

Magnetic resonance in $Pb_xNb_yO_z$ -ceramics as a system containing chemical fluctuation regions

© V.S. Vikhnin, H.R. Asatryan, R.I. Zakharchenya, A.B. Kutsenko, S.E. Kapphan*

A.F. Ioffe Physical-Technical Institute, Russian Academy of Sciences,
194021 St. Petersburg, Russia

* FB Physik, Universität Osnabrück,
49069 Osnabrück, Germany

E-mail: hike.asatryan@mail.ioffe.ru

The simulation of chemical fluctuation regions in the PMN-like relaxors by growth of the $Pb_xNb_yO_z$ -ceramics was performed. Different $Pb_xNb_yO_z$ -clusters (chemically and structurally) coexist in such a ceramics. Hole polarons and bi-polarons, „ Cr^{3+} — two polaronic holes“ paramagnetic complexes were considered for an explanation of EPR spectra in $Pb_xNb_yO_z$ -ceramics. Dynamical averaging and light induced effects, and significant effects of reduction treatment giving a co-existence of Nb^{5+} and Nb^{3+} ions as well as of strong internal magnetic field were discovered in such a ceramics. The latter could be related to antiferromagnetic phase realization in $Pb_xNb_yO_z$ -clusters containing high enough concentration of magnetic Nb^{3+} host lattice ions. Such a situation leads to antiferromagnetic resonance on Nb^{3+} ions as well as to EPR of Cr^{3+} -related paramagnetic complexes in Nb^{3+} -induced internal magnetic field. Charge transfer vibronic excitons (CTVE) in free and in CTVE-phase states were detected in $Pb_xNb_yO_z$ -ceramics by photoluminescence studies.

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1. Introduction

It is known that the ordering in ferroelectric relaxors is controlled mainly by co-operative behavior of polar clusters [1,2]. One of polar cluster models is the cluster of ferro-ordered localized charge transfers corresponding to bipolaronic electron-hole pairs [3,4]. This is the cluster of localized charge transfer vibronic excitons (CTVE) (see [3–5] and references therein). Another source of the polar cluster formation could be chemical fluctuation regions with ferro-ordering (for example, these are some kinds of Nb-rich regions with different Pb–Nb–O compositions in ferroelectric relaxor PMN). For study such a situation we will investigate in the present paper the limiting case of $Pb_xNb_yO_z$ -ceramics which only consists of different type $Pb_xNb_yO_z$ -clusters.

The chemical analysis study achieved that average normalized concentration of O-ion for as grown $Pb_xNb_yO_z$ -ceramics equals approximately to 3.5. That is, the Nb^{3+} ions have here relatively low concentration with respect to Nb^{5+} ion contribution. Nevertheless, a situation becomes principally different for the samples after reduction treatment. Indeed, such an average O-ion concentration becomes approximately 3 after essential sample reduction in the hydrogen atmosphere. It reflects the co-existence of different $Pb_xNb_yO_z$ -clusters with chemical compositions inclusive in average the Nb^{5+} as well as Nb^{3+} ions with approximately the same concentration. Note that corresponding Nb^{3+} ion significant contribution could be responsible for an appearance of magnetic behavior for such a $Pb_xNb_yO_z$ -ceramics. The latter is related with paramagnetic properties of Nb^{3+} ion ($S = 1$). As a

result, antiferromagnetic ordering of Nb^{3+} ion spins will be predicted here due to antiferromagnetic exchange interaction between these ions.

Co-existence of $Pb_xNb_yO_z$ -clusters with different chemical composition inclusive of Nb^{5+} as well as Nb^{3+} ions in the reduced ceramic Pb–Nb–O samples (Fig. 1) will be the main suggestion of our model. We assume that $Pb_xNb_yO_z$ -ceramics consists of non-magnetic $Pb^{2+}Nb_2^5O_6^{2-}$, $Pb_5^2+Nb_4^5+O_{15}^{2-}$, and $Pb_2^2+Nb_2^5+O_7^{2-}$ clusters on the one hand, and of antiferromagnetic $Pb_2^2+Nb_2^3+O_5^{2-}$, $Pb^{2+}Nb_2^3+O_4^{2-}$, and $Pb^{2+}Nb_{1/2}^3+Nb_{1/2}^5+O_3^{2-}$ clusters on the other.

