

Department of Earth Sciences University of Hamburg Summer semester 2018

MASTER THESIS

Temperature-induced Structural Transformations in the Ferroelectric Solid Solution $(1-x)PbTiO_3 - xBiNi_{0.5}Ti_{0.5}O_3$ across the Morphotropic Phase Boundary

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Supervised by Prof. Dr. Boriana Mihaylova Dr. Kaustuv Datta Temperature-induced Structural Transformations in the Ferroelectric Solid Solution (1 - x)PbTiO₃-xBiNi_{0.5}Ti_{0.5}O₃ across the Morphotropic Phase Boundary

Abstract

Powder X-ray diffraction and Raman spectroscopy are used to investigate the average and local structure, respectively, of the ferroelectric solid-solution (1-x)PbTiO₃-xBiNi_{0.5}Ti_{0.5}O₃ at room temperature as a function of composition (x = 0, 0.10, 0.20, 0.30, 0.40, 0.50, 0.55, 0.60, 0.65 and 0.70) as well as for five different compositions (x = 0, 0.20, 0.50, 0.55, and 0.70) as a function of temperature (100 K - 1040 K). The volume and the tetragonal strain of the unit cell decrease when the amount of $BiNi_{0.5}Ti_{0.5}O_3$ (BNT) increases. Anomalous Raman scattering is observed in the paraelectric phase for all analyzed compositions (x = 0, 0.20, 0.50,0.55, and 0.70), indicating the presence of local-scale ferroic species. The displacive character of the paraelectric-to-ferroelectric phase transition is suppressed with the increase of x, being gradually replaced by an order-disorder mechanism that becomes dominant in the vicinity of the morphotropic phase boundary ($x_{MPB} = 0.55$). A high degree of local-scale orientational disorder has been observed at the MPB, where a more energetically favourable state of the A-site cations becomes dominant and, simultaneously, tetragonal distortions and antiferrodistortive tilting related to the B-site cation vibrations are competing. These processes, together with a strong coupling between the A-site and B-site cation subsystems observed exactly at the MPB, could represent the origin of the excellent piezoelectric properties exhibited at this composition.

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1 Introduction

A material is said to be *ferroelectric* if it exhibits a spontaneous polarization, switchable under an external electric field. Ferroelectricity usually disappears above a critical temperature called the Curie temperature (T_c) and the material is then said to be in a paraelectric state [11]. Ferroelectricity has been discovered in 1921 in the hydrogen-bonded KNaC₄H₄O₆·4H₂O, known as Rochelle salt, and later in the 1940s in the perovskite oxide BaTiO₃, which revolutionized the ferroelectric industry [12]. Due to their superior electromechanical and dielectric properties, ferroelectric ceramics are widely used in a variety of applications including sensors, actuators, nonvolatile memories, and ultrasonic transducers [13, 14, 15].

The ferroelectric nature of PbTiO₃ (PT) has been discovered by Shirane et al. [16] in 1950. PT is one of the most important ferroelectric perovskite oxides, attracting great theoretical and technological interest [17]. PbTiO₃ has a high Curie temperature ($T_c = 763$ K), a low dielectric constant, and a high remnant polarization ($P_r=75 \ \mu C/cm^2$). However, the large tetragonality (c/a = 1.064) of lead titanate leads to a high spontaneous strain occurring at the transition temperature and makes the compound too fragile for practical applications. In order to access the high temperature properties of PbTiO₃, different doping modifications have to be used [18, 19]. Very popular materials are ferroelectric solid solutions with a morphotropic phase boundary (MPB) between the rhombohedral and the tetragonal ferroelectric phases, where a compositionally induced phase transition takes place and the physical properties of the material are strongly enhanced [20].

A well known PbTiO₃-modification is the solid solution PbZr_{1-x}Ti_xO₃ (PZT), which is currently dominating the ferroelectric ceramics market [21]. PZT ceramics with the composition near the MPB have a $T_c = 385^{\circ}$ C and exhibit excellent electromechanical properties [22]. The biggest disadvantage of PZT is its high Pb content, as new EU regulations restrict the use of lead considering its negative effects on the environment and human health. Consequently, in the last decades many compounds with the perovskite structure have been studied in the search for nontoxic lead-free or lead-poor alternatives to PZT [21, 22].

Piezolectric ceramics from the perovskite families $PbTiO_3$ -BiMeO₃ (Me = Sc³⁺, Fe³⁺, In³⁺...) and $PbTiO_3$ -BiMe[']Me^{''}O₃ (Me['] = Mg²⁺, Ni²⁺, Zr²⁺..., and Me^{''} = Ti⁴⁺, Nb⁵⁺...) have attracted much attention due to their high Curie temperature combined with superior piezoelectric properties at the morphotropic phase boundary and reduced content of Pb [7, 18, 23, 24, 22, 25].

The ferroelectric solid solution $(1-x)PbTiO_3-xBiNi_{0.5}Ti_{0.5}O_3$ (PT-BNT) appears to be a promising candidate with a high Curie temperature and good piezoelectric and mechanical properties [7, 26]. Furthermore, Hu et al. [26] also reports weak ferromagnetic activity at room temperature, which gives this compound a multiferroic character. At x = 0.55 PT-xBNT exhibits a peak in the piezoelectric and electromechanical response [6, 25], making this

composition suitable for a wide range of applications [18]. From a structural point of view it has been shown that, between the tetragonal phase (P4mm) for compositions below x_{MBP} and the rhombohedral phase (R3m) above x_{MBP} , an additional monoclinic phase (Pm) should be considered [27].

Since the macroscopic polarization in a ferroelectric system is highly influenced by the degree of local distortion [12], it is crucial to understand the structural behaviour not only in terms of long-range ordering, but also in terms of short-range (approximately the size of one cation-anion polyhedron) and medium-range order (approximately a few adjacent cation-anion polyhedra). The aim of this thesis is to analyze the temperature-evolution of the atomic short-range and medium-range order (up to a few unit cells in the case of perovskite-type materials) in a range of compositions across the morphotropic phase boundary and evaluate the changes in the atomic structure produced by variations in the chemistry. For this, powder X-ray diffraction was used to characterize the average crystal structure of the samples at ambient conditions, while the temperature-induced structural transformations and the effect of the compositional variations on the mesoscopic-scale coupling processes are studied by Raman spectroscopy.

2 Ferroelectricity

A material is said to be *ferroelectric* if it exhibits spontaneous polarization in the absence of an external electric field and can switch between different orientation states of polarization under the application of an electric field (Figure 1a) [11].

If no electric field has been previously applied, the direction of the polarization is not uniform throughout the compound. Ferroelectric ceramics, the most used ferroelectric materials, consist of a very large number of randomly oriented grains. At the paraelectric-to-ferroelectric phase transition, regions with different orientations of the polarization develop independently inside each grain, restricted however to the crystallographic directions available in that grain. These regions are called *ferroelectric domains* and are separated by domain walls. Each domain consists of unit cells with the same orientation of the electric dipoles (Figure 1b).



Figure 1: a. Formation of dipole moments: paraelectric (PE) state vs. different ferroelectric (FE) states, before and after the application of an external field; b. Ferroelectric domains and domain walls (blue dotted line); c. Hysteresis loop: P is the polarization, E is the electric field and P_S , P_R , and E_C are the saturation polarization, the remnant polarization, and the coercive field, respectively.

The macroscopic polarization P is defined as the dipole moment per unit volume and in a linear approximation it is proportional to the applied electric field E:

$$P = \epsilon_0 \chi_e E$$
,

where χ_e is the electric susceptibility of the material and ϵ_0 is a fundamental physical quantity called the dielectric constant of vacuum. The electric susceptibility measures the ease of polarization of a material when an electric field is applied and is directly related to the dielectric constant ϵ , which describes the permittivity of a material relative to the permittivity of vacuum [12]:

 $\epsilon = 1 + \chi_{\rm e}$

2 Ferroelectricity

A distinctive feature of ferroelectric materials is the behaviour of the polarization during the poling process, when a large electric field is applied to an untreated, randomly oriented ceramic (Figure 1c): as the domains begin to align to the direction of the electric field E, the polarization P increases (dotted line) until almost all domains have the same orientation and the saturation polarization P_S is reached. When the electric field is removed, some of the domains return to their original state, while most of them remain aligned, leading to a non-zero polarization when E reaches zero, which is called remnant polarization (P_R). In order to switch the direction of the polarization an electric field with a certain strength E_C , called coercive field, has to be applied in the opposite direction. The behaviour of the polarization plotted against the electric field is known as the *hysteresis loop*.

2.1 Perovskite-type structure

Although ferroelectricity also appears in hydrogen-bonded compounds [28] and different polymers [29], materials with the perovskite structure are the most technologically important ferroelectrics due to their high tolerance to doping (chemical element substitution), which allows the optimization of specific physical properties [11, 30].

The perovskite structure has the general formula ABX_3 , where A and B are two different cations and X is an anion (Figure 2). The A-site and B-site cations are twelve-fold and six-fold coordinated by X-site anions, respectively. In the majority of perovskite ferroelectrics the X site is occupied by oxygen. The structure can also be thought as a network of corner-sharing BO_6 octahedra, with every eight BO_6 unities surrounding an A-filled cuboctahedron.



Figure 2: Two representations of the cubic perovskite unit cell: a. with the origin in B: A(1/2, 1/2, 1/2), B(0, 0, 0), O(1/2, 1/2, 0) and b. with the origin in A: A(0, 0, 0), B(1/2, 1/2, 1/2), O(1/2, 0, 0).

In the paraelectric state, ABO₃ perovskites with a primitive unit cell have a cubic structure (Pm $\overline{3}$ m), which is distorted to lower symmetry below T_c . Reasons for this symmetry lowering are, among others, distortion and tilting of the BO₆ octahedra [31]. A powerful tool to predict the stability of a compound with perovskite structure is the tolerance factor, introduced by

Goldschmidt [32] in 1926. The tolerance factor t is defined as:

$$t=\frac{r_A+r_O}{\sqrt{2}(r_B+r_O)},$$

where r_A is the ionic radius of A, r_B is the ionic radius of B, and r_O is the ionic radius of oxygen.

