '3' of the $O^{2-}$ ion EP tensor coincides with the shortest (Nb–O) direction and this tensor has axial symmetry, so that $\alpha_{11} = \alpha_{22} \neq \alpha_{33}$. The results obtained are shown in Fig. 3.

So, a substantial temperature dependence of the one of the principal components ($\alpha_{11}$) of the oxygen ion EP tensor is observed in $LiNbO_3$ crystal. Nevertheless, the shortest (Nb–O) distance in stoichiometric $LiNbO_3$ is practically independent of temperature in this temperature range [6], that is not surprising, because EP of a ion is in proportion with cube of its ionic radius, which is a temperature-dependent quantity. These results make it possible to realize computer simulations of peculiarities of structure ordering and dynamics of ions in $LiNbO_3$ structure, such as, for example, the isomorphic phase transitions, diffusion of $Li^+$ ions and mobility of $OH^-$ groups.

### *References*

1. N.D. de Leeuw, S.C.Parker, C.R.A.Catlow, G.D.Price, *Phys. Chem. Minerals*, **27**, 332 (2000).
2. S.V.Yevdokimov, A.V.Yatsenko, *Cryst. Repts.*, **48**, 594 (2003).
3. S.Tinte, M.Sepliarsky, M.Stachiotti et al., *Z. Phys. B*, **104**, 721 (1997).
4. A.V.Yatsenko, *Physica B*, **305**, 287 (2001).
5. S.N.Khrykina, A.V.Yatsenko, *Functional Materials*, **9**, 86 (2002).
6. H.Lehnert, H.Boysen, F.Frey et al., *Zeitschr. Kristallogr.*, **212**, 712 (1997).
7. V.K.Semenchenko, I.T.Bodnar', V.P.Yarunichev, *Optika i Spektr.*, **54**, 685 (1983).
8. H.Iwasaki, T.Yamada, N.Niizeki, *Jap. J. Appl. Phys.*, **7**, 185 (1968).
9. U.Shlarb, K.Betzler, *Phys. Rev. B.*, **48**, 15613 (1993).
10. R.I.Shostak, A.V.Yatsenko, in: TNU, Ser. Fiz., Math., Biol., **17**, 89 (2001).

## Обчислення дипольної електронної поляризовності іонів у $LiNbO_3$ у температурному діапазоні (273 ÷ 873)K

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З використанням модифікованого рівняння Лорентц-Лоренца проведено обчислення дипольної електронної поляризовності іонів кисню у кристалі $LiNbO_3$ стехіометричного складу в діапазоні температур (273 ÷ 873) К. Ці результати забезпечують можливість проведення комп'ютерного моделювання особливостей структурного упорядкування та динаміки іонів у $LiNbO_3$.