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# Original Crystal-Chemical Behaviors in $(\text{Ba,Sr})_2\text{Ln}(\text{Fe,Nb,Ta})_5\text{O}_{15}$ Tetragonal Tungsten Bronze: Anion-Driven Properties Evidenced by Cationic Substitutions

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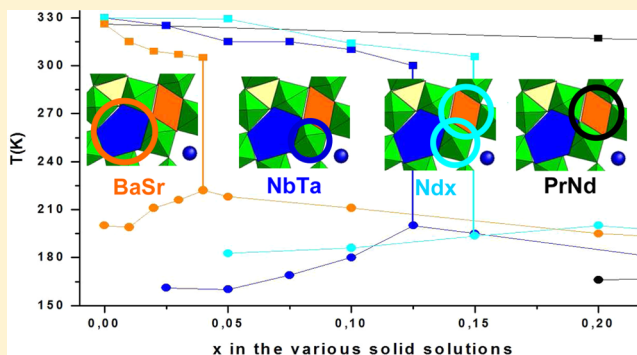
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**ABSTRACT:** From room-temperature composite multiferroics to relaxor to ferroelectric crossovers, many original behaviors were recently evidenced in compounds and/or solid solutions related to the  $\text{Ba}_2\text{LnFeNb}_4\text{O}_{15}$  (Ln = rare earth) family of tetragonal tungsten bronze (TTB) materials. We show how an empirical crystal chemistry approach, while yielding unexpected results, allowed for a better understanding of these original and sometimes specific behaviors. A survey of the dielectric properties of four solid solutions derived from the  $\text{Ba}_2\text{NdFeNb}_4\text{O}_{15}$  ferroelectric TTB is presented. We also show how the diversity of compositions and chemical substitution patterns unveils the anionic driving force behind the relaxor to ferroelectric crossovers. We finally discuss the probable involvement of aperiodic modulations in these crossovers and the fact that these modulations may constitute an additional degree of freedom to control the properties of TTB structured functional materials.



## 1. INTRODUCTION

In the wide panel of functional materials, ferroics<sup>1</sup> are the centerpiece of many fundamental and technological breakthroughs of the highest importance to our society. We rely on ferromagnets for information storage and on ferroelectrics to design capacitors and memories. Ferroic properties can be triggered in many crystal structures and chemical systems, the most proficient (and the most studied) being probably the oxides with perovskite structure, in which the three kinds of primary ferroic orders are encountered. Perovskite-based ferroics have been and are still the subject of extensive research and controversy, which allow the fundamental knowledge on ferroics to progress.

When two ferroic properties are combined in a unique material, this one is labeled a multiferroic<sup>2</sup> and becomes subject to the highest interest from the material sciences communities, because of the potential such a combination offers for the development of a new generation of functional materials.<sup>3,4</sup> Among multiferroics, magnetoelectric multiferroics are currently attracting a renewed interest, as the superposition and the coupling of magnetic and dielectric properties may allow for new concepts in information storage and in the developing field of

spintronics. But single-phase magnetoelectric multiferroics are scarce and mostly related to perovskite. It is thus of the highest interest to increase the structural and chemical diversity of systems investigated for such properties and to look for alternative ways to design ferroic and multiferroic materials. In this view, oxides crystallizing with the tetragonal tungsten bronze (TTB) structure form another proficient class of ferroics, in which ferroelectrics and ferroelastics are abundant, while ferroelectric and magnetic orders can both be found in TTB fluorides.<sup>5,6</sup> The present paper aims at enlightening the potentialities of  $(\text{Ba,Sr})_2\text{Ln}(\text{Fe,Nb,Ta})_5\text{O}_{15}$  TTBs (Ln = La, Pr, Nd, Sm, Eu, Gd) for ferroic and other properties. Traditional, empirical, and simple solid state and crystal chemistry approaches unveil how the anionic sublattice of the  $(\text{Ba,Sr})_2\text{Ln}(\text{Fe,Nb,Ta})_5\text{O}_{15}$  TTB may govern many of their chemical, structural, and physical properties.

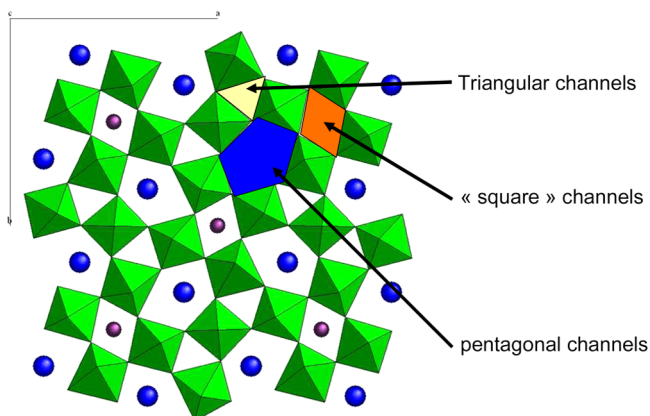
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## 2. ABOUT FERROELECTRIC TTBS

The TTB structural type is related to the potassium tungstate  $K_{0.475}WO_3$ , the structure of which was elucidated by Magneli.<sup>7</sup> The characteristic feature of the TTB structure is the three types of open channels that develop within its octahedral framework (Figure 1), which allowed solid state chemists to perform a wide



**Figure 1.** Crystal Structure of  $Ba_2LaFeNb_4O_{15}$  TTB projected along [001]. Green octahedra contain Fe and Nb, Ba in blue, La in purple.

range of substitutions, either in these channels or within the octahedral framework itself. The TTB crystal structure can be described as a three-dimensional framework with formulation  $A_2BC_2M_5O_{15}$ , where corner-sharing octahedra (M) define pentagonal (A), square (B), and triangular (C) channels. A prototype of TTB ferroics is the oxide  $Ba_2NaNb_5O_{15}$ ,<sup>8</sup> also one of the first and most significant among TTB niobates representatives.  $Ba_2NaNb_5O_{15}$  presents an interesting range of physical properties including ferroelectricity and ferroelasticity (i.e., it is a multiferroic). These attracting characteristics gave rise to extended investigations on chemical systems related to this TTB niobate. Thus, many new ferroelectric—and relaxor—compositions were discovered.<sup>9</sup>

