Ordering of A-cations in lead-free oxides with a filled tetragonal tungsten bronze structure

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Abstract. By X-ray powder diffraction, the structure of polycrystalline lead-free oxides $K_xBi_2 Nb_{10}O_{30}$ and $Na_x Sr_x Nb_{10} O_{30}$ was refined with an emphasis on ordering in the A-sites of the tetragonal tungsten bronze crystal lattice. It was shown that the studied oxides have different types of cationic ordering, which does not change at ferroelectric phase transition. The results are consistent with the piezoresponse force microscopy data.

1. Introduction

The oxygen framework of the tetragonal tungsten bronze (TTB) structure forms three different c-oriented channel positions (A1, A2 and C). The resulting favorable structural modifications are one of the reasons why TTB-based materials are considered the second most important structural class of ferroelectrics after perovskites. The coexistence of different cations favorable in both the octahedral framework as well as in the A sites and the amount of disorder are closely related to the complex dielectric properties of these materials [1-5]. The classification of TTB oxides [3, 6, 7] by completeness of filling the A positions in square and pentagonal channels include stuffed, filled, and unfilled groups. As shown in [8, 9], the presence of a structural vacancy in the unfilled phases $(Ba, Sr)_x Nb_{10} O_{30}$ is accompanied by the formation of polar nanoregions (PNR) responsible for relaxor properties. However, the formation of such inhomogeneities in TTB oxides is not necessarily associated with the presence of structural vacancies, and can occur not only in an unfilled structure. Such regions can also be found in the filled compounds as a consequence of the specific distribution of A-cations [10].

2. Filled TTB structure

To reveal the general regularities of the A-cation distribution in the TTB structure, the most suitable are widespread filled oxides represented by the structural formula $A_1 \frac{A_2}{2} B_{10} O_{30}$, where $A_1$ and $A_2$ show cationic positions in the square and pentagonal channels. Here, we consider only filled oxides of the composition $M_1 x M_2 y B_{10} O_{30}$, where $M_1$ and $M_2$ are two different cations. The cation distribution in these oxides can be described by the parameter $s$ - the probability for the $M_1$ cation to occupy an A1 position in the square channel; $0 \leq s \leq 1$. Accordingly, the structural formula of $M_1 x M_2 y B_{10} O_{30}$ oxides is written as $(M_1 x M_2 y) B_{10} O_{30}$ and accounting the lack of vacancies in the filled structure $(M_1 x M_2 y) B_{10} O_{30}$.
The s parameter fully describes the structural ordering in the considered compounds, including the "special" configurations [10]:

\[ s = 1 \] - ordered structure were each of the A1 and A2 sublattices is occupied by cations of one certain type (structural formula \( \text{M1}_{2} \text{M2}_{2} \text{B}_{10} \text{O}_{30} \)).

\[ s = 0 \] - partially ordered structure in which M2 cations fill two A1 positions, and four A2 positions are statistically occupied by an equal number of M1 and M2 cations in accordance with \((\text{M2})_{2} (\text{M1}_{1/2} \text{M2}_{1/2})_{2} \text{Nb}_{10} \text{O}_{30} \).

\[ s = 1/3 \] disordered TTB structure, in which six cations M1 and M2 are statistically distributed over six A1 and A2 positions M1 and M2: \((\text{M1}_{1/3} \text{M2}_{2/3})_{3} (\text{M1}_{1/3} \text{M2}_{2/3})_{2} \text{Nb}_{10} \text{O}_{30} \).

The structural ordering in filled TTB oxides is supposed to be the key for understanding the variety of TTB-type materials properties.

