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Polar cluster formation due to point charge centres in $\text{KTaO}_3:\text{Li}$

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Abstract

Experiments on second-harmonic generation (Eden S, Auf der Horst C and Kapphan S 1998 *J. Korean Phys. Soc.* **32** 411) have revealed oxidation and reduction processes to have a great influence on the values of the intensities obtained. This influence is explained in the present paper by the fact that the oxidation–reduction treatment changes the concentration of the free charges connected with oxygen vacancies, and these charges influence the impurity cluster formation, which causes changes in the second-harmonic intensities. It is shown that polarized impurity clusters are stabilized by charges placed at their boundaries because of the compensation of the depolarization field.

1. Introduction

$\text{KTaO}_3:\text{Li}$ is one of the model solid solutions showing impurity dipole ordering effects, which can be detected either by dielectric spectroscopy or by optical methods [1, 2]. On increasing the Li concentration, at first, Li clusters appear and then, at a larger Li concentration, a long-range order is developed. In the present paper we are concerned with dilute $\text{KTaO}_3:\text{Li}$, in which the Li clusters are comparatively small. However, their existence was clearly seen by the second-harmonic generation (SHG) method [3, 4] as well as by means of birefringence [5]. Indeed, due to the randomness of the Li-ion distribution, there is a wide distribution of Li–Li lengths. The Li ions at comparatively short distances are organized into clusters with a preferred orientation of the Li dipole moments, while the polarization orientation in different clusters remains random.

Experiments [6] showed a rather strong influence of the oxidation and reduction treatment on the SHG intensities. It was seen that the oxidation treatment of the samples results in a decrease of the SHG intensities (figure 1). It is interesting that the influence of the reduction treatment looks similar to the influence of an external field (see figures 2): both increase the SHG intensities. Indeed, if one compares the values of the intensities obtained in the field 160 kV m^{-1} (figure 2) with the data obtained in zero field (figure 1), then it is apparent that the

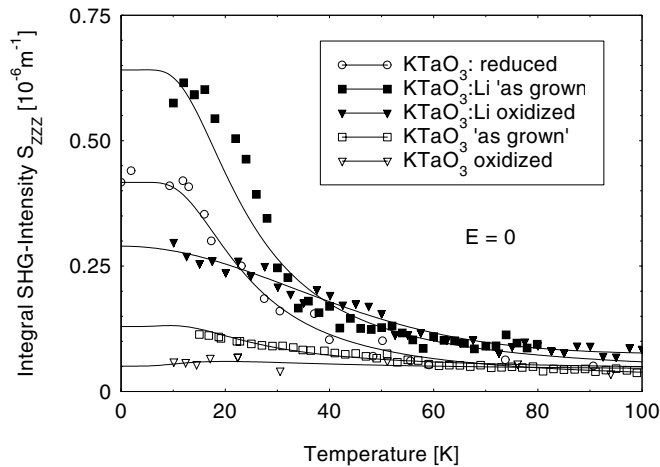


Figure 1. The dependence of the SHG intensities in $\text{KTaO}_3:\text{Li}$ with $x = 0.008$ and nominally pure KTaO_3 on the oxidation treatment. Reduction and oxidation: at 1000 C for 4 h at ambient pressure (H_2 and O_2 respectively).

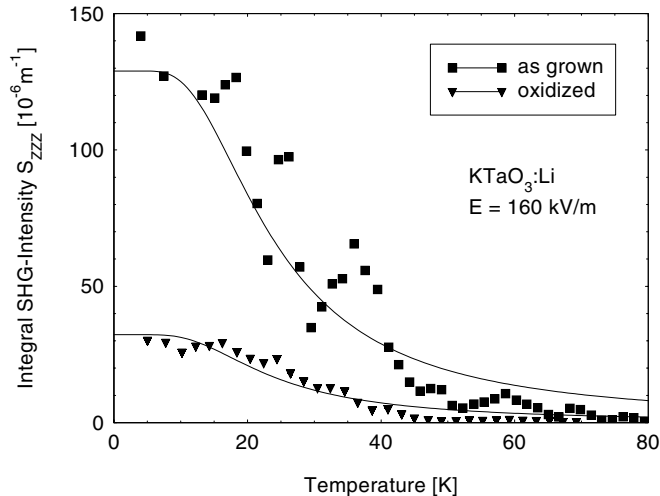


Figure 2. The dependence of the SHG intensities in $\text{KTaO}_3:\text{Li}$ with $x = 0.008$ on the oxidation treatment in the dc field 160 kV m^{-1} .

former are much larger than the latter. In [6] it was assumed that the oxygen vacancies should play an important role in this effect, but the rather small concentration of these vacancies produced during an ordinary reduction treatment of the samples was insufficient to allow the effect to be connected with the scattering of light by the vacancies themselves, at least if they are distributed uniformly over the bulk. Very probably the electrons trapped by these vacancies should play an important role, or/and surface effects are important. Besides these experiments there were others showing a strong influence of the charge carriers on some properties of KLT, similar solid solutions and even nominally pure perovskites [7–11]. These findings were supported by studies of the oxide thin-film degradation effect [12–15] and photocurrent [16–21].