If t = 1, the compound has the ideal cubic structure (Figure 3a). If t is larger than 1, the B-site cation is smaller than the ideal value and can move from the center of the oxygen cage, which leads to a small polar distortion at the B-site (Figure 3b). If t < 1, the A-site cation is too small to fill the oxygen cuboctahedron and rotations and tilting of the BO₆ octahedra take place in order to compensate for the empty space (Figure 3c). In the latter case, the materials are called A-site driven and are generally not ferroelectric, since the inversion symmetry is preserved [4]. An important exception in this case are materials with Pb²⁺ as the A-site cation [31]. The perovskite structure is stable within the limits t = 0.88 to 1.09. Outside these boundaries, other aristotype structures are preferred, for example the ilmenite structure for t < 0.88 [22].



Figure 3: Tolerance factor t

Although the tolerance factor cannot be used to predict the existence of ferroelectricity, Eitel et al. [22] reported that perovskites with t < 1 adopt a monoclinic or rhombohedral structure, while for t > 1 the tetragonal symmetry is preferred.

2.2 Paraelectric-to-ferroelectric phase transition

Ferroelectric phase transitions are an important class of transformation processes with significant technological implications [33]. The ferroelectric state appears when the short-range forces caused by repulsion between the atoms are overcome by long-range Coulomb forces caused by dipole-dipole interactions. This happens at a critical temperature called the Curie temperature (T_c). In the case of perovskites, the structure changes from centrosymmetric to polar and develops ferroelectric properties [34, 35]. Figure 4 shows the possible structures resulting from the deformation of the cubic $Pm\overline{3}m$ perovskite structure due to displacements of the B cation [1].



Figure 4: Space groups resulting from the distortion of the cubic ABO_3 structure due to B-site cation displacements. Howard, 2005 [1]

A phase transition is usually accompanied by a maximum in the dielectric constant ϵ , whose behaviour above the Curie temperature is described by the Curie-Weiss law:

$$\epsilon = \frac{C}{T - T_0},$$

where C is the material-dependent Curie constant and T_0 is the Curie-Weiss temperature. According to the Landau-Ginzburg-Devonshire's mean field theory [36], the transition is said to be of *first-order* if the change in the order parameter (the net polarization, in this case) at the transition temperature is discontinuous. In this case the Curie-Weiss temperature is slightly lower than the Curie temperature. A *second-order* transition takes place when the low-temperature and high-temperature phases merge continuously, without any discontinuity in the order parameter and T_c and T_0 coincide (Figure 5) [4].



Figure 5: The behaviour of the spontaneous polarization (P_S) and the dielectric constant (ϵ) at a first-order (a.) vs. second-order (b.) phase transition. Damjanovic, 1998 [2]

From a structural point of view, a transition is called to be *displacive* if the magnitude of

the local displacements $(|\delta \vec{r}|)$ follows the temperature-dependent behaviour of the macroscopic order parameter (the net polarization) in a range including the transition temperature (Figure 7a). If the magnitude of the local distortions remains unchanged while the macroscopic order parameter shows the behaviour of the phase transition, the transition is called to be of *orderdisorder* type. In this case only the orientation vectors of the local distortions $\left(\frac{\delta \vec{r}}{|\delta \vec{r}|}\right)$ change at the transition temperature and the local atomic displacements lose the long-range order (Figure 7b) [37].

This behaviour can be explained through a quantum mechanical approach: in a crystal the atoms are connected by harmonic forces and vibrate in double-well potentials (Figure 6).

Figure 6: One-dimensional model of interatomic interactions (after Dove, 2002 [3])

In an order-disorder transition, the potential barrier between the two wells is stronger than the interaction between neighbouring atoms, therefore the atoms will prefer one of the two wells, even at temperatures above T_c . However, in the paraelectric phase the occupancy is random and the positions of the atoms are not correlated. On cooling, the interactions between adjacent atoms become stronger, which leads to the formation of short-range order. On further cooling below T_c , the long-range order develops as most of the atoms will be localized on the same side of the potential barrier (Figure 7d) [4].

Displacive transition

Order-disorder transition



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Figure 7: Displacive (a. and c.) vs. order-disorder (b. and d.) phase transition. Figures c. and d. from Dove, 1997 [4]

2 Ferroelectricity

In a displacive phase transition the interatomic forces are stronger than the potential barrier. At high temperatures the atoms do not feel the existence of potential barriers and they effectively vibrate around the central points of the potential, which correspond to the equilibrium position in the paraelectric state. On cooling, the interatomic forces become stronger and neighbouring atoms are slightly displaced to the same side of the double-well potential. This displacement becomes stronger on further cooling and below T_c all atoms are displaced to one side of the origin by the same distance, which leads to the development of the long-range ferroelectric order within a single domain (Figure 7c) [3, 4]. A displacive phase transition is considered to be driven by a so called soft mode, which is a phonon whose frequency drops to zero when a phase transition is approached. The set of atomic vector displacements of the soft mode represents the difference between the atomic equilibrium position in the two phases, while the soft mode wavenumber correlates with the order parameter [12].

For many materials, the atomistic origin of their ferroelectricity is still not deeply understood. Although perovskites exhibit the same aristotype structure, small variations in the chemistry can lead to a completely different ferroelectric behaviour [35]. Moreover, most of the ferroelectric materials do not exhibit a pure displacive or pure order-disorder transition, but a combination of both mechanisms.

3 PbTiO₃-based ferroelectric solid solutions

The solid-solution $x PbZrO_3-(1-x)PbTiO_3$ (PZT) is the most widely used ferroelectric ceramic, with applications including medical devices, capacitors, memory chips and sensors [14, 38]. The exceptional dielectric and piezoelectric properties of PZT appear especially in compositions located in the vicinity of the morphotropic phase boundary (MPB). The term MPB was originally introduced to describe a composition-induced phase transition from a tetragonal to a rhombohedral phase, accompanied by strong enhancement of the dielectric and piezoelectric properties [20]. Nowadays it is accepted that either a single low-symmetry phase (monoclinic, triclinic) or a coexistence of multiple phases can be found at the MPB, acting as a bridge between the tetragonal and rhombohedral phases in a solid solution [11, 21, 23]. In MPB compositions the environments of the A- and B-site cations are distorted and the energetic barrier which exists between different long-range order distortion directions is lowered, which allows optimal domain reorientation during the poling process and leads to enhanced electromechanical properties [21, 22].

In the last decades, much effort has been done to find non-toxic Pb-free or Pb-poor alternatives to PZT with similar or even better piezoelectric properties, using both experimental and theoretical methods [5, 21, 22, 39]. The search for systems with a morphotropic phase boundary has proven to be difficult, as there was no initial indicator for the composition at which the MPB should appear and for each solid solution a large number of compositions had to be investigated [21].

Bi-based ferroelectrics are an appealing alternative to pure Pb-compounds, since Bi³⁺ has the same electronic configuration as Pb²⁺, with a stereochemically active (6s)² lone electron pair, but, unlike lead, it is non-toxic in its oxide form [14]. In 2001 Eitel et al. [22] observed that the Curie temperature of (1-x)PbTiO₃-*x*BiMeO₃ systems at x_{MPB} increases as the tolerance factor of the non-PbTiO₃ end member of the solid solution decreases. This relationship between the transition temperature and the tolerance factor led to the discovery of the solid solution PbTiO₃-BiScO₃ with a very high Curie temperature at x_{MPB} ($T_c > 720$ K), which intensified the search for other Bi-containing ferroelectrics with an MPB [39].

In 2004 Suchomel et al. [21] established that in $(1-x)PbTiO_3-xBiMe'Me''O_3$ systems the position of the morphotropic phase boundary shifts towards the PbTiO₃ end member as the tolerance factor of the BiMe'Me''O₃ end member decreases. In 2005 Grinberg et al. [39] stated that in a solid solution x_{MPB} as well as T_c at x_{MPB} can be predicted using the average ionic radius and the B-cation displacement of the non-PbTiO₃ end member.

A large number of PbTiO₃-BiMeO₃ and PbTiO₃-BiMe[']Me^{''}O₃ systems with a high Curie temperature at the morphotropic phase boundary was predicted based on these theoretical studies, where Me, Me['] and Me^{''} are metal cations with ratios that give an average B-site cation valence of +3: Me = Sc³⁺, Fe³⁺, In³⁺ etc.; Me['] = Mg²⁺, Ni²⁺, Zr²⁺ etc. and Me^{''} =

Ti⁴⁺, Nb⁵⁺ etc. Although many of these solid solutions exhibit superior piezoelectric properties at x_{MPB} [7, 18, 23, 24, 22, 25], they also have several disadvantages, for example:

- $(1-x)PbTiO_3-xBiFeO_3$ (PT-xBF) exhibits a very high Curie temperature at the composition near the morphotropic phase boundary ($T_c > 870$ K), but it also has high conductivity and large dielectric loss, and therefore poor dielectric properties [7, 40].
- (1-x)PbTiO₃-xBiScO₃ (PT-xBS) has a high Curie temperature T_c = 720 K and excellent piezoelectric properties (d₃₃ = 460 pC/N). Unfortunately, the high cost of scandium makes this solid solution unsuitable as industrial material [18].
- (1-x)PbTiO₃-xBiNi_{0.5}Ti_{0.5}O₃ (PT-xBNT), which is the subject of this thesis, has a high Curie temperature (*T_c* ~ 680 K) and good piezoelectric properties (d₃₃ ~ 260 pC/N) at the morphotropic phase boundary composition [7]. It also exhibits good mechanical properties, including high density and excellent fracture toughness [26]. However, PT-xBNT has leakage current as well as relatively low resistance and a large coercive field (E_c), which influences the poling process and limits the mobility of the domain walls [18]. Some of these issues have already been addressed: Kang et al. [18] solved the leakage current problem by doping the PT end member with strontium (*y* = 0.05): (1-*x*)Pb_{1-y}Sr_yTiO₃-*x*BiNi_{0.5}Ti_{0.5}O₃; Jiang et al. [41] used, instead of the conventional sintering technique, a microwave sintering method which reduces the volatilization of Bi and Pb during sample preparation and improves the electrical properties of PT-BNT; Choi et al. [6] reported that the addition of MnO₂ improves dielectric losses and the poling behaviour, but at the same time the remnant polarization and the piezoelectric coefficient d₃₃ are strongly reduced.