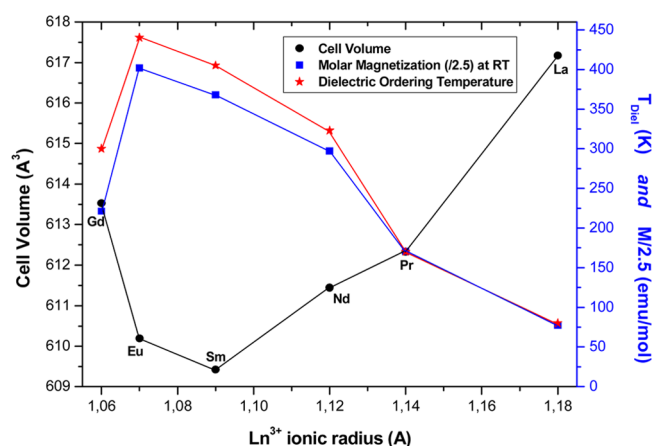
Another remarkable feature of TTB ferroics is the occurrence of modulated crystal structures, directly connected with their physical properties. Many studies presented some experimental evidence of structural modulations associated with ferroelectric and/or ferroelastic states.<sup>10–19</sup> These modulated states have been thoroughly investigated in several TTB systems,  $Ba_2NaNb_5O_{15}$ ,<sup>10–14</sup>  $Sr_{1-x}Ba_xNb_2O_6$ ,<sup>15,16</sup> and more recently in  $Ca_{1-x}Ba_xNb_2O_6$ .<sup>20,21</sup> Accurate structural models have been built for both systems, allowing some understanding of these modulated states. However, if some empirical relationships were established that correlate the structural and physical properties of TTB ferroelectrics,<sup>22–24</sup> their crystal-chemistry remains a puzzling topic, as the microscopic mechanism that induce and control the modulated phases in TTBS is not yet fully described.

This crystal chemical flexibility of the TTB framework is clearly established, given the wide range of chemical substitutions allowed in TTBS.<sup>23</sup> Any of these substitutions affect the whole octahedral framework the TTB matrix is built of, but, although the radius difference between cations occupying the square and pentagonal sites is frequently a relevant parameter,<sup>24</sup> the most sensitive site is usually the square channel which is at the center of the perovskite columns. Any distortion of this site will yield correlated distortions of the rest of the octahedral framework and can induce a structural modulation. In the prototype TTBS

$Ba_2NaNb_5O_{15}$  and  $Sr_{1-x}Ba_xNb_2O_6$ , these modulations can affect both the atoms lying in the channels and the anionic framework.

## 3. ABOUT THE $Ba_2LnFeNb_4O_{15}$ TTBS

TTBS have been quite disregarded, with respect to perovskites, for multiferroic properties, at least for the praised class of multiferroics that combine ferromagnetism and ferroelectricity. Yet, the family of  $Ba_2LnFeNb_4O_{15}$  ( $Ln = La, Pr, Nd, Sm, Eu, Gd$ ) TTB niobates, which we reinvestigated a few years ago<sup>25</sup> has revealed as a unique room temperature multiferroic composite system. In this system, the dielectric properties arise from the TTB matrix, while the in situ formation of barium ferrite secondary phase ( $BaFe_{12}O_{19}$ , BFO) is responsible for the magnetic properties. The outstanding feature of this system is that ferroelectric and magnetic properties evolve with respect to a unique crystal-chemical parameter (Figure 2).<sup>25,26</sup>



**Figure 2.** Cell volume and physical properties of TTB multiferroic composites with respect to rare earth ionic radius.

Besides the “multiferroic composites” aspect, unexpected dielectric behaviors were also discovered in this family of TTBS, as exemplified by the ferroelectric to relaxor evolutions in the  $Ba_{6-2x}Eu_{2x}Fe_{1+x}Nb_{9-x}O_{30}$  (referred to as “Eux” in the following) and  $Ba_2Pr_xNd_{1-x}FeNb_4O_{15}$  solid solutions (referred to as “Pr–Nd” in the following).<sup>27,28</sup>

In the  $Eu_x$  system, the ferroelectric state is destabilized upon decreasing the rare earth content, and a relaxation phenomenon may be correlated with the disappearance of the ferroelectric transition as both signatures seem to collapse in a unique relaxor behavior when further decreasing the europium content. The most surprising point in this system is the disappearance of the ferroelectric state while the niobium content increases within the TTB phase.

In the Pr–Nd solid solution, while for the unsubstituted Nd and Pr compounds, purely ferroelectric and relaxor (respectively) behaviors were observed, a coexistence of ferroelectric and relaxor behaviors was confirmed in all the substituted samples. The associated phase transition sequence, going through “relaxor–ferroelectric–paraelectric” states upon heating, was also observed in some perovskite systems.<sup>29,30</sup>

These rather unusual behaviors emphasize the flexibility of the  $Ba_2LnFeNb_4O_{15}$  TTBS, which supposedly allows for tuning the relaxor to ferroelectric crossovers on scanning the composition in these two solid solutions, although they rely on very different substitution mechanisms.

