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# Structural study of cubic pyrochlores based on quantum mechanical simulation

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**Abstract**

In the ideal $A_2B_2O_6O'$ pyrochlore structure, the *x*-value of O atom position is a variable parameter. In $Bi_{1.5}ZnNb_{1.5-x}Ta_xO_7$ (BZNT) cubic pyrochlores, the *x*-values alter with the different compositions of Nb/Ta. In this work, a series of initial models for BZNT were established by analyzing X-ray diffraction data. Then three structure modifying methods, including Rietveld refinement, Rietveld refinement with energy and geometry optimization based on quantum mechanics, were employed to obtain the precise models using Materials Studio. Moreover, the reflectivities of BZNT were computed by quantum mechanical simulation based on the refined models. Comparing the simulation results from different modifying models with the experimental results, it is found that Rietveld refinement with energy optimization is the most accurate method for BZNT pyrochlores. According to the simulation results, the different reflectivities correspond well with various *x*-values of O atom positions in BZNT pyrochlores.


*Keywords:* Microscopic structure; Optical properties; Simulation

## 1. Introduction

Ternary oxides in the $Bi_2O_3$–ZnO–$Nb_2O_5$ (BZN) systems exhibit high-dielectric constants, low-dielectric losses and compositionally tunable capacitance [1–5]. Based on the nominal composition and the indexed x-ray powder diffraction patterns, the $Bi_{1.5}ZnNb_{1.5}O_7$ (α-BZN) composition is identified to have a cubic pyrochlore structure $A_2B_2O_7$, with the Zn ions occupying both A and B sites [2]. Considering similar ionic radius and electronegativity of $Nb^{5+}$ and $Ta^{5+}$, previous works reported the structural trends and dielectric properties of $Bi_{1.5}ZnNbTa_{1.5}O_7$ (BZNT) [6,7].

In order to distinguish the oxygen atoms in the two different networks, the $A_2B_2O_7$ for ideal oxide pyrochlore is often written as $A_2B_2O_6O'$. The $A_2O'$ network features four-coordinate O′ ions and two-coordinate A cations. The $B_2O_6$ framework consists of [$BO_6$] octahedral sharing all vertices to form large cavities [8]. The ideal cubic pyrochlore structure is highly symmetrical, which belongs to space group $Fd\bar{3}m$. The ideal cubic structure has four distinct sites occupied by the A (site 16*d*), B (site 16*c*), O (site 48*f*) and O′ (site 8*b*) ions. Because of high symmetry, the positions of all ions except O ion are fixed. The O ions in 48*f* sites have a single variable parameter along the *x*-direction. In this model, it has extensive displacive disorder on both A and O′ sites. The disorder plays an important role in the physics of BZN since the dielectric properties are believed to be closely associated with the $A_2O'$ network [9] (see Fig. 1).

In this work, the properties of new compounds $Bi_{1.5}ZnNb_{1.5-x}Ta_xO_7$ (BZNT, $x = 0$, 0.5, 1.0, 1.5) were experimentally obtained, which Nb ions were replaced by Ta ions gradually. Three structure modifying methods, including Rietveld refinement, Rietveld refinement with energy and geometry optimization, were applied to obtain the precise structure. Moreover, the quantum mechanical simulation based on the three models was adopted to compute the optical properties of BZNT. Through comparing the simulation results and experiment data, precise models for BZNT were obtained.

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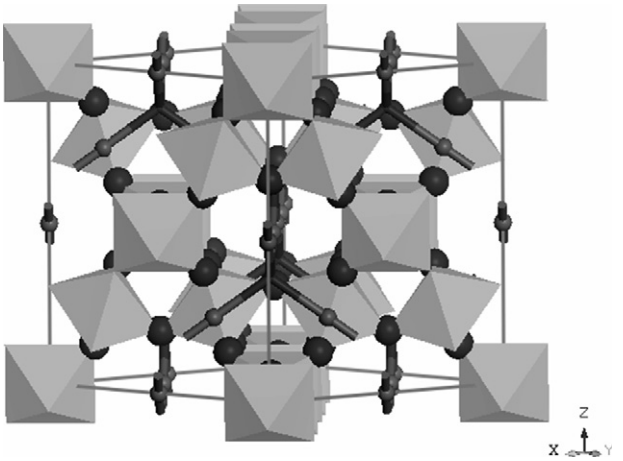


Fig. 1. The cubic BZNT structure ( ) represents A sites; the tetrahedra represents B sites; ( ) represents O atoms.

