

Relaxor-like and spectroscopic properties of niobium modified barium titanate

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Abstract. Dielectric susceptibility measurements on niobium-modified barium titanate ceramics for Nb compositions extending up to the solubility limit (18%) show that these materials display relaxor-like properties for compositions larger than $\sim 6\%$ Nb. Raman spectra exhibit extra modes attributed to local responses related with the substitution of niobium for titanium ions. The behaviour of this barium titanate modification, in which Nb^{5+} aliovalent cations are substituted for Ti^{4+} , is discussed by comparison with the zirconium-modified series, in which, oppositely, only a size difference characterizes the substitution on the B site. It is emphasized that electrical random fields created in the former case are more efficient in inducing a relaxor behaviour than elastic random fields created in the latter. The nature of the complex defects expected from the inherent high concentration of barium vacancies is discussed in connection with photoluminescence spectra.

PACS. 77.84.-s Dielectric, piezoelectric, ferroelectric, and antiferroelectric materials – 77.84.Dy Niobates, titanates, tantalates, PZT ceramics, etc – 61.43.-j Disordered solids

1 Introduction

One of the interesting properties of ferroelectric relaxors, as far as applications are concerned, is the broad dielectric peak which makes them suitable for DRAM or high performance capacitor dielectrics in a wide temperature range. However, most of relaxor compounds are complex lead-based perovskites $\text{A}(\text{B},\text{B}')\text{O}_3$ with $\text{A} = \text{Pb}$, such as lead magnesio-niobate (PMN) or lanthanum modified lead zirconate titanate (PLZT) which have been the subjects of many studies. Due to environmental concerns, specific work has been devoted to lead-free relaxors over the last few years. Promising compounds are modified barium titanate ceramics. Barium titanate is used for a long time as a dielectric in many electrical components and devices, but it exhibits a rather narrow dielectric permittivity *vs.* temperature $\varepsilon'(T)$ peak. The idea of incorporating ions to this material in order to change its properties has been suggested and realized many years ago [1], but its transformation into a lead-free relaxor has been systematically investigated only very recently [2]. Various modifications have been considered and prepared, namely homovalent or heterovalent substitutions on the A- or on the B-site [2], but the more interesting ones from the fundamental as well as for the technological points of view are the B-site substitutions. In a previous article [3], we reported

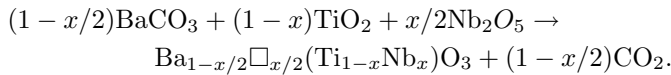
and discussed the properties of zirconium modified barium titanate $\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramics and their relaxor behaviour for $x > 27\%$. It was shown in this work that these compositions, referred to as BTZ100x in what follows, displayed all the characteristics of usual relaxors, with a freezing (Vogel-Fulcher) temperature of about 145 K for BTZ40, below which a breaking of ergodicity takes place. In addition, some specific features of the Raman spectra and their evolution with temperature were reported and discussed. It should be pointed out that Zr substitution on B-site is homovalent, and is not predicted, accordingly, to affect in a drastic way the charge state of BaTiO_3 . In other words, Zr^{4+} ions do not act as random electric field sources. However, the Zr^{4+} ion size (72 pm) is about 20% larger than that of Ti^{4+} ion (60.5 pm) in 6 coordination, and random elastic fields are thus expected from this substitution, which are very likely responsible for relaxor properties [4] which appear in BTZ for $x > 27\%$. It has been briefly suggested [2] that heterovalent substitutions could induce a relaxor behaviour above much smaller concentrations (~ 0.04). The radius of the pentavalent niobium ion is close (64 pm) to that of tetravalent titanium. The difference in their valencies would be, in that case, the more relevant parameter, and the corresponding random fields are thus expected to be of electrical nature. The aim of the present work is to report the electrical and spectroscopic properties of highly niobium modified barium

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titanate (referred to as BTN), and to discuss them in terms of defects and charges, by comparison with the results already obtained and published on the zirconium modified compositions [3]. Small substitution ratio $\text{BaTiO}_3\text{:Nb}$ ceramics and single crystals were already studied and are known for their electrical conductivity properties [5]. The second section of the paper is devoted to a brief description of the experimental details. Section 3 deals with dielectric measurements, and Section 4 with the spectroscopic experiments, which include Raman scattering and photoluminescence spectra. The discussion of these results and their comparison with those previously obtained on BTZ will be the subject of Section 5.

