Vol 11 No 7, July 2002
1009-1963/2002/11(07)/0714-06

Chinese Physics

© 2002 Chin. Phys. Soc.
and IOP Publishing Ltd

First principles study on the ferroelectricity of the perovskite ABO_3 ferroelectrics*

Wang Yuan-Xu(王渊旭)†, Zhong Wei-Lie(钟维烈), Wang Chun-Lei(王春雷), Zhang Pei-Lin(张沛霖), and Su Xuan-Tao(苏绚涛)

Department of Physics, Shandong University, Jinan 250100, *China*

(Received 30 May 2001; revised manuscript received 8 March 2002)

In order to understand well the different ferroelectric behaviour of quantum paraelectrics and ferroelectrics and the origin of the ferroelectricity of the solid solution $KTa_{0.5}Nb_{0.5}O_3$(KTN), we calculated the electronic structure of $CaTiO_3$, $BaTiO_3$ and KTN by first principles calculation. From total energy analysis, it is shown that, with increasing cell volume, the crystals ($CaTiO_3$, $SrTiO_3$) will have a ferroelectric instability. For $BaTiO_3$, the ferroelectricity will disappear as the cell volume is decreased. From the density of states analysis, it is shown that the hybridization between B d and O p is very important for the ferroelectric stability of ABO_3 perovskite ferroelectrics. This is consistent with the analysis of band structure.

Keywords: ferroelectrics, electronic band structure, phase transition
PACC: 7115, 7780

1. Introduction

Perovskite ABO_3 materials have been extensively studied because of their technical importance and the fundamental interest in the physics of their phase transitions. $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$ are perovskites with the same B and A cations in the same column of the periodic table. $BaTiO_3$ is a classic ferroelectric with a Curie temperature 393K. The crystals $SrTiO_3$ [1] and $CaTiO_3$ [2] are incipient ferroelectrics or quantum paraelectrics. They show in their dielectric constant a Curie–Weiss-like behaviour on approaching low temperatures, but finally the dielectric constant saturates and does not exhibit a ferroelectric phase transition. The Curie–Weiss-like behaviour signifies an incipient ferroelectricity, the actual paraelectricity at low temperatures is stabilized by quantum fluctuations.[1] Most perovskite ferroelectrics that have been widely used are solid solutions (such as $PbZr_{1-x}Ti_xO_3$ (PZT)) and complex compounds (two or more kinds of atoms occupy the same crystallographic positions, such as $PbMg_{1/3}Nb_{2/3}O_3$). First principles calculations on these complicated systems are just beginning.

The origin of the different behaviour of $BaTiO_3$ on the one hand and $SrTiO_3$ and $CaTiO_3$ on the other hand has been the subject of some investigations. Wang *et al*[3] studied the electronic structure of $CaTiO_3$ by first principles calculation and concluded that it is an incipient ferroelectric. Bersuker *et al*[4] showed that the main contribution to the instability of the cubic configuration is due to the formation of new covalent bonds by distortion, and the additional covalence increases in the sequence of $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$. Zhong and Vanderbilt[5] calculated quantum fluctuation effects on cubic $SrTiO_3$ and $BaTiO_3$. They found that, for $SrTiO_3$, quantum fluctuations suppress the ferroelectric transition completely and, for $BaTiO_3$, quantum fluctuations reduce the transition temperature by 35–40K.

Solid solution $KTa_{1-x}Nb_xO_3$ (KTN) belongs to the class of random dipole ferroelectrics.[6] The substitute impurities (such as Nb) reside in off-centre positions and thus have a dipolar character. They are randomly distributed in a strongly polarizable host lattice ($KTaO_3$). The interaction between the impurity and host lattice results in ferroelectricity. This description is valid for low impurity (such as Nb) concentration range. Random field theory[7] and the transverse field Ising model[8] have been successfully used in this connection. For the range of high Nb concentration, very little theoretical study has yet been done. Sepliarsky *et al*[9] calculated the phase diagram of $KTa_{0.5}Nb_{0.5}O_3$ using an atomic-level simula-

*Project supported by the State Key Program for Basic Research of China (Grant No 1998061408).
†Corresponding author: wangyx@sdu.edu.cn

tion approach that they developed, based on the traditional Buckingham potential. Peng *et al*[10] determined the equilibrium configuration of B-site cations (Ta and Nb) in the tetragonal ferroelectric phase of $KTa_{0.56}Nb_{0.44}O_3$ by a total energy calculation in combination with a 'leverage law' approximation.