The present paper considers different models, which are able to explain these experimental findings in a unified approach. We think that electrons have shallow levels at Li nanocluster *boundaries* and that the filling of these levels leads to the enlargement and stabilization of the Li-correlated clusters due to the joining of smaller ones. The excitation of the electrons from these levels leads to the breaking of the large (merged) clusters into smaller ones. Thus, our idea is that just the electrons appearing during the reduction treatment (or disappearing during the oxidation treatment) are responsible for the stabilization of comparatively large ordered Li clusters, which influence the SHG intensities.

2. Charge–dipole interaction in the matrix of polarizable ions

In this section we consider a reason for the coupling between a lone Li dipole and an electron (coupling with a hole was described in [17]). First we study the charge–dipole interaction in the simple cubic lattice by taking into account the polarization of the surrounding media. The energy of the charge–dipole interaction can be expressed as the product of the field produced by the charge on the lattice site in the n th cell, e_n , and the dipole moment, $U = -\mathbf{d} \cdot \mathbf{e}_n$. It is convenient to represent the field e_n as an integral of the Fourier transform over the Brillouin zone, and then the electric field can be found as the sum of the bare electric field and the field produced by the polarized lattice sites:

$$\mathbf{e}(\mathbf{k}) = \mathbf{e}^0(\mathbf{k}) - \hat{\phi}(\mathbf{k})\hat{\chi}(\mathbf{k})\mathbf{e}^0(\mathbf{k}) \quad (1)$$

where $\mathbf{e}^0(\mathbf{k})$ is the Fourier transform of the unscreened field, which at small \mathbf{k} is $\mathbf{e}^0(\mathbf{k}) = q(\mathbf{i}\mathbf{k}/k^2)$; here q is the value of the charge producing the field and $\hat{\phi}(\mathbf{k})$ is the Fourier transform of the tensor of the dipole–dipole interaction, which in the coordinate system when the z -axis is directed along the \mathbf{k} -vector takes the form

$$\phi_{\alpha\beta} = \left(-\frac{4\pi}{3}\gamma + c_{\perp}k^2 \right) \delta_{\alpha\beta} + [4\pi + (c_{\parallel} - c_{\perp})k^2] \delta_{\alpha 3} \delta_{\beta 3}. \quad (2)$$

Here we have introduced a coefficient, γ , showing the difference from the simple cubic lattice; in the simple cubic lattice this coefficient equals 1. The c_{\parallel} - and c_{\perp} -coefficients are responsible for the dispersion of the transverse and longitudinal fluctuations respectively; the directions denoted by the numbers 1 and 2 are transverse while 3 corresponds to the longitudinal direction.

For the cubic lattice and when the z -axis is directed along the wavevector \mathbf{k} the susceptibility $\chi_{\alpha\beta}$ is described by

$$\chi_{\alpha\beta} = \frac{\delta_{\alpha 1} \delta_{\beta 1} + \delta_{\alpha 2} \delta_{\beta 2}}{\chi_0^{-1} - \frac{4\pi}{3}\gamma + c_{\perp}k^2} + \frac{\delta_{\alpha 3} \delta_{\beta 3}}{\chi_0^{-1} + 4\pi - \frac{4\pi}{3}\gamma + c_{\parallel}k^2}. \quad (3)$$

where χ_0 is the site polarizability. The substitution of the Fourier transforms into the initial equation gives

$$\begin{aligned} \mathbf{e}_n &= q \frac{\mathbf{r}_n}{l^3} - q \sum_{\mathbf{k}} \left(4\pi - \frac{4\pi}{3}\gamma + c_{\parallel}k^2 \right) \frac{1}{\chi_0^{-1} + 4\pi - \frac{4\pi}{3}\gamma + c_{\parallel}k^2} \frac{\mathbf{i}\mathbf{k}}{k^2} e^{-\mathbf{i}\mathbf{k} \cdot \mathbf{r}_n} \\ &= \frac{1}{(1 + 4\pi\chi_0 - \frac{4\pi}{3}\gamma\chi_0) l^3} \left[1 - e^{-l/r_{c\parallel}} - \frac{l}{r_{c\parallel}} e^{-l/r_{c\parallel}} \right] \end{aligned} \quad (4)$$