**Table 1.** Phase Content and TTB Composition for the Ba<sub>2</sub>LnFeNb<sub>4</sub>O<sub>15</sub> Composite Multiferroic TTBS, According to X-ray Microprobe Data and to Calculations from an Hypothetical Chemical Mechanism

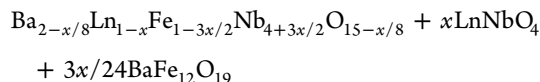
X-ray Microprobe (Hypothesis: Full Occupancy of Octahedral Sites, O Content Calculated for Neutrality)						
Ln	Ba	Ln	Fe	Nb	O	
Pr	1.95(2)	0.95(2)	0.96(2)	4.04(2)	14.91	
Nd	1.98(2)	1.01(2)	0.96(2)	4.04(2)	15.03	
Sm	1.88(2)	0.85(2)	0.87(2)	4.13(2)	14.78	
Eu	1.92(2)	0.80(2)	0.86(2)	4.14(2)	14.76	
Calculated for Different $x$ Values with Ba <sub>2-x/8</sub> Ln <sub>1-x</sub> Fe <sub>1-3x/2</sub> Nb <sub>4+3x/2</sub> O <sub>15-x/8</sub>						
$x = \text{LnNbO}_4$	$3x/24 = \text{BaFe}_{12}\text{O}_{19}$	Ba	Ln	Fe	Nb	O
0.02	0.0025	1.9975	0.98	0.97	4.03	14.9975
0.06	0.0075	1.9925	0.94	0.91	4.09	14.9925
0.1	0.0125	1.9875	0.9	0.85	4.15	14.9875
0.15	0.01875	1.98125	0.85	0.775	4.225	14.98125
0.2	0.025	1.975	0.8	0.7	4.3	14.975

The structural studies of the Ba<sub>2</sub>LnFeNb<sub>4</sub>O<sub>15</sub> TTBS (powder X-ray and neutron diffraction) did not yield a satisfying structural model so far and suggested a modulation affecting the anionic framework is likely in this family.<sup>31</sup> To allow insightful studies on the structural properties of this TTB system, its crystal growth by the flux method has been successfully developed.<sup>32,33</sup> As reported recently,<sup>34</sup> the single crystals obtained are large enough to perform advanced chemical, structural, and physical characterizations, ultimately with all experiments performed from a unique crystal.

We will discuss in this paper some aspects of the chemical and crystal-chemical mechanisms which generate the original behaviors encountered in the (Ba,Sr)<sub>2</sub>LnFe(Nb,Ta)<sub>4</sub>O<sub>15</sub> TTBS. We will show that some of these mechanisms are specific to this system, while others may be specific to the TTB framework. We will particularly emphasize the original dielectric behaviors encountered in the (Ba,Sr)<sub>2</sub>LnFe(Nb,Ta)<sub>4</sub>O<sub>15</sub> TTBS, i.e., the relaxor to ferroelectric crossovers.

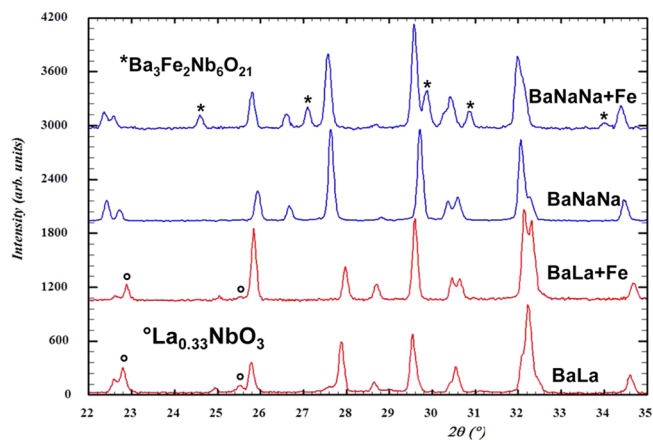
#### 4. ABOUT THE SPECIFICITIES OF Ba<sub>2</sub>LnFeNb<sub>4</sub>O<sub>15</sub> COMPOSITE MULTIFERROIC TTBS

Composites, as multiphased systems, are generally not considered worthy of crystal-chemical investigations, since the specific properties of a composite system usually relies more on the nature, quality, and properties of interfaces than on the crystal chemistry of the bulk materials associated in the composites. However, the Ba<sub>2</sub>LnFeNb<sub>4</sub>O<sub>15</sub> TTBS do not correspond to such kinds of composites. The TTB multiferroics appear as a specific composite system, the properties of which are controlled by a unique crystal-chemical parameter: the radius of the Ln<sup>3+</sup> ion inserted in the square channel of the TTB framework (cf. Figure 2). The presence of barium ferrite, responsible for the ferromagnetic properties of the composites, is related to the partial accommodation of the rare earth in the TTB matrix. As a consequence, a mechanism involving all the cations forming the TTB phase, and dedicated to maintain electrical neutrality, results in the formation of two secondary phases, fergusonites LnNbO<sub>4</sub> and BFO. It has been proven<sup>26</sup> that an excess of iron oxide in the ceramic forces the release of some barium by the TTB matrix, to yield the BFO phase. The corresponding chemical mechanism, starting from a Ba<sub>2</sub>LnFeNb<sub>4</sub>O<sub>15</sub> composition, could be resumed as follows:<sup>35,36</sup>



And it is remarkable that a unique parameter,  $x$  the amount of rare earth *not* accommodated in the TTB framework, can account for the formation of all the phases encountered in this chemical system. Table 1 illustrates this point and gathers the chemical composition of several TTBS extracted from X-ray microprobe measurement, as well as composition calculated from the above formula for various  $x$  values.

As the release of barium by the TTB framework is a crucial point concerning the in situ formation of BFO, we tried to produce new multiferroic composites from other Ba-containing TTBS, namely, the well-known Ba<sub>2</sub>NaNb<sub>5</sub>O<sub>15</sub> and a relaxor TTB (BaLaNb<sub>5</sub>O<sub>15</sub><sup>37</sup>), by adding excess hematite during the preparation of these compounds. Since a very small amount of barium is needed to yield a significant quantity of BFO, we expected these tests to be straightforward. In order to have a better knowledge of the reactivity of these systems, we added the excess hematite either with the reacting product (before the formation of the TTB) or between calcination and sintering of the ceramics (after formation of the TTB). To our surprise, we did not succeed inducing in situ BFO formation by adding hematite to either of the studied systems (Figure 3), and both elaboration protocols yielded the same results. If secondary phases actually formed (perovskite and hexagonal tungsten



**Figure 3.** Part of the XRD patterns of BaLa (red) and BaNaNb (blue) TTBS, following firing (lower pattern) and sintering (upper pattern, "+Fe") with addition of hematite  $\alpha\text{-Fe}_2\text{O}_3$  (2%, weight). Secondary phases contributions are marked; all the others contributions belong to the TTB phase. No evidence of barium hexaferrite BaFe<sub>12</sub>O<sub>19</sub> was found from XRD and MEB analyses.



bronze related phases), no mechanism yielding BFO formation could be activated. This last result shows how particular the  $\text{Ba}_2\text{LnFeNb}_4\text{O}_{15}$  multiferroic composites are and suggests that the presence of iron within the TTB framework may be requested for the mechanism yielding BFO formation to be activated. As other iron-containing TTB ceramics display some similar multiferroic properties,<sup>38,39</sup> it would be interesting to check the eventual involvement of this mechanism in these TTB systems.