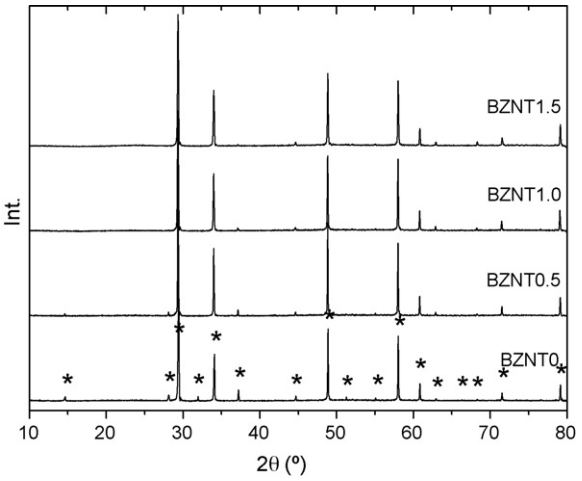


Fig. 2. X-ray diffraction patterns of $Bi_{1.5}ZnNb_{1.5-x}Ta_xO_7$ ($x = 0$, 0.5, 1.0, 1.5).

The structure–property relationship had also been investigated. Further analysis showed the three modifying methods can be applied well to different material systems. The Rietveld refinement with energy method can be applied successfully to establish the microscopic structure for ceramic system, especially for the pyrochlores.

## 2. Experimental procedure

### 2.1. Initial model establishment

$Bi_{1.5}ZnNb_{1.5-x}Ta_xO_7$ ($x = 0$, 0.5, 1.0, 1.5) samples (denoted as BZNT0, BZNT0.5, BZNT1.0, BZNT1.5, respectively) were prepared by conventional solid-state powder processing techniques. The samples were sintered at 1000, 1020, 1040 and 1060 °C for 3 h separately [10]. Phase structures of the sintered ceramics were studied by X-ray diffractometer (Rigaku, Dmax-2400), Cu Kα, 40 kV, 10 mA, 10–80° with the scanning step 2°/min. The XRD patterns are shown in Fig. 2.

In order to index the peaks from XRD data, we carried out some pretreatment work, which included $K\alpha_2$ removed and background subtraction. Peak detection method was performed to search the peaks of XRD data. Indexing program TREOR90 was used to test experimental powder pattern in all of crystal systems. Then Pawley refinement was employed to check the indexing results, and to obtain the space group and the refined lattice parameters [11]. The result indicated that the space group of BZNT series is $Fd\bar{3}m$. Table 1 shows the lattice parameters of $a$ value for cubic BZNT. The atom positions for BZNT pyrochlore were placed according to Levin et al. [8] (see Table 2).

Table 1
The lattice parameters for cubic BZNT pyrochlores

| | $a$ (Å) |
|---|---|
| BZNT0 | 10.5433 |
| BZNT0.5 | 10.5425 |
| BZNT1 | 10.5466 |
| BZNT1.5 | 10.5384 |

### 2.2. Model modification and computation

In the cubic BZN pyrochlore, O ions in 48*f* sites have a single variable parameter along the *x*-direction. It was assumed that this variable equals to 0.3196 in all initial models for BZNT. However, the actual parameter will alter imaginably along with the change of Nb/Ta ratio in the BZNT. In addition, this variable was expected to be a significant factor for BZNT properties. So how to determine this parameter was a primary factor before computing the BZNT properties. Thus, three different methods were introduced to solve this difficulty.

The first method known as Rietveld refinement was introduced to adjust the model according to the experiment data. The Rietveld refinement finds a set of powder diffraction simulation parameters that lead to optimum agreement between the simulated powder diffraction pattern and the experiment data. The parameters being refined are the atomic positions and other factors influencing the scattering strength of the atoms [12]. The agreement between simulation and experiment is quantified by a measure of similarity, which is called weighted profile R-factor ($R_{wp}$). The smaller the $R_{wp}$ is, the better the agreement between the simulation and experiment results is.

As to the second approach, Rietveld refinement with energy optimization was employed to obtain the accurate models for BZNT pyrochlores. Rietveld refinement with energy incorporates a precise description of potential energy in conjunction with the $R_{wp}$ in the Rietveld refinement process, optimizing

Table 2
Initial atoms position for the $Bi_{1.5}ZnNb_{1.5-x}Ta_xO_7$ (BZNT)

| Atom | Occupancy | Wyckoff position | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|
| Bi(A)/Zn(A) | 0.75/0.25 | 16*d* | 0.5 | 0.5 | 0.5 |
| Nb(B)/Ta(B)/Zn(B) | 0.75 − *x*/*x*/0.25 | 16*c* | 0 | 0 | 0 |
| O | 1 | 48*f* | 0.3196 | 0.125 | 0.125 |
| O′ | 1 | 8*b* | 0.375 | 0.375 | 0.375 |

a combined figure of merit. This method tries to balance two different and possibly conflicting objectives, i.e. matching the simulated pattern with experimental diffraction data and minimizing the potential energy of the structure. In our work, Pareto optimization was applied automatically to calculate a set of possible optimal refinement solutions with changing energy weights. The corresponding Rietveld refined and Rietveld refinement with energy optimization were both carried out using the Reflex module of Materials Studio.

