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First-principles calculation of influences of La-doping on electronic structures of KNN lead-free ceramics*

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The electronic structures of lead-free piezoceramic $(K_{0.5}Na_{0.5})NbO_3$ (KNN) and La-doped KNN ($(K_{0.5}Na_{0.5})_{0.994}La_{0.006}NbO_3$) are studied by using first principles calculation on the basis of density functional theory (DFT). The results reveale that the piezoelectricity stems from strong hybridization between the Nb atom and the O atom. At the same time, the K or Na atoms are replaced by the La doping atoms, which brings about the anisotropic relaxation. The La doping reduces the forbidden band, at the same time it makes Fermi surfaces shift toward the energetic conduction band (CB) of KNN. With the increase of La-doping intent, the phase structure of KNN extends from O-phase to T-phase and improves the piezoelectric properties of KNN.

Keywords: $(K_{0.5}Na_{0.5})NbO_3$ (KNN), piezoelectricity, first-principles calculation, electronic structure

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1. Introduction

Piezoelectric material is one of the important functional materials, which can realize the mutual conversion between mechanical energy and electrical energy, and has been widely used in modern industry and defense field. The macroscaled bulk piezoelectric materials can be used in underwater acoustic transducer, medical B-ultrasonic probe, ultrasonic motor, oil logging detector, non-destructive testing, and acceleration sensor, and so on.[1–5] At present, the further development of new bulk piezoelectric material system is one of the key research directions in the field of piezoelectric materials.[6]

For a long time, lead-based material, represented by lead zirconate titanate (PZT), has attracted more and more attention because of its outstanding piezoelectric, electromechanical and dielectric properties. Based on this kind of piezoelectric material, the sensors, transducers, and other devices have been used in engineering. However, there are still many dangerous factors from the main ingredient in PZT. Due to the toxicity of lead, the preparation, use and disposal of lead-based piezoelectric materials will be harmful to human body and the environment. To adapt sustainable development strategies, there is a need to end the use of plumbum and synthesize lead-free piezoelectric ceramics systems which can be applied to green technology and be environmentally friendly. In view of the harmfulness of lead-based piezoelectric material, it is a crucial and urgent task to develop new lead-free piezoelectric ceramic materials. According to previous research, numerous lead-free ceramic systems can be produced, such as $BaTiO_3$, $(K,Na)NbO_3$ (KNN), and $(Bi,Na)TiO_3$ based ceramics.[7–9] But in recent years, the new potassium sodium niobate based bulk piezoelectric materials are considered to be the most promising lead-free piezoelectric material system due to their excellent electric performances, high Curie temperature.[10–13] Actually, one thinks that the polymorphic phase boundary (PPB) is a critical component of KNN-based piezoelectric material. With the composition near PPB of KNN-based ceramics, we can obtain outstanding piezoelectric properties.

According to some previous researches, donor doping in the KNN may induce the PPB's production and could improve the piezoelectric property of KNN-based ceramics. For instance, the piezoelectric coefficient d_{33} of the ceramics can be enhanced obviously from 220 $pC{\cdot}N^{-1}$ to 274 $pC{\cdot}N^{-1}$–710 $pC{\cdot}N^{-1}$ after being doped with the donor ions Bi^{3+}, La^{3+}, and Nb^{5+}. The La_2O_3, CeO_2, and other lanthanide oxides have acted as donor dopants or additives in the BNT-based and $BaTiO_3$-based unleaded piezoceramics, and have achieved good effects.[14,15]

But these achievements usually focus on experiments, but not on theoretical studies. Traditional experiments show that the piezoelectric property of KNN can be improved mostly through doping. This supports us to ascertain the doping

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mechanisms and influences on piezoelectric property from an atomic perspective.