2 Experimental details

The various compositions were obtained from BaCO_3 (Cerac 99.9%), TiO_2 (Aldrich 99.99%) and Nb_2O_5 (Fluka 99.9%) by solid state synthesis using the following chemical reaction:



A calcination for 15 hours at 1100 °C was followed by a 4-hours sintering at 1400 °C. Both heat treatments were conducted under dry oxygen atmosphere. Room temperature X-ray diffraction analyses allowed to determine the limit of the solid solution ($x \approx 0.18$) in which the structural type was still perovskite. For higher x values, the X-ray diffraction pattern showed the powder to be heterogeneous, *i.e.*, not a single phase. Diameter shrinkages $\Delta\Phi/\Phi$ were systematically determined as $\Phi_{\text{initial}} - \Phi_{\text{final}}/\Phi_{\text{initial}}$, and were in the range 0.14 to 0.18.

Prior to dielectric measurements, gold electrodes were deposited on the circular faces of the cylindrical platelets about 7 mm in diameter and 1 mm thick. The study was performed under dry helium from 75 to 450 K using a Wayne-Kerr component analyzer 6425, in the frequency range $10^2 - 10^5$ Hz.

Because of the difference in the ionic valency between titanium and niobium ions, constitutional barium vacancies characterize niobium modified BaTiO_3 , in such a way that the exact stoichiometry of this compound should be written as $\text{Ba}_{1-x/2}\square_{x/2}(\text{Ti}_{1-x}\text{Nb}_x)\text{O}_3$, where \square stands for barium vacancy. This means that, in BTN15, for instance, the concentration of barium vacancies is 7.5%, *i.e.*, about one vacancy every 2.4 unit cells along one of the 3 directions of the space. As will be discussed later on, such a high content of vacancies is expected to give rise to complex defects.

Raman scattering investigations were performed below room temperature on two samples, representative of a ferroelectric (BTN2.5) and a relaxor-like (BTN15) composition. The sample was stuck to the cold finger of a cryostat, and the scattered light was analyzed by a Dilor Z24 spectrometer. The exciting light for the Raman spectra was the 514.5 nm line of an Argon ion laser. More details

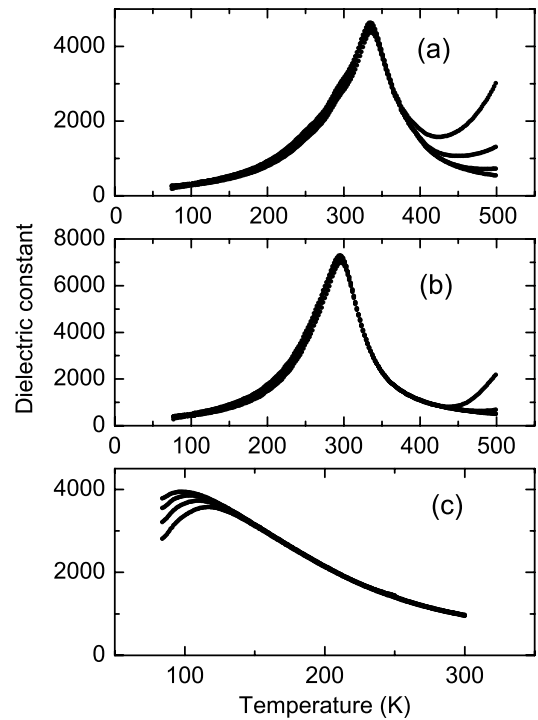


Fig. 1. Real part of the dielectric permittivity as a function of the temperature for BTN2.5 (a), BTN5 (b) and BTN15 (c). Only 4 of the 8 frequencies investigated have been plotted, namely 10^2 , 10^3 , 10^4 and 10^5 Hz from top to bottom in each plot. The increase in the dielectric permittivity observed for BTN2.5 and BTN5 at high temperature is very likely related with electrical conductivity.

