Anharmonic metastable charge transfer vibronic exciton in potassium tantalate

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Abstract. Charge Transfer Vibronic Excitons (CTVEs) are bi-polaronic excitons characterized by specific recombination luminescence. The latter has been investigated with respect to the influence of IR pumping and led to the experimental evidence of a non-linear CTVE. Such an essentially anharmonic CTVE with respect to the charge transfer and lattice displacements was predicted recently [Vikhnin, 2003 Sol. St. Commun 127 2832], and should manifest a well-defined metastable behavior. It is shown that an IR pumping recalls practically the same CTVE-recombination emission band as that induced initially by a UV-pumping. Such an effect is characterized by relaxation time \( \tau \) after the UV-pumping (for example, \( \tau \sim 60 \text{ sec. at 3 K} \)). This behavior is explained as a result of occupation of a metastable anharmonic CTVE minima. An additional IR-pumping could transfer the occupation from the anharmonic CTVE state to the harmonic CTVE which is active for recombination luminescence. The temperature dependence of \( \tau \) for the anharmonic CTVEs with metastable behavior shows that the relaxation time is controlled by resonance as well as by phonon-induced tunneling.

1. Introduction
Investigations of charge-transfer excitons interacting with lattice were opened in pioneering work of Agranovich and Zakhidov [1]. Further development of the studies in this direction had led to Charge Transfer Vibronic Excitons (bi-polaronic excitons – CTVEs, see [2,3] and references therein) discovery. Note that CTVE is polaronic electron – hole correlated pair (or triad) which is well localized from each other at the distances on the order of lattice constant. The CTVE approach is related with ionic-covalent solids with pronounced electron-lattice interaction and is based on the self-consistent calculations of the interacting charge transfer and lattice distortions for these bipolaronic states.

The main purpose of the present work is to clarify the existence of anharmonic CTVEs recently predicted [2]. Therefore, our attention was focused on the experimental evidence of an appearance of a mainly non-linear (anharmonic with respect to charge transfer as well as with respect to lattice vibrations) CTVE. This is an important issue of charge transfer excitations in studies of ionic-

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covalent compounds on the one hand, and for spectroscopic applications on the other. To demonstrate the existence of the new anharmonic CTVE and reveal its dynamical properties, we conducted laser excitation and analyzed in the visible range the characteristic luminescence [4-8] from ferroelectric oxides. The sample we studied is a model incipient ferroelectric KTaO$_3$ with ionic-covalent bonding in this context.

2. Co-existence of harmonic CTVE-I and anharmonic CTVE-II

As it was shown in [2], the CTVE state is well described in the harmonic approximation (CTVE-I state in accord with the classification in [2]) with respect to O$\rightarrow$Ta charge transfer, $q$, as well as to active lattice ions displacement, $x$, which is a stretching mode variable for O-Ta vibrations. However, CTVE should not be such a single topical case. Another type of CTVE, namely, well described in the framework of essentially anharmonic approach with respect to "$q$-$x$" variables, could be also the cases in ionic-covalent solids with pronounce vibronic interaction. Topical model for such an anharmonic, CTVE-II state [2] could be described by the following adiabatic potential:

$$U_{\text{CTVE-II adiabatic}} \approx (\Delta E)q + \frac{1}{2} Cqx + \frac{K}{2} x^2 + \frac{\alpha}{2} q^2 + \frac{W_1}{2} q x^2 + \frac{W_2}{3} q^3 + \frac{\beta}{4} q^4 + \ldots$$  \hspace{1cm} (1)

The shape of CTVE-II potential well is mainly controlled by all terms in (1) except the first one, which is only important for the CTVE-II energy determination. Such an anharmonic potential well, together with harmonic CTVE-I potential well (related mainly with the first four harmonic terms in (1)), exists under the condition of co-existence with CTVE-I (see figure 1, and reference [2]). Potential (1) minimization with respect to $q$, $x$ leads to the CTVE-II state criterion:

$$\left(\frac{W_2}{2} + \frac{4W_1K^2}{C^2}\right)^2 > 4\beta\left(\frac{2}{C}\right)^2\left(\frac{2K\alpha}{C} - \frac{C}{2}\right)$$  \hspace{1cm} (2)

A key feature of CTVE-II is its metastability. Here an absence of effective adiabatic-type

**Figure 1.** Scheme of the topical transitions leading to IR-induced recombination luminescence in the visible range. (1) IR-pumping of CTVE-II; (2) relaxation with phonons emission of the CTVE-excited state; (3) recombination luminescence in the visible range (4) tunnel relaxation of CTVE-I as the bottleneck of its relaxation to the ground state.
Frank-Condon recombination transitions with light emission as well as of effective vibration relaxation (which could be only realized by the transitions through strong potential barrier in our case) is responsible for such a metastable behavior.

