Manifestation of Polaronic States in Ferroelectric Relaxor PMN

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Small polaron states in the model ferroelectric relaxor PMN were confirmed in this work by detection of the characteristic IR-absorption accompanied by light-induced polaron transport. The mechanism of an influence of mobile polaronic clusters on the polar cluster reorientations and, as a result, on the co-operative phenomena in relaxor is developed. Here mobile polaronic clusters can move on the interfaces of polar clusters with carrying of their polarizations. The latter are moving self-consistently with polaronic clusters, and are involved to the reorientation-like motion. The polar cluster–polar cluster interaction between such type reorienting polarizations of different clusters can be a possible origin of phase transitions in PMN-like relaxors. Semi-empirical Hartree-Fock calculations of electronic polaron states in some model ABO_3-systems performed are in a good agreement with the experiment.

INTRODUCTION

The ordering in ferroelectric relaxors is usually connected with co-operative behaviour in polar cluster (PC) system. That is why the determination of new degrees of freedom in relaxors which can influence the co-operative effects for PCs can be of significant importance.

In the present work we report the experimental results on IR absorption study in model ferroelectric relaxor PMN. These results can be consider as a direct effect of small or intermediate polarons in PMN-like relaxors, and support the necessity of the involving of polaron degrees of freedom to the PC-model construction. Here we also propose the mechanism of such a polaron influence on the co-operative effects. For instance, it is polaron contribution to glass-like state formation for ferroelectric relaxors of PMN-type. Last, we had got a semi-quantitative confirmation of polaronic origin of the

absorption effect detected from the side of quantum-chemical calculations. Namely, there were semi-empirical Hartree-Fock calculations of electronic polarons in some ABO_3 model systems in the framework of intermediate neglect of differential overlap (INDO) approximation.
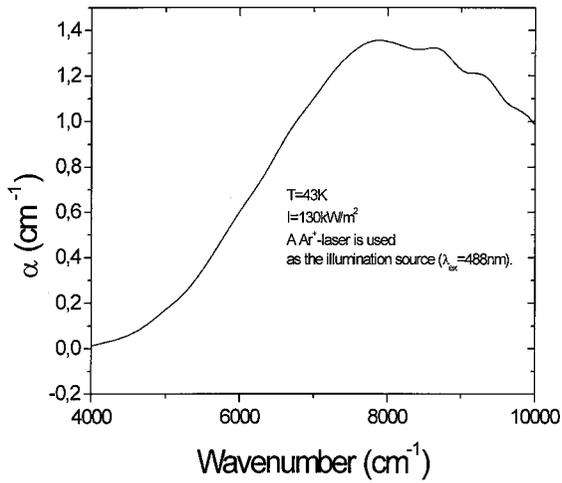
POLARONIC IR-ABSORPTION IN PMN