3.1 (1-x)PbTiO₃-xBiNi_{0.5}Ti_{0.5}O₃

While PbTiO₃ is a well known ferroelectric material, the studies about the other end member of the (1-x)PbTiO₃-xBiNi_{0.5}Ti_{0.5}O₃ solid solution are scarce. BiNi_{0.5}Ti_{0.5}O₃ (BNT) has a low structural stability and cannot be synthesized at ambient conditions [42]. Only recently Inaguma and Katsumata (2002, [42]) used high pressure (6 GPa) to stabilize a BiNi_{0.5}Ti_{0.5}O₃ perovskite with an orthorhombic unit cell. Takenaka et al. [25] reports that a minimum of 30% PbTiO₃-amount is required for the solid solution (1-x)PbTiO₃-xBiNi_{0.5}Ti_{0.5}O₃ to adopt a perovskite structure at room temperature.

The morphotropic phase boundary of the PT-*x*BNT system has been reported at slightly different compositions, but all within the range $0.51 \le x_{MPB} \le 0.55$ (Table 1).

These small variations are probably related to the accuracy of the sample preparation as well as to the method used to determine the position of the MPB. According to our in-house

	Kang et al. [18]	Takenaka et al. [25]	Zhang et al. [7]	Choi et al. [6]
X _{MPB}	0.53 - 0.55	0.55	0.52 - 0.54	0.51

Table 1: Position of the morphotropic phase boundary in $(1-x)PbTiO_3-xBiNi_{0.5}Ti_{0.5}O_3$

X-ray diffraction analyses, which will be discussed in detail in Chapter 7, the MPB is at x = 0.55.

Previous studies [6, 7, 27] showed that for $x < x_{MPB}$ PT-xBNT is tetragonal with the space group P4mm and the spontaneous polarization is oriented along the pseudocubic $\langle 001 \rangle_c$, while for $x > x_{MPB}$ PT-xBNT adopts a rhombohedral structure (R3m) and is $\langle 111 \rangle_c$ -polarized. At $x = x_{MPB}$, the structure reportedly changes from the $\langle 001 \rangle_c$ -polarized state to the $\langle 111 \rangle_c$ polarized state through a lower symmetry monoclinic phase (Pm) [27]. The presence of this intermediate monoclinic phase, which was first discovered by Noheda [43] in PZT, can be explained also from a theoretical group-subgroup point of view, as Pm is a subgroup of both P4mm and R3m. The phase diagram of PT-xBNT can be seen in Figure 8.



Figure 8: Calculated (grey line, after Stringer et al. [5]) and measured (red circles [6] and blue squares [7]) Curie temperature for the solid solution $(1-x)PbTiO_3-xBiNi_{0.5}Ti_{0.5}O_3$. The red dashed line represents the Curie temperature extrapolated from the experimental data [6].

Stringer et al. [5] investigated the behaviour of the transition temperature in the solid solution systems $(1-x)PbTiO_3-xBiMe'Me''O_3$ as a function of x and found that the Curie

temperature can be expressed using the following polynomial equation:

$$T_c(x) = a + bx + cx^2,$$

where $a = T_c(0) = 768$ K, and b and c are material dependent constants. The behaviour of the transition temperature can be categorized based on the sign of the *b* and *c* coefficients: 1. b > 0 and c > 0, which is the case that gives the highest paraelectric-to-ferroelectric transition temperatures, as the Curie temperature increases with the BiMe[']Me^{''}O₃ content (example: $(1-x)PbTiO_3-xBiFeO_3)$; 2. b < 0 and c < 0, which is the most common case, in which the transition temperature decreases as the amount of the non-PbTiO₃ end member is increased; 3. b > 0 and c < 0: with increasing BiMe[']Me^{''}O₃ content, the Curie temperature is first enhanced above the T_c of PbTiO₃, but after reaching a maximum it starts to decrease. This is the case of $(1-x)PbTiO_3-xBiNi_{0.5}Ti_{0.5}O_3$.

The Curie temperatures determined by Choi et al. [6] via differential scanning calorimetry and permittivity-temperature measurements (Figure 8, red circles) and Zhang et al. [7] through thermal depoling experiments (Figure 8, blue squares) show indeed a maximum of the T_c at x = 0.10 and a shift of the transition temperature downward to room temperature for increasing values of x, but are up to 30 K lower then the values predicted by Stringer et al. (Figure 8, grey solid line), especially in the region near the morphotropic phase boundary. Moreover, there is no experimental data available for the Curie temperatures in the range above x = 0.57, therefore a cubic-to-rhombohedral transition temperature has been estimated via extrapolating the value of T_c for the cubic-to-tetragonal transition (red dashed line [6]).

From an atomistic point of view, the origin of the strong ferroelectricity of $PbTiO_3$ can be found in the hybridization of the 3d states of Ti^{4+} with the 2p states of O^{2-} as well as the hybridization between the 6s states of lead and the 2p states of oxygen, which leads to a large strain stabilizing the tetragonal phase [35]. On the other hand, Bi^{3+} has the same electronic configuration as Pb^{2+} and is therefore ferroelectrically active, but the d-electron state of Ni^{2+} is partially occupied, which disfavours hybridization [26]. The ionic radii after Shannon [9] for the twelve-fold coordinated Pb^{2+} cation, six-fold coordinated Ti^{4+} and Ni^{2+} cations and the six-fold coordinated O^{2-} anion as well as the respective electronic configuration are summarized in Table 2. According to Okawa et al. [8], the ionic radius for the twelve-fold coordinated Bi^{3+} cation is 1.45 Å.

The calculated tolerance factors for different compositions using the ionic radii given in Table 2 can be seen in Figure 9:

Cation	Electronic configuration	Ionic radius (Å)
Pb^{2+}	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ²	1.49
Bi ³⁺	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ²	1.45
Ti ⁴⁺	[Ar] 3p ⁶	0.605
Ni ²⁺	[Ar] 3d ⁸	0.69
O ²⁻	[He] 2s ² 2p ⁶	1.4

Table 2: Electronic configuration and ionic radii [8, 9]



Figure 9: Tolerance factor as a function of composition x

The behaviour of the tolerance factor matches remarkably well the behaviour expected for $(1-x)PbTiO_3-xBiNi_{0.5}Ti_{0.5}O_3$. For compositions below $x_{MPB} t$ is slightly larger than 1, which indicates that the B-site cation can move freely within the oxygen cage, leading to a tetragonal deformation of the crystal structure. Because nickel has a larger ionic radius than titanium while bismuth has a slightly smaller ionic radius than lead, the tolerance factor decreases with increasing concentration of BiNi_{0.5}Ti_{0.5}O_3. This suggests that tiltings of the BO₆ octahedra may develop, favouring a rhombohedral unit cell. A competition between the tetragonal and rhombohedral phases appears to take place at the MPB-composition with t = 1.

It should be noted that, in the absence of a calculated value for twelve-fold coordinated bismuth, previous studies use the ionic radii of eight-fold coordinated Pb and Bi [42] or approximations of the missing ionic radius which can vary between 1.26 Å [31] and 1.36 Å [21] to calculate the tolerance factor of the perovskite structure. This should be taken into

account when comparing different studies, as the tolerance factors may vary substantially depending on the corresponding ionic radii used.

4 Methods

4.1 Basic concepts

A crystal is a solid characterized by a three-dimensional periodic arrangement of atoms, ions, or molecules and can be mathematically described by using the concept of crystal lattice. The crystal lattice is defined by a discrete translational symmetry with the translation vectors \vec{a} , \vec{b} and \vec{c} , whose directions form the x-, y-, and z-axes of the crystallographic coordination system. The repeating unit within a crystal is called a unit cell. The lengths of the translation vectors $(a = |\vec{a}|, b = |\vec{b}| \text{ and } c = |\vec{c}|)$ and the angles between them $(\angle(\vec{a}, \vec{b}) = \gamma, \angle(\vec{a}, \vec{c}) = \beta$ and $\angle(\vec{b}, \vec{c}) = \alpha)$ represent the lattice parameters of the unit cell (Figure 10a).

The smallest unit cell which contains exactly one lattice point is called a primitive unit cell. A particular type of primitive cells is the Wigner-Seitz cell, which is built around a lattice point by connecting it with its nearest neighbours and drawing perpendicular planes through the midpoints of the connecting lines (Figure 10b) [44].



Figure 10: a. Primitive unit cell in a crystal lattice; b. Two-dimensional representation of the Wigner-Seitz cell

The orientation of a plane in a crystal lattice is described by the Miller indices (*hkl*), where *h*, *k*, and *l* are three integers representing the reciprocals of the plane intercepts with the crystallographic axes (Figure 11). One set of (*hkl*) indices does not describe only one lattice plane, but an infinite set of parallel planes separated by an interplanar distance d_{hkl} .



Figure 11: The plane intercepts on the x-, y- and z-axes are $\frac{1}{2}$, $\frac{2}{3}$ and $\frac{1}{2}$, respectively. Their reciprocals are 2, $\frac{3}{2}$ and 2. The common denominator is 2, therefore the Miller indices of the plane are (434).