where $l \equiv r_n$, $l = |\mathbf{l}|$ and $r_{c\parallel} = \sqrt{c_{\parallel}/(\chi_0^{-1} + 4\pi - \frac{4\pi}{3}\gamma)}$ is the longitudinal correlation radius. One can express the result obtained in terms of the dielectric permittivity, $\varepsilon = \varepsilon_{\infty} + 4\pi/(\chi_0^{-1} - \frac{4\pi}{3}\gamma)$:

$$U = -dq \frac{(\varepsilon - \varepsilon_{\infty})\gamma + 3}{3(\varepsilon - \varepsilon_{\infty} + 1)} \left[\frac{\mathbf{r}}{r^3} - \frac{\mathbf{r}}{r^3} e^{-r/r_{c\parallel}} - \frac{\mathbf{r}}{r^2 r_c} e^{-r/r_{c\parallel}} \right]. \quad (5)$$

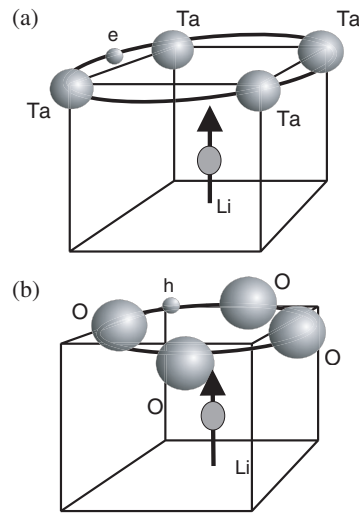


Figure 3. Electronic (a) and hole [17] (b) states at a Li dipole in KLT.

The longitudinal correlation radius is $\sqrt{\varepsilon/\varepsilon_\infty}$ times lower than the transverse correlation radius and its value is less than the lattice parameter. This implies that the last two terms are negligible in comparison with the first one. Moreover, due to the very large value of ε in the ferroelectrics ($\varepsilon \gg 1$), the factor in this expression is simply $dq\gamma/3$. Hence the final expression is

$$U \simeq -\gamma q \frac{\mathbf{d} \cdot \mathbf{l}}{3l^3} \quad (6)$$

(one should divide the result by $4\pi\varepsilon_0$ in the International System where ε_0 is the dielectric constant). Thus we see that the dipole–charge interaction in the highly polarizable dielectrics is enhanced due to the interaction of the charge with longitudinal phonons. Straightforward computations of the field produced by a point charge in a lattice consisting of polarizable ions [22, 23] have shown that, at small distances, the enhancement of the charge–dipole interaction is even larger than that given by the asymptotic expression derived.

The formula derived allows one to estimate the potential of a microscopic dipole embedded in a lattice of polarizable ions. For example, for $\text{KTaO}_3\text{:Li}$ we have $\gamma = 0.2$, $r^2 = 3a^2/4$ where $a \approx 4\text{Å}$, $d = 0.6\text{Åe}$ and the estimate of the interaction energy for the Li dipole with an electron located on the nearest four Ta sites (figure 3) is of 28 meV but the electronic energy level position is smaller due to the electronic dispersion effect. However, another situation arises if the electron is situated in the field of an ordered Li cluster controlled by the same interaction (see the next section).

The interaction of the charges with the Li orientable dipoles showing an r^{-2} -variation with distance could lead to a large polaron energy, as the integral of this interaction over the space diverges with the size of the integration. However, for KLT there are different reasons preventing the formation of such a polaron. Indeed, the Li–Li interaction destroys the polar region around the electron, as it is stronger than the charge–Li interaction for large enough Li concentrations ($>1\%$); the thermal fluctuations of the Li dipole moment also destroy the polaronic state, at least at temperatures larger than the interaction energy of the charge with a Li dipole. Hence at some distances the interaction energy will show a change with distance stronger than a r^{-2} -variation. That is, if one takes into account the fact that the average dipole moment on a Li site is proportional to the field and that the field produced by a charge

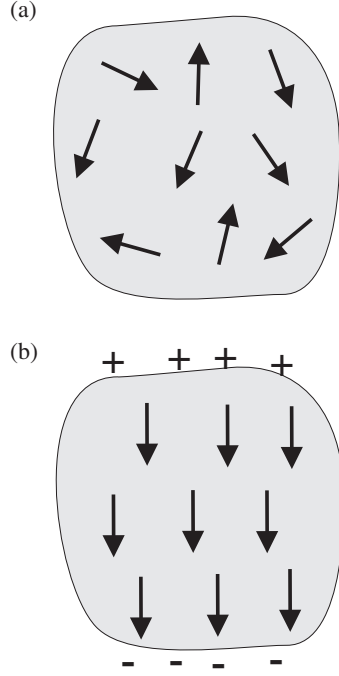


Figure 4. Dipole ordering ((a) \rightarrow (b)) due to the compensation of the depolarization field by free carriers.