We perform the direct measurement of optical absorption in the IR-region with the purpose to detect the characteristic polaron absorption [1–6] connected with IR-illumination induced polaron transport which can be considered as a "passport" of polaron effect-as it was in the case of uniaxial relaxor SBN [6]. The scheme of the light induced transport of small or intermediate polarons is presented on the Fig. 1. There are two steps transition of one polaron from one cell to another one. Namely, the first step is the adiabatic light absorption in the framework of the Frank-Condon principle, and with the transition to the potential curve belonged to the neighbouring cell. The second one is the successive set of the phonon emission processes corresponding to the relaxation process up to reaching the minimum of the potential in another, neighbouring cell (see Fig. 1). Namely the first step related light absorption is the key process there.
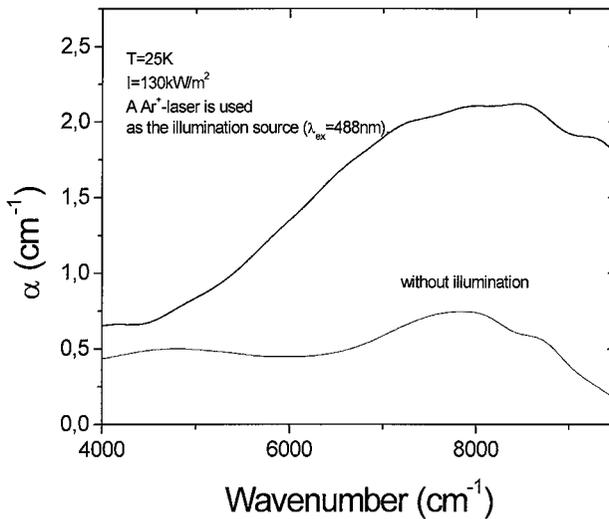
The experiment made from 2 K up to room temperature was performed under the same conditions as in the [6]. It confirms the above mentioned assumption about polaronic state absorption (see Figs. 2–5).
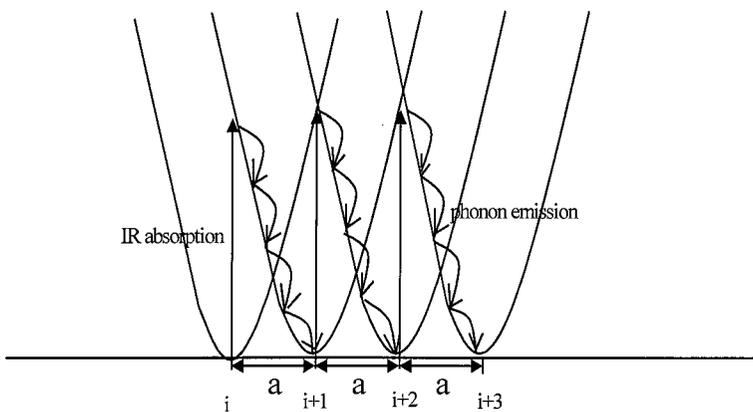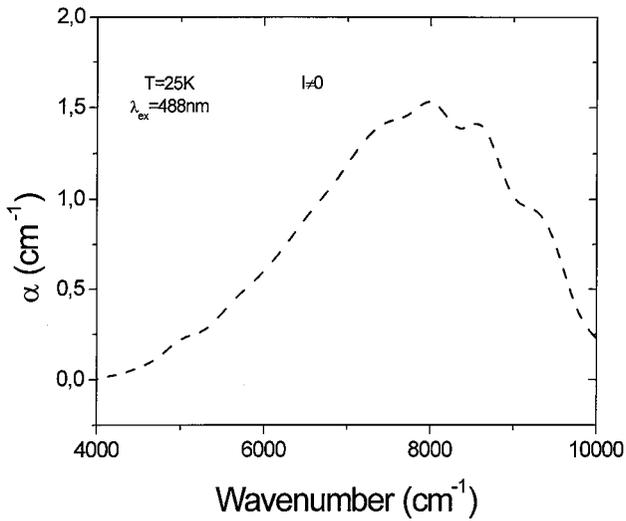

Figure 1. Light-induced transport of polarons accompanied by characteristic IR-absorption.
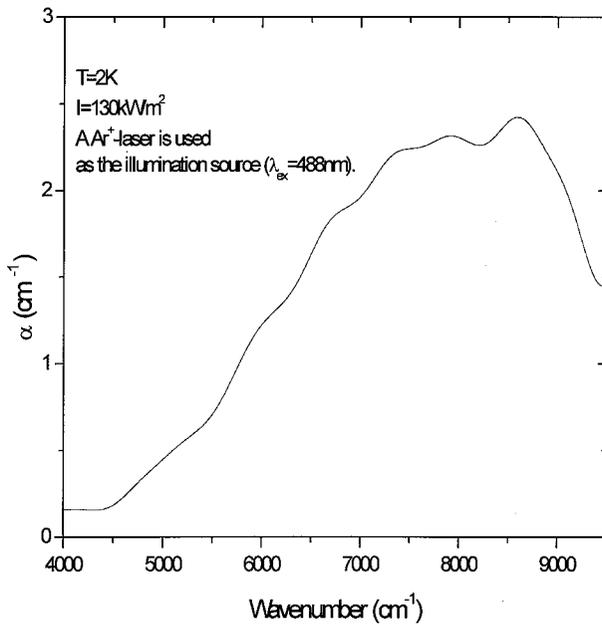
Figure 2. Light-induced IR absorption effect of free polarons ($T = 43$ K).