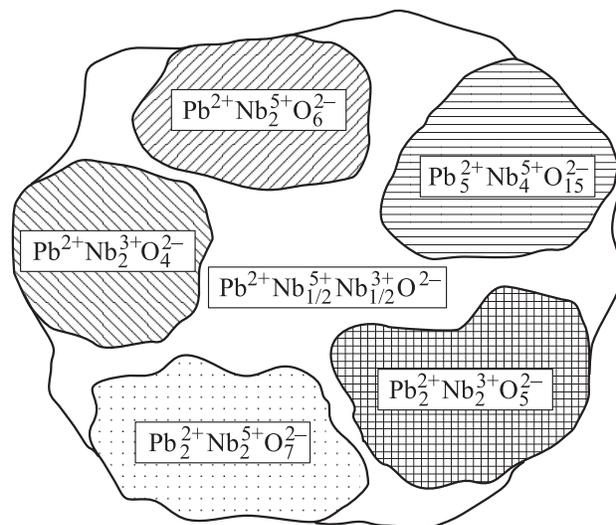


Figure 1. Co-existence of different Pb–Nb–O-clusters with different chemical composition and with different structure in $Pb_xNb_yO_z$ -ceramics.

2. Experimental results and their interpretation

Let us consider some new effects detected by EPR and by photoluminescence in $\text{Pb}_x\text{Nb}_y\text{O}_z$.

1. **Light induced effects in EPR.** Significant increasing of definite EPR-lines due to illumination (for instance, by mercury lamp during 0.5 h) takes place for as grown $\text{Pb}_x\text{Nb}_y\text{O}_z$ ceramic samples. Indeed, b and b' doublet is essentially increased by such illumination (Fig. 2). In contrast with it, a central a -line (with respect to doublet b and b') at least is not increased by the same illumination (or is slightly decreased by light) (Fig. 2). We assume that such a behavior could be related with EPR manifestation of polaronic and bi-polaronic states in $\text{Pb}_x\text{Nb}_y\text{O}_z$ ceramic samples. Indeed, b and b' doublet lines could be considered as a result of $|0\rangle \rightarrow |\pm 1\rangle$ transitions of triplet spin state ($S = 1$). Here splitting between $|0\rangle \rightarrow | + 1\rangle$ and $|0\rangle \rightarrow | - 1\rangle$ lines formation could be explained as a result of uniaxial in-cluster field action. It is naturally to assume that the photoinduced triplet could be related with pairs of self-localized carriers. These self-localized pairs of carriers in ferroelectric oxides become polaronic pairs. Such a conclusion seems rather natural because small polaron states are responsible for well defined carrier ground state in ferroelectric oxides in accord with conductivity investigations on the one hand, and calculations

of polaronic levels positions in many ferroelectric oxides (for instance, on the basis of semi-empirical Hartree–Fock approach in the INDO approximation) on the other. So, active here $|0\rangle$, $| + 1\rangle$ and $| - 1\rangle$ triplet spin states could be treated as the states of photoinduced triplet hole bi-polaron (b and b').

The central a -line (with respect to doublet b and b') could be interpreted as a free polaronic hole effect. Its g -factor value ($g = 3.015$) is high enough and could be explained as a result of direct contribution to the g -factor of the orbital Zeeman effect for the ground double degenerating state for oxygen related hole, $2p_x$ and $2p_y$. Such a ground state decreases its energy due to an interaction with $4d_{xy}$ -type ground states of two neighboring Nb-ions. The a -line intensity will decrease with illumination due to transfer of free hole state occupation to the hole bi-polaronic state (two hole strong correlation appearance with bi-polaron formation) on the one hand, and will increase with the same illumination due to direct generation by light of the free hole polaron on the other. We have to deal here with a competition of these two opposite tendencies which lead finally to rather weak change on the experiment of the intensity of induced by light a -line under discussion.