can be found in reference [3]. All the vibration spectra reported in this article are corrected by the population factor $n(\omega) + 1$. The same Raman spectrometer was used for the photoluminescence spectra, but the 488 nm line of the Ar^+ laser was selected. The spectral range of the Z24 spectrometer extends from 1.5 to 3.5 eV. However, the upper limit of the photoluminescence spectra is determined by the energy of the exciting light, *i.e.*, 2.54 eV for the blue laser line used.

3 Dielectric experiments and phase diagram

Dielectric susceptibility measurements have been done as a function of temperature at frequencies extending from 10^2 to 2×10^5 Hz on the whole series of BTN samples. The results at some of these frequencies are represented in Figure 1 for the three compositions BTN2.5 (a), BTN5 (b), and BTN15 (c). Contrary to what was observed in BTZ [3], a niobium content as low as 2.5% (Fig. 1a) confers to barium titanate a “diffuse phase transition” character [6]. A very broad, but non-dispersive, dielectric susceptibility peak is observed. In addition, the well known phase transitions of barium titanate, which were

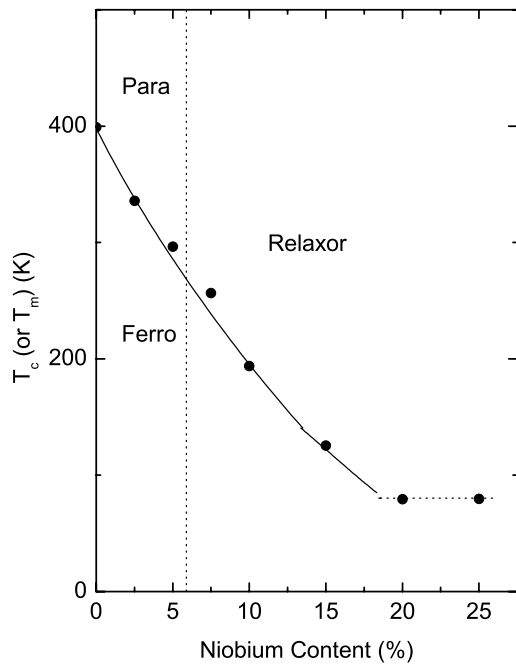


Fig. 2. Phase diagram for niobium doped barium titanate, as determined from dielectric measurements. The temperatures for concentrations larger than 6% are those of the dielectric maximum measured at 10^3 Hz. The solubility limit is 18% Nb. Lines are guides for the eyes.

still detected in low zirconium content BTZ as anomalies in the dielectric susceptibility, are restricted in BTN2.5 to the paraelectric to ferroelectric transition at 334.5 K for this composition (~ 400 K in BaTiO_3 and 391 K in BTZ2.5 [3]). An other smeared transition is visible in the plot, and measured at 285 K by differentiation. In the 5% compound (Fig. 1b), the dielectric susceptibility maximum is determined as ~ 297 K, and the above mentioned smeared anomaly has completely disappeared. A dispersive behaviour is obtained for Nb concentration $x \gtrsim 0.06$. Figure 1c illustrates this behaviour for BTN15. Only 4 of the 8 frequencies studied have been reported in order not to clutter up the figure. The temperature T_m of the dielectric susceptibility maximum decreases from 117 to 98 K when the frequency varies from 10^5 to 10^2 Hz. A conventional analysis gives a Vogel-Fulcher temperature of 25 K for this composition, to be compared with 145 K in BTZ40 [3].