First-principles calculations based on density functional theory (DFT) have gradually shown their importance in the study of the physical mechanism of materials in recent years. This method does not need relying on any empirical parameters. By purely solving the material's intrinsic quantum mechanical equations, one can obtain the atomic, electronic structure and related physical properties of the material, and thus presenting a method of studying the relationship between the microstructure and macroscopic properties of materials. This method does not need to worry about the influence caused by the characterization test and data processing in the experiment. It can intuitively and effectively observe the local atomic structure, electronic structure, and system energy of the material, and give a corresponding physical explanation for the change of the performance of material. For example, by comparing and calculating the electronic structures of $PbTiO_3$ and $BaTiO_3$, the researchers found that the ferroelectricity of these two materials originates from the hybridization of the 3d orbital of Ti and the 2p orbital of O, and the difference in ferroelectric behavior between the two is due to the strong hybridization between 6s and O 2p in Pb, but Ba shows almost complete ionicity in $BaTiO_3$.

Tan *et al.*[16] directly compared the piezoelectric properties of single crystals of $KNbO_3$ (KN) and $K_{0.5}Na_{0.5}NbO_3$ (KNN) with ceramics through the first-principles method and orientation averaging method, and found that the KNN ceramics has obviously higher piezoelectric performance than KN, comparing with KN, d_{33} is increased by about 70%, which is consistent with experimental observations, while the d_{33} mainly comes from the contributions of d_{15} and d_{33} in the single crystal. Further research found that the Born effective charges of the two are not much different from each other, but the large ion displacement caused by the smaller radius of Na can enhance ferroelectricity; at the same time, Na also causes the ion displacement of itself and adjacent O with strain response to be increased significantly, this is what causes higher piezoelectricity in KNN. Peng *et al.*[17] used the first-principles calculation method to calculate the elasticity and piezoelectric coefficients of orthogonal phase KNN at different Na concentrations, and reasonably estimated the piezoelectric coefficients of ceramics by using the orientation average method. It was found that when the Na content was 0.5625, the highest piezoelectric performance, the d_{33} of the ceramic can reach 88.6 pC/N. The study found that the orientation dependence of piezoelectric properties of single crystals is extremely sensitive to the change in the concentration of Na, and high shear piezoelectric moduli d_{15} and d_{24} have a strong relationship with the piezoelectric properties of enhanced polycrystalline KNN ceramics. Li *et al.*[18] used DFT combined with VCA method to study the piezoelectric coefficient of $K_{1-x}Na_xNbO_3$ system in detail, and predicted the components of morphotropic phase boundary (MPB). At the same time, the structural parameters, bulk modulus, and forbidden band width of the system were calculated, and it was pointed out that when $x = 0.5$, its polarization direction of intensity turned from [011] to [001] to have lower energy barriers than that the pure $KNbO_3$ has, and this results in the enhanced piezoelectric characteristics.

What is studied in this paper is the electronic structure of $(K_{0.5}Na_{0.5})NbO_3$ and La-doped $(K_{0.5}Na_{0.5})NbO_3$ lead-free piezoceramics through first principles calculations on the basis of DFT.

It is found that the main contribution to enhanced piezoelectricity of La-doped KNN is the hybridization of O 2p and Nb 4d orbitals. The relative mechanism is also discussed.

We believe that this research can provide the necessary theoretical basis for its practical application.

2. Methods and parameters

In this study, the density functional theory (DFT) calculation was conducted with the Vienna *ab-initio* simulation package.[19] The electron–ion interaction was described by projector augmented-wave (PAW) pseudopotential. In the exchange and correlation functional, the Perdew–Burke–Ernzerhof (PBE) version of the generalized gradient approximation (GGA) exchance–correlation was applied.[20,21] In the DFT calculation, the kinetic energy cutoff of 520 eV was used for the wave functions expansion. Brillouin zone integration was conducted on the grid with $2 \times 2 \times 2$ for geometry optimization and $4 \times 4 \times 4$ k-grid mesh for calculation of density of states. To calculate the electronic structure of $K_{0.5}Na_{0.5}NbO_3$, we used the unit cell lattice that has $a = b = 3.996$ and $c = 4.063$ in the tetragonal phase to build a supercell in the [001] direction for $K_{0.5}Na_{0.5}NbO_3$ as shown in Fig. 1(a). La atom replaces a Na atom or a K atom thatwas chosen randomly as shown in Fig. 1(b). The energy and force converged respectively to 1.0×10^{-5} eV·atom^{-1} and 0.02 eV·Å^{-1} to achieve high accuracy.