behaves as r^{-2} , then the interaction energy at such distances will be proportional to r^{-4} . This implies that the polaronic energy will be proportional to inverse distance between the polaron and a Li impurity. If the susceptibility behaves as $E^{-1/2}$, as in the hydrodynamic model [24], the interaction energy will change with distance as r^{-3} , which leads to a logarithmic singularity after the integration over the space. The latter effect can provide a large polarization contribution to the polaronic energy even if the Debye screening effect is included.

3. A nanosize cluster locked by electrons

We consider a nanocluster of volume V_{nc} locked by n_e electrons (figure 4). The free energy in this case takes the form

$$\begin{aligned}
 F = F_0 + \int dV & \left[\frac{1}{2}\alpha P^2 + \frac{1}{3}C P^3 + \frac{1}{4}\beta P^4 \right. \\
 & + A n_e P^2 + A' n_p P^2 - B(n_e + n_p)P + \frac{1}{2}K u_{\alpha\alpha}^2 - W u_{\alpha\alpha} P^2 - E P \left. \right] \\
 & + \int d\nu_+ [\kappa(\nabla P)^2 + D n_e(\nabla P)] + \int d\nu_- [\kappa(\nabla P)^2 + D n_p(\nabla P)] \\
 & + \int \int dV d\nu_+ [-H P(\nabla P) + F P(\nabla P)^2 + G_+ P^2(\nabla P)] \\
 & + \int \int dV d\nu_- [H P(\nabla P) + F P(\nabla P)^2 + G_- P^2(\nabla P)] + U n_e n_p \quad (7)
 \end{aligned}$$

where P is the polarization inside the cluster, $u_{\alpha\beta}$ is the tensor of displacements, n_p is the concentration of positive charges. The first integral describes the energy of the bulk of the

cluster, the second integral is taken over the region where ∇P is finite (v_+ and v_- respectively for the regions with the positive and negative gradients of polarization) and, finally, the third integral describes the interaction between the bulk and surface of the cluster. Let us exclude the u -tensor by making the substitution $u_{\alpha\alpha} = (W/K)P^2$. In this case the nonlinearity constant, β , will be renormalized: $-\tilde{\beta} = \beta - W^2/2K$.

In order to estimate the integrals we will use the approximate behaviour of the polarization with distance in the surface region of the cluster:

$$F = F_0 + [(\frac{1}{2}\alpha + An_e + A'n_p)P_0^2 + \frac{1}{3}CP_0^3 + \frac{1}{4}\tilde{\beta}P_0^4 + \frac{1}{6}\gamma P_0^6 - B(n_e + n_p)P]V_{nc} + \frac{k}{\xi}P_0^2S - D(n_e + n_p)P_0S + 2\left[HP_0^2S + \frac{F}{2\xi}P_0^3 - (G_+ - G_-)P_0^3S\right]V_{nc}. \quad (8)$$

Now one can rewrite this expression in the polynomial form

$$F = F_0 + A_1P_0 + A_2P_0^2 + A_3P_0^3 + A_4P_0^4 + \dots \quad (9)$$

where

$$\begin{aligned} A_1 &= -[B(n_e + n_p)L + EL + D(n_e + n_p)]S = a_{11}L + a_{12} \\ A_2 &= \left[\left(\frac{1}{2}\alpha + An_e + A'n_p\right)L + \frac{k}{\xi}P_0^2 + 2HSL\right]S = a_{21}L + a_{22} \\ A_3 &= \left[\frac{1}{3}C + \frac{F}{\xi} - (G_+ - G_-)S\right]LS = a_3L \\ A_4 &= \frac{1}{4}\tilde{\beta}LS = a_4L. \end{aligned} \quad (10)$$