2. **Cr^{3+} -related polaron complexes.** In accord with photoluminescence studies of the $\text{Pb}_x\text{Nb}_y\text{O}_z$ -ceramics under discussion these samples contain unwanted Cr^{3+} impurity [6]. Its existence was confirmed by the detection of characteristic for $3d^3$ shall of Cr^{3+} ion very narrow R -lines [6] of a luminescence. Note that some specific charge compensation for Cr^{3+} impurity on Nb^{5+} site is topical for the case of $\text{Pb}_x\text{Nb}_y\text{O}_z$ -clusters with Nb^{5+} ion state (for PbNb_2O_6 -, $\text{Pb}_5\text{Nb}_4\text{O}_{15}$ -, and $\text{Pb}_2\text{Nb}_2\text{O}_7$ -clusters). Indeed, an extra ($2-$) charge on the Cr^{3+} site here needs corresponding charge compensation. It is realized due to two oxygen hole trapping on the Cr^{3+} ion of the Nb^{3+} site. In reality we deal with Cr^{3+} ion extra-charge compensation under the conditions of hole-hole correlation as well as of essential hole-lattice polarization and lattice deformation interactions. As a result, hole bi-polaron trapping to the first coordination sphere of Cr^{3+} impurity ion takes place here. We suppose in the present work that charge compensation of Cr^{3+} ion located on Nb^{5+} site is namely realised due to trapping of two oxygen-related holes to the first coordination sphere of such Cr^{3+} ion. As a result, neutral „impurity–two hole“ complex with related three-particle „Negative-U“ effect is appeared. Corresponding holes can be in small polaron states as well as in large (intermediate) polaron states. These aspects were discussed also in [6,7]. But in the present work we will extend such a model for real case of a co-existence of low and high total spin states on the one hand, and establish the links between magnetic states of such a „ Cr^{3+} — two polaronic holes“ paramagnetic complex and its structure with important consequences for this complex spin-orientation relaxation and related dynamical averaging effects on the other.

Let us discuss this aspect in more details. Here the paramagnetic complex with core-like Cr^{3+} ion ($S = 3/2$)

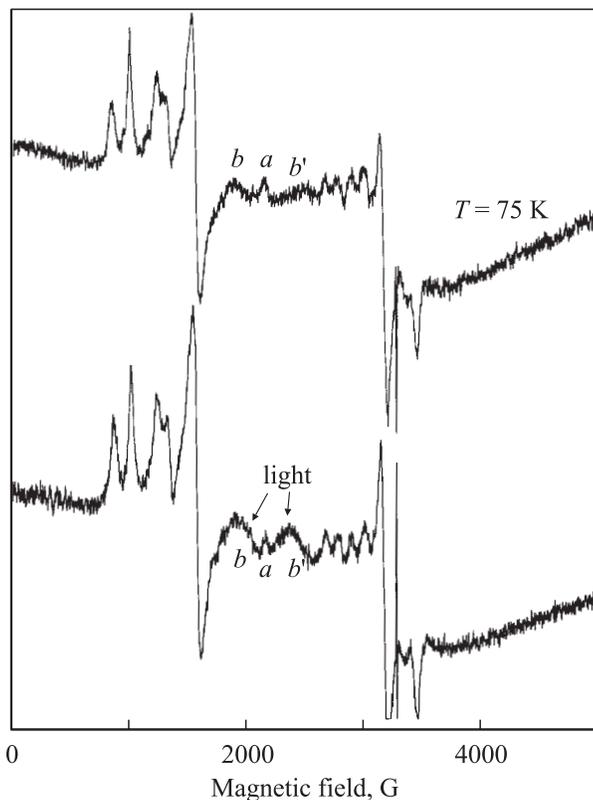


Figure 2. EPR spectra of $\text{Pb}_x\text{Nb}_y\text{O}_z$ -ceramics registered at $T = 75$ K without and with simultaneous light irradiation in the microwave cavity, and light induced center manifestation.