Finally, geometry optimization based on quantum mechanics was applied to obtain the variable parameters of O atoms for BZNT. Quantum mechanics provides a reliable way to calculate what the electrons and atomic nuclei do in any situation based on fundamental physical laws and without using free parameters. The implementation of geometry optimization uses a Hessian function in the mixed space of internal and cells degrees of freedom, so that both lattice parameters and atomic coordinates can be optimized. This geometry optimization can update the cell construction based on first-principles pseudopotentials and plane waves in the framework of the density-functional theory (DFT) [13–15].

In DFT calculation, different approximate functions perhaps bring varied optimization results. In order to eliminate the effect of different functions, we employed several approximate functions to optimize the BZNT pyrochlores. The geometry optimization was carried out using CASTEP module of Materials Studio. In the optimization process, the all electron potentials were replaced by norm-conserving pseudopotentials. The wave functions were expanded in plane wave up to energy cutoff of 600 eV. Integrals over the Brillouin zone were replaced by a grid of $4 \times 4 \times 4$ K-point sampling. In addition, the SCF tolerance was 1e–6 eV/atom.

The optical properties of the series of BZNT based on above three refinement results were simulated. Using CASTEP module, we calculated the total energy of the BZNT system and its optical properties. The generalized-gradient approximation (GGA) PBE function with separate XC function was adopts for optics calculation. The calculated parameters were the same as that used in geometry optimization.

## 3. Results and discussion

The final modified single variable parameters of O atoms of BZNT pyrochlore are shown in Table 3. The other atoms, including in A (site 16*d*), B (site 16*c*) and O′ (site 8*b*), have no movements, as their positions have been settled in the space group $Fd\bar{3}m$. From Table 3, we can see the *x*-value is relatively close by using Rietveld refinement and Rietveld refinement with energy method. The comparison between the experimental data and final modify model by Rietveld refinement and Rietveld refinement with energy methods is shown in Table 4. The accordance becomes more precise with the decreasing $R_{wp}$. It seems that Rietveld refinement is more precise to refine model from Table 4. However, comparing the reflectivities simulated by these two methods (see Fig. 3b and c) with experiment results (see Fig. 3a), it is obvious that Rietveld refinement with energy is a better refine method for BZNT pyrochlore.

Table 3
The variable parameter of O atoms position for different modification method in BNZT pyrochlore (Method 1 represents Rietveld refinement; Method 2 represents Rietveld refinement with energy; Method 3 represents geometry optimization, respectively)

| | BZNT0 | BZNT0.5 | BZNT1 | BZNT1.5 |
|---|---|---|---|---|
| Method 1 | 0.32210 | 0.34352 | 0.33854 | 0.34830 |
| Method 2 | 0.32113 | 0.32118 | 0.32428 | 0.32429 |
| Method 3 | 0.40046 | 0.41898 | 0.41907 | 0.29468 |

Table 4
The $R_{wp}$ of refine results by using different methods

| | BZNT0 | BZNT0.5 | BZNT1 | BZNT1.5 |
|---|---|---|---|---|
| Method 1 | 10.44 | 7.72 | 8.57 | 8.46 |
| Method 2 | 10.62 | 8.26 | 8.67 | 8.55 |

Further analysis shows Rietveld refinement will be likely applied to chemically unviable structures only occasionally. In some system with large number of degrees of freedom, the information content of the powder pattern is too low to determine accurately all the degrees of freedom. In addition, the other reason is that the refine model using Rietveld refinement was unsteady state in some instances, for the minimum of the potential energy was not considered. Then Rietveld refinement with energy can balance the minimum of energy and matching between the simulated patterns with experimental diffraction data.

Comparing reflectivity simulation results based on geometry optimization and experiment data (see Fig. 3a and d), geometry optimization has almost no positive effect on modifying the BZNT pyrochlore. This viewpoint conflicts the common opinion about geometry optimization based on quantum mechanical. In order to eliminate effect of the different approximate function for optimization, several functions were applied to optimize BZNT0, including GGA (RPBE), GGA (PW91), GGA (PBE) and LDA (CA-PZ) function. The different functions we used have some diversities for optimization [13–15]. However, the optimization results from the different functions for the *x*-value of O atom position of BZNT0 are similar (0.39974–0.40101). The same trends are also observed for the other BZNT pyrochlores. Thus, the influence of different approximate functions on the optimization results can be excluded.