When refining the complex TTB structure, it is desirable to reduce the number of refined parameters; therefore, it is advisable to choose a cation distribution model (i.e., parameter s) by an independent method. As usual, a larger ion is placed in a pentagonal channel A2, but sometimes an acceptable convergence is achieved under other assumptions. In [11], it was experimentally shown that for tetragonal lead-free tantalates and niobates \( \text{M1}_{2} \text{M2}_{4} \text{B}_{10} \text{O}_{30} \) (M=K, Na, Rb, Ag, Bi and M2= K, Ba, Sr) the cation distribution over the A1 and A2 positions depends only on the difference in the ionic radii of elements [12] regardless of their valence. Based on this assumption, we selected three compounds as model filled structures: \( \text{K}_{4} \text{Bi}_{2} \text{Nb}_{10} \text{O}_{30} \); \( \text{K}_{2} \text{Sr}_{4} \text{Nb}_{10} \text{O}_{30} \); and \( \text{Na}_{2} \text{Sr}_{2} \text{Nb}_{10} \text{O}_{30} \). All of them are known as promising base for lead-free active materials. In accordance with the values of the ionic radii of the M1 and M2 cations, these compounds probably realize each of the considered special configurations:

\( \text{K}_{4} \text{Bi}_{2} \text{Nb}_{10} \text{O}_{30} \) is a ferroelectric with a diffused maximum of dielectric permittivity at \( T_{m} = 372 - 400 \) °C [13-15]. The cited works describe the crystal lattice as orthorhombic, but these data are not supported by convincing experiments. The previously obtained crystal data were interpreted taking into account the orthorhombic cell by analogy with \( \text{Na}_{2} \text{Ba}_{4} \text{Nb}_{10} \text{O}_{30} \). However, a detailed study of \( \text{K}_{4} \text{Bi}_{2} \text{Nb}_{10} \text{O}_{30} \) structure was not carried out.

\( \text{Na}_{2} \text{Sr}_{2} \text{Nb}_{10} \text{O}_{30} \) is a ferroelectric relaxor with a maximum of dielectric permittivity at \( T_{m} = 230 \) °C [3, 16]. Structure refinement of the nanostructured powder was conducted in [16] with the assumption of a partially ordered structure with A1 sites filled by strontium, and A2 sites statistically occupied by equal amounts of sodium and strontium: \((\text{Sr})_{2} (\text{Sr}_{1/2} \text{Na}_{1/2}) \text{Nb}_{10} \text{O}_{30} \).

Structure and surface piezoresponse of partially ordered \( \text{K}_{2} \text{Sr}_{4} \text{Nb}_{10} \text{O}_{30} \) were studied in details in our previous works [10, 17].

3. Experiment

The dense ceramic \( \text{K}_{4} \text{Bi}_{2} \text{Nb}_{10} \text{O}_{30} \) and \( \text{Na}_{2} \text{Sr}_{4} \text{Nb}_{10} \text{O}_{30} \) samples were synthesized by solid state reactions followed by uniaxial hot pressing under \( P = 40 \) MPa at \( T = 1150 \) °C for 40 min. Samples for X-ray diffraction studies were carefully milled and annealed at 1200 °C to eliminate the effects of texturing and residual mechanical stresses [17].

Powder X-ray diffraction (PXRD) data for the sample phase qualification and precise PXRD data for profile analysis were collected using the DRON-7 diffractometer, filtered Co-Kα radiation, standard attachment. Temperature studies were carried out with the Anton Paar 1000 temperature attachment with the temperature stability not worse than ±0.5 degrees. Rietveld data were collected within the broad angular interval with the scanning step 0.04 deg and counting time 10 sec. Data processing was performed with the PowderCell package [18]. Surface piezoelectric response data
were measured with Veeco Multimode VS SPM under the same experimental conditions as in [10, 17].

4. Structure refinement
X-ray powder patterns of the \( K_4Bi_2Nb_{10}O_{30} \) and \( Na_2Sr_4Nb_{10}O_{30} \) samples at room temperature and in the paraelectric state show the formation of pure TTB structure without any impurity phases (Figures 1,2). Both samples show tetragonal cell symmetry because additional splitting testifying lowering the lattice symmetry, was not found as at 18 °C and at paraelectric state.