The phase diagram derived from the dielectric measurements is reported in Figure 2. It is poorer than for BTZ because of the already mentioned smearing of the transitions other than paraelectric to ferroelectric. In the dispersive region ($x \gtrsim 0.06$) the reported values are the temperatures T_m determined from a measurement at 10^3 Hz. The comparison with the phase diagram obtained for BTZ [1,3] shows that the slope of the $T(x)$ line is steeper and the concentration above which a relaxor-like behaviour appears smaller for BTN than for BTZ. These observations will be discussed in more detail in Section 5.

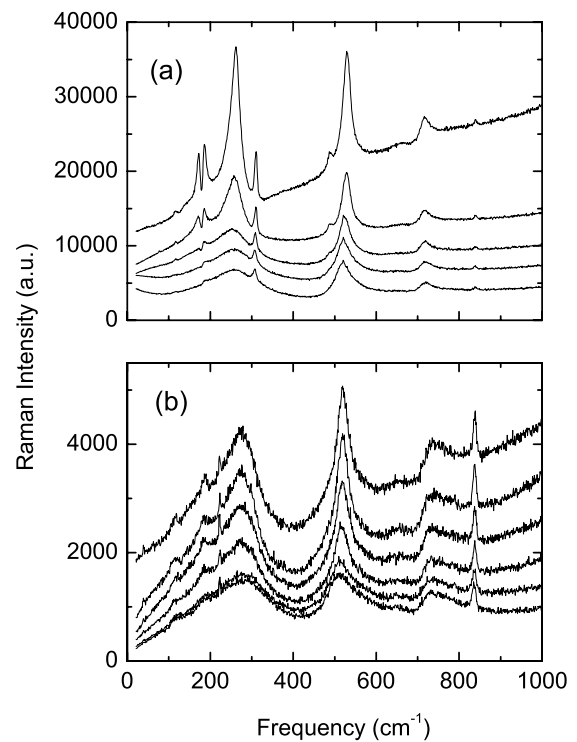


Fig. 3. Raman spectra at various temperatures for: (a) BTN2.5: from top to bottom: 13, 100, 200, 250 and 270 K; (b) BTN15: from top to bottom: 13, 40, 85, 130, 235 and 300 K.

4 Raman scattering and photoluminescence spectra

4.1 Raman scattering

Raman spectra of BTN2.5 have been recorded below room temperature, *i.e.*, in ferroelectric phase(s). Because of their ceramic character, the spectra recorded in parallel and crossed polarizations are similar. They are represented in Figure 3a for various temperatures. A striking fact is the continuous increase of the “baseline” with the Raman shift. This is related with a photoluminescence phenomenon which will be the subject of the next subsection. Most of the features already described for BTZ [3] can be recognized, and are very reminiscent of those previously reported and analyzed for pure barium titanate [7]. More specifically, the $B_1 + E$ line at 311 cm^{-1} , the high frequency LO mode at 719 cm^{-1} and the interference effect at $\sim 180 \text{ cm}^{-1}$ are observed in the ferroelectric tetragonal phase. The mode located at 488 cm^{-1} , which is labelled, according to Scalabrin *et al.* [7], as E(TO), seems to disappear on heating above 200 K, in the same way as in BTZ05, where it was no longer detected at 270 K. This mode could thus be thought as a signature of the rhombohedral phase, but this assertion is worth to be confirmed on pure barium titanate single crystals. Two other features missing in BaTiO_3 were reported in BTZ [3]. The first one, located at 119 cm^{-1} in BTZ05 and which transforms into a dip for the relaxor composition BTZ40, was attributed