4 Methods

An important concept in crystallography is the reciprocal lattice, which was first introduced in the 1921 by P. Ewald [45] in order to simplify the interpretation of diffraction patterns. The reciprocal lattice is the Fourier transform of the direct lattice, where each point of the reciprocal lattice corresponds to a set of (hkl)-lattice planes from the direct lattice and represents the endpoint of a vector which is perpendicular to the respective (hkl)-planes and has the magnitude $d^* = 1/d_{hkl}$. The vector basis of the reciprocal lattice is given by:

$$ec{a}^* = rac{ec{b} imes ec{c}}{ec{a} \cdot (ec{b} imes ec{c})} \qquad ec{b}^* = rac{ec{c} imes ec{a}}{ec{b} \cdot (ec{c} imes ec{a})} \qquad ec{c}^* = rac{ec{a} imes ec{b}}{ec{c} \cdot (ec{a} imes ec{b}),}$$

where \vec{a} , \vec{b} and \vec{c} build the basis of the direct lattice. The Wigner-Seitz cell of the reciprocal space is called the first Brillouin zone. The physical meaning of the reciprocal space is that it represents the crystal in terms of energy and momentum.

4.2 Lattice dynamics

Atoms in a crystal are not static, but oscillate about their equilibrium position. At low temperatures, when the dynamic atomic displacements from the equilibrium configuration are small, the collectivized atomic vibrations can be described using a concept derived from classical mechanics, namely the harmonic oscillator [4]. Figure 12 shows a diatomic chain, where neigbouring atoms with masses m_1 and m_2 are connected by forces that behave like linear springs.



Figure 12: Atomic vibrations in a diatomic molecule

If we consider u_n as the displacement of the *n*-th atom from its equilibrium position and k as the spring constant, the equations of motions for the two atoms are:

$$m_{1}\frac{d^{2}u_{n}}{dt^{2}} = k(u_{n+1} + u_{n-1} - 2u_{n})$$

$$m_{2}\frac{d^{2}u_{n+1}}{dt^{2}} = k(u_{n+2} + u_{n} - 2u_{n+1})$$
(4.1)

and can be solved by describing the atomic displacements as travelling waves:

$$u_n = X_1 e^{i(nqa\pm\omega t)}$$

$$u_{n+1} = X_2 e^{i((n+1)qa\pm\omega t)}, \qquad (4.2)$$

where ω is the angular frequency, q is the wavevector, a is the lattice constant and X_1 and X_2 are the oscillation amplitudes of the m_1 and m_2 atoms, respectively. The substitution of u_n and u_{n+1} to the equations of motion leads to:

$$(2k - m_1\omega^2)(2k - m_2\omega^2) - 4k^2\cos^2 qa = 0$$
(4.3)

with the solution:

$$\omega^{2} = k \left(\frac{1}{m_{1}} + \frac{1}{m_{2}} \right) \pm k \sqrt{\left(\frac{1}{m_{1}} + \frac{1}{m_{2}} \right)^{2} - \frac{4 \sin^{2} qa}{m_{1} m_{2}}}$$
(4.4)

The plot of ω against k is called the *dispersion relation* and gives a complete description of the lattice vibrations of a crystal (Figure 13a). Since $\omega(q) = \omega(q + 2\pi)$, it suffices to consider only the wavevectors q in the range $\left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$, which corresponds to the first Brillouin zone. Equation 4.4 has two solutions which lead to different dispersion curves. The lower branch, which increases linear with q, is called the acoustic branch and corresponds to sound waves. The upper branch shows a much weaker dispersion and is called the optical branch, because it induces dipole moments in ionic crystals and can interact with light [46]. In the case of the acoustic branch all atoms of the unit cell vibrate in the same direction, while the optical branch is generated by different atoms species vibrating in opposite directions (Figure 13b).



Figure 13: a. Dispersion relations for a diatomic chain; b. Optical longitudinal and transverse and acoustic longitudinal and transverse phonon modes

A vibration where all atoms in a crystal move with the same frequency is called a normal

mode. The quantised vibrational modes of a crystalline lattice are called *phonons*. A normal mode has the energy

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega,\tag{4.5}$$

and is occupied by *n* phonons with the individual energy:

$$E = \hbar \omega$$
, (4.6)

where \hbar is the reduced Planck's constant. The energy of the whole crystal can be considered as the superposition of all the individual normal modes in the crystal [46].

The one-dimensional model can be extended to a three-dimensional model, for which the solution for the equation of motion (Equation 4.1) of an atom is written as the normal mode:

$$u = A e^{i(qr - \omega t)}, \tag{4.7}$$

where the wavevector q describes the wavelength and the direction of the wave propagation and A is a vector representing the amplitude and the direction of the vibration, which can be parallel to the direction of propagation, in which case the mode is called to be *longitudinal*, or perpendicular to the direction of propagation and the mode is called to be *transverse* [3].

A crystal with N atoms in the primitive unit cell has a total of 3N normal modes, from which 3 are acoustic modes and the other 3N-3 are optical modes. A wave with the wavevector q oriented along a direction of high symmetry in the crystal can be characterized as being either longitudinal or transverse and is called TA, LA, TO or LO, which stand for transverse acoustic, longitudinal acoustic, transverse optic and longitudinal optic, respectively. Along non-symmetry directions the vibrations are not always pure longitudinal or pure transverse and might exhibit a mixed character, in which case they are called *quasimodes* [47].

Although this case will not be discussed in this thesis, it should be noted that when the temperature increases the thermal energy gained by the atoms and the displacements from the equilibrium configuration become larger. In this case the lattice vibrations are better described by an anharmonic model (Figure 14).



Internuclear distance

Figure 14: The potential energy as a harmonic versus anharmonic oscillator. E_0 , E_1 ... represent discrete energy levels.

4.3 Powder X-ray diffraction

Powder X-ray diffraction (XRD) is a powerful method which can be used for both quantitative (phase identification in a polycrystalline sample) and qualitative (structural characterization) analyses. X rays are electromagnetic waves with an energy between 100 eV and 100 keV, corresponding to a wavelength of 10^{-12} to 10^{-8} m, which is also the magnitude of the interatomic distances. Therefore X rays can penetrate through a sample bulk, which makes them suitable for the study of different phenomena in a crystal, for example: atomic substitutions, strain distributions, and phase transitions [48].

When interacting with the sample, the X rays are scattered by the electron shells of atoms. The scattering amplitude of an atom, called the atomic form factor f(q), depends on the number of electrons (Z) of the atom and the scattering direction and is defined as the Fourier transform of the electron density distribution:

$$f(q) = \int
ho(r) e^{i \overline{q} \cdot \overline{r}} dV$$
,

where ρ is the electron density, \overline{q} is the scattering vector and \overline{r} is the atomic position in the real space. As a consequence, light atoms as well as neighbouring elements in the periodic table are hard to be distinguished by X rays [49].

When a sample is irradiated with a monochromatic X-ray beam, the beam falls on a set of (*hkl*)-lattice planes at an angle θ . If the waves diffracted by the planes are in phase, which means that the path difference between two rays is an integer multiple of the wavelength ($\Gamma = n\lambda$), then the interference between the X-rays is said to be constructive and an intensity peak can be observed in the resulting diffraction pattern. Constructive interference occurs when Bragg's Law is satisfied:

$$n\lambda = 2d_{hkl}sin\theta$$

where *n* is an integer, λ is the wavelength, d_{hkl} is the distance between adjacent (*hkl*)-lattice planes and θ is the Bragg angle and represents half of the angle between the incident and the scattered beams (Figure 15).



Figure 15: Bragg's Law

In a powder the crystallites are randomly oriented, which means that if the sample is rotated through a range of 2θ -angles, a very large number of crystallites will satisfy the Bragg's Law for each set of (*hkl*)-planes. Every crystalline substance has a unique diffraction pattern, where the peak position depends on the lattice parameters and interatomic distances, the intensity of the peaks contains information about the type and the arrangement of the atoms in the crystal lattice and the width and the shape of the peaks are indicators for the size and shape as well as the mechanical properties of the crystallites [44, 48].

4.4 Raman spectroscopy

Raman spectroscopy is a technique based on interactions between electromagnetic radiation in the visible/near-visible region (light) and optical phonons. The quanta of light are called photons and have the energy:

$$E = h\nu = rac{hc}{\lambda},$$

where *h* is the Planck's constant, *c* is the speed of light, ν is the frequency, and λ is the wavelength.

Atoms vibrate at frequencies between 10^{12} and 10^{14} s⁻¹, which correspond to the infrared range and therefore a transition between different energy levels can be induced by infrared radiation. In a Raman scattering experiment the sample is irradiated with monochromatic visible light, which has a much higher energy and therefore cannot be absorbed by a phonon in a crystal, but will excite it from the initial energy state to a virtual high-energy state by disturbing the valence electron density of states [50]. Since this state is not stable and exists only for a very short time, the system immediately returns to its initial state while a new photon with energy equal to the energy of the incident photon is released. This process is called Rayleigh scattering. Apart from the elastically scattered light, there is also a small amount of incident light that is scattered inelastically in a process called Raman scattering. Based on the initial vibrational state of the crystal, two different situations may occur:

- 1. The crystal is excited from the ground state to a virtual state by an incoming photon with energy $h\nu_0$, but returns to a phonon excited state and the resulting photon is scattered with a lower energy of $h(\nu_0 \nu_1)$. This process is referred to as Stokes Raman scattering.
- 2. The crystal is already in a vibrational excited state before the interaction with an incoming photon with energy $h\nu_0$, goes again to a higher energy state but returns to the ground energy while a photon with a higher energy $h(\nu_0 + \nu_1)$ is scattered. This process is called anti-Stokes Raman scattering (Figure 16a).



Figure 16: a. Rayleigh and Raman scattering; b. Stokes, Rayleigh and anti-Stokes peaks

A phonon can generate a Raman peak only when the atomic vibrations cause a change in the polarizability, which describes the ease with which the electron density of states changes upon an external field. In the case of optical phonons, the difference between the position of positively-charged nucleons and the center of gravity of negatively-charged e⁻ shells leads to the formation of an instantaneous electric dipole, which interacts with the electric field of light.