### 5. ABOUT RELAXOR TO FERROELECTRIC CROSSOVERS IN $(\text{Ba,Sr})_2\text{LnFe}(\text{Nb,Ta})_4\text{O}_{15}$ TTBS

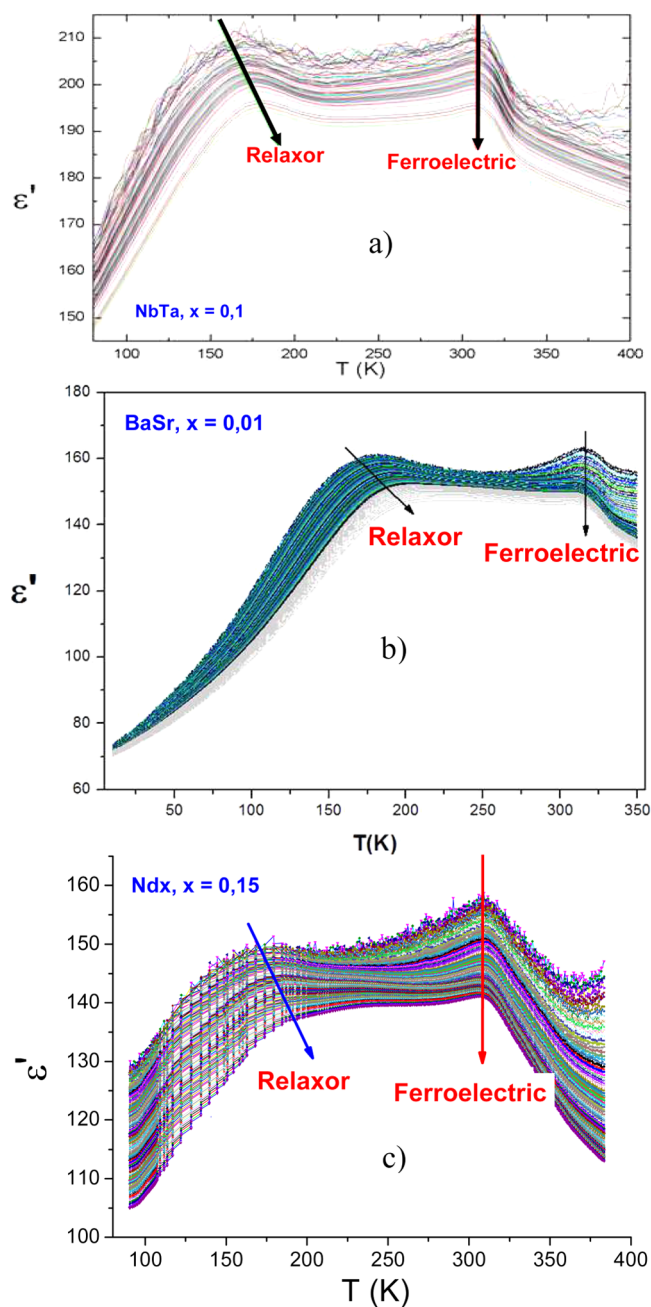
Following the relaxor to ferroelectric crossover discovered in the  $\text{Ba}_2\text{Pr}_x\text{Nd}_{1-x}\text{FeNb}_4\text{O}_{15}$  solid solution (referred to as “PrNd” in the following), a search for similar crossovers in systems derived from the  $\text{Ba}_2\text{NdFeNb}_4\text{O}_{15}$  ferroelectric TTB was undertaken. The purpose of the present paper is to give a wide (and early) view of the dielectric behavior observed in the studied systems, in order to evaluate the driving force at work within these solid solutions, from different but complementary substitution schemes. As the TTB framework can be divided in four cationic sublattices, i.e., the octahedral framework and the pentagonal, square and triangular channels, our approach is to study solid solutions involving substitutions in these different cationic sublattices. However, as the triangular channels are empty in the  $\text{Ba}_2\text{NdFeNb}_4\text{O}_{15}$  TTB, substitutions schemes involving these channels were not considered. The PrNd substitution scheme involving solely the square channel, we studied two systems based on substitutions within the two other cationic sublattices (octahedral sites and pentagonal channels) and one system involving all cationic sublattices except triangular channels.

The  $\text{Ba}_2\text{NdFe}(\text{Nb}_{1-x}\text{Ta}_x)_4\text{O}_{15}$  solid solution (NbTa in the following) was investigated concerning the substitution within the octahedral framework.<sup>31,40</sup> As this framework is usually considered as the origin of ferroelectricity in TTB niobates, the substitution of  $\text{Nb}^{5+}$  ions by the ferroelectrically less active  $\text{Ta}^{5+}$  ions should have a significant effect on the dielectric properties of the ceramics. Actually, a relaxor to ferroelectric crossover was found in this system for  $0 < x < 0.15$ , which is illustrated with the dielectric response of ceramics with  $x = 0.1$  (Figure 4a).

The  $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{NdFeNb}_4\text{O}_{15}$  (BaSr in the following) solid solution, involving substitution in the pentagonal channels, was also investigated,<sup>41</sup> in order to evaluate the influence of this channel on the ferroelectric properties of TTBS. Again a relaxor to ferroelectric crossover was found, although limited to a narrow range of compositions ( $0 < x < 0.05$ ). Figure 4b displays the dielectric properties of a ceramic with  $x = 0.01$ , in which this crossover is found.