For ferroelectricity in perovskites, the hybridization between B d and O p states is essential,[11] and the realization of the hybridization may depend to some extent on the space available to the B cation. It is therefore expected that the different tendency to become ferroelectric in $BaTiO_3$, $SrTiO_3$ and $CaTiO_3$ may be connected to their cell volumes. In this paper, we calculate the electronic structure of these perovskites by the full potential linearized augmented plane wave (FLAPW) method. The total energy as a function of the displacement of the Ti cation, and the density of states (DOS) of Ti and O at different cell volumes are obtained. It is shown that in incipient ferroelectrics the tendency to become ferroelectric is checked by their smaller cell volumes. With increasing cell volume, $CaTiO_3$ and $SrTiO_3$ will become ferroelectric. If the cell volume is decreased, ferroelectricity in $BaTiO_3$ will disappear. The origin of ferroelectricity of the solid solution KTN is also studied.

2. Method

The calculations presented in this paper were performed within the generalized gradient approximation to the density functional theory, using the FLAPW method. In this method no shape approximation on either potential or the electronic charge density is made. We use WIEN97[12] implementation of the method, which allows the inclusion of local orbits in the basis, improving upon linearization and making possible a consistent treatment of semicore and valence states in one energy window, hence ensuring proper orthogonality. The generalized gradient approximation (GGA) has been used.[13] In the FLAPW method, the unit cell is divided into two parts: (1) non-overlapping atomic spheres (centred at the atomic sites) and (2) an interstitial region. The FLAPW method expands the potential in the following form

$$V(r) = \sum_{lm} V_{lm} Y_{lm}(\hat{r}), \quad \text{inside sphere} \qquad (1)$$

$$V(r) = \sum_{K} V_K \mathrm{e}^{\mathrm{i}Kr}, \quad \text{outside sphere} \qquad (2)$$

where $Y_{lm}(\hat{r})$ is a linear combination of radial functions times spherical harmonics.

In the cubic phase of $CaTiO_3$, the lattice parameters we used are a=0.38950nm.[14] The atomic coordinates are Ca(0.5, 0.5, 0.5), Ti(0, 0, 0), O(0, 0.5, 0) (0, 0, 0.5). The atomic sphere radii (Ri) 2.0, 2.2 and 1.1 are used for Ca, Ti and O, respectively, in the calculations. For the case of $BaTiO_3$, the lattice parameters we used are a=0.4000nm. The convergence parameter $RK_{\max}$ (R_{mt} $^*K_{\max}$, where $K_{\max}$ is the plane-wave cut-off and R_{mt} is the smallest of all atomic sphere radii), which controls the size of the basis sets in these calculations, is set to be 8.0. We have used $5 \times 5 \times 5$ meshes, which represent 200 k-points in the first Brillouin zone.

A supercell of K_2TaNbO_6 is constructed by superposing a $KTaO_3$ unit cell on a $KNbO_3$ one along the [001] direction. The neutron diffraction crystallographic data for tetragonal $KTa_{0.56}Nb_{0.44}O_3$ reported by Hewat *et al*[15] is used for the structural parameters in the calculation. Along the [001] direction, the displacement of Ta, Nb is Δ(Ta, Nb)=$-0.012c$. The lattice parameters we used are a=7.5728 a.u., b=7.5728 and c=15.1456 a.u. The atomic sphere radii (R_i) 2.0, 1.5, 1.8 and 1.6 a.u., are used for K, Ta, Nb and O, respectively. The atomic coordinates in the ferroelectric phase are K(0, 0, 0.01105)(0, 0, 0.51105), Ta(0.5, 0.5,0.75505), Nb(0.5, 0.5, 0.75505), O(1)(0.5, 0.5, 0)(0.5, 0.5, 0.5), O(2)(0.5,0, 0.1793) (0, 0.5, 0.1793)(0.5, 0, 0.6793)(0, 0.5, 0.6793). The convergence parameter $RK_{\max}$, and the meshes used are the same as above.