to a local mode related with zirconium. The second, a high frequency line ($\sim 780 \text{ cm}^{-1}$), was associated with the occurrence of relaxor properties, but without any further comment. These two features are also observed in BTN2.5, at 117 and 838 cm^{-1} , respectively (Fig. 3). According to Freire and Katiyar [8], the low frequency mode, labelled as $E(\text{TO}_2)$, corresponds to a motion of the barium ions against the BO_6 octahedra. The substitution of Zr or Nb for Ti on the B-site results in an increase in the weight of the BO_6 unit, which in turn lowers the frequency of the mode from 180 cm^{-1} in pure barium titanate to 119 cm^{-1} in the modified compounds. The closeness of the atomic weights of Zr ($M = 91.22$) and Nb ($M = 92.91$) explains why these low lying lines exhibit almost the same frequencies in BTZ and BTN. On the contrary, the high frequency mode peaks at different frequencies in BTZ and BTN (~ 780 and 838 cm^{-1} respectively). According to the same analysis [8], these lines could be thought as the local counterparts of the $E(\text{LO}_4)$ mode, which appears at 722 cm^{-1} in pure barium titanate. It is depicted by these authors as an internal deformation of the BO_6 octahedron. Force constants between the B cation and oxygen ions are not expected to be the same for Zr^{4+} and Nb^{5+} , at least because of their different charges, and this could be a reason for the higher line frequency displayed by the BTN compositions.

Some of the Raman spectra obtained for BTN15 are presented in Figure 3b. These spectra look very much like those recorded in the paraelectric cubic phase of pure barium titanate, *i.e.*, they are mainly constituted by three broad bands located at ~ 280 , 520 and 720 cm^{-1} , which are labelled as $A_1(\text{TO})$ and $E(\text{TO})$ modes in the tetragonal phase [7]. The two local features at 119 and 838 cm^{-1} still persist, and this last line is even stronger than in BTN2.5, despite the lower signal level recorded in BTN15 by comparison with BTN2.5. This increase in the intensity with the niobium content reinforces our assertion on the local character of this line. Such a local mode was already observed in lanthanum doped barium titanate, where it appears at 840 cm^{-1} , with an intensity increasing with the La content [9]. But the most important information which is provided by Figure 3b is the strong variation, with the temperature, of the 280 and 520 cm^{-1} lines, whose behaviour has been already explained in terms of space and time Fourier transform of the correlation function of the polarization in many relaxor compounds [3, 10, 11]. In order to show the variation with temperature of the Raman intensity, we have selected the isolated 520 cm^{-1} line for which the integrate intensity can be easily calculated. The corresponding data are plotted in Figure 4. The integrated Raman intensity begins to increase on cooling for temperatures lower than $\sim 200 \text{ K}$, while it was already increasing at 300 K in BTZ, and the plateau reflecting the saturation of the correlation function of the polarization, *i.e.*, the ergodicity breaking, appears below $\sim 40 \text{ K}$, in rather good agreement with the Vogel-Fulcher temperature of 25 K obtained from dielectric results. In compounds which exhibit a real ferroelectric phase transition, such as low La PLZT compositions [12] or ferroelectric BTZ [3], a conti-

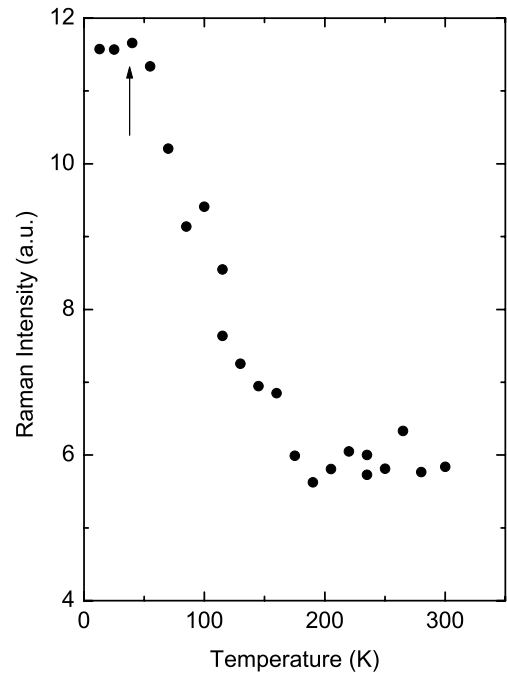


Fig. 4. Variation with temperature of the integrated Raman intensity of the 520 cm^{-1} line in BTN15. A plateau is observed below about 45 K .