Figure 3. IR absorption without and with illumination: polaronic clusters and free polarons co-existence at $T = 25$ K.

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Figure 4. Light-induced IR absorption: free polarons at $T = 25$ K.

Figure 5. Increasing of light-induced IR-absorption with temperature lowering ($T = 2$ K).

Indeed, there are

(i) the peak of the IR-absorption without any optical pumping in the visible region;

(ii) the increasing of the light induced IR absorption namely in the region of the absorption peak without addition pumping;

(iii) these peaks positions well coincide with the polaronic absorption peaks in another ferroelectric oxides (for $LiNbO_3$, SBN, and $SrTiO_3$);

(iv) the pure light induced IR absorption is increased with temperature lowering;

(v) increasing of the experiment temperature smoothly decrease the absorption band detected, and at $T = 300$ K it is not detected at all.

All these facts can be explained by the assumption that we have to deal with small (or intermediate) polaron absorption corresponding to effect presented on the Fig. 1.

1. Indeed, the parameters for local potentials for different ferroelectric oxides under discussion are not so different, and approximate coincidence of the polaronic absorption quanta for them can be predicted. In other words, the IR absorption with approximately the same energy quanta of the light induced absorption is the positive argument for polaronic origin effect.

2. If the absorption peak in the region of 8000 cm^{-1}, for absorption without illumination, coincides with light induced peak we can conclude that we have to deal with some number of *long living polarons*. For example, it will be for polaron clusters, which can be responsible for IR absorption peak without illumination.

3. Note also, that these *polaron clusters are not so dense* because the IR absorption induced transport of the polarons is realized here for the same approximately energy quanta as for the light induced absorption case which can be connected with free polarons.

4. The temperature induced pronounce decreasing of this absorption peak as well as increasing of it with temperature lowering can be explain as a consequence of kinetic effects. Namely, the probability of polaron liberation via excited states is increased with temperature increasing. As a result, the polaron probability to go away (up to trapping to some defect) is increased with temperature. On the other hand, the liberation has pronounce decrease with temperature lowering, and the light induced absorption is a maximal at lowest temperature.

Last not least, let us discuss also the nature of the absorption line shape in real PMN-crystal. We have to deal here with parallel action of the following mechanisms:

(i) a classical broadening mechanism of polaronic absorption by Reik [1, 2] as well as

(ii) an inhomogeneous broadening due to random internal fields in the framework of component concentration spatial fluctuations in real sample.

(iii) But the third mechanism can also give significant contribution to broad line shape of the polaronic absorption detected. This is the superposition of a set of different bands with above mentioned (i)–(ii) broadening origins in the framework of *multi-band structure* existence. The nature of such a multi-band structure of polaronic absorption can be connected with two following effects.

First, this is the absorption with adiabatic polaron transitions from initial cell to the potentials curves of not nearest neighbouring cells which are nevertheless located in the same direction as the direction of the main mechanism of light-induced polaron transport with nearest neighbouring cells effect in the framework of Frank-Condon Principle. Such transitions take part under the action of significant anharmonicity for the case.

Second, these are the adiabatic, Frank-Condon type polaron transitions with light-induced polaron transport also between not nearest neighbouring cells but in another directions. The directions of light-induced polaron transport are different here from the direction of the main mechanism of light-induced polaron transport between nearest neighbouring cells. This process also has important contribution of the cell potential anharmonicity but in addition it is strongly dependent on crystal anisotropy.