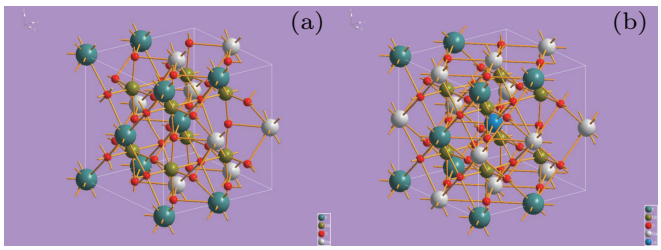


Fig. 1. Structure diagram of (a) pure and (b) La-doped KNN.

3. Results and discussion

3.1. Electric field gradient

The perturbed angular correlation (PAC) is the basis of hyperfine interaction (HFI). The PAC supplies an uncommon method to investigate the piezoelectric material's electric performances by the electric field gradient (EFG) extracted from the measuring HFI. Tables 1 and 2 list the properties of structural relaxation and EFG which are brought in at the La atomic site.

Table 1. Comparison of coordination between La-doped KNN and undoped KNN.

	d(K/Na–O)	d(Nb–O1) [001]	d(Nb–O2) [110]
KNN	2.88	1.85	2.01
La-doped KNN	2.94	1.99	2.01

For the diverse atom sites, the bond distances are obtained at the force of no more than 0.01 eV·Å^{-1}. As can be seen from Table 1, compared with the bond distance of Na(K)–O in pure KNN, the bond distance of La-doped KNN is large, which shows that compared with the valence bond distance of the pure system, the bond distance of the La-doped system is short. In the undoped system and La-doped system, the relaxations of Nb–O octahedra are both anisotropic. For the undoped system, Nb–O1 bond distance in the orientation of [001] is longer than Nb–O2 bond distance. This shows that the Nb–O octahedron extends in an orientation of [001]. But for the La-doped system, the Nb–O1 bond distance in the orientation of [001] is shorter than Nb–O2 bond distance. This shows that the Nb–O octahedron condenses in an orientation of [001]. Moreover, the variations in the bond distance (0.09 Å) between the two orientations in La-doping system are greater than those in undoped system (0.04 Å), which suggests that the replacement of La causes the KNN structure to be more crooked. And it means that the La replacement may be the crucial element in reducing the phase transition temperature, thus improving the piezo-electric property.

Table 2. EFG of $(K_{0.5}Na_{0.5})NbO_3$ and La-doped $(K_{0.5}Na_{0.5})NbO_3$.

	KNN			La-doped KNN		
	K (Na)	Nb	O	K (Na)	Nb	O
V_{xx}	−0.007	−1.700	−0.469	−0.07	−1.186	−0.469
V_{yy}	−0.007	−1.700	−0.469	−0.07	−1.186	−0.469
V_{zz}	+0.014	+3.400	+0.938	+0.14	+2.371	+0.938
η	0	0	0	0	0	0

The main part of EFG tensor is in the orientation of [001] which has an asymmetric parameter of $\eta = 0$. As can be seen from Table 2, the obtained EFG value on K or Na site in $(K_{0.5}Na_{0.5})NbO_3$ are as follows: $V_{xx} = 0.007$, $V_{yy} = 0.007$, and $V_{zz} = 0.014$. For the La-doped $(K_{0.5}Na_{0.5})NbO_3$, the EFG values are $V_{xx} = 0.07$, $V_{yy} = 0.07$, and $V_{zz} = 0.14$. The discrepancies in these values show that La atoms doped in $(K_{0.5}Na_{0.5})NbO_3$ ceramics change the distributing of charge and promote the bond energy. From the above outcomes we can infer that the addition of La^{3+} shortens the bond distance of Nb–O1. At the same time, it exacerbates the Nb–O octahedron's distortion in an orientation of [001]. The increase of distortion is a key factor of improving the piezoelectric performances. Moreover, the EFG tensor's main part is in an orientation of [001] which has a nonsymmetrical parameter of $\eta = 0$.