3. Results and discussion

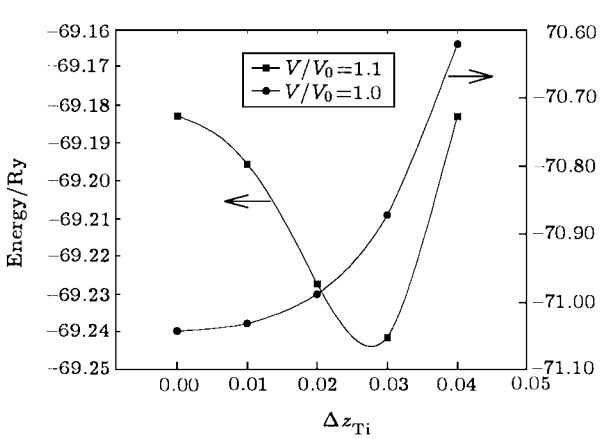


Fig.1. Total energy (E(Ry)+3520)×100 of cubic $CaTiO_3$ as a function of the displacement Δz of the Ti atom in the [001] direction for different volumes.

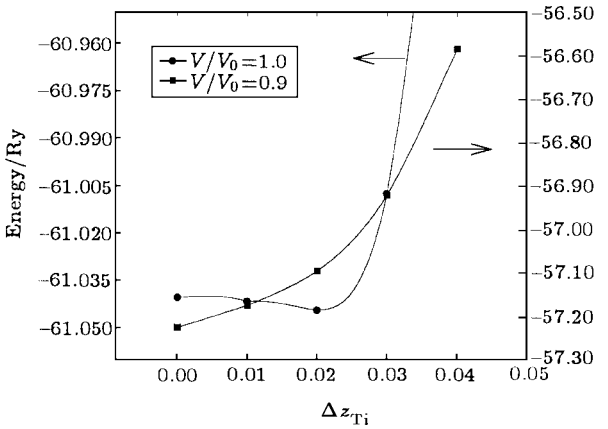


Fig.2. Total energy $(E(\mathrm{Ry})+3520)\times 100$ of cubic $BaTiO_3$ as a function of the displacement Δz of the Ti atom in the [001] direction for different volumes.

In order to understand the tendency of the $CaTiO_3$ cubic perovskite to suffer a ferroelectric transition, we have calculated the electronic properties of $CaTiO_3$ for different displacements of the Ti atom in the [001] direction. The incipient ferroelectricity of $CaTiO_3$ was studied using the FLAPW method in a previous paper.[3] Figure 1 shows the total energy as a function of the Ti atom displacement for different volumes. At the experiment, for equilibrium volume (V/V_0=1.0), $CaTiO_3$ is not energetically favoured with the proposed ferroelectric distortion. However, with a 10% volume expansion (V/V_0=1.1), the same displacement results in a shallow, but well-defined double well. This implies that there is a tendency to become ferroelectric in the cubic $CaTiO_3$ crystal. This is consistent with the experimental results[2] that point out that $CaTiO_3$ is an incipient ferroelectric. From our calculation, the ferroelectric state can be induced by a negative pressure. The tendency of $SrTiO_3$ to suffer a ferroelectric transition was studied by Fabricius *et al*[16] For a 5% volume expansion, $SrTiO_3$ shows an instability and would undergo a ferroelectric transition. For a 10% volume expansion, it has a shallow well. This means that $SrTiO_3$ is an incipient ferroelectric. $BaTiO_3$ is a typical ferroelectric. In order to understand the volume effect on $BaTiO_3$, we have calculated the electronic properties of $BaTiO_3$ for a different displacement of the Ti atom in the [001] direction for different volumes. Figure 2 shows the total energy as a function of the Ti atom displacement for different volumes. In the experiment, for equilibrium volume (a=7.5 a.u.), $BaTiO_3$ has a double well. For a 10% volume reduction (about a=7.3 a.u.), the tendency to ferroelectricity does not exist. In contrast to $CaTiO_3$ and $SrTiO_3$, the ferroelectric state of $BaTiO_3$ will disappear when subjected to a positive pressure.

From the total energy analysis, it can be seen that the volume effect of II–IV perovskites $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$ is very important for their ferroelectricity. The lattice constants of $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$ (for a 10% volume reduction), at which the ferroelectric transition no longer exists, are respectively a=7.36, 7.38 and 7.32 a.u. respectively. To have a ferroelectric transition, the lattice constants of $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$ are respectively 7.598, 7.618 and 7.551 a.u. Generally speaking, in II–IV perovskites, the lattice constant should be about 7.6 a.u. for a ferroelectric transition to occur. When the lattice constant is about 7.3 a.u., there is no ferroelectric transition. So we can conclude that different cell volumes will mainly result in different ferroelectric behaviours between quantum paraelectrics ($CaTiO_3$ and $SrTiO_3$) and ferroelectrics ($BaTiO_3$).