The energy change of geometry optimization shows that energy decreases with increment of *x*-value, except for BZNT1.5. For example in BZNT0 pyrochlore, the band length of B–O is from 2.002 to 2.443 Å gradually. Moreover, the length of O–O becomes closer simultaneously from 2.924 to 2.666 Å. Then system energy reaches the minimal value and the system is steady state. In the BZNT1.5, band length of B–O decreases gradually due to the smaller radius of Ta than Nb atoms. The stress is relieved by the optimization process. However, in the actual ceramics, the stress cannot be eliminated absolutely. Thus, the geometry optimization result is preferably applied to single crystal instead of ceramic.

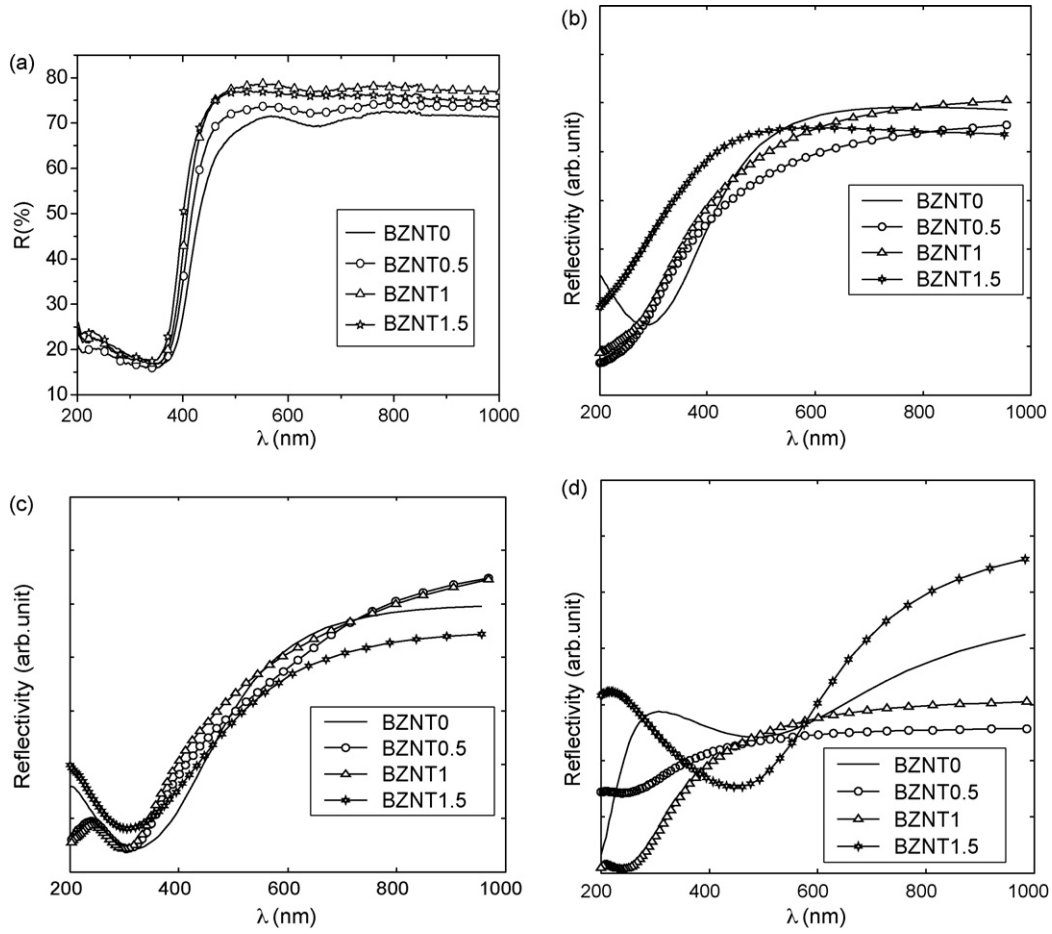


Fig. 3. Reflectivity results of BZNT by experiment and simulation based on different modify methods (a) experiment; (b) Rietveld refinement; (c) Rietveld refinement with energy; (d) geometry optimization.

## 4. Conclusions

The Rietveld refinement, Rietveld refinement with energy and geometry optimization are employed to materials system in different principles. In BZNT pyrochlore, Rietveld refinement with energy is the more accurate modification method than the rest. When we use this method, it is very important to balance the relationship between the simulated pattern with experimental results and minimum of the potential energy of the structure. Moreover, we can obtain that different reflectivities for BZNT are due to differences of *x*-value of O atom positions.

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