nous increase of the Raman integrated intensity of most of the lines is observed, without any saturation, reflecting the onset of ferroelectric long range order. This is actually the case of BTN2.5.

4.2 Photoluminescence spectra

Figure 3 clearly shows an increase of the background with the Raman shift at low temperature in BTN2.5 as well as in BTN15. This trend is usually attributed to a luminescence effect. To check this assertion, the spectra have been recorded up to the higher absolute wavenumber limit of the spectrometer after a change in the exciting laser line from 514.5 to 488 nm , as mentioned previously. The result is presented in Figure 5a for the 2.5% Nb compound at 13 K (top) and room temperature (bottom). The strong peak at 2.54 eV is the (attenuated) exciting line, and the Raman spectrum is visible in the spectral region 2.45 to 2.54 eV . A very broad band extends between 1.5 and 2.5 eV . Its maximum shifts to lower energies and its intensity decreases on heating. A very narrow line (0.019 eV wide) located at 1.605 eV is also visible at 13 K , but vanishes on heating.

These phenomena are strongly enhanced in the 15% Nb composition, as illustrated in Figure 5b. Two narrow lines are now present at ~ 1.592 (line 1) and 1.610 eV (line 2). Their energy positions do not change very much with temperature, but their linewidths increase from 0.0214 to 0.0384 eV for line 1, and from 0.0101 to 0.0196 eV for line 2 when the temperature increases from 13 to 300 K . In addition, their intensity strongly decreases

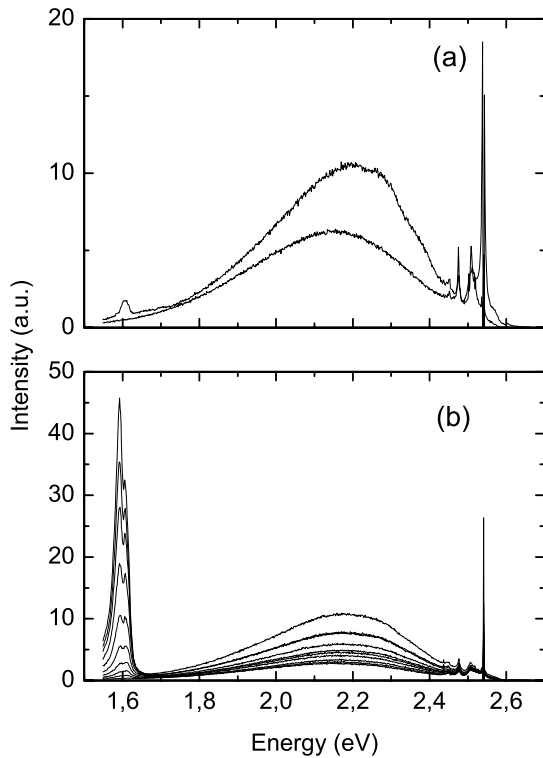


Fig. 5. Photoluminescence spectra: (a) BTN2.5 at 13 K (upper curve) and room temperature; (b) BTN15 at temperatures varying from 13 K to 300 K from top to bottom.

on heating, and it could be thought of a thermal quenching by a non radiative channel. A fit of the integrated intensity of these lines with the usual expression for thermal quenching [13]: $I \sim (A + B \exp(-E_{TQ}/kT))^{-1}$ gives energies of 53 and 77.6 meV for lines 1 and 2 respectively. A similar analysis for the broad band extending from about 1.7 to 2.5 eV would give an energy of ~ 19 eV but, as discussed in the next section, such a treatment of the data is probably not appropriate.