and with definite internal magnetic structure due to exchange interaction between holes with $S = 1/2$ within bipolaron, as well as between the same holes and core-like Cr^{3+} ion takes place. We have the case of the formation of three type states with total spin values $S = 5/2$, $S = 3/2$, and $S = 1/2$ respectively. Ferromagnetic-type state with $S = 5/2$ is the ground state of our system for the case of a weak vibronic interaction for polaronic holes and of a corresponding weak „Negative-U“ effect which could not compensate a Coulomb hole-hole repulsion in this case. Such a situation is characterized by $h^+-Cr^{3+}-h^+$ complex linear chain geometry and by ferromagnetic ordering of all three spins for three centres forming the complex under discussion. That is, such a geometry corresponds to $S = 5/2$ total spin. To the contrary, the $S = 3/2$ complex state is characterized by antiferro-ordering for trapped h^+-h^+ holes. This $S = 3/2$ state becomes ground complex state due to strong „Negative-U“ effect for h^+-h^+ pair in the framework of strong vibronic coupling for holes accompanied by essential h^+-h^+ distance decrease. This situation is characterized by near right angle geometry for the complex, $h^+_h+Cr^{3+}$. At last, $S = 1/2$ state of the complex is excited state with respect to both limiting situations discussed above. Now let us treat the EPR related aspects.

3. Dynamical averaging effect and the main EPR spectrum origin. As it is seen, linear chain and near right angle geometries are related with different type of hole-hole exchange interaction, and with corresponding different spin-structure. As a result, spin-lattice relaxation transition with the change of a spin value, $|S = 5/2\rangle \leftrightarrow |S = 3/2\rangle$, is accompanied by spin-flip process for a single hole. The latter means that linear chain geometry — near right angle geometry relaxation transition in reality is the spin-flip transition which influences on the EPR. For instance, such a transition could directly take part in the formation of EPR lines dynamical averaging phenomenon, and of spin-lattice relaxation.

The next significant aspect here is related with strong enough vibronic reduction of corresponding exchange interaction due to strong enough difference of an vibronic effect contribution to $S = 5/2$ linear chain, and to $S = 3/2$ near right angle states under discussion. The latter leads to important decrease of corresponding exchange splitting between $|S = 5/2\rangle$ and $|S = 3/2\rangle$ state energies up to the values of the same order as room temperature equivalent value. As a result, we have to deal with strong acceleration with temperature of such spin-flip relaxation accompanied by linear chain geometry — near right angle geometry reorientation transitions in room temperature region. The latter allows to use the $|S = 5/2\rangle \leftrightarrow |S = 3/2\rangle$ relaxation transitions as an origin of dynamical averaging phenomenon within our experiments. Indeed, as it is shown on the Fig. 3, the d -group of EPR lines manifests the transformation with temperature which can be treated as dynamical averaging effect in 75–230 K region. It is important for such an explanation that both type of active states, $|S = 5/2\rangle$ as well as $|S = 3/2\rangle$, could be realized in the framework of the EPR experiment. Moreover, we have to deal here