3. IR-induced recombination luminescence after UV-excitation: manifestation of anharmonic metastable CTVE-II state

The consequence of UV-excitation of KTaO$_3$, which results in the characteristic recombination luminescence in the visible region, has been further studied in our experiments with respect to the influence of an additional IR pumping. It was detected that after switching off the UV pumping a following IR pumping could induce practically the same CTVE-I recombination emission band as it was by the UV-pumping (see figure 2). Such an IR induced luminescence can be observed during some definite, long enough time characterized by $\tau$. It was observed that the decay time $\tau$ was approximately 15 sec at 50 K, and increased to ~ 60 sec at 4 K. This experimental result suggests an IR-induced transition from some metastable state to an active one (CTVE-I) from which recombination luminescence was emitted.

The mechanism for appearance of the visible recombination luminescence after switching off the UV-pumping is understood based on the properties of CTVE-II. Namely, this effect can be interpreted based on the possibility of previous occupation of the metastable CTVE-II state by UV-pumping, and on the possibility of occupation transfer to the active CTVE-I state from which the recombination luminescence is created. The CTVE-II $\rightarrow$ CTVE-I transition can only be induced by additional IR-pumping (see figure 1). Note that CTVE-II states in KTaO$_3$ really manifest the metastable behavior as described in figure 1. The measurements of the temperature dependence for the CTVE-II characteristic relaxation time $\tau$ show that this relaxation time could be controlled by resonance tunnel transitions with dissipation in the lower excited state [9] in a parallel way with phonon-induced tunnel transitions [10]. The latter follows from a rather slow CTVE-II decay rate which could be explained by tunnel mechanism on the one hand and from the rather smooth behavior in its increase with temperature on the other, explaining significant contribution from resonance tunneling. In summary of the experimental results, we conclude that the metastable, anharmonic, and luminescence silent CTVE-II state could be responsible for the IR-induced visible luminescence from KTaO$_3$ that is of the same spectroscopic characteristics as the CTVE-I recombination luminescence in the crystal.

![Figure 2](image-url)
4. Polaronic clusters and possibility of photo-induced ferroelectric-ferroelastic phase transition: anomalous Raman scattering in KTaO3

Unusual Raman scattering lines at 463 cm$^{-1}$ and 155 cm$^{-1}$ induced by strong enough pumping with laser wavelength at 334 nm, 351 nm, and 458 nm were detected from the KTaO3 crystals. These new lines manifest pronounce decrease of their intensities with temperature lowering. At temperature below 30 K, lines at 463 cm$^{-1}$ and 155 cm$^{-1}$ were no longer detectable. The nature of such Raman lines could be explained by clusters of a space charge appearance with a formation of a new, in-cluster, and local phonon lattice dynamics. These centers could be small polarons which form the space charge clusters. Indeed, the occupation of polaronic cluster sates decreases with temperature lowering for the case in which Fermi level position is lower than the polaron in-cluster state energy. As a result, corresponding polaronic cluster lines may decrease with temperature lowering. New local and quasi-local vibrations, such as that at 463 cm$^{-1}$ and at 155 cm$^{-1}$ in our case, in polaronic clusters could be formed.

While the 463 cm$^{-1}$ Raman line could be related with electronic self-localized Jahn-Teller polarons, the 155 cm$^{-1}$ Raman line could be related with hole self-localized polarons both within corresponding polaronic clusters. In such a case, Raman lines from self-organized quasi-1D polaronic needle-like clusters and related TO phonon mode softening due to electrostriction effect in their vicinity and due to co-operative Jahn-Teller effect (CJTE) for electronic polarons may appear along with the that of the normal modes. The CJTE could be the possible explanation of an effect of giant dielectric constant increase [11,12] with optical pumping in SrTiO3 and in KTaO3 incipient ferroelectrics. Indeed, strong CJTE tetragonal distortion along the main axis of each needle-like electronic polaron cluster as well as strong enough electrostriction for KTaO3 and for STO3 cases lead together to pronounce softening of active ferroelectric mode in these incipient ferroelectrics accompanied by giant photo-induced dielectricity manifested in [11,12].

Last but not least, the increase of optical pumping could lead to real light-induced ferroelectric-ferroelastic phase transition in incipient ferroelectrics KTO and in STO in accord with the polaronic cluster mechanism proposed.

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