Study of the energy band structure of xBa (Sc1/2Nb1/2)O3-(1-x)(K1/2Na1/2)NbO3 perovskite solid solution

Hongjun Ye¹, Zhuo Xing¹

¹Xijing University, Xi'an, 710123, China

Abstract. As an important branch of the research on smart materials, the piezoelectric and ferroelectric materials play an important role in the devices with functions of sensing and energy conversion of electricity, magnetism, sound, light, force, and heat, etc., and provide a strong hardware support for the development of artificial intelligence and data science. This paper studied the properties of the potassium sodium niobate (K1/2Na1/2) NbO3-based doped solid solution, calculated the xBa(Sc1/2Nb1/2)O3-(1-x)(K1/2Na1/2)NbO3 solid solution by using the First-Principles software based on quantum mechanics, and by changing the value of x, studied the energy band structure of several doping amounts. In the end, it found that Nb4d and Sc3d electrons contributed to the valence band maximum, and had a hybrid phenomenon with O2p between the energy band -7eV to and -2eV. Also, due to the doping of the Atom B, the energy band gap changed regularly.

1. Introduction
The (K1/2Na1/2) NbO3 (KNN) is currently a major research direction of lead-free piezoelectric ceramics in the world, though its piezoelectric and ferroelectric properties are still not comparable to that of lead titanate PbTiO3 (PT). To improve and enhance the performance of KNN, the method usually adopted is the solid solution technique. Because Barium scandium niobate (Sc1/2Nb1/2) O3 (BSN) has a similar structure with KNN, i.e. the perovskite structure, it is often used to form a solid solution with KNN. In addition, the simple structure of perovskite is very convenient for theoretical research, making its solid structure naturally a hot spot in theoretical research and calculation. Through the First-Principles calculations, this paper studied the xBSN-(1-x)KNN perovskite structure solid solution aiming for different doping amount values of x. It formed the energy band diagram and calculated the state densities when x=0, 0.1, 0.125, 0.2, 1, then compared and analyzed the five cases. After that, it found that the band gap had fluctuated with the doping amount x, with the largest value when x=0.125.

2. Calculation method
In this paper, the calculation was based on the Density Functional Theory (DFT), and the software adopted was the CASTEP module of Material Studio. The PBE [3] exchange potential based on the Generalized Gradient Approximation (GGA) [1-2] was also used in the calculation. The ultrasoft pseudopotentials [4] was adopted for the atomic structure. The Monkhorst-Pack sampling method [5]
was adopted for all the wave vector grid divisions of the first Brillouin zone. For all the calculated energy cutoff, the fine quality was selected for the grid quality parameters. All these settings not only met the accuracy requirements, but also made the calculation results comparable with those of other calculations.

3. Results and discussion

3.1. Optimization of primitive cell
The calculations in this paper were based on the doping with cubic phase KNbO3 as the matrix, and in all subsequent calculations, supercells were established on the basis of the matrix. Therefore, the unit cell of cubic phase KNbO3 must be optimized first, to minimize the energy of the unit cell and keep it in the most stable state. In the results of optimization, the lattice constant a was 3.95Å.

3.2. Establishment of supercell and solid solution
The doping amounts (values of x) in this paper were 0, 0.1, 0.125, 0.2, and 1 in five cases, respectively. The corresponding number of atoms, the corresponding molecular formula, and the establishment of supercells are shown in Table 1.

| x     | Ba | Na | K | Sc | Nb | Supercell            | Molecular Formula            |
|-------|----|----|---|----|----|-----------------------|------------------------------|
| 0     | 0  | 1  | 1 | 0  | 2  | 1×1×1(1)              | KNN---                     |
| 0.1   | 2  | 9  | 9 | 1  | 19 | 1×4×5 (20)            | 0.1BSN-0.9KNN             |
| 0.125 | 2  | 7  | 7 | 1  | 15 | 2×2×4 (16)            | 0.125BSN-0.875KNN         |
| 0.2   | 2  | 4  | 4 | 1  | 9  | 1×2×5 (10)            | 0.2BSN-0.8KNN             |
| 1     | 2  | 0  | 0 | 1  | 1  | 1×1×1 (1)             | BSN---Ba(Sc1/2Nb1/2)O3    |

The superlattice established in this paper is shown in Figure 1. Different elements are identified on the atoms, and also, different colors are used to distinguish different elements. The red color stands for O atoms, white color stands for Sc atoms, light blue stands for Nb atoms, green color stands for Ba atoms, purple color stands for K atoms, and dark blue stands for Na atoms.
3.3. Energy band and state density
The Energy Band Diagram, State Density Diagram, Fractal State Density Diagram and Atomic State Density Diagram of various doping amounts are similar. Taking $x=0.2$ as an example, the laws of energy band and state density with various doping amounts are illustrated below.