SOME POLARONIC RELATED MODELS IN RELAXORS

(i) First, let us consider the model of polaronic clusters moving on polar cluster interfaces [7, and the present work]. Note, that such a polaronic cluster stabilizes resulting double-cluster "PC + polaronic cluster" due to compensation of depolarisation field [8]. Moreover, because adiabatic behaviour for these two interacting clusters is fulfilled the clusters are mutually fitting of their properties for both of their. As a result, the rotation-like motion of the polaronic cluster on the PCs interface is accompanied by corresponding rotation of local polarization of PC

- Corresponds to polaronic cluster region.
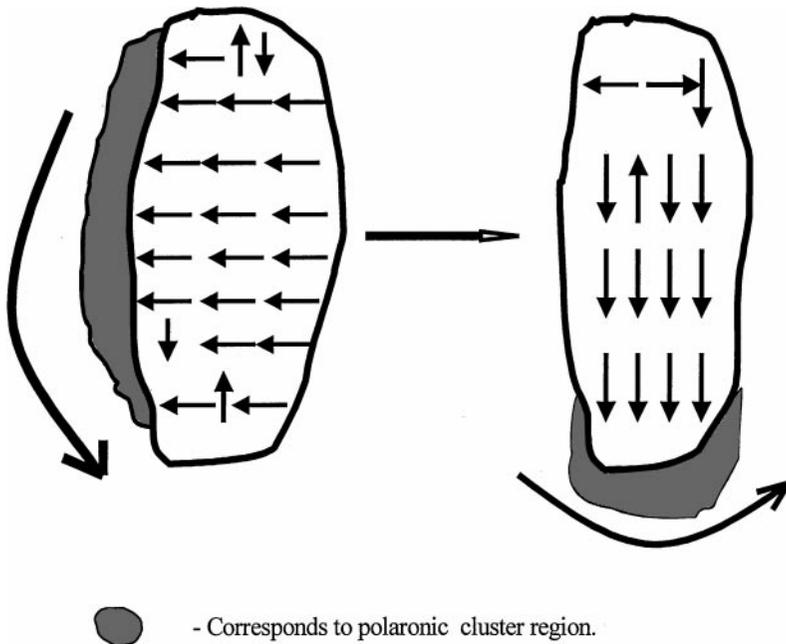
Figure 6. A mechanism of local polarisation reorientations. Polarization reorientation of polar cluster is induced by reorientation of self-consistent polaron cluster on the interface of this polar cluster.

(both take place with the dissipation)—see Fig. 6. This is a new mechanism of PC-polarization changes—due to its reorientations induced by the motion of self-consistent polaronic clusters. As a result of these polarization reorientations our system of double-clusters mentioned above becomes in co-operative regime. Now indirect interaction via phonons between PCs can lead to the local PC polarizations ordering. For instance, it can be a glass-like low temperature phase as it is for the PMN-case. Indeed, the PC-PC of such a reorienting clusters can follow to $\sim r^{-3}$ space decay law with its average zero value for the definite but rather long distance (averaging on the all angles). Such a behaviour is a characteristic both for electric dipole-dipole, and for elastic dipole-dipole interactions (the latter is actual here due to local piezo-effect for each PC, [9, 10]). Here the mean field is not appeared, and we have to deal with a glass-like ordering, where the width of symmetrical part of internal field distribution function is much larger than a contribution of each odd moment of this function.
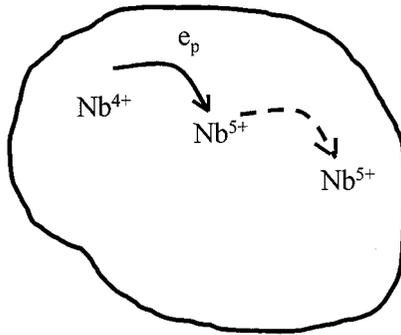
Figure 7. Nb-rich chemical fluctuation region in PMN: electronic polaron hopping motion. Local dipole moment fluctuations lead here to dielectric losses.