3.2. Band structure

For calculating the band structure, we employ a k-point route along the F–g–B–G–g points of the symmetry. Figure 2 reveals the calculating band structure of KNN, showing that the band structure is compact and level, which is because of the credit of atoms and several hundred electrons in super cell. At the same time, band structures are generally level and compact far below Fermi energy. The energy bands of solid solution in Fig. 2 are of direct-gap. The top of valence band (VB) and the bottom of conduction band (CB) are at G-point. In accordance with the results of Adachi's experiment,[22] there exists a direct energy gap in pure KNN (the experimental value is 3.11 eV). It can be seen that our calculation results are more logical than the experimental results. In addition, we calculate the energy gap which is narrower than the experimental value. In the results calculated from first principles there arises a narrow energy gap problem, which is because the incontinuity of exchange-interrelation potential is not taken into consideration in the frame of DFT. At the same time, we underestimate the interrelation among excited electrons in the multi-particle system. This does not influence our succedent analysis.

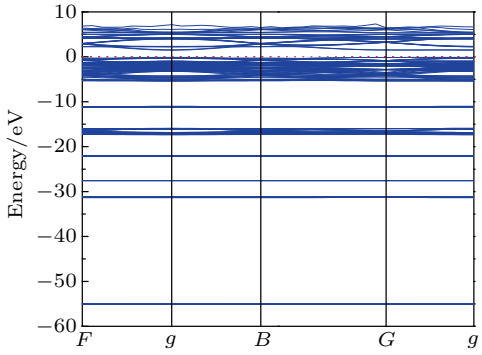


Fig. 2. Calculated band structure for $K_{0.5}Na_{0.5}NbO_3$.

Figure 3 shows that K and Na atoms are severally replaced by La atoms. Through the comparison of this with the band structure of undoped KNN in Fig. 2, we can see that Fermi energy shifts towards CB. At the same time this causes Fermi surface to enter into the CB. The lower levels of doped KNN are nearly −19 eV, CB is approximately in a range from −0.34 eV to 4.50 eV, at the same time the energy gap is 1.563 eV. The lower levels of undoped KNN system are nearly −15 eV, and CB is nearly in a range of 2.28 eV–7.55 eV.

The results show that the incorporation of La atoms makes the lower levels and CB shift towards the low-level direction, and thus reducing the energy gap. Compared with the radius of K^{+1} and Na^{+1}, the radius of La^{3+} is large, so the additional electrons are brought in. The electrons of the 6s-layer of La atom are simply excited to 3d orbit. Comparing with the K atom's 4s-layer and Na atom's 3s-layer, La atoms have one more electron, and after being doped with La atoms, they are easy to lose the electrons to turn into donor atoms. So when Fermi surface shifts to CB, the band structure shifts toward the low-level orientation. In addition, the descent velocity at VB's roof is slower than that at CB's base, so energy gap shows restored state.

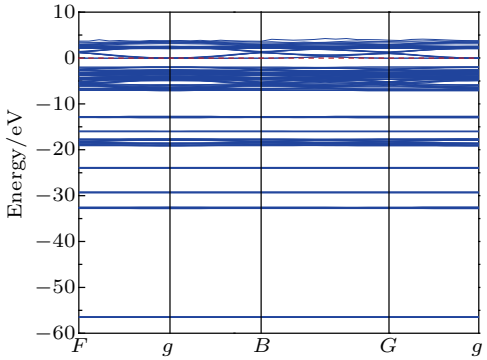


Fig. 3. Calculated band structure for $(K_{0.5}Na_{0.5})_{0.94}Li_{0.06}NbO_3$.