A Raman spectrum (Figure 16b) is the plot of the scattered light intensity given in counts per second against the phonon energy given in wavenumbers ω , were a wavenumber is defined as:

$$\omega = \frac{1}{\lambda} = \frac{\nu}{c}.$$

The population of the ground state is normally higher than that of the excited state, at least at room temperature. Consequently, Stokes scattering is more probable to occur than anti-Stokes scattering, and therefore the peaks resulting from Stokes scattering have a higher intensity (Figure 16b) [50]. For this reason only the Stokes part of the spectrum is usually collected during a Raman experiment. A wide range of information about a sample can be obtained from the analysis of the position, width and intensity of a Raman peak [46].

5 Experimental

5.1 Sample preparation

The Raman measurements were carried out on pressed powder pellets. For the pure lead titanate experiments we used commercially available $PbTiO_3$ powder from Sigma-Aldrich with a purity of 99.9%. The $(1-x)PbTiO_3-xBiNi_{0.5}Ti_{0.5}O_3$ polycrystalline ceramics with x = 0.10, 0.20, 0.30, 0.40, 0.50, 0.55, 0.60, 0.65, and 0.70 were synthesized by Prof. Jun Chen (University of Science and Technology Beijing, China) using the conventional solid-state reaction method [51]. Powders of NiO, PbO, TiO and Bi₂O₃ compounds were mixed together in stoichiometric proportions and ball milled in ethanol for 12 hours. This process was followed by a calcination at 850°C for 5 hours and another ball milling in ethanol for 12 hours. In the next step the powder mixtures were uniaxially pressed into pellets with a diameter of 10 mm and a thickness of 1 mm and hydrostatically compacted at 200 MPa at room temperature. During the last step the pellets were sintered in a covered crucible at 1100°C for 2 hours.

The chemical composition of the samples was verified by electron microprobe analysis using a Cameca Microbeam SX100 equipped with a wavelength-dispersive detector. While the ratios of the A-site cations follow the expected trend (Figure 17a), the nickel amount at the B site is slightly higher than expected for a few compositions, but still follows the 1:1 trend within uncertainties. This deviation occurs most probably due to the presence of small amounts of secondary parasitic phases, detected by XRD at x = 0.70 (Figure 17b). Spatial inhomogeneity of PT-*x*BNT at x = 0.50 and 0.70 has also been observed by Raman spectroscopy and it has been taken into account during data analysis.



Figure 17: A-site (a.) and B-site (b.) cations

5.2 X-ray powder diffraction

The high-resolution X-ray diffraction patterns were collected at the Mineralogical-Petrographic Institute in Hamburg with a STOE STADI-MP diffractometer in Bragg-Brentano geometry over a 2θ -range between 20° - 90° at room temperature. The monochromatic CuK_{α 1} radiation

with the wavelength $\lambda = 1.54056$ Å was generated at 40 kV and 30 mA. A germanium (111) monochromator was used.

The Rietveld refinement was performed with the TOPAS-Academic V6 software [52]. For the refinement with a pseudo-Voigt function we used the macro PV_Peak_type (see [53, p. 40]), which describes the profile width as a function of 2θ using the relationships:

$$FWHM = ha + hb * tan\theta + \frac{hc}{cos\theta}$$
$$\eta = lora + lorb * tan\theta + \frac{lorc}{cos\theta},$$

where FWHM is the full width at half maximum, η is the pseudo-Voigt mixing parameter and *ha*, *hb*, *hc*, *lora*, *lorb*, and *lorc* are the refineable parameters [53]. The position and the displacement parameters of the Pb/Bi atoms as well as the Ti/Ni atoms were constrained to be identical during the refinement, respectively. Isotropic atomic displacement parameters were used for all atoms. A Chebyshev polynomial function with six parameters was used for the background refinement. The peak asymmetry due to the axial divergence was taken into account by using the simple_axial_model macro (see [53, p. 156]).

5.3 Raman Spectroscopy

The Raman spectra were collected at the Mineralogical-Petrographic Institute in Hamburg with a Horiba Jobin-Yvon T64000 triple-grating spectrometer equipped with an Olympus BH41 microscope and a liquid nitrogen cooled charged coupled device (CCD) detector. The 514.5 nm green line of an Ar⁺ laser in backscattering geometry was used to excite the Raman scattering. The laser was focused on the sample through a 50x long-working distance objective and the diameter of the laser spot on the sample surface was ~2 μ m. The spectral resolution was 2 cm⁻¹ and the accuracy of the peak position was ~0.35 cm⁻¹. Multiple spectra were collected at room temperature from different points of each compound to verify the repeatability of the data. No polarization, orientation, or spatial dependence of the Raman spectra has been detected.

Temperature dependent *in situ* Raman experiments were performed on cooling from 870 to 100 K every 10 K using a Linkam THMS-E600 stage with a temperature accuracy of 0.1 K and on heating from room temperature to 1040 K using a Linkam TS1200 EV-1015 stage with a temperature accuracy of 1 K. The temperature change on heating has been set to 50 K below T_c and 10 K above T_c . The acquisition time has been set individually for each sample, varying between 15 and 60 seconds, and has been taken into account during data evaluation.

The collected spectra were analyzed by OriginPro 2016G. The instrumental background was removed. The Raman intensities of the spectra were temperature-reduced by the Bose-

Einstein phonon occupation factor:

$$I_{Reduced} = rac{I_{Measured}}{n(\omega, T) + 1}$$

with

$$n(\omega, T) = rac{1}{e^{rac{\hbar\omega}{k_BT}-1}},$$

 $\hbar = 1.05457266 \times 10^{-34}$ Js, and $k_B = 1.380658 \times 10^{-23}$ J/K. In order to obtain the phonon wavenumbers ω , the full widths at half maximum FWHM, and the integrated intensities I, the obtained intensities were divided by the acquisition time, normalized to [0,1] and then fitted using a pseudo-Voigt function:

$$PV = \mu L + (1 - \mu)G,$$

where L and G are the Lorentzian and Gaussian peak-shape functions and $\mu \in [0, 1]$ is a weight coefficient. The criterion used to determine the maximum number of fitted peaks was $\delta I/I < 1/2$ for each peak, where I is the magnitude and δI the uncertainty of the integrated intensity.

Group-theory analysis 6

Group theory analysis is a mathematical method used to represent the normal vibrational modes of a system as symmetry species of the corresponding point group called *irreducible* representations and can be used to predict whether a certain phonon is Raman active or not [4]. Each irreducible representation is labelled by a combination of characters called Mulliken symbols [54], which are described in Table 3:

А	non degenerate, symmetric with respect to rotation about the principal
	axis
В	non degenerate, anti symmetric with respect to rotation about the
	principal axis
Е	doubly degenerate
F	triply degenerate
subscript 1	symmetric with respect to a vertical mirror plane perpendicular to the
	principal axis
subscript 2	anti symmetric with respect to a vertical mirror plane perpendicular to
	the principal axis
subscript g	symmetric with respect to a center of symmetry
subscript u	anti symmetric with respect to a center of symmetry
/	symmetric with respect to a mirror plane horizontal to the principal
	axis
//	anti symmetric with respect to a mirror plane horizontal to the principal
	axis

Table 3: Mulliken symbols for irreducible representations

As mentioned in Chapter 4.2, phonons can be described as pure longitudinal or pure transverse only if their wavevector is oriented along the directions of the crystal polar axes. However, in polycrystalline materials the directions of the phonon wavevectors are randomly oriented with respect to the crystallographic axes of the grains, which leads to interaction between different vibrational modes and formation of quasimodes, rather than polar phonons [55].

This behaviour can be mathematically described using the Loudon model [56], in which the energy of the quasi-phonon depends on the energy of the ordinary modes as well as on the angle θ between the quasimode wavevector and the polar axis of the single domain. In the case of an uniaxial crystal, two simplified situations may occur:

1. The short-range covalent forces are stronger than the long-range ionic-type forces:

$$|\omega_A - \omega_E| \gg \omega_{ALO} - \omega_{ATO}$$
 and $\omega_{ELO} - \omega_{ETO}$,

which leads to a mixing of the polarization and quasi-A and quasi-E modes arise:

$$\omega_{q(LO)}^{2} = \omega_{ALO_{x}}^{2} \cos^{2} \theta + \omega_{ELO_{x}}^{2} \sin^{2} \theta$$
$$\omega_{q(TO)}^{2} = \omega_{ATO_{x}}^{2} \cos^{2} \theta + \omega_{ETO_{x}}^{2} \sin^{2} \theta$$
(6.1)

2. The long-range ionic forces are stronger than the short-range covalent forces:

$$|\omega_A - \omega_E| \ll \omega_{ALO} - \omega_{ATO}$$
 and $\omega_{ELO} - \omega_{ETO}$,

which leads to a mixing of the symmetry and quasi-LO and quasi TO-modes arise:

$$\omega_{q(A_x)}^2 = \omega_{ATO_x}^2 \cos^2 \theta + \omega_{ALO_x}^2 \sin^2 \theta$$

$$\omega_{q(E_x)}^2 = \omega_{ETO_x}^2 \cos^2 \theta + \omega_{ELO_x}^2 \sin^2 \theta$$
(6.2)

By averaging over θ in the Equations 6.1 and 6.2, where $\langle \cos^2 \theta \rangle = \langle \sin^2 \theta \rangle = 1/2$, the following simplified equations are obtained [57]:

$$\begin{aligned}
\omega_{Q(TO_x)} &= \sqrt{(\omega_{ATO_x}^2 + \omega_{ETO_x}^2)/2} \\
\omega_{Q(LO_x)} &= \sqrt{(\omega_{ALO_x}^2 + \omega_{ELO_x}^2)/2} \\
\omega_{Q(A_x)} &= \sqrt{(\omega_{ATO_x}^2 + \omega_{ALO_x}^2)/2} \\
\omega_{Q(E_x)} &= \sqrt{(\omega_{ETO_x}^2 + \omega_{ELO_x}^2)/2}
\end{aligned}$$
(6.3)

A rigorous peak assignment is difficult for solid solutions, since the Raman features are broad and the compositional disorder leads to an additional relaxation of the selection rules [55]. In order to characterize the peaks observed in PT-xBNT for different compositions, the steps below were followed:

1. Experimental data obtained by Raman spectroscopy for single crystal PbTIO₃ [58, 59] were examined (Table 4). The cubic PbTiO₃ structure has four triply degenerate optic modes: three F_{1u} modes and one F_{2u} mode, where the lowest frequency F_{1u} is considered to be the soft mode [60]. At the transition from cubic ($Pm\overline{3}m$) to tetragonal (P4mm), every F_{1u} mode splits into one A_1 and one E mode, while the F_{2u} mode splits into one B_1 and one E mode, while the F_{2u} mode splits into one B_1 and one E mode, while the F_{2u} mode splits into one B_1 and one E mode, the transition from cubic parallel and perpendicular the polar axis, respectively. The A_1 and E modes are both infrared and Raman active, while B_1 is only Raman active. At the Γ -point long-range electrostatic forces split the IR-active modes into TO and LO modes [61].