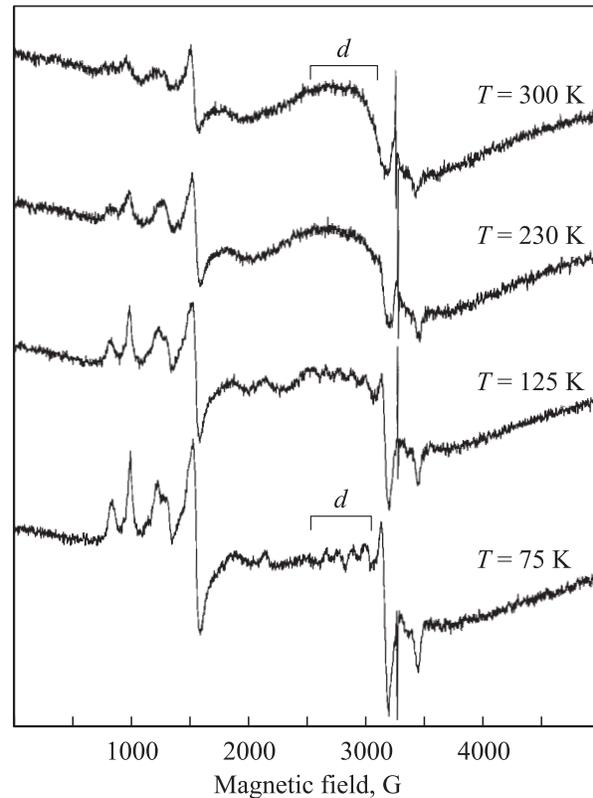


Figure 3. Temperature dependences of EPR spectra of $Pb_xNb_yO_z$ -ceramics at $\nu = 9.35$ GHz in 300–75 K range. Manifestation of broad and intensive EPR-line (spectrum denoted by bracket „ d “) appearing with temperature for magnetic fields in the $2150 \leq H \leq 3100$ Gs region.

with not only a simple co-existence of $|S = 5/2\rangle$ and $|S = 3/2\rangle$ states, but with their multiple co-existence taking into account realization of „ Cr^{3+} — two polaronic holes“ paramagnetic complexes within three different Pb–Nb–O clusters containing Nb^{5+} ions (Fig. 1). Namely this model has explained the main EPR line spectrum structure (Figs 3, 2). It was done by WINEPR SimFonia Program for powder spectra treatment. It is important to underline that EPR-lines connected with $|S = 5/2\rangle$ state as well with $|S = 3/2\rangle$ state both are taking part in d -line group (Fig. 3) formation but are responsible for different EPR lines in this group as it is following from the computer analysis of the powder spectra mentioned above. We conclude that $|S = 5/2\rangle \leftrightarrow |S = 3/2\rangle$ fluctuation mechanism could be effective here for dynamical averaging effect explanation. Last not the least, such a model could explain also not only the averaging effect alone but strong intensity increase with temperature of the averaged spectra. The latter could be due to direct contribution of spin-flip relaxation transition $|S = 5/2\rangle \leftrightarrow |S = 3/2\rangle$ to microwave absorption as a result of mixed absorption transitions appearance. Here usual external microwave magnetic field as well as resonance microwave component of the spectrum of internal magnetic field fluctuations related to $|S = 5/2\rangle \leftrightarrow |S = 3/2\rangle$ relaxation transitions both together