**Figure 1.** Diagram of Supercell.

**Figure 2.** Energy Band Diagram a and State Density Diagram b when $x=0.2$. 
Figure 3. Partial State Density Diagram c and Atomic State Density Diagram d when x=0.2.

From the Energy Band Diagram a, the energy band type of $x\text{Ba}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3-(1-x)(\text{K}_{1/2}\text{Na}_{1/2})\text{NbO}_3$ is a direct band gap. Combined with the Partial State Density Diagram c, the Electron s occupies positions with low energy levels. It is severely bound by the nucleus and locates in the inner layer. The results at an around Fermi level are provided by Electrons p and d. Similar to the Energy Band Diagrams of all ABO3 (Atom A can be Ba, Pb, K and Na atom, Atom B can be Ti and Nb atom) perovskite structures [6-7], the valence band maximum of $x\text{Ba}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3-(1-x)(\text{K}_{1/2}\text{Na}_{1/2})\text{NbO}_3$ is provided by the 2p of the O atom. However, from Diagram d, Nb4d and Sc3d also contribute to the valence band maximum, and have a hybrid phenomenon between the energy band -7eV to and -2eV. The conduction band bottom is mainly provided by Nb and Sc. The electrons of K and Na are mainly located in the positions with low energy level, which are far away from the Fermi level, and have little effect on the electrical performance of the system. The K electrons are less bound by the nucleus, therefore, they are located in the positions with higher energy levels and closer to the Fermi level. In addition, in the Atomic State Density Diagram (d), two Ba atoms at different positions are calculated. It's found that the state densities of the two Ba atoms are exactly the same, which may reflect that the covalent interaction between Ba and other atoms is small, as well as its ionicity.

3.4. Band gap

From the calculations, it's found that the band gap of the solid solution can be effectively regulated by the doping amount, as shown in Table 2. As the doping amount increases, the band gap of the solid solution first increases and then decreases. When the doping amount is 0.125, the band gap reaches the maximum value of 1.970 eV. It should also be noted that, due to the defects of the Density Functional Theory itself [8], the calculated band gap will be smaller than the actual value, causing that the band gap of BSN (Ba(Sc1/2Nb1/2)O3) is 0. However, the underestimated band gap value will not affect the overall trend of the band gap value changing with the doping amount.
Table 2. Band Gap.

| x     | xBa\(\frac{\text{Sc}}{2}\)N\(\frac{\text{b}}{2}\)O\(_3\) \(-x\)\(\frac{\text{K}}{2}\)N\(\frac{\text{a}}{2}\)\(\text{NbO}_3\) | Band gap(eV) |
|--------|--------------------------------------------------|--------------|
| 0      | KNN---(K1/2Na1/2)NbO3                            | 1.603        |
| 0.1    | 0.1BSN-0.9KNN                                    | 1.647        |
| 0.125  | 0.125BSN-0.875KNN                                | 1.970        |
| 0.2    | 0.2BSN-0.8KNN                                    | 0.898        |
| 1      | BSN---Ba(Sc1/2Nb1/2)O3                            | 0            |

4. Conclusions
This paper calculated the energy band and state density of xBa(Sc1/2Nb1/2)O3-(1-x)(K1/2Na1/2)NbO3 solid solution with different doping amounts x by the First-Principles, and by comparison, found that they shared common laws, that is, the valence band maximum was mainly provided by the 2p electrons of the O atom, and the conduction band bottom was mainly provided by Nb and Sc atoms of Atom B. This law is consistent with the energy band law of the perovskite ABO3 structure. However, some new characteristics also emerge due to the doping of other elements. Nb4d and Sc3d also contribute to the valence band maximum, and have a doping phenomenon with O2p between the energy band -7eV to and -2eV. This may be the reason for the regular fluctuations of the band gap. The band gap increases at first, reaches the maximum value of 1.970 when x=0.125, and then gradually decreases.

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