Measured [58]	Measured [59]	Phonon assignment after Foster et al. [58]
88	88	ETO1
128	128	ELO1
149	147	A ₁ TO1
194	189	A ₁ LO1
219	220	ETO2
290	289	$B_1 + E$
360	359	A ₁ TO2
441	439	ELO2
465	465	A ₁ LO2
505	505	ETO3
647	646	A ₁ TO3
687	723	ELO3
795	796	A ₁ LO3

	Table 4:	Phonon	modes	in	single-crysta	al PbTiO ₃
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2. The quasi-phonons were calculated based on the single-crystal data by using Equation 6.3 and our measurements were assigned to the corresponding values (Table 5).

Calculated based on [58]	Measured [59]	In-house measurements	Quasi-phonon assignment
		89	ET01
110	109	108	<i>q</i> E1
122		126	q⊤O1
164	161	143	qLO1
173		154	qA1
		219	ETO2
		289	$B_1 + E$
298	310	298	q⊤O2
348		350	qE2
416		397	qA2
453	451	448	qLO2
		506	ETO3
580	559	546	q⊤O3
603		602	qE3
725		729	qA3
743	773	774	qLO3

Table 5: Quasi-phonons in polycrystalline Pb
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It can easily be seen that, while the ordinary ETO and B_1+E phonons are preserved also in polycrystalline PbTiO₃, the positions of the other Raman peaks match the wavenumbers of the calculated quasi-phonons remarkably well. These are characteristic to a tetragonal structure, which means that this peak assignment could only be applied to compositions up to x = 0.55. For larger values of x, PT-xBNT has a rhombohedral (R3m) structure. Similar to the cubic-to-tetragonal transition, in the rhombohedral ferroelectric phase each of the three F_{1u} modes splits into $A_1 + E$ modes and the F_{2u} mode splits into $A_2 + E$, where A_2 is not a Raman-active mode. Moreover, based on previous studies [27], an additional monoclinic phase (Pm) should exist at the morphotropic phase boundary, where each E mode transforms into A'+A'' modes, while the A_2 mode transforms into an A'' mode. Therefore 9A'+6A''phonon modes exist in the monoclinic symmetry, from which 7A'+5A'' are Raman active [62]. The space groups discussed above and their corresponding phonon modes are summarized in Table 6.

	Pb/Bi	Ni/Ti	01	O2
	1a	1b	3с	-
Pm3m	F _{1u}	F_{1u}	$2F_{1u}+F_{2u}$	
	1a	1b	1b	2c
P4mm	$A_1 + E$	$A_1{+}E$	$A_1{+}E$	$A_1{+}B_1{+}2E$
	1a	1b	1b	2c
Pm	2A'+A"	2A'+A"	2A'+A"	3A'+3A''
	1a	1a	3b	-
R3m	$A_1 + E$	$A_1 + E$	$A_1 + A_2 + 2E$	

Table 6: Space groups of PT-xBNT with the Wyckoff positions and the corresponding phonon modes. The phonons corresponding to the heavier Pb/Bi cations are acoustic phonons.

3. During the last step we compared the positions of the Raman peaks obtained for a large range of compositions with the results obtained above. The phonon wavenumbers for all compositions measured at room temperature are summarized in Table 10 (Appendix A). The behaviour of phonon wavenumbers with the composition together with the five main spectral regions characterised by related atomic vibrations [23, 63] can be seen in Figure 18.

The peaks in the spectral ranges 40-200 cm⁻¹, 200-450 cm⁻¹ and 450-890 cm⁻¹ result from the splitting of the $3F_{1u}$ cubic phonons corresponding to the B-site cations and O-anions, respectively. The B_1 + E mode at ~ 300 cm⁻¹ results from the splitting of the F_{2u} cubic mode.



Figure 18: Room-temperature Raman spectra as a function of composition x

7 Results and discussion

7.1 Powder X-ray diffraction

Figure 19 shows the high-resolution X-ray diffraction patterns of the $(1-x)PbTiO_3-xBiNi_{0.5}Ti_{0.5}O_3$ compounds with different compositions x at ambient conditions. The XRD patterns of the PT-xBNT solid solution were indexed to a perovskite-type tetragonal structure with the space group P4mm for $x \le 0.50$ and to a rhombohedral structure with the space group R3m for $x \ge 0.60$. The transition between the two phases can easily be observed as the large splitting between the (100) and (001) peaks near 22° and the (200) and (002) peaks near 45°, which is typical for the tetragonal phase [18], is reducing as the BiNi_{0.5}Ti_{0.5}O₃ content is increasing. The peaks merge at x = 0.60, indicating that the rhombohedral phase is dominant.



Figure 19: X-ray powder diffraction patterns of $(1-x)PbTiO_3-xBiNi_{0.5}Ti_{0.5}O_3$ at room temperature

A special case is represented by the MPB-composition (Figure 20a), where the peaks exhibit additional splitting. This composition cannot be refined using a pure tetragonal or pure rhombohedral model, which indicates a phase coexistence. Different models have been used during the Rietveld refinement (Figure 20b, 20c and 20d: P4mm + Pm, P4mm + R3m and P4mm + Pm + R3m, respectively). However, none of these models was satisfying and the results obtained by Pandey et. al [27], suggesting a coexistence of a tetragonal P4mm and monoclinic Pm phase, could not be reproduced. This problem will therefore be the subject

of a future study, where the structure at the morphotropic phase boundary is going to be analyzed using complementary methods to the conventional X-ray powder diffraction, namely neutron powder diffraction and pair-distribution-function analysis.



Figure 20: Additional peak splitting at $x = x_{MPB}$ (a.) and Rietveld refinement of PT-0.55BNT using different structural models (b., c., and d.)

Figure 21a shows the behaviour of the lattice parameters with increasing x: the **c** axis is decreasing while the **a** axis is increasing, which leads to a decrease of the $\frac{c}{a}$ -ratio and reduces the tetragonal strain (Figure 21c). The effect of the composition appears to be stronger for the **c** axis than for the **a** axis, which can be explained by the fact that the covalency of the bonds between the B-site cations and the four surrounding oxygen anions in the (ab)-plane is stronger than the covalency of the bonds between the B-site cations and therefore compression and elongation of the B-O bonds in the (ab)-plane are energetically unfavourable [63].



Figure 21: a. Unit-cell parameters, b.volume and c. $\frac{c}{a}$ -ratio of the PT-*x*BNT unit cell as a function of composition *x*

The volume of the unit cell also decreases with increasing the amount of BNT (Figure

21b), but with different slopes in the tetragonal versus rhombohedral phase. An anomaly can be seen at x = 0.30, where the volume is smaller than expected. The values of the unit-cell parameters, volume, and c/a-ratio can be seen in Table 11, Appendix A.

7.2 Raman spectroscopy

Figure 22 shows the Raman spectra of the PT-*x*BNT solid solution with x = 0, 0.20, 0.50, and 0.55 over a wide range of temperatures across T_c . As can be seen, the overall Raman intensity of the spectra decreases as the amount of BNT is increasing and simultaneously, the Raman peaks are getting broader due to the presence of compositional disorder. Moreover, Raman scattering could be measured even at temperatures up to 250 K above the Curie temperature, at least for compositions with high content of PbTiO₃. This is actually forbidden by the selection rules of the cubic symmetry and therefore indicates the presence of local ferroic distortions. A similar effect has been already observed in other PbTiO₃-based solid solutions and ascribed to off-centered A- and B-site cations [23, 64, 65].



Figure 22: Raman spectra at different temperatures and compositions

For better comparison, the normalized Raman spectra of PT-xBNT are given in Figure 23. It is apparent that the Raman signal near 50 - 60 cm⁻¹ originating from off-centered A-site cations as well as near 200 - 280 cm⁻¹ originating from off-centered B-site cations persist well above T_c , confirming the presence of local dipoles in the paraelectric state. The wavenumbers of all measured Raman peaks between 100 K and 1040 K for x = 0, 0.20, 0.50, 0.55, and 0.70 can be seen in Figure 30, Appendix A.



Figure 23: Raman spectra with normalized intensities to [0, 1]

x	T_c calculated (°C)	T_c calculated (K)	T_c measured (°C)	T_c measured (K)
0	495	768	495	768
0.20	492	765	490	763
0.50	440	713	408	681
0.55	425	698	400	673
0.70	375	648	325 (estim.)	598

The Curie temperatures used in the temperature-dependent plots (T_c measured) are summarized in Table 7.

Table 7: Curie temperature for different compositions calculated using the equation given by Stringer et al. [5] and measured by Choi et al. [6] and Zhang et al. [7]



A-site cation vibrations

Figure 24: A-site cationic vibrations as a function of composition (a.) and temperature (b.)