5 Discussion

The purpose of this study was to compare the electrical properties and the Raman responses of barium titanate ceramics doped with either zirconium [3] or niobium. These two Zr^{4+} and Nb^{5+} cations have been chosen because of their differences with titanium: Zr^{4+} is isovalent but larger in size by about 20% than Ti^{4+} , while Nb^{5+} has approximately the same size as Zr^{4+} but a different charge. The comparison of the results of the previous [3] and the present work reinforces the general idea that electric random fields are more efficient in ferroelectric materials than elastic (dilatational) random fields in lowering the ferroelectric transition temperature and in inducing a relaxor behaviour, as was already demonstrated in a previous theoretical study [4]. First, the concentration above which a dispersive behaviour is observed in the dielectric properties is much smaller ($\sim 6\%$) for the Nb doped than for

the Zr doped ($\sim 27\%$) compounds. Secondly, the Vogel-Fulcher temperature is significantly lowered (*e.g.*, from 145 K for BTZ40 to 25 K for BTN15) on changing the substituting ion from Zr^{4+} to Nb^{5+} . However, and contrary to BTZ, the question of the relaxor behaviour of BTN is still open. In the former compound, a clear pyroelectric depolarization peak was observed [3], which can be considered as the signature of a relaxor phase at low temperature: below the Vogel-Fulcher temperature, a breaking of ergodicity occurs, and an average non-zero polarization can be stabilized if induced under electric field from high temperatures. On restoring ergodicity (*i.e.*, above the freezing temperature), this field-induced macroscopic polarization disappears and gives way to a depolarizing current peak. In BTN, the first results reported in this article are limited to liquid nitrogen temperature, and a dielectric and pyroelectric study at lower temperature is clearly needed to confirm the relaxor character of this compound for Nb contents higher than $\sim 6\%$. These experiments are under way, but strong hints at a relaxor behaviour are already given by the observation of an increase of the imaginary part of the dielectric susceptibility with frequency, and by the closeness of the maximum temperatures for its real and imaginary parts.

The question of the nature of the charged defects in BTN can be addressed. As stated previously (Sect. 2), 7.5% of barium vacancies (\square) are needed for charge compensation in BTN15, and such a high concentration is expected to give rise to complex defects, associating, *e.g.*, Nb^{5+} ions and \square vacancies. Photoluminescence spectra can give an idea of the defects involved in the behaviour of BTN. The low energy lines around 1.6 eV speak in favour of such complex defects: only one weak line is observed in BTN2.5, while two strong and thermally quenched lines characterize the photoluminescence spectrum of BTN15. The energies of the temperature quenching are 53 and 77.6 meV, *i.e.*, within the range of phonon excitations and could be interpreted in terms of a non-radiative recombination channel between localized-center states in the configuration-coordinate model [13]. The complex defects are suggested to play the role of these localized centers. ESR measurements could provide more information to check this assertion.

Broad luminescence bands centered around 2.3 eV have been observed in perovskites for a long time, but their explanation is still controversial. Earlier works [14] attributed this feature to exciton recombination, but more recent investigations [15,16] showed that, because of the occurrence of O^- and cationic states within the band gap of $BaTiO_3$, donor-acceptor pair recombination is more likely. Trivalent titanium cations are known to exist in barium titanate, but it has been shown [17] that, even for small niobium contents (typically $\sim 0.15\%$ Nb), Ti^{3+} ions reduce Nb^{5+} to Nb^{4+} , in such a way that all these charged species are expected to contribute to donor-acceptor pair luminescence. The electronic structure of strongly doped barium titanate remains however to be investigated, both theoretically and experimentally, and time resolved luminescence spectra could help in determining the nature of the involved states.

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