 (ii) Second, polaronic clusters are trapped by nano-size anti-ferroelectric ordered microregions. Such anti-ferroelectric micro-regions were detected in PMN—like systems recently [11]. The origin of such a trapping connects with potential well appearance for polaronic cluster due to elastic field of this anti-ferroelectric region which attracts polaronic cluster. As a result, the polaronic cluster moves within this potential well with creation of characteristic dielectric losses effect.
(iii) Third, polaronic clusters are trapped by charged chemical fluctuation regions [12] with formation of the charge compensation. Simultaneously a new type of losses connected with electron polarons and hole polarons hoppings is appeared here (Figs. 7, 8). Note, that such
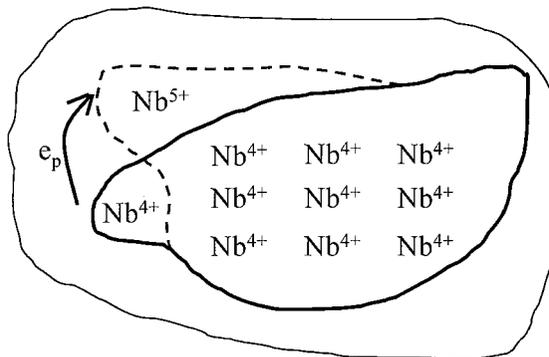
Figure 8. Polaronic clusters (drops) in chemical fluctuation regions in PMN and their shape changing due to single polaron successive motion on such a cluster interfaces.

a charged chemical fluctuation regions are appeared more often in non-crystalline relaxors.

QUANTUM CHEMICAL MODELLING OF POLARONIC STATES

We had used semi-empirical Hartree-Fock method in the framework of INDO-approximation in our calculations of the electron polarons in ferro-electric perovskite-like crystals $BaTiO_3$, $KNbO_3$, and $KTaO_3$. For instance, in $BaTiO_3$ we relaxed 6 O atoms around the central Ti atom, where the electron polaron is mainly localized, and kept fixed all other atoms. (We restricted ourselves to the cubic $BaTiO_3$ phase.) As a result of geometry optimization, we found that the energy minimum of the system corresponds to outward displacement of four nearest equatorial O atoms by 1.53% a_o (lattice constant) and relaxation of remaining two nearest O atoms inwards, by 1.1% a_o along the z axis. The total energy gain of a system due to lattice relaxation around Ti atom is 0.24 eV.

Due to combined breathing mode and the Jahn-Teller (JT) effect, initially three-fould degenerate ground state of a system with the symmetry t_{2g} splits into two levels, nondegenerate and twofold degenerate. As a result of asymmetric geometry relaxation a considerable electron density is localized on the Ti $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ atomic orbitals. In fact, about 80 percent of an extra electron density is localized on Ti atom, which confirms a model of small-radius electron polaron in $BaTiO_3$. Another two empty levels with e_g symmetry are located close to CB bottom. The calculated t_{2g} ground state symmetry agrees well with the experimentally detected [13]. We have calculated also the electron polaron optical absorption energy, using the ΔSCF scheme, and found it to be 0.69 eV. The absorption process corresponds to a charge transfer to the nearest Ti atom. This absorption band has been detected

TABLE I Optical absorption energies of electron polarons in ABO_3 perovskite-like ferroelectrics and relevant lattice relaxation energies as calculated by means of INDO method

Polaron absorption and lattice relaxation energies in ABO_3			
Crystal	Type of polaron	Absorption energy (eV)	Relaxation energy (eV)
$BaTiO_3$	Electron polaron	0.69	0.24
$KNbO_3$ [15]	Electron polaron	0.78	0.21
$KTaO_3$ [15]	Electron polaron	0.75	0.27

recently experimentally under picosecond laser excitation [14], with absorption energy ≈ 0.6 eV. Our calculated electron polaron energy for BaTiO$_3$ (0.69 eV) is also close to Nb^{4+} polaron absorption band detected recently around 0.72 eV in uniaxial relaxor SBN [6]. This also lies in the same energy range as our previous ABO$_3$ electron polaron calculations, Table I.

ACKNOWLEDGEMENTS

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