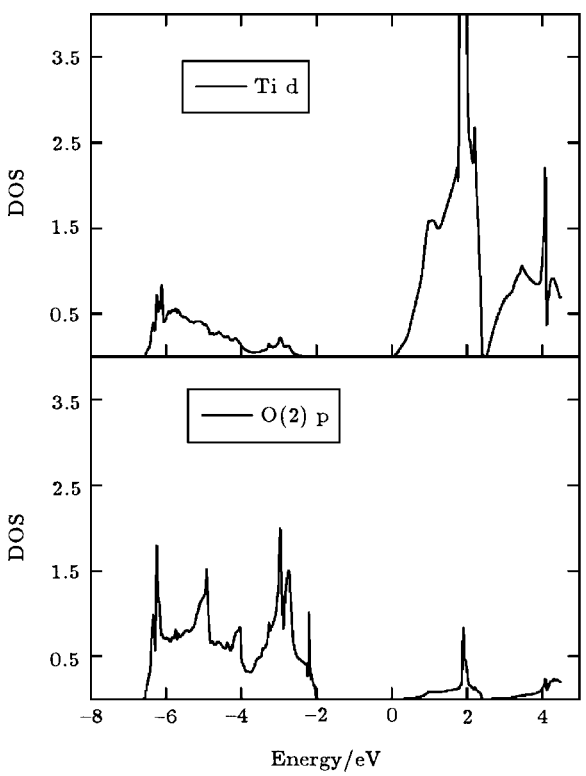


Fig.3. The DOS of Ti d and O(2) p in $CaTiO_3$ at Δz =0.03 Ti for V/V_0=1.0.

Figure 3 shows the density of states (DOS) of Ti d and that of O(2) p of $CaTiO_3$ at Δz=0.03 for V/V_0=1.0. Figure 4 shows the DOS of Ti d and that of O(2) p of the same crystal at Δz=0.03 for V/V_0=1.1. Comparing Figs.3 and 4, we can see that the DOS of Ti d and O(2) p in different volumes are similar, but

the DOS of Ti d and O(2) p for V/V_0=1.1 are much higher than that for V/V_0=1.0. It can be seen that, for V/V_0=1.0, Ti d and O(2) p do hybridize to some extent but the hybridization is not as important in the case of V/V_0=1.1. From the analysis of the DOS of Ti d and O p, we can conclude that, with a 10% volume expansion (V/V_0=1.1), $CaTiO_3$ has a tendency to become ferroelectric. This is consistent with the conclusion from the total energy analysis.

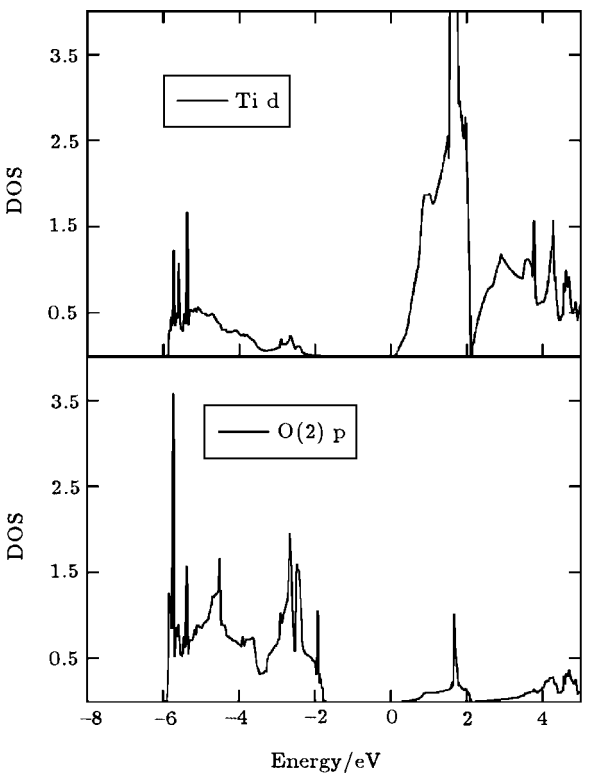


Fig.4. The DOS of Ti d and O(2) p in $CaTiO_3$ at Δz=0.03 Ti for V/V_0=1.1.

