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Chemical order and local structure of the lead-free relaxor ferroelectric $Na_{1/2}Bi_{1/2}TiO_3$

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The A-site mixed perovskite sodium bismuth titanate $(Na_{1/2}Bi_{1/2})TiO_3$ (NBT) is investigated by means of first-principles calculations based on density functional theory. By studying different geometries with varying occupations of the A-site, the influence of chemical order on the thermodynamic stability and local structure is explored. We find that the hybridization of Bi 6*sp* with O 2*p*-states leads to stereochemically active Bi^{3+} lone pairs and increases the stability of structures with high Bi concentrations in {001}-planes. This goes along with displacive disorder on the oxygen sublattice, which up to now has been neglected in experimental studies. The calculated ordering energies are, however, small as compared to the thermal energy and therefore only short-range chemical order can be expected in experiments. Thus, it is conceivable that chemically ordered local areas can act as nucleation sites for polar nano-regions, which would explain the experimentally observed relaxor behavior of NBT.

1. Introduction

The mixed perovskite $(Na_{1/2}Bi_{1/2})TiO_3$ (NBT) is one rare example of A-site mixed relaxor ferroelectrics. NBT-based materials show extraordinarily high strains and are promising environmentally friendly alternatives to the toxic lead-containing standard material in piezoelectric applications $Pb(Zr,Ti)O_3$ (PZT). Additionally, the fact that Bi^{3+} is iso-electronic to Pb^{2+}, both exhibiting a lone pair effect, has encouraged further studies on structural, chemical and electrical properties of this material by both experimental and theoretical methods [1–20]. Pure NBT ceramics show strong ferroelectric properties with large remanent polarization [1], but they are difficult to pole due to their high coercive field and conductivity caused by oxygen vacancies [2]. For overcoming these problems NBT-based solid solutions have been studied. Especially, recent results on $(Na_{1/2}Bi_{1/2})TiO_3-BaTiO_3-(K_{1/2}Na_{1/2})NbO_3$ (NBT-BT-KNN) solid solutions revealed promising piezoelectric properties [3,21].

After Smolenskii discovered NBT in 1960 [4], structural, vibrational and dielectric properties have been investigated in detail [1,3,5–17]. Neutron powder diffraction studies showed that NBT above 540 °C is in its cubic prototype phase (space group $Pm\overline{3}m$). On cooling it undergoes two reversible phase transformations. Between 400 and 500 °C a tetragonal structure with space group symmetry *P*4*bm* exists with in-phase $a^0a^0c^+$ octahedral tilting and anti-parallel cation displacements along [001], the tetragonal distortion from cubic is rather small with 0.14% [5,6]. Below 255 °C a rhombohedral *R*3*c* structure is stable with anti-phase $a^-a^-a^-$ octahedral tilting and ion displacements along the [111]-direction of the pseudo-cubic cell with $\alpha = 89.83°$ [6]. High-resolution single-crystal X-ray diffraction revealed that there might exist monoclinic-like deviations from *R*3*c*-symmetry [7], local deviations from the average structure were also subject of an earlier work of Thomas et al. [8]. Recently, an additional intermediate orthorhombic phase in the temperature range 280–320 °C having *Pnma*-symmetry and $a^-b^+a^-$ octahedral tilting bridging the rhombohedral and tetragonal phase was found by TEM and electron diffraction [9,10]. Already at 200 °C *Pnma*-modulation of the *R*3*c*-phase starts, which can be understood as formation of twin planes with *Pnma*-symmetry within the *R*3*c*-host. The same authors refined the tetragonal phase above 400 °C in the centrosymmetric space group *P*4/*mbm*, the phase transition from *Pnma* to *P*4/*mbm* occurs between 320 and 370 °C. All these information are summarized in Fig. 1.

In the temperature range of the diffuse phase transition from the rhombohedral to the tetragonal phase (200–320 °C), NBT exhibits peculiar antiferroelectric [11], relaxor-like behavior [1] with electric field-induced phase transitions [3,12].

The origin of the relaxor behavior is still controversial, but in B-site mixed perovskites it is associated with heterovalent disorder [22,23]. NBT has aliovalent cations on the A-site (Na^+ and Bi^{3+}) in the exact ratio 1:1. For B-site mixed perovskites chemical

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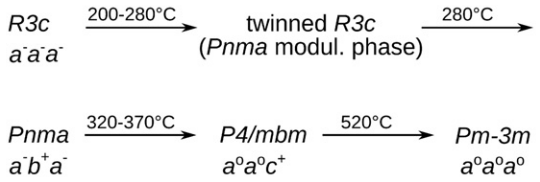

Fig. 1. Phase transitions of NBT with variation in temperature.

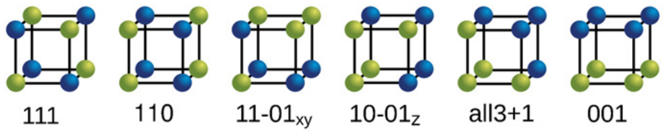

Fig. 2. $2 \times 2 \times 2$ perovskite supercell configurations, the simple cubic sublattice of A-atoms is only shown (Bi: green, Na: blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ordering is generally understood [24]. Order, commonly rock salt (111)-order, occurs when the charge difference between the cation species occupying the same crystallographic site is $\Delta q > 2$, while for charge differences $\Delta q < 2$ disorder is found. For $\Delta q = 2$ disordered, partially ordered and fully ordered examples can be found depending on size and/or bonding preferences of the different cations. In contrast, A-site ordering is much less common. There exist only a few examples where A-site order is experimentally found. Knapp and Woodward reported on (001)-order for $(Na_{1/2}La_{1/2})(Mg_{1/2}W_{1/2})O_3$ driven by cooperative effects of both A-site and B-site ordering [25]. More examples can be found in a review recently published by King and Woodward [26]. They show that A-site order commonly occurs in {001}-layers, but that charge differences between the cations of $\Delta q = 2$ are not sufficient to cause ordering. Systematic oxygen vacancies, vacancies in the A-sublattice or B-site ordering are necessary to stabilize chemical A-site order in mixed perovskites.