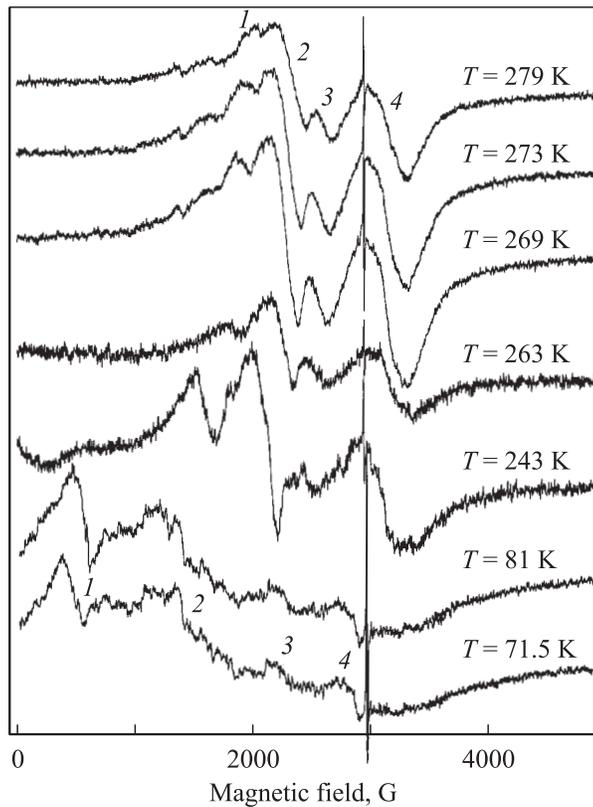


Figure 4. Temperature dependence of antiferromagnetic resonance lines (two doublets, 1 and 2, 3 and 4) accompanied by EPR-lines of defects in internal magnetic field for strongly reduced $\text{Pb}_x\text{Nb}_y\text{O}_z$ -ceramics. Essential line shifts, line broadenings, intensities decreasing, and multi-line structure appearance with temperature lowering are presented.

form the cross-type absorption effect. As a result, we have pronounced enhancement of the microwave absorption which could be related to the experiment situation (Fig. 3).

Note in the conclusion of this section that another type unwanted paramagnetic impurity centers in the $\text{Pb}_x\text{Nb}_y\text{O}_z$ -ceramics, namely, related with Cu^{2+} ions, could not be disregarded. A possibility of different type unwanted paramagnetic centers in the considering $\text{Pb}_x\text{Nb}_y\text{O}_z$ ceramics was discussed previously in [7].

4. Antiferromagnetic $\text{Pb}_x\text{Nb}_y\text{O}_z$ -clusters, antiferromagnetic resonance, and EPR in internal magnetic field. Strong reduction treatment of the $\text{Pb}_x\text{Nb}_y\text{O}_z$ -ceramics under consideration leads to principally new situation for the relative contribution of Nb^{5+} and Nb^{3+} charge states of Nb ion to such a ceramics. Namely, the contribution of Nb^{3+} ions is significantly increase and reaches the contribution of Nb^{5+} ions. Antiferromagnetic clusters are appeared here namely on the basis of above mentioned (see the introduction and Fig. 1) three type micro-regions containing Nb^{3+} paramagnetic ions with $3d^2$ shell and $S = 1$. The antiferromagnetic ordering is created there due to $\text{Nb}^{3+}-\text{O}-\text{Nb}^{3+}$ super-exchange interaction via intermediate oxygen ion. Such clusters were detected in the present work by antiferromagnetic resonance [8,9], AFMR

(Fig. 4). Note that magnetic ordering mentioned above is accompanied by internal local magnetic field appearance with characteristic temperature dependence. Characteristic antiferromagnetic ordering features, namely, strong AFMR line shifts with temperature lowering up to an appearance of near zero field AFMR lines on the one hand, as well as resonance line intensity decreasing and line width increasing with the same temperature lowering on the other (Fig. 4) support such an interpretation. Moreover, as it is following from Fig. 4, we have to deal with AFMR induced by two different Nb^{3+} rich antiferromagnetic clusters (for example, by $\text{Pb}_2^+\text{Nb}_2^+\text{O}_5^{2-}$ and by $\text{Pb}^{2+}\text{Nb}_2^+\text{O}_4^{2-}$ -clusters) because two basic doublets (AFMR lines 1, 2 and 3, 4 on Fig. 3) take place on the experiment.