Here we introduced the equality $V_{nc} = LS$ where L is the linear size of the cluster and S is the sectional area. The stability condition gives the equation of state

$$A_1 + 2A_2P_0 + 2A_3P_0^2 + 4A_4P_0^3 = 0. \quad (11)$$

We consider the case where $A_2 > 0$, $A_4 > 0$. In this case there are three possible solutions of this equation, P_{01} , P_{02} and P_{03} , while only one of these corresponds to the steady state. One of the solutions (let it be P_{01}) corresponds to the polarization arising in the field A_1 . The two other solutions correspond to the spontaneous polarization appearing due to symmetry breaking; it exists even in the absence of the field. We will take it that the nanocluster is stabilized if one of the solutions corresponding to the appearance of a spontaneous polarization is stabilized (let it be P_{02}). Hence the condition for the creation of the cluster locked by the free charges is of the form

$$F(P_{01}) = F(P_{02}). \quad (12)$$

This equation can give also the minimal size, L_{\min} , in terms of the cluster size, L , of the cluster. With the assumption of small L -values, when only the terms linear in L are taken into account, one can obtain that

$$L_{\min} \simeq \frac{-a_4^2a_{12}^2 + 3a_3a_4a_{12}a_{22} - 36a_3^2a_{22}^2}{2a_4^2a_{11}a_{12} - 3a_3a_4(a_{11}a_{22} + a_{12}a_{21}) + 72a_3^2a_{21}a_{22} - \frac{27}{64}a_3^2a_{22}^2}. \quad (13)$$

If $F(P_{01}) < F(P_{02})$, then the clusters do not appear, while in the reverse case, they can appear and grow. The result also depends on the number of the free charges available. In the case where these free charges are plentiful, they can be used in order to produce the internal field in the cluster compensating the depolarization field. However, if the charges are few, then the clusters do not appear.

In the case where the number of the electrons is sufficient to compensate the depolarization field completely, one can use the following approximate relations facilitating the approach to the problem:

$$n_e = -\frac{1}{4\pi}(\nabla P)_{v_+}, \quad n_p = \frac{1}{4\pi}(\nabla P)_{v_-} \quad (14)$$

together with the stability condition. Here the former gradient is taken in the region of v_+ where the polarization gradient is positive, and the latter is taken in the region of v_- where the gradient is negative. This implies that the positive charges arising due to the change of the polarization at the cluster surface are fully compensated by the electrons and that the negative charges on the other side of the cluster are fully compensated by positively charged oxygen vacancies or/and holes.

It is important to state that the clusters appear mainly at those points in the crystal where the local density of the Li ions is higher than the average one. It is obvious that the correlation of the Li dipoles inside such clusters is larger than the average correlation. Hence a local phase transition could happen in the cluster before the phase transition in the whole crystal. However, such local instability is prevented by the depolarization field, while this field can be compensated by the free charges, which can be collected at boundaries of the cluster.

4. Discussion

In the present paper we have shown that, in a lattice consisting of polarizable sites, the dipole–charge interaction is enlarged due to local field effects. This enlargement resembles the well-known enhancement of the dipole–dipole interaction, due to the indirect interaction, over that of the transverse optical phonons [2, 25, 26]. However, in the present case the longitudinal optical phonons are the most important, since the charges do not interact with the transverse phonons.

Another finding in the present paper is the stabilization of nanoclusters by free charges like electrons, which can be caught by a cluster—on the one hand—and which will produce a stabilizing field for this cluster, compensating the depolarization field partly or completely—on the other hand. Thus both the cluster and free charges will be self-trapped. This model corresponds to experimental data [6], in which a strong dependence of the SHG intensity on the oxidation–reduction treatment of KLT was found (see also figure 1). Indeed the SHG intensities reflect $\langle P^2 \rangle$, which is proportional to the average number of Li impurities in Li clusters (the so-called cluster size) [4]. Hence the increase of the cluster size due to the increase of the number of free charges (figure 1) or due electric field influence (figure 2) results in a linear increase of the SHG intensities.

Another experimental finding [19] showed that the illumination of the samples in a field decreases the SHG intensities, which can be explained now as the excitation of the electrons from the locked domains that breaks up these domains, but the illumination should be done in a field in order to take electrons away.

Thus the experiments on the SHG performed in [6] can be explained if one takes into account that the oxidation–reduction treatment of $\text{KTaO}_3\text{:Li}$ changes the concentration of oxygen vacancies. These point defects are known to have shallow trap levels when two electrons occupy the vacancy. Hence the electrons can be easily released from the vacancies and they can occupy in other trap levels in the bulk or surface. In particular, these electrons can occupy energy levels existing at the boundaries of polarized impurity domains, which results in their stabilization. The reduction treatment increases the number of free electrons and, hence, there are more possibilities for organizing the polarized impurity clusters or enlarging

the existing clusters. This increases the SHG intensities in agreement with experiment. The reverse is true when the sample is oxidized: the clusters are broken into smaller ones due to the lack of electrons in this case. This decreases the SHG intensities, also in agreement with experiment. Thus one can govern the average impurity-polarized cluster size by using an oxidation–reduction treatment of the samples.

Acknowledgments

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