Nonetheless, many authors reported on chemical order in NBT. Park suggested a low degree of Bi/Na-order in NBT with an ordered face-centered structure (space group $Fm\overline{3}m$) for the high-temperature cubic phase based on single-crystal XRD measurements [13]. Dorcet and Trolliard recently proposed the same type of order based on TEM images and electron diffraction. According to them ordering occurs in nanometer sized domains embedded in a disordered matrix [10]. Rock salt type order was also deduced from Raman spectra, which indicated an additional strong lattice disorder [14]. Chemical short-range order emerging as segregation planes with correlated cation displacements along $\langle 001 \rangle$ (comparable to Guinier-Preston-Zones in metal alloys) leading to asymmetric streak patterns in diffuse scattering was suggested by Kreisel et al. [15]. Besides these streaks Thomas et al. [16] could identify additional satellite reflections in their reciprocal space maps which are thought to have their origin in a modulated domain structure. Structural polar disorder of the Bi-sites is assumed by Shuvaeva et al. to explain XAFS results [17]. They find that statistically disordered Bi-displacements deviating from the [111]-direction lead to few short Bi–O bonds of 2.22 Å. However, this short bond length never appeared in average crystal structures deduced from diffraction methods implying that strong local disorder exists in NBT due to the mixed cationic A-site.

Theoretical methods, in contrast, have only scarcely been used for studying this material. Xu and Ching investigated the electronic structure of pure NBT and its solid solution with $BaTiO_3$ by means of an orthogonalized linear combination of atomic orbitals (OLCAO) method, but they only considered the rock salt type of chemical order and did not include structural relaxations [18]. Burton and Cockayne conducted a cluster expansion-supported search on the ground state structure of NBT based on *ab initio*-calculations [19]. They predicted a monoclinic structure (space group *Pm*, unique *c*-axis) within a 40-atom supercell with "criss-cross" rows of Na and Bi perpendicular to [001] (cf. 10–01_z configuration in Fig. 2 for cation order). In our recent study, we compared first-principles calculations and TEM images of the solid solution of NBT and $BaTiO_3$ within the composition range of the morphotropic phase boundary, showing that in this material the distribution of Ba/Bi/Na is homogeneous, hence no distinctive chemical order occurs [20].

With respect to the massive discrepancies between general empirical models, experimental and theoretical work, it thus appears to be a worthwhile task to revisit the problem of chemical order in NBT.

In order to gain insights into the chemical ordering tendency and the consequences for the local structure we investigated six different cation configurations in $2 \times 2 \times 2$ (pseudo)cubic perovskite supercells using total energy calculations based on electronic density functional theory [27,28].

We present total energies and densities of states of these configurations in structurally relaxed configurations. Regarding the tendency for chemical ordering we discuss the observed total energy differences in the light of thermodynamics by comparing the values with mixing energies at elevated temperatures. We analyze the local structure induced by the different cation orders and identify the driving forces for the observed atomic displacements by discussing selected densities of states.

In doing so, we focus on the high-temperature cubic phase, where mobility is sufficiently high to allow for cation redistribution. However, the displacive disorder on the oxygen sublattice induced by cation order is also relevant for the low temperature phases of NBT, because the chemical order installed at high temperatures will be frozen in.

2. Method

The Vienna Ab-initio Simulation Package (VASP) [29–32] was used to perform fully relaxed total energy calculations. Projector Augmented Plane Waves [33,34] were applied with the LDA exchange correlation functional [35]. An $8 \times 8 \times 8$ Monkhorst-Pack *k*-point mesh for the primitive cell was used for Brillouin zone integration [36]. In all calculations, the plane-wave energy cutoff was set to 750 eV resulting in a numerical error of less than 1 meV/atom.

The valence electron configurations of the PAW data sets were:

$$\text{Bi } 5d^{10}6s^26p^3, \quad \text{Na } 2p^63s^1, \quad \text{Ti } 3s^23p^64s^23d^2 \quad \text{and} \quad \text{O } 2s^22p^4.$$

Calculations were performed with relaxation of atomic positions at the experimental cell volume (lattice constant a=3.9137 Å). Forces were optimized to less than 0.005 eV/Å.

Additional calculations with the PBE exchange correlation functional [37] lead to the same conclusions.

In a $2 \times 2 \times 2$ perovskite supercell there are eight A-atoms on a simple cubic sublattice. For a 1:1 composition there exist six distinctive arrangements of A-atoms, the resulting configurations are shown in Fig. 2. Three of these configurations correspond to layered structures along the three high-symmetry (pseudo)cubic directions [001], [110] and [111]. In '10-01_z' and '11-01_{xy}', there are only columns of same cations present. In the '10-01_z' configuration these columns are arranged along [10(0)]- and [01(0)]-directions alternately stacked along the *z*-axis, while in the '11-01_{xy}' configuration they are arranged along [(0)11]- and [(0)01]-directions when looking along the *x*-axis and along