The possible ordering of A-cations in the TTB structure, unlike in perovskites, is difficult to reveal by the appearance of additional superstructural reflections. \( K_4Bi_2Nb_{10}O_{30} \) is an exception, because due to the large difference in the A-cation scattering factors, the ordered type of their distribution is accompanied by the appearance of reflections (110), (200), (210), and (220), which are intense enough to be detected by PXRD.

The main goal of this study is determination of the cation distribution over positions in the square and pentagonal channels. For the TTB structure, it is preferable to start solving the problem from the paraelectric phase with a minimal set of variable atomic parameters. For the purpose, XRD powder data for \( K_4Bi_2Nb_{10}O_{30} \) were collected at 530 °C and for \( Na_2Sr_4Nb_{10}O_{30} \) at 400 °C, that is, well above the corresponding ferroelectric phase transition temperatures.

As an initial model for refining the structure of the paraelectric phase, we used the data of the filled TTB single crystal \( K_6Ta_{10.8}O_{30} \), space group \( D_{4h}^5 = P4/mmbm \), № 127. The trigonal C sites were considered vacant; tetragonal and pentagonal channels A1 and A2 occupied by cations in 2a and 4g Wyckoff positions; \( Nb^{5+} \) ions occupy positions in two nonequivalent octahedra B1(2c) and B2(8j).

In the \( D_{4h}^5 \) space group, there are three atomic parameters of cations: the \( x \) coordinate of the A atom in the 4g position and the \( x, y \) coordinates of niobium in the B2 (8j) position. These parameters with the corresponding occupation factors were refined. Also at Rietveld refinement lattice constants, background polynom, and the overall temperature factor B were minimized. The reflections were fit to a pseudo-Voigt function for the peak shape with the refining coefficients U, V, W of the Caglioti function:

\[
H = Utg^2\Theta + Vtg\Theta + W
\]

4.1. \( K_4Bi_2Nb_{10}O_{30} \)
The noticeable intensities of (110), (200), (210), and (220) low-angle reflections for \( K_4Bi_2Nb_{10}O_{30} \) can be explained only by a high ordering degree \( s \approx 1 \). Therefore, in the initial approximation, we used a model close to a fully ordered structure, in which A1 (2a) positions are occupied mainly by bismuth, A2 (4g) - by potassium cations. The refined crystal data for \( K_4Bi_2Nb_{10}O_{30} \) at 530 °C (paraelectric state) are summarized in Table 1 and Figure 1.

![Figure 1. Rietveld XRD data for \( K_4Bi_2Nb_{10}O_{30} \) sample at T=530 °C. The 2Θ peak positions are shown by vertical dashes.](image-url)
The XRD data for $K_4Bi_2Nb_{10}O_{30}$ in the ferroelectric state was got at 18 °C. At this temperature, $K_4Bi_2Nb_{10}O_{30}$ exhibits ferroelectric properties, and no additional splittings compared to the high-temperature phase were found. Thus, to refine the structure, we used the polar tetragonal space group $C_{4v} \cong P4bm$. The atomic and profile data obtained for the paraelectric phase were used as an initial approximation.

Table 1. X-ray Rietveld data for $K_4Bi_2Nb_{10}O_{30}$ in paraelectric state.

| Crystallography data |
|-----------------------|
| Symmetry tetragonal   | Space group $D_{4h}^5$ |
| Lattice: a= 12.6582(9) Å | c=3.9482(5) Å | V= 632.62 Å³ |

| Experiment conditions for data collection |
|------------------------------------------|
| Radiation Co Kα $\lambda_1 = 1.78897$ Å $\lambda_2 = 1.79285$ Å | Measuring range 2θ = 10-80 degr |
| Step 0.04deg Counting time 10 sec |

| Rietveld data |
|---------------|
| profile PsVoigt2 U: 0.3574 V: -0.2297 W: 0.0551 |
| R-values (%) Rp=7.36 Rwp=10.02 Rexp=0.38 |
| zero shift : -0.139 |