A third system relying on substitutions within three cationic sublattices was studied:  $\text{Ba}_{6-2x}\text{Nd}_{2x}\text{Fe}_{1+x}\text{Nb}_{9-x}\text{O}_{30}$  (referred to as Ndx, note that in figures the values reported as “ $x$ ” are actually “ $1 - x$ ”).<sup>42</sup> For this latter one, the compound  $\text{Ba}_2\text{NdFeNb}_4\text{O}_{15}$  is obtained for  $x = 1$  ( $1 - x = 0$ ), and this substitution scheme guarantees the full occupancy of pentagonal and square channels (as long as the ceramics are single phased). As for the other systems, a relaxor to ferroelectric crossover is found for  $0 < x < 0.20$ , and Figure 4c displays the typical dielectric response of a ceramic with  $x = 0.15$ .

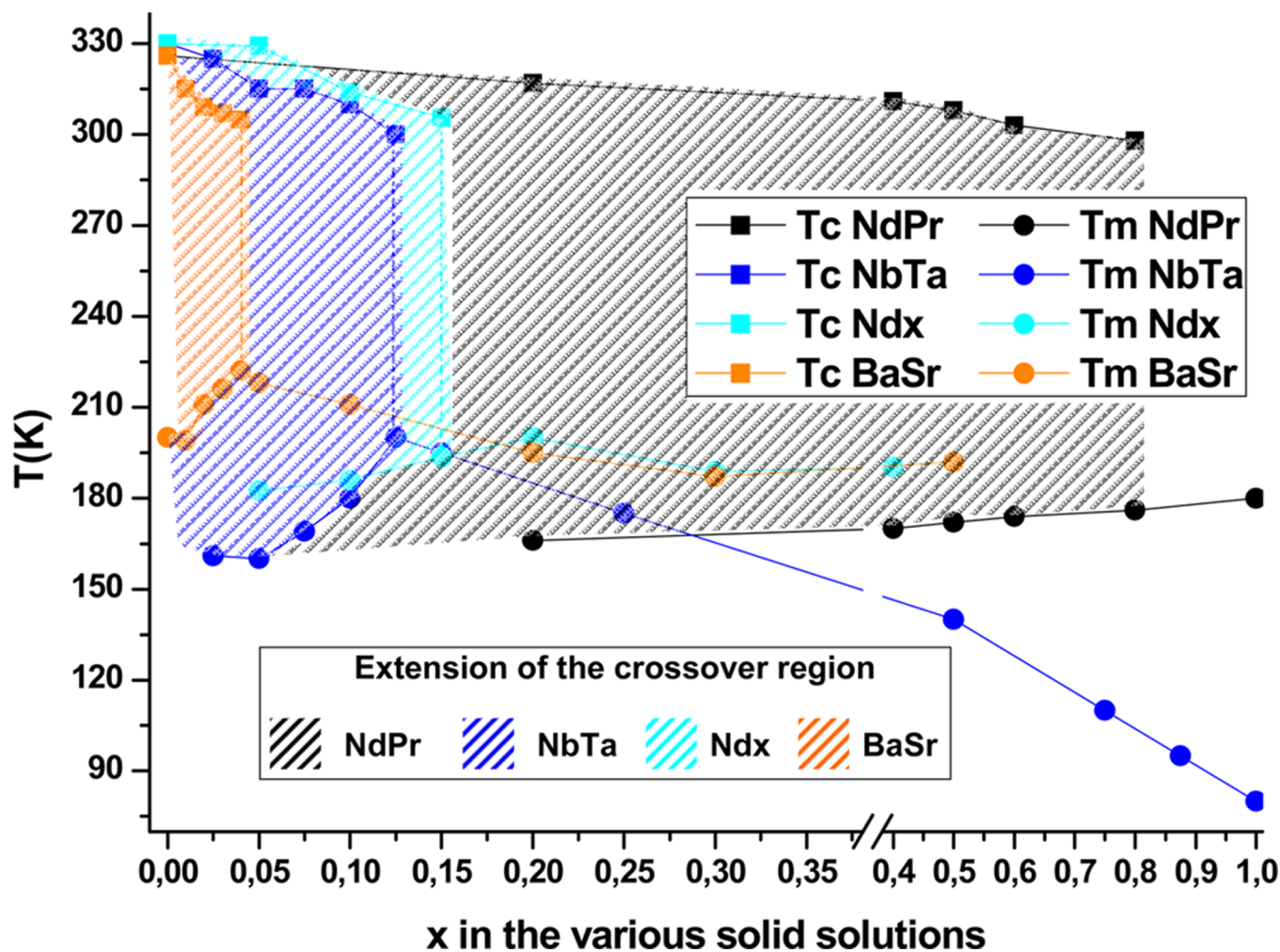
It is worth noting the similarities in shape and amplitudes of the dielectric responses obtained in the three solid solutions, as illustrated by Figure 4. The global results obtained from these solid solutions are summarized in Figure 5, which displays the compositional dependence of the ferroelectric ( $T_C$ ) and relaxor



**Figure 4.** Dielectric response in the frequency range 1 kHz–1 MHz, showing a relaxor to ferroelectric crossover of (a) a ceramic from the NbTa system, with  $x = 0.1$ ; (b) a ceramic from the BaSr system with  $x = 0.01$ ; (c) a ceramic from the Ndx system with  $x = 0.15$  (for sake of consistency with Figure 5, 0.15 is actually the value of “ $1 - x$ ”).

( $T_m$ ) transition temperatures and highlight the extension of the relaxor to ferroelectric crossover regions.

Several striking observations emerge from Figure 5, the first one being that in all the studied systems,  $T_C$  remains relatively stable with the substitution, before a brutal collapse of the ferroelectricity. The stability of  $T_C$  is surprising because in most solid solutions based on a ferroelectric, any substitution will significantly affect the ferroelectricity, which is sensible to any modification of the crystalline lattice. On the contrary here the ferroelectric state is hardly sensible to substitutions (until its disappearance), even to those affecting all but one of the cationic sublattices (Ndx).