The internal local magnetic field in the ferromagnetic clusters discussed above leads also to significant EPR lines shift for impurity-related paramagnetic centers are located in the inter-cluster interface regions. We assume that EPR active impurity centers Cr^{3+} , Cr^{3+} with two oxygen-related holes, and $\text{Cr}^{3+}-\text{V}_\text{O}^{2+}$ on the one hand, and Cu^{2+} , $\text{Cu}^{2+}-\text{V}_\text{O}^{2+}$, and $\text{V}_\text{O}^{2+}-\text{Cu}^{2+}-\text{V}_\text{O}^{2+}$ on the other are realized in inter-cluster interfaces for antiferromagnetic clusters under discussion. So, the AFMR and EPR signals are co-existed in the super-high-frequency response and both are under the action of internal magnetic field of Nb^{3+} ion system. Taking into account an increasing of such an internal magnetic fields with temperature lowering, and its random behavior in the framework of random interface structure we have to deal here with extended distribution for the resonance magnetic field shifts of AFMR and EPR lines under discussion. This type multi-line phenomenon inducing with temperature lowering was detected experimentally namely in reduced samples containing Nb^{3+} .

5. CTVE-manifestation in $\text{Pb}_x\text{Nb}_y\text{O}$ -ceramics. Free CTVE and CTVE-phase states. Charge Transfer Vibronic Excitons (CTVEs) are characteristic long living dipole excitation in ferroelectric oxides (see [3–5] and references therein). They are polaronic electron-hole pairs or triads. In this work we have detected

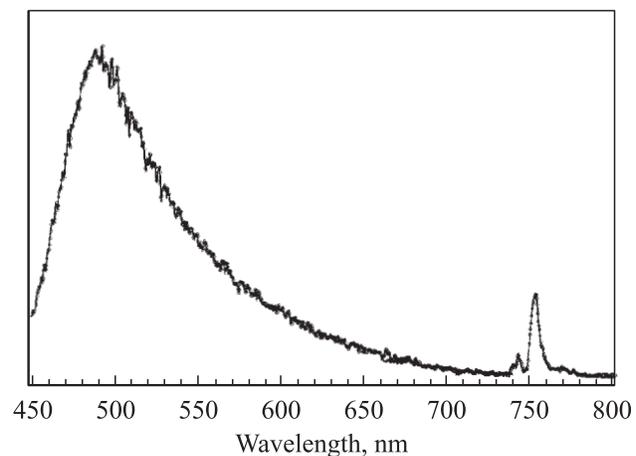


Figure 5. Photoluminescence intensity spectral dependence for ceramics powders of $\text{PbNb}_{x1}\text{O}_{y1}$. Photoluminescence was excited by N_2 -laser ($\lambda = 337$ nm), $T = 293$ K.

CTVEs in $Pb_xNb_yO_z$ -ceramics (Fig. 5). Here CTVEs with $O \rightarrow Nb^{5+}$ charge transfer was directly manifested by photoluminescence studies. The band-band excitation by pulse N_2 laser was used. We had detected a photoluminescence line related with recombination of $O \rightarrow Nb^{5+}$ CTVE at ~ 500 nm. This line coincides in a good approximation with corresponding photoluminescence line of $O \rightarrow Nb^{5+}$ CTVE in Nb_2O_5 -ceramics. Note, that $O \rightarrow Nb^{3+}$ CTVEs were not obtained on the experiment. This is an indication that $O \rightarrow Nb^{3+}$ CTVE is characterized by more high excitation energy than for $O \rightarrow Nb^{5+}$ case.

Special interest is caused by a detection of two red luminescence lines (at ~ 740 and at ~ 760 nm) which can be connected with recombination of $O \rightarrow Nb^{5+}$ CTVEs in the CTVE-phase state. Such a phase is related with an appearance of a system of strongly correlated CTVEs when in each cell the CTVE is appeared [3–5]. Note that recombination of free CTVEs explains an origin of „green“ luminescence which is a general enough phenomenon for ferroelectric oxides. As it was shown recently [5], „red“ luminescence phenomenon is also related with CTVE-recombination but in the CTVE-phase state. Here strong „red“ luminescence signal corresponding to more low luminescence quantum is related to CTVE-recombination in the lowest, ferroelectric CTVE-phase. Vice versa, weak „red“ luminescence signal corresponding to more high luminescence quantum is related to CTVE-recombination in the excited, antiferroelectric CTVE-phase.

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