| Structure data |
|----------------|
| Name | Z | ion | wyck | x | y | z | SOF |
| A1 | 83 | Bi3+ | 2a | 0.0000 | 0.0000 | 0.0000 | 0.8985 |
| 19 | K+ | 0.0089 |
| A2 | 19 | K+ | 4g | 0.1775 | 0.6775 | 0.0000 | 0.9856 |
| 83 | Bi3+ | 0.0145 |
| B1 | 41 | Nb5+ | 2c | 0.0000 | 0.5000 | 0.5000 | 1.0000 |
| B2 | 41 | Nb5+ | 8j | 0.2844 | 0.4203 | 0.5000 | 1.0000 |
| O1 | 8 | O2- | 2d | 0.0000 | 0.5000 | 0.0000 | 1.0000 |
| O2 | 8 | O2- | 8i | 0.2904 | 0.4236 | 0.0000 | 1.0000 |
| O3 | 8 | O2- | 4h | 0.2899 | 0.7899 | 0.5000 | 1.0000 |
| O4 | 8 | O2- | 8j | 0.1551 | 0.5040 | 0.5000 | 1.0000 |
| O5 | 8 | O2- | 8j | 0.4328 | 0.3582 | 0.5000 | 1.0000 |

For the ferroelectric phase at 18 °C, the result is obtained with the reliability factors Rp = 7.95; Rwp = 10.91; Rexp = 0.39(%) and tetragonal lattice parameters a = 12.6210(9) Å; c = 3.9175(5) Å. The occupancy factors for A1 and A2 positions within the experimental accuracy coincide with those obtained for the paraelectric phase.

4.2. Na$_2$Sr$_2$Nb$_{10}$O$_{30}$

An analysis of the convergence of sensitive weak reflections clearly indicates that in Na$_2$Sr$_2$Nb$_{10}$O$_{30}$ the A -cations distribution is most close to the disordered configuration (s = 1/3). Therefore, in the initial model, positions A1 and A2 were statistically filled with sodium and strontium cations. The resulting crystal data for Na$_2$Sr$_2$Nb$_{10}$O$_{30}$ at 400 °C (paraelectric state) are summarized in Table 2 and Figure 2. The use of a partially ordered (s = 0) model according to [16] resulted in a significant decrease in data convergence.
Despite the acceptable overall reliability factors, the two reflections (510 and 411) are explained only by the presence of about 5% of the second phase - ordered (s = 1), in which A1 positions are occupied by sodium ions, and A2 positions are occupied by strontium ions.

The XRD data for $Na_2Sr_4Nb_{10}O_{30}$ in the ferroelectric state was got at $18 \, ^\circ C$. The same structure refinement algorithm was used as for $K_4Bi_2Nb_{10}O_{30}$.

The results with reliability factors $R_\text{p}=6.72; \, R_{\text{wp}}=9.23; \, R_{\text{exp}}=1.26$ (%) show the same as for paraelectric state occupancies. Lattice parameters $a = 12.3454(9) \, \text{Å}; \, c = 3.8926(5) \, \text{Å}$ within the experiment accuracy coincide with data for nanosrtuctured powders [16]: $a = 12.3495 (6) \, \text{Å}; \, c = 3.8911 (2) \, \text{Å}$.

**Table 2.** X-ray Rietveld data for $Na_2Sr_4Nb_{10}O_{30}$ in paraelectric state.

| Crystallography data |
|-----------------------|
| **Temperature** 400°C |
| **Symmetry** tetragonal | **Space group** $D_4^5$ | **Space group number** 127 |
| **Lattice:** | $a=12.4170(9) \, \text{Å}$ | $c=3.8937 (5) \, \text{Å}$ | $V= 600.41 \, \text{Å}^3$ |

| **Experiment conditions for data collection** |
|---------------------|
| **Radiation** Co Kα | $\lambda_1 = 1.78897 \, \text{Å}; \, \lambda_2 = 1.79285 \, \text{Å}$ |
| **Measuring range** $2\Theta$ | =10-100 degr |
| **Step** 0.04deg | **Counting time** 10 sec |