In order to reveal the roles the atoms Nb, Ta and O play in the ferroelectricity of KTN, we have calculated its DOS and the electronic band structure and valence charge density by first principles calculations. Figure 5 shows the DOS of Ta d, Nb d and O(1) p of ferroelectric KTN. In Fig.5, around −5.5eV, there is a sharp peak for both Ta d and Nb d. This indicates that the numbers of Ta d and Nb d electrons in the same energy range (around −5.5eV) increase greatly, and thus there is a strong hybridization between B (Ta and Nb) d and O p (particularly at −5.5eV) in the ferroelectric KTN. It is this hybridization that weakens the short-range repulsions and stabilizes the ferroelectric structure. In short, both atoms Ta and Nb play similarly important roles in the ferroelectricity of KTN.

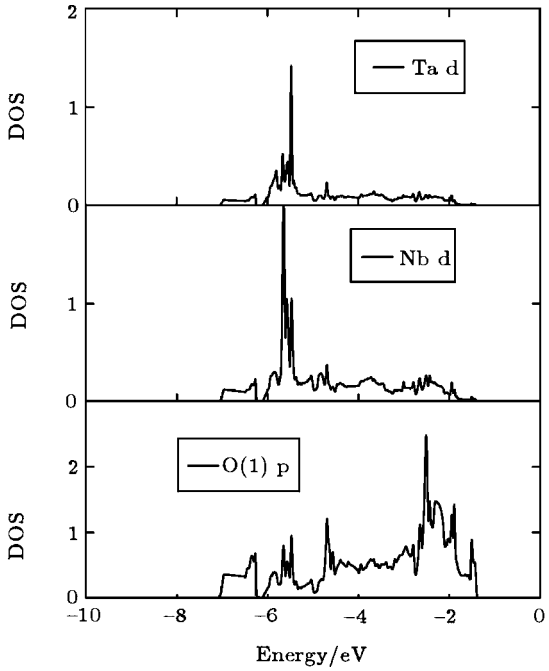


Fig.5. The DOS (Ta, Nb, O) of ferroelectric KTN.

Concerning the different behaviour of $KTaO_3$ and $KNbO_3$, Postnikov *et al*[17] studied their electronic structure and compared the three DOS of Ta, Nb and O. For the displacement of atom Nb, there is a DOS peak arising from the binding between O 2p and Nb 4d, which is absent in the DOS of $KTaO_3$. They pointed out that this is because the ionic Ta has a slightly larger size than Nb, the covalent part of the Ta–O bond is more saturated and practically no energy lowering results from the symmetry-breaking displacement of the Ta atom towards three of its neighbours in the O_6 cage.

Comparing our results of KTN with those of $KTaO_3$ in Ref.[17], the atom Ta behaves differently in these two crystals. The difference results mainly from the different crystal structures of $KTaO_3$ and ferroelectric KTN. As is well known, cell volume is a very important factor in the ferroelectricity of perovskite ferroelectrics. The lattice constant for pure $KTaO_3$ is a=7.53 a.u.[18] and that in KTN is 7.5728 a.u. Increased cell volumes give the atom Ta more free space in ferroelectric KTN. In other words, the covalent part of the Ta–O bond is less saturated than that in pure $KTaO_3$, and off-centre displacement of Ta in KTN is thus energetically favourable.

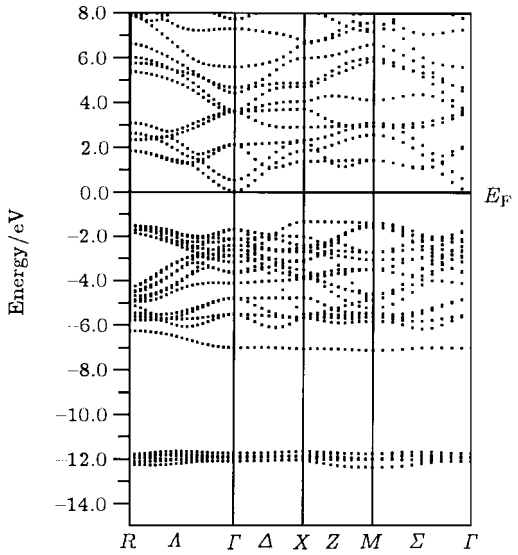


Fig.6. The electronic band structure of ferroelectric KTN.