3.3. Density of states

Figure 4 shows the total density of states (DOS)for KNN and fractional DOS for every atom of KNN. Figure 4 shows that the electronic states under the Fermi energy mostly focus on three energy area: −5 eV to 0 eV, 0 eV to −10 eV, and 0 eV to −15 eV. The VB in −5 eV–0 eV is mostly composed of O 2p electrons, Nb 4d electrons, and a few p electrons of K/Na.This demonstrates that between the O atom and Nb atom, this area is mostly composed of a strong p–d covalent coaction. The VB of −15 eV is mostly O-2s electrons, K-3p electrons, and Nb-s, p, d electrons, which demonstrates that this area is mostly comprised of s–p orbital hybrid between O and K. Moreover, comparing with Na atoms at A-site, near −10 eV there are mostly K-2p electrons; so we can conclude that compared with the orbital hybrid in Na and O, the orbital hybrid in K and O is large.

According to Figs. 5(a) and 5(b), La atom substitutes for K and Na atoms, separately. In conclusion, VB around Fermi surface after doping is mostly composed of O-2p, Nb-4d, and a few p and d electrons of K atom and La atom. The CB mostly consists of Nb-4d, La-4d, and a few s electrons of K atom and Na atom. Comparing with pure DOS (Fig. 4), the contribution of K and Na atoms decrease as La atom substitute for K atom and Na atom separately, and La-doping is conductive to the CB. This causes Fermi surface to shift toward high-energy CB, and reflects the influence of doping on piezo-electric performance of KNN ceramics.

3.4. Formation energy of doping element

The formation energy is the energy that is required when doping atoms substitute for replaced atom. When the formation energy is weaker, the doping atom enters into lattice location more easily. We calculate formation energy of La atom when it replaces K and Na atoms in KNN separately.

Here is the formula for doping formation energy, the formation energy ($\Delta E_{\text{formation}}$) is defined as follows:

$$\Delta E_{\text{formation}} = E_{\text{bulk+La}} - E_{\text{bulk}} - E_{\text{substituted atom}} + E_{\text{La}},$$

where $E_{\text{bulk+La}}$ is the total energy of the bulk doped La atom, E_{bulk} is the total energy of KNN, $E_{\text{substituted atom}}$ and E_{La} are the total energy of the substituted atom and La atom, respectively.

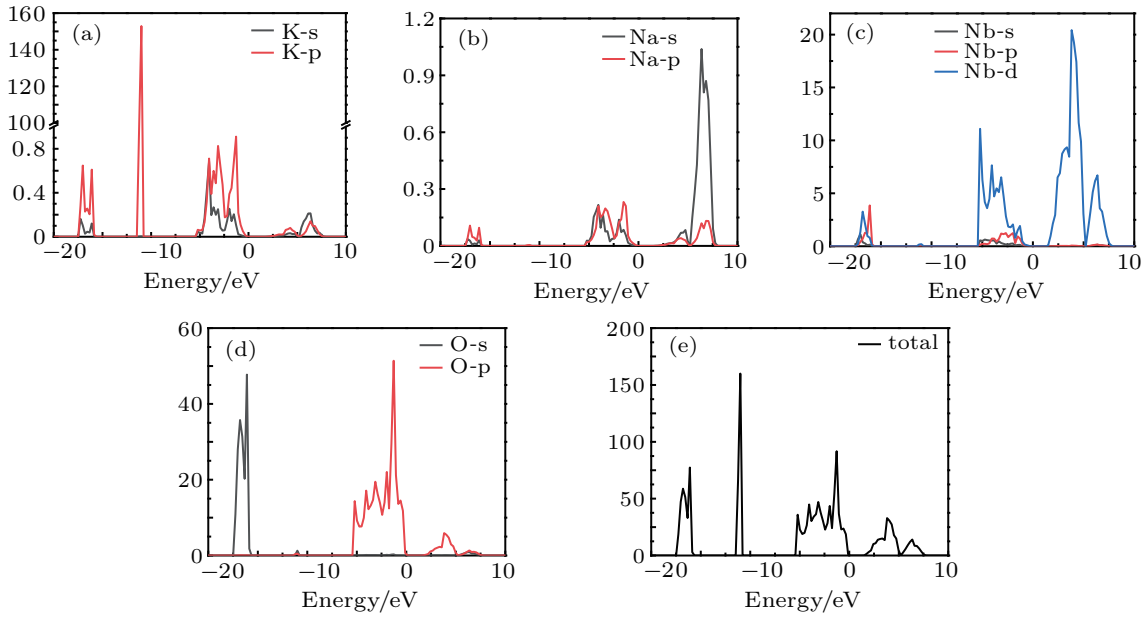


Fig. 4. Total and partial DOSs of KNN.