The Raman peaks in the spectral range below 90 cm⁻¹ are related to the vibrations of the heavier A-site cations against the BO₆ octahedra along the a-axis [64, 66]. The development of their wavenumbers, FWHMs and normalized intensities as a function of composition and temperature can be seen in Figure 24a and 24b, respectively.

In pure lead titanate the ETO1 mode softens when approaching the Curie temperature, but exhibits a minimum in wavenumber and a maximum in FWHM at T \sim 790 K > T_c . However, in doped PT the behaviour of the ETO1-mode (now called peak 2) is clearly affected by the presence of BNT, which is reflected by the appearance of an additional Raman peak (peak 1) at $\omega \sim 45$ cm⁻¹.

It can easily be seen that, while the maxima in the width and intensity of peak 2 in PT-0.20BNT are still visible in the vicinity of T_c , they are obviously weaker compared to pure lead titanate, which indicates that the softening of peak 2 is suppressed in the presence of BNT.

At x = 0.50, where the ratio between the Pb and Bi atoms is 1:1, peak 2 shows a minimum in wavenumber and a maximum in FWHM as a function of composition (Figure 24a). On the other hand, Figure 24b shows that at this composition the FWHMs and the intensities of peak 1 one peak 2 coincide and show almost no temperature-dependence up to 380 K, where they merge and peak 1 becomes dominant.

In compositions with $x \ge 0.55$, peak 2 exists only up to the room temperature, while peak 1 is the dominant mode in the whole temperature range and the high values of the full width at half maximum combined with a monotonous behaviour across the Curie temperature indicate a high degree of structural disorder.

It is well known that the temperature dependence of the modes in the low-frequency range can predict the displacive nature of the phase transition [67]. Therefore, the evolution of the A-site cation vibrations with the composition indicates a gradual change in the character of the phase transition, from almost pure displacive driven by a soft mode in undoped lead titanate to order-disorder for $x \ge 0.50$.

While peak 1 has already been observed in other lead titanate-based solid solutions [23, 64], its nature is still not entirely clear. Datta et al. [64] suggests that the appearance of this low-frequency peak is related to a new, energetically favourable state of the A-site cations.



A-BO₃ vibrations

Figure 25: A-BO₃ vibrations as a function of composition (a.) and temperature (b.)

The peaks in the spectral region $100 - 200 \text{ cm}^{-1}$ arise from BO₃-translations against the A-site cation vibrations [68]. The Raman peak around 160 cm⁻¹ is considered to correspond

to the A_1TO1 soft mode in single-crystal PbTiO₃, which is related to the displacements of the BO₆ octahedra relative to the A-site cations along the polar axis [60, 63, 64].

The temperature dependence of the wavenumbers (Figure 25a) shows that in pure lead titanate the quasimodes with an LO component (qE1 and qA_11) soften as the phase transition approaches from below and disappear at T_c , which may be explained by the fact that in the paraelectric phase the long-range electrostatic forces favouring the LO-TO splitting are vanishing [57].

In PT-0.20BNT the short-range forces prevail over the long-range electrostatic forces and the two-dimensional qE1- and qTO1-modes observed in pure PbTiO₃ mix into a single peak, which will be addressed as peak 3. This new mode exhibits a minimum in the energy and a maximum in the intensity and FWHM at the Curie temperature. However, in this case no soft mode behaviour can be observed, but the energy of the mode starts to decreases linearly with the temperature at 310 K, mirrored by a local maximum in the intensity and FWHM. Peak 3 is preserved within the whole temperature range for all compositions.

A similar behaviour can also be observed in the case of the one-dimensional qA_11 and qLO1-modes (Figure 25b), which merge at x = 0.30. The position of the resulting peak (called peak 4) is being shifted to higher wavenumbers as x increases. The disappearance of this mode before or near the Curie temperature can be observed in all compositions (760K, 600 K, 660 K, 750 K and 670 K for x = 0, 0.20, 0.50, 0.55 and 0.70, respectively).

In PT-0.50BNT the position of peak 4 decreases linearly with the temperature and disappears at T = 660 K, while peak 3 is being shifted to higher wavenumbers "in steps" at 260 K, 380 K and 660 K. Between 380 K and 660 K peak 3 shows a sudden drop in the FWHM and intensity, which does not seem to affect the behaviour of peak 4. However, it is worth noting that 380 K is the temperature where peak 1, which is considered to introduce a new state of the A-site cations, becomes dominant.

The absence of a softening behaviour in PT-*x*BNT compounds with $x \ge 0.50$ together with the obtained intensity- and FWHM-values indicate a high degree of structural disorder, similar to the case of the A-site cation vibrations.

The softening of peak 3 at x_{MPB} in the composition-dependent plot (Figure 25b) together with the maximum in the FWHM indicate a strong coupling between the A-site cation and B-site cation subsystems.



B-site cation vibrations

Figure 26: B-site cationic vibrations as a function of composition (a.) and temperature (b.)

The peaks in the spectral range 180 - 380 cm⁻¹ are associated with B-site cationic vibrations [68]. The Raman peaks around 230 cm⁻¹ (peak 5) and 280 cm⁻¹ (peak 6) are related to the vibrations of the B cation within the oxygen cage [63, 68]. Peak 6 originates from the splitting of the cubic F_{2u} mode, which results into the B_1 +E modes in the tetragonal phase and into the A_2 +E modes in the rhombohedral phase, with A_2 not being Raman active. Regarding the peak around 350 cm⁻¹ (peak 7), pair-distribution-function analysis applied by Datta et al. [64] revealed that the oxygen anions vibrate along the A-O bonds in the {111}_{pc} planes, which results into the tilting of the BO₆ octahedra about the $\langle 111 \rangle_{pc}$ directions.

Figure 26a shows that the splitting of peak 5 and peak 6, which is a characteristic feature for the tetragonal symmetry [62], is reducing with increasing BNT content and appears to follow the trend observed for the *c*- and *a*-lattice parameters, with the red shift in the wavenumber of peak 5 being more pronounced than the blueshift in the wavenumber of peak 6. The two peaks merge at x = 0.50 and the resulting peak will still be called peak 6 for simplicity. This behaviour indicates that the tetragonal distortion within the BO₆ octahedra are gradually inhibited by the addition of BNT [64].

Let us now inspect the temperature-dependent behaviour of PT-*x*BNT compounds with $x \ge 50$ (Figure 26b). One can easily observe that the wavenumbers of peak 6 as well as peak 7 are almost identical for x = 0.50, 0.55, and 0.70 and they remain constant across a wide temperature range, until the two peaks merge at at 650 K, 670 K, and 670 K, respectively. However, when analysing the FWHM and the intensity of the peaks for the three compositions, an interesting behaviour can be observed. At x = 0.50, both the FWHM and the intensity of the peak associated with the B-O vibrations are stronger than those of the peak associated

with the tilting of the BO₆ octahedra. At the MPB, the ratio between the intensities and the FWHMs of peak 6 and peak 7 is almost 1:1, respectively, while at x = 0.70 the width and the intensity of peak 7 become more pronounced in the whole temperature range. Moreover, an almost identical behaviour can be observed in another PbTiO₃-based solid solution, namely (1-x)PbTiO₃-xBiMg_{0.5}Ti_{0.5}O₃ (Figure 31, Appendix A).

This leads to the following model: below the morphotropic phase boundary, in the tetragonal phase, the tetragonal distortions within the BO₆ octahedra dominate over the tilting of the BO₆ octahedra, i.e. polar distortions dominate over antiferrodistortive structural distortions. At the morphotropic phase boundary these two different states are competing while above x_{MPB} , in the rhombohedral phase, the tilting of the BO₆ octahedra becomes dominant. This matches surprisingly well the prediction made by the tolerance factor in Chapter 3, which anticipated tetragonal distortions for compositions with $x < x_{MPB}$ and antiferrodistortive rotations for $x > x_{MPB}$.

Internal BO₆ octahedral vibrations

The peaks in the range $450 - 780 \text{ cm}^{-1}$ are related to internal octahedral modes involving mixed B-site cation and oxygen vibrations and are strongly affected by the strength of the B-O bond [68]. In Pb-based B-site-complex ABO₃-type relaxor ferroelectrics, which show double-perovskite structure due to the existence of local chemical B-site order, the Raman scattering in the spectral range $450 - 650 \text{ cm}^{-1}$ has been assigned to the symmetrical and antisymmetrical bending of the BO₆ octahedra, while the Raman scattering in the higher-energy range between 720 and 820 cm⁻¹ has been assigned to the symmetrical and anti-symmetrical stretching of the BO₆ octahedra [68, 65]. However, in the absence of single crystals to experimentally distinguish the Raman peaks that arise from doubling on the unit cells and are present in both cubic and ferroelectric states from the Raman signal that results exclusively from ferroic distortions, we will further discuss the internal BO₆ vibrations only in terms of a lower-energy and a higher-energy range arising from two different main types of interactions between the B-site cations and oxygen anions.

Before discussing the temperature dependence of these peaks in detail, it is worth noting that the intensity of the broad Raman features resulting from the two different types of interactions is highly sensitive to the occupancy of the B site. Figure 27 shows the room-temperature Raman spectra of the $(1-x)PbTiO_3-xBiNi_{0.5}Ti_{0.5}O_3$, $(1-x)PbTiO_3-xBiMg_{0.5}Ti_{0.5}O_3$, and $(1-x)PbTiO_3-xBiNi_{0.5}Zr_{0.5}O_3$ solid solutions at a wide range of compositions. If we compare PT-*x*BNT and PT-*x*BMT, one can observe that the range between 450 and 650 cm⁻¹ is very similar for both solid solutions, while the Raman scattering between 720 and 780 cm⁻¹ shows a different trend depending on the type of dopant element at the B-site. In PT-*x*BMT the lower-energy region (450 to 650 cm⁻¹) is more pronounced at room temperature compared to the high-energy range (720 and 780 cm cm⁻¹) for all compositions, while in PT-*x*BNT

the latter becomes dominant with increasing x (Figure 26a and Figure 26b). It should be mentioned that these differences are strongly reflected by the relative peak-intensities, but can be hardly seen in the peak-wavenumber behaviour. On the other hand, PT-xBNT and PT-xBNZ show a similar behaviour between 720 and 780 cm⁻¹, but are different in the 450 and 650 cm⁻¹ range, especially for $x \ge 0.20$.