| **Rietveld data** |
|-------------------|
| **profile** PsVoigt2 | **U:** 0.4375 | **V:** -0.2891 | **W:** 0.0941 |
| **R-values (%)** | $R_p=7.26$ | $R_{wp}=9.95$ | $R_{exp}=1.04$ |

| **zero shift** | -0.1285 |

| **Structure data** |
|-------------------|
| **Name** | **P.No.** | **ion** | **wyck** | **x** | **y** | **z** | **SOF** |
| A1 | 11 | Na$^+$ | 2a | 0.0000 | 0.0000 | 0.0000 | 0.3389 |
| 38 | Sr$^{2+}$ | 0.6589 |
| A2 | 38 | Sr$^{2+}$ | 4g | 0.1811 | 0.6811 | 0.0000 | 0.6637 |
| 11 | Na$^+$ | 0.3437 |
| B1 | 41 | Nb$^{5+}$ | 2c | 0.0000 | 0.5000 | 0.5000 | 1.0000 |
| B2 | 41 | Nb$^{5+}$ | 8j | 0.0797 | 0.2092 | 0.5000 | 1.0000 |
| O1 | 8 | O$^{2-}$ | 2d | 0.0000 | 0.5000 | 0.0000 | 1.0000 |
| O2 | 8 | O$^{2-}$ | 8i | 0.0800 | 0.2200 | 0.0000 | 1.0000 |
| O3 | 8 | O$^{2-}$ | 4h | 0.3000 | 0.8000 | 0.5000 | 1.0000 |
| O4 | 8 | O$^{2-}$ | 8j | 0.6600 | 1.0000 | 0.5000 | 1.0000 |
| O5 | 8 | O$^{2-}$ | 8j | 0.1500 | 0.0700 | 0.5000 | 1.0000 |
5. Summary
Based on the XRD powder diffraction data, the type of structural ordering for oxides was established. The results are consistent with the [11] criterion for the distribution of A-cations in the filled TTB structure. For the ferroelectric phase of both compounds, the tetragonal cell symmetry is proved. At cooling from paraelectric to ferroelectric state, the ordering degree \( s \) does not change, consequently this phase transition is not accompanied by the order-disorder phenomena.

The A cations in \( K_4Bi_2Nb_{10}O_{30} \) are distributed over the A1, A2 positions in tetragonal and pentagonal channels according to the ordered configuration with the occupancy parameter \( s = 0.899 \) (0.90). According to the refinement results, the sample has two types of defects:

1. The refined composition \( K_{3.96}Bi_{1.86}Nb_{10}O_{30} \) is not quite stoichiometric.
2. In violation of the main ordered motive, some cations appear not in “their own” positions. The refined structural formula \( (K_{0.009}Bi_{0.899})_2(K_{0.985}Bi_{0.015})_4 Nb_{10}O_{30} \) indicates that the vacancies associated with the deviation of stoichiometry are concentrated in the square channels A1.

A similar deviation from the ordered structure was described earlier for \( Na_2Ba_4Nb_{10}O_{30} \) [20].

The composition of the \( Na_2Sr_4Nb_{10}O_{30} \) powder sample corresponds to the stoichiometric one. Sodium losses due to evaporation at the synthesis were avoided using the hot pressing method. The obtained result on the disordered cation distribution does not coincide with that described earlier for the nanostructured powders [16]. Probably, this discrepancy testifies the possibility of variations of the cation ordering in \( Na_2Sr_4Nb_{10}O_{30} \) under varied preparation conditions.

The assumption, the structural order can influence the various charged subsystems formation is confirmed by the piezoresponse force microscopy (PFM) data.

The possibility of such electrically active nano/meso-sized regions for \( K_2Sr_4Nb_{10}O_{30} \) were investigated previously by us in [10] where their sizes were estimated. Similar PFM studies for \( K_4Bi_2Nb_{10}O_{30} \) and \( Na_2Sr_4Nb_{10}O_{30} \) demonstrate the presence of different subsystems in them, determining the meso-sized regions electrical activity.

6. References

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