**Figure 5.** Ferroelectric ( $T_C$ , squares) and relaxor ( $T_m$ , discs) transition temperatures in the NdPr (black), NbTa (blue), Ndx (cyan), and BaSr (orange) systems. Shaded areas indicate the relaxor to ferroelectric crossover regions.  $T_m$  values are taken at 1 MHz except for Ndx system (100 kHz). For Ndx system, the values actually used in the figure on the horizontal axis correspond to “1– $x$ ”.

The second surprising observation concerns the disappearance of ferroelectricity, which is associated with a maximum of  $T_m$  in BaSr and NbTa. The maxima of  $T_m$  are also found close to the composition for which the ferroelectricity disappear in Ndx and PrNd. On one hand, indications were found, in subsequent investigations on the PrNd system, that the ferroelectric and relaxor states are relatively independent<sup>43</sup> (as far as this is possible for two dielectric states occurring in the same material). On the other hand, this second observation suggest a link between the ferroelectric and relaxor behavior, the nature of which remains to be determined.

The third puzzling observation concerns the extension of the crossover region, and thus the stability of the ferroelectric state, that decreases according to the following: PrNd > Ndx > NbTa > BaSr. This means that the substitution of  $Sr^{2+}$  for  $Ba^{2+}$  is more detrimental to the ferroelectric state than the substitution of  $Ta^{5+}$  for  $Nb^{5+}$ , the latter being without doubt the most ferroelectrically active ion in all the compositions.

Finally the most remarkable observation is the fact that all the chosen substitution schemes yield, qualitatively, to the same kind of dielectric behavior, i.e., a relaxor to ferroelectric crossover. The only significant differences found from one system to the other concern the extension of the crossover region. This means that the driving force of the dielectric behaviors encountered in these

systems does not lie with the cationic sublattices. Of course, this does not mean that the dielectric properties in these TTB solid solutions are independent of the cationic sublattices, as otherwise the dielectric behavior would be the same whatever the cationic substitution, which is obviously not the case. The point made here is that although the dielectric responses of these ceramics is that of their whole crystalline network, and not that of the anionic or one of the cationic frameworks, the specific origin, the driving force of this dielectric response should be looked for within the anionic framework. Although relationships between the dielectric response of these materials and their cationic contents inevitably exist, when looking at the solid solutions presented in this study, their dielectric behavior cannot be rationalized with respect to the TTB matrix solely on the basis of one or several cationic sublattices.

For example, let one consider the pentagonal sites as the driving force of the behavior encountered in these solid solutions, as the substitution of as few as 5% of  $Ba^{2+}$  ions by  $Sr^{2+}$  ions suppress the ferroelectricity. It appears then rather difficult to explain how the homovalent substitution of  $Ta^{5+}$  for  $Nb^{5+}$  ions, which also have the same ionic radii in six coordination (0.64 Å), influence the pentagonal site to lead to the suppression of the ferroelectric state. One could call for a different mechanism

involved in both solid solutions, but then it would be troublesome to explain their rather identical dielectric behaviors.

The fact that the cationic sublattices have only an indirect influence on the dielectric properties of these systems is made particularly clear by the  $\text{Nd}_x$  system. In this solid solution, the ferroelectricity disappears, although the content of ferroelectrically active niobium increases in the octahedral sites (it was also the case in the “Eux” system), thus forbidding consideration that the ferroelectricity has its sole origin in this cationic sublattice.

Thus, the similar dielectric behaviors found for the four solid solutions, all derived from the ferroelectric  $\text{Ba}_2\text{NdFeNb}_4\text{O}_{15}$  TTB, actually indicate that the driving force of these original behaviors lies in the common ground of all the studied systems: the anionic framework. This point is also supported by earlier studies,<sup>44,45</sup> in which the substitution of oxygen by fluorine leads to a dramatic decrease of  $T_C$  for very small fluorine contents (1.7% in  $\text{Ba}_{2-x}\text{Na}_{1+x}\text{Nb}_5\text{O}_{15-x}\text{F}_x$ <sup>44</sup>). The replacement of  $\text{Ba}^{2+}$  by  $\text{Na}^+$  in this system cannot account for the change of  $T_C$  as in the similar solid solution  $\text{Ba}_x\text{Na}_{5-2x}\text{Nb}_5\text{O}_{15}$ , the  $\text{Ba}_{1.93}\text{Na}_{1.14}\text{Nb}_5\text{O}_{15}$  compound actually displays a  $T_C$  of 858 K,<sup>46</sup> higher than that of the  $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$  prototypical ferroelectric TTB.

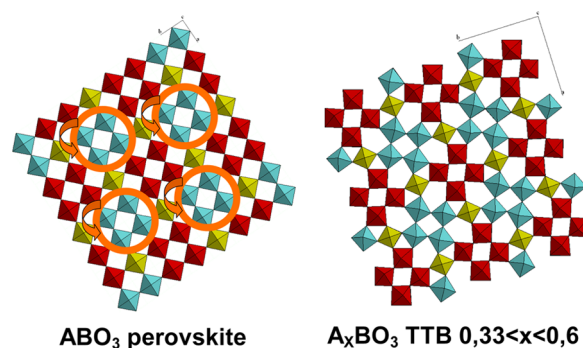
However, if each studied solid solution allows for understanding *how* the TTB framework responds to a given substitution, and if the previous comparison of several substitution schemes reveal *what*, in the TTB framework, is involved in the original dielectric responses encountered, the reason *why* TTBs possess these anion-driven properties remains to be discovered.