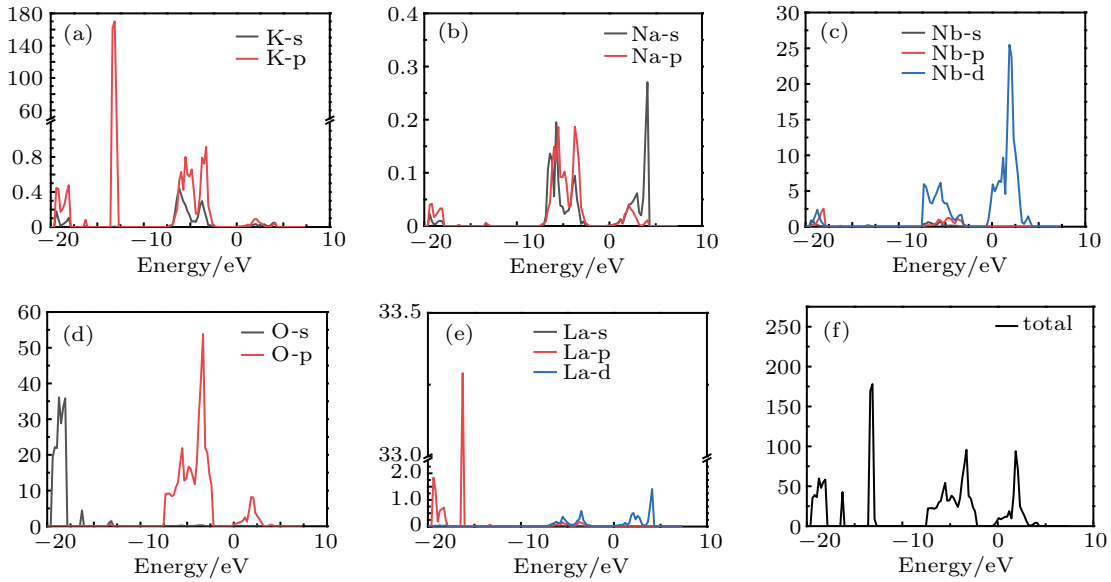


Fig. 5. Total and partial DOSs of La-doped KNN.

The formation energy of the substituted atom La is shown in Table 3. Negative formation energy indicates that the material is stable, and the lower the formation energy, the more stable the material is. The calculation results of formation energy show that the system is still stable after being doped with La atoms.

Table 3. Calculated formation energy (in unit eV).

$E_{(\mathrm{KNN-La})}$	$E_{(\mathrm{KNN})}$	$E_{(\mathrm{La})}$	Formation energy/eV
−318.54	−311.39	−4.29	−2.88

4. Conclusions

We investigated the electronic structures of the lead-free piezoceramics $(K_{0.5}Na_{0.5})NbO_3$ and the La modified $(K_{0.5}Na_{0.5})NbO_3$ by the first principles calculations. The calculations prove that the La-doping reduces the energy gap and makes Fermi surface to shift toward high-energy CB, and K and La atoms can substitute for Na atom more easily. La doping leads to anisotropic relaxation. This is the main reason for the lowering of the phase transition temperature from the orthorhombic to the tetragonal phase or the change of the lattice structure to the tetragonal phase. This can improve the piezoelectric property of KNN. At the same time, we calculate the EFG, band structure, total DOS, and fractional DOS. It can be confirmed that the main contribution to piezoelectricity is from the hybridization of O-2p and Nb-4d orbitals. This makes the Nb–O octahedron distorted. And it is a probable method to improve the piezoelectricity of KNN materials.

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