Figure 27: Raman spectra of a. $(1-x)PbTiO_3-xBiNi_{0.5}Ti_{0.5}O_3$, b. $(1-x)PbTiO_3-xBiMg_{0.5}Ti_{0.5}O_3$, and c. $(1-x)PbTiO_3-xBiNi_{0.5}Zr_{0.5}O_3$ with different compositions x at room temperature

Since the high-energy Raman scattering (720-780 cm⁻¹) arises from the B-O bond stretching, one should take a closer look at the four cations occupying the B position:

Atom	Atomic number	Electron configuration	Ionic radius (Å)
Ti	22	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ²	0.605
Zr	40	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$	0.78
Mg	12	$1s^2 2s^2 2p^6 3s^2$	0.72
Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$	0.69

Table 8: Electronic configuration and ionic radii [9, 10]

As can be seen, the Ni²⁺-cation has a smaller ionic radius than Mg^{2+} and Zr^{4+} and, simultaneously, is the only ion with a partially unoccupied d orbital, which could be the reason why the two Ni-containing solid solutions have different behaviour than the Mg-containing solid solution. However, although Raman spectroscopy clearly indicates a high dependence of the internal BO₆ vibrations with the cation occupying the B position, complementary methods like X-ray diffraction and pair-distribution-function analyses are required to study in detail the B-O bond lengths as well as the O-B-O and B-O-B angles as a function of the type and the amount of the B-site cations substituting titanium before drawing any conclusions.



Let us now discuss the temperature-dependent behaviour of the Raman scattering in the range 450-780 cm⁻¹ in PT-*x*BNT (Figure 28b and Figure 29b).

Figure 28: Internal BO₆ vibrations in the 450 - 650 cm⁻¹ range as a function of composition (a.) and temperature (b.)

In undoped lead titanate the $qTO3 \mod (\sim 550 \text{ cm}^{-1}, \text{ called peak 9})$ softens and merges with the ETO3 mode ($\sim 500 \text{ cm}^{-1}$, called peak 8) at T $\sim 620 \text{ K}$. The $qE3 \mod (\sim 630 \text{ cm}^{-1},$ peak 10), which corresponds to the A₁TO3 mode in single-crystal PbTiO₃, is also softening and merges at the Curie temperature with the ETO3 phonon. This is clearly reflected by the temperature-dependent behaviour of the FWHMs and intensities of the three peaks (Figure 28b).

In PT-0.20BNT the displacive behaviour at high temperatures remains preserved, but peak 9 has a large red shift in the wavenumber compared to $PbTiO_3$ and merges with peak 10 at T \sim 600 K. The resulting peak softens considerably above the Curie temperature and merges with peak 8 at T \sim 850 K, exhibiting a maximum in the FWHM and intensity.

One can easily observe that the compounds with $x \ge 0.5$ have, once again, very similar behaviours. While PT-0.50BNT and PT-0.55BNT appear to have almost identical trends for all three analyzed parameters (ω , FWHM and fractional intensity), PT-0.70BNT exhibits a drop in the wavenumber of peak 9 at T = 400 K, which is mirrored by a large jump in the FWHM and intensity. The order-disorder character is very pronounced for $x \ge 0.5$, where no anomalies can be seen around the Curie temperature.



Figure 29: Internal BO₆ vibrations in the 720 - 780 cm⁻¹ range as a function of composition (a.) and temperature (b.)

The linear decrease with the temperature of the wavenumbers of peak 11 (\sim 715 cm⁻¹) and peak 12 (\sim 780 cm⁻¹) appears to have the same slope for both peaks (Figure 29b), but this slope is changing gradually with increasing BNT-amount and becomes almost 0 at x = 0.70, where only a slight change in the wavenumber can be observed across the whole temperature range.

For $x \ge 0.50$ a similar behaviour as in the case of the B-site cation vibrations can be observed. At x = 0.50 the intensity of peak 12 is higher than the intensity peak 11. This behaviour changes at x = 0.55, where the two peaks switch intensities and at x = 0.70 peak 11 becomes dominant.

8 Conclusions

The Raman scattering related to the off-centered A-site cations (\sim 40 - 60 cm⁻¹) and offcentered B-site cations (\sim 200 - 280 cm⁻¹) persists well above the Curie temperature, indicating structural inhomogeneities and the presence of short-range ferroic order in the paraelectric phase.

Moreover, the characteristic temperatures at which the peaks merge and the modes with an LO component arising from A-site and B-site cation vibrations as well as A-BO₃ vibrations disappear match reasonably well the experimentally obtained Curie temperatures for x = 0, 0.20, 0.50, and 0.55 (Table 9), which may indicate that the T_c of PT-0.70BNT is higher than the one estimated initially.

x	T_c measured (K)	T_c deduced (K)
0	768	760
0.20	763	760
0.50	681	660
0.55	673	670
0.70	598 (estimated)	670

Table 9: Measured versus deduced Curie temperature

The addition of BNT obviously suppresses the displacive character of the phase transition, which dominates at low values of x, and at x = 0.50 the phase transition appears to already have an almost pure order-disorder mechanism. From this point of view, PT-0.20BNT could be considered as an intermediate state, with both displacive and order-disorder characteristics.

For compositions with $x \ge 0.50$ the following main processes can be observed in the range related to the A-site cation vibrations, B-site cation vibration as well as A-BO₃ cation vibrations (40 - 400 cm⁻¹):

- at x = 0.50 two energetically different states of the A-site cations are competing in the low frequency range, while the tetragonal distortions dominate over the antiferrodistortive tilting of the BO₆ octahedra,
- at x = 0.55 the lower energetic state of the A-site cations is dominant, while the tetragonal distortions and the antiferrodistortive tilting of the BO₆ octahedra are competing, showing a high degree of structural instability,
- at x = 0.70 the lower energetic state of the A-site cations remains dominant together with the antiferrodistortive tilting becoming the dominant state of the B-site-cation vibrations.

This behaviour indicates a strong coupling within the A-site and B-site cation subsystems at the morphotropic phase boundary and may represent the origin of the enhanced piezoelectric properties exhibited at this composition.

In the higher-energy range (> 450 cm⁻¹) the broad Raman feature between 720 and 780 cm⁻¹ becomes dominant with respect to the Raman band between 450 and 650 cm⁻¹ when the temperature as well as the amount of BNT are increasing.

While the spectral range related to the A-site- and B-site-cation subsystems has been already thoroughly investigated by numerous studies, the contribution of the internal BO_6 octahedral vibrations to the behaviour exhibited at the morphotropic phase boundary is still not clear. Raman spectroscopy analysis reveals that the behaviour of the highest-energy feature as a function of *x* could indicate a significant contribution to the compositionally-driven phase transition, and therefore the processes that take place in this spectral range require further investigation using complementary methods.

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Peak label	0	0.10	0.20	0.30	0.40	0.50	0.55	0.60	0.65	0.70	
peak 1		43	43	43	44	45	47	49	49	49	
peak 2	88	83	76	74	73	71	73	76	76	76	ETO1
-	111										quasiE1
peak 3	125	123	114	120	120	111	104	105	111	112	quasiTO1
-	143	151	152								quasiLO1
peak 4	154	170	175	170	177	179	183	184	184	179	quasi A_11
peak 5	217	221	230	239	249						ETO2
peak 6	289	288	283	281	279	266	265	265	265	268	$B_1{+}E$
-	296										quasiTO2
peak 7	350	343	339	335	333	334	334	334	335	337	quasiE2
-	395	397	396	395	395	391	393	396	398	400	quasiA ₁ 2
-	447	449	447	440							quasiLO2
peak 8	506	508	512	510	494	480	476	474	475	466	ETO3
peak 9	554	580	595	598	570	547	544	543	547	523	quasiTO3
peak 10	629	623	625	622	617	611	612	613	612	614	quasiE3
peak 11	728	716	719	719	721	720	719	719	719	718	quasi A_13
peak 12	771	767	767	762	764	766	764	765	766	768	quasiLO3

A Appendix

Table 10: Wavenumber of the Raman-active quasi-phonons in PT-xBNT for different compositions x at room temperature following the peak assignment for polycrystalline lead titanate

х	а	a (err)	с	c (err)	α	α (err)	volume	volume (err)	c/a
0.1	3.913	1.71E-4	4.113	1.95E-4	90		62.997	0.006	1.051
0.2	3.917	5.3E-5	4.102	6.6E-5	90		62.967	0.002	1.047
0.3	3.925	1.1E-4	4.081	1.29E-4	90		62.897	0.005	1.040
0.4	3.933	9.7E-5	4.064	1.15E-4	90		62.886	0.004	1.033
0.5	3.943	0.01303	4.038	0.01303	90		62.797	0.005	1.024
0.6	3.969	7.4E-5	3.969	7.4E-5	89.998	0.0132	62.566	0.004	1
0.65	3.969	1.29E-4	3.969	1.29E-4	89.995	0.0130	62.555	0.006	1
0.7	3.969	2.1E-4	3.969	2.1E-4	89.999	0.0110	62.543	0.002	1

Table 11: Unit-cell parameters



Figure 30: Wavenumbers of the Raman peaks as a function of temperature and composition x



Figure 31: Behaviour of peak 6 (280 cm $^{-1})$ and peak 7 (335 cm $^{-1})$ in (1-x)PbTiO_3- $x{\rm BiMg}_{0.5}{\rm Ti}_{0.5}{\rm O}_3$

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