## 6. STRUCTURAL ASPECT: IS THERE AN APERIODIC DEGREE OF FREEDOM?

The TTB framework possesses a very rich crystal-chemistry, due to its chemical flexibility which is clearly established. Almost the full range of cations available in the periodic classification,<sup>9</sup> from the small  $\text{Li}^+$  to the highly charged  $\text{W}^{6+}$  via most of the alkali, alkaline earth, and transition metals, some p-elements such as  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$  and eventually lanthanides and actinides ( $\text{Th}^{4+}$ ,  $\text{U}^{4+}$ ) can be introduced in the TTB framework. Moreover oxygen can easily be replaced by fluoride in the anionic framework.<sup>45</sup>

Any chemical substitutions will affect the octahedral framework the TTB matrix is built of, but the most sensible cationic site in the  $(\text{Ba,Sr})_2\text{LnFe}(\text{Nb,Ta})_4\text{O}_{15}$  TTBs, as we pointed out,<sup>25,34</sup> is the square channel at the center of perovskite columns. The relationship existing between the perovskite and TTB frameworks may be a reason for the central role played by these channels. The TTB framework can be derived from the perovskite one by rotating some perovskite columns of  $45^\circ$ , yielding the three kind of channels characteristics of the TTB structure (Figure 6). Any distortion of these square channels will yield correlated distortions of the octahedral framework (i.e., of the anionic framework which defines the octahedral sites), due to the three-dimensional network formed by corner-sharing connections between octahedra. These correlated distortions can induce a structural modulation, which is eventually incommensurate, depending on their periodicity with respect to that of the TTB lattice.

Such is the case of the prototype ferroelectric TTB  $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ , which has been studied in detail in the 1980s.<sup>10,11</sup> For this material, a complicated succession of phase transitions has been elucidated, involving of course a ferroelectric state, but also a ferroelastic state which is responsible for two incommensurate phases in  $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ . In these phases, modulations mainly affect the anionic framework. In more recent



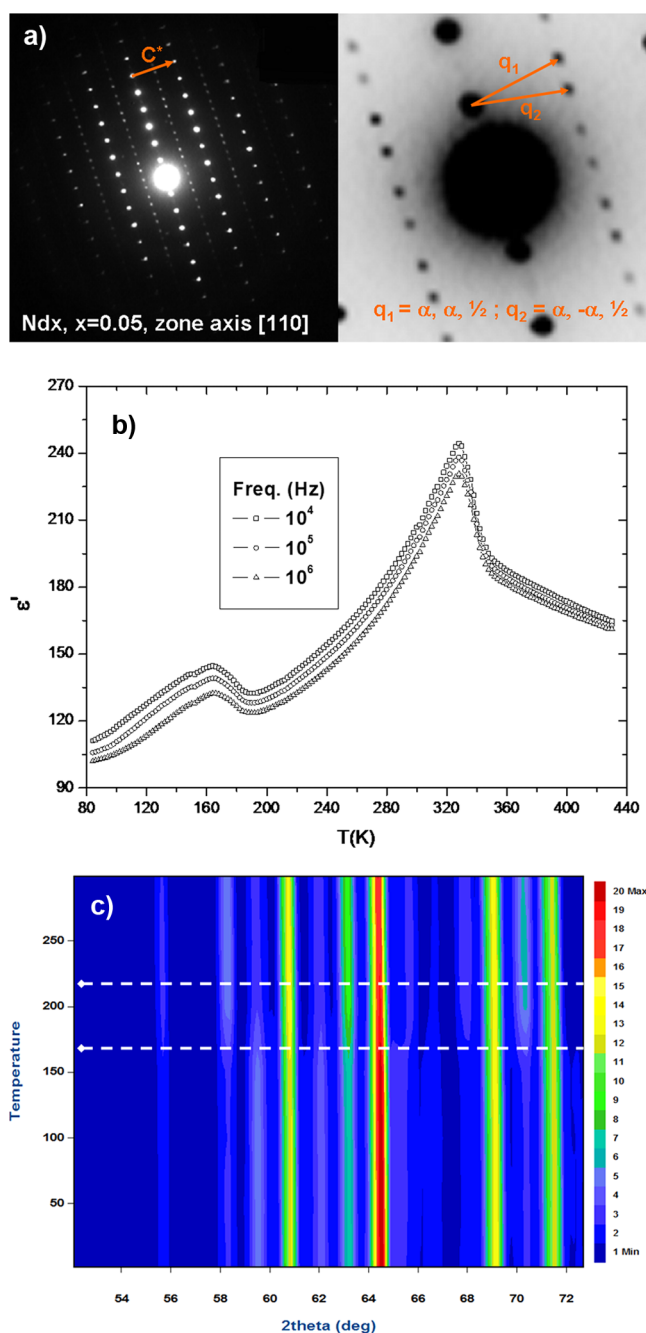
**Figure 6.** Structural relationship between perovskite and TTBs: By rotating the blue perovskite columns by  $45^\circ$ , one goes from the perovskite framework to the TTB framework, with minor rearrangements for the other octahedra.

studies,<sup>16,20,21</sup> models of the modulated phases in several TTB systems were established within the superspace formalism. These studies confirmed that the anionic sublattice is the most affected by the structural modulation.

Thanks to the development of a crystal growth method,<sup>32,33</sup> a similar kind of modulation was recently brought to light in the  $\text{Ba}_2\text{LnFeNb}_4\text{O}_{15}$  TTBs.<sup>33,34</sup> Moreover, recent TEM studies indicated that such modulations are also present in ceramics from the  $\text{Nd}_x$  system (Figure 7a). These aperiodic modulations are also present at room temperature in the paraelectric state in  $\text{Ba}_2\text{LnFeNb}_4\text{O}_{15}$  single-crystals.<sup>34</sup> Furthermore,  $\text{Ba}_2\text{NdFeNb}_4\text{O}_{15}$  ferroelectric TTBs can present an additional low temperature anomaly (Figure 7b and ref 25) very similar to the relaxor transition observed in the above-mentioned solid solutions, although with a very limited dielectric dispersion. A temperature-dependent neutron diffraction study of such a  $\text{Ba}_2\text{NdFeNb}_4\text{O}_{15}$  TTB revealed significant modification of the diffraction pattern (Figure 7c) in a temperature range (150–200 K) encompassing the previously mentioned dielectric anomaly. These modifications essentially appear as intensity and shape modification of existing TTB Bragg positions, but may not be taken into account by a conventional (i.e., three-dimensional) structural model, consistent with previous observations from XRD.<sup>25</sup> Thus, they likely are contributions from an aperiodic modulation, which would then be involved in the original dielectric behavior observed in many  $(\text{Ba,Sr})_2\text{LnFe}(\text{Nb,Ta})_4\text{O}_{15}$  TTBs. This would be particularly consistent with the large thermal hysteresis of the ferroelectric transition observed in the  $\text{PrNd}$  system<sup>43</sup> as well as others TTB systems,<sup>47</sup> as such a hysteresis as been previously described in incommensurate ferroelectrics.<sup>48</sup> With large subcentimetric single-crystals available for various compositions,<sup>34</sup> and the availability of superspace models,<sup>20,21</sup> the ground is set for a deeper exploration of the crystal chemistry of modulated TTBs. These studies will bring a formal proof of structure-properties relationships in  $(\text{Ba,Sr})_2\text{LnFe}(\text{Nb,Ta})_4\text{O}_{15}$  TTBs, particularly for the aperiodic modulations taking place in their crystal structure, and their related anion-driven properties.

It has to be highlighted that the structural relationship existing between the perovskite and TTB frameworks supports the idea that similar useful chemical, physical-chemical, and physical properties can be found in both kind of materials. In fact the  $\text{PbNb}_2\text{O}_6$  TTB, for example, can be formulated as a  $\text{Pb}_{0.6}\text{NbO}_3$  phase, i.e., can be related to a cation deficient perovskite formulation  $\text{A}_x\text{BO}_3$  (with a stability range  $0.33 < x < 0.6$  in general). Actually one can find in the literature TTB materials





**Figure 7.** (a) Left: electron diffraction pattern of a  $\text{Nd}_x$  ceramic with  $x = 0.05$ , along the  $[110]$  zone axis, showing the doubling of  $c^*$ ; right: enlargement showing the satellite peaks of the incommensurate modulation, and the modulation vectors. (b) Real part of the permittivity of a  $\text{Ba}_2\text{NdFeNb}_4\text{O}_{15}$  ceramic, showing a dielectric anomaly around 160 K. (c) Temperature dependence of the neutron diffraction pattern of  $\text{Ba}_2\text{NdFeNb}_4\text{O}_{15}$  in the range  $53^\circ < 2\theta < 73^\circ$  (instrument G4-1, LLB, Saclay,  $\lambda = 24266 \text{ \AA}$ ) showing significant modifications in the temperature range 150–200 K.

studied for ferroelectric properties, of course, but also for piezoelectricity,<sup>49</sup> nonlinear optical properties,<sup>50</sup> luminescence,<sup>51</sup> mixed conduction,<sup>52</sup> photocatalysis,<sup>53</sup> and magnetism.<sup>54</sup> It appears then rather reasonable to further consider that most of the properties obtained from a perovskite phase may be induced in a TTB phase by adequate substitutions. Obtaining the relevant formulations for TTB-structured materials would then be made

easier by the crystal chemical flexibility of their three-dimensional framework. Obviously these properties would be influenced, to some extent, by structural modulations affecting the anionic framework. The systematic presence of structural modulations in  $\text{Ba}_2\text{LnFeNb}_4\text{O}_{15}$  relaxor single crystals,<sup>34,55</sup> along with similar observations in other TTB systems ( $\text{BaNaNa}$ , SBN, KNSBN,  $\text{Ba}_2\text{LnTi}_2\text{Nb}_3\text{O}_{15\dots}$ ), suggest that they are rather a feature of the TTB framework than a peculiarity of the  $(\text{Ba,Sr})_2\text{LnFe}(\text{Nb,Ta})_4\text{O}_{15}$  TTBs. Therefore, if the underlying mechanism generating these modulations is understood, it should be possible to tune or even design the properties of TTB materials by taking advantage of these modulations and of the crystal-chemical flexibility of TTBs. This is illustrated by the relaxor to ferroelectric crossovers found in  $(\text{Ba,Sr})_2\text{LnFe}(\text{Nb,Ta})_4\text{O}_{15}$  TTBs, in which perturbations of the anionic framework by cationic substitutions generate these unexpected behaviors. Thus, in TTB materials presenting aperiodic modulations, these modulations may constitute an extra degree of freedom to control their physical-chemical properties, which could be considered as an aperiodic degree of freedom. Formally establishing this aperiodic degree of freedom requires the study of TTB's superspace crystal chemistry.

## 7. CONCLUSION

The study of TTB systems of the general formulation  $(\text{Ba,Sr})_2\text{LnFe}(\text{Nb,Ta})_4\text{O}_{15}$  allowed for the discovery of the very specific multiferroic composites and of multiple relaxor to ferroelectric crossovers. If each of these findings individually bears a significant level of interest, a survey of the dielectric behavior of a set of solid solutions, derived from the ferroelectric  $\text{Ba}_2\text{NdFeNb}_4\text{O}_{15}$  TTB, unravels the anionic driving force behind the relaxor to ferroelectric crossovers. Advantage could be taken of the sensitivity of the anionic sublattice to cationic substitutions, to tune the properties of  $(\text{Ba,Sr})_2\text{LnFe}(\text{Nb,Ta})_4\text{O}_{15}$  TTBs. This sensitivity is likely related to incommensurate modulation detected in many TTBs, including those belonging to the  $(\text{Ba,Sr})_2\text{LnFe}(\text{Nb,Ta})_4\text{O}_{15}$  family. Finally, it appears that only a fine understanding of the crystal chemistry of this system, which appears now to be within reach thanks to the existence of large single crystals of various compositions, may allow for a rationalization of these original behaviors, i.e., multiferroic composites, relaxor to ferroelectric crossovers, and those that possibly remain to be discovered or designed.

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### Notes

The authors declare no competing financial interest.

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## DEDICATION

Dedicated to Dr. Annie Simon on the occasion of her recent retirement.



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