Figure 6 shows the electronic band structure of ferroelectric $KTa_{0.5}Nb_{0.5}O_3$. In Fig.6, there are many valence bands in the range from -7eV to -2eV. Comparing Figs.5 and 6, we can conclude that they arise mainly from O p and partly from Ta d and Nb d because there is a sharp DOS peak of Ta d and Nb d around -5.5eV. These bands overlap each other and are dispersive. This implies that the hybridization between B d and O p in the ferroelectric phase is strong. Another characteristic is that the bandgap of ferroelectric KTN is indirect. The indirect bandgap of ferroelectric KTN is 1.2eV wide. The conduction bands (Ta d and Nb d) are very close to the valence band (O p). This also implies a stronger d–p hybridization in the ferroelectric KTN. From the examination of the electronic band structure of KTN, we can conclude that there is a strong hybridization between B d and O p in the ferroelectric KTN. This hybridization is very important for the ferroelectricity of $KTa_{0.5}Nb_{0.5}O_3$. This is consistent with the analysis of DOS. Singh[19] has shown the band structure of $KTaO_3$ and $KNbO_3$. The main difference between the band structures of $KNbO_3$ and $KTaO_3$ is a 0.6 eV large bandgap in the tantalates and a stronger dispersion of one of the bands between M and R points, which is about 1eV higher in $KNbO_3$ than in $KTaO_3$. The larger bandgap in $KTaO_3$ implies the absence of ferroelectricity in $KTaO_3$. In ferroelectric KTN, the bandgap is about 1.2eV, which is small, implying ferroelectricity in KTN.

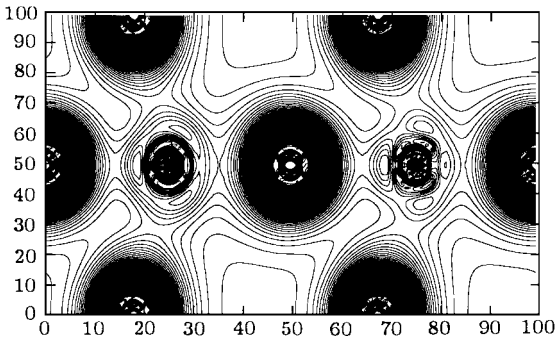


Fig.7. The valence charge density contour of ferroelectric KTN in the (100) plane.

Figure 7 shows the valence charge density contour of ferroelectric KTN in (100) plane. The atoms Ta and Nb are at points (75,50), (25,50), while the atom O(1) is at (50,50). In Fig.4, there is an obvious sharing of charge between atoms B (Nb and Ta) and O due to B d and O p hybridization. So we can see that the interaction between Ta and O, Nb and O is a very strong covalent interaction. The hybridization between B (Ta and Nb) d and O p is strong.

4. Conclusion

In summary, we have studied the nature of the different ferroelectric behaviours of quantum paraelectrics ($CaTiO_3$, $SrTiO_3$) and ferroelectrics ($BaTiO_3$) by a first principles calculation. We have calculated the total energy as a function of the displacement of the Ti cation, DOS of Ti d and O p, for different cell volumes. From the calculated total energy, it is shown that, in perovskites $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$, the ferroelectric phase transition exists when the lattice constant is about 7.6 a.u. and it will disappear if the lattice constant is reduced to about 7.3 a.u. In incipient ferroelectrics $SrTiO_3$ and $CaTiO_3$, the tendency to become ferroelectric is checked by their small cell volumes. For KTN, from the DOS analysis, it is shown that the hybridization between B (Ta, Nb) d and O p is very important for the ferroelectric stability of $KTa_{0.5}Nb_{0.5}O_3$. The behaviour of Ta is similar to Nb, but is different from its behaviour in pure $KTaO_3$. This is consistent with the result from the analysis of band structure. In short, for ferroelectricity in perovskites, the hybridization between B d and O p states is essential, and the realization of the hybridization may depend to some extent on their cell volumes.

References

[1] Müller K A and Burkard H 1979 *Phys. Rev.* B **19** 3593

[2] Lemanov V V, Sotnikov A V, Psminova E, Weihnacht M and Kunze R 1999 *Solid State Commun.* **110** 611

[3] Wang Y X, Zhong W L, Wang C L and Zhang P L 2001 *Solid State Commun.* **117** 461

[4] Bersuker I B, Gorinchoi N N and Fedorco T A 1994 *Ferroelectrics* **153** 1

[5] Zhong W and Vanderbilt D 1996 *Phys. Rev.* B **53** 5047

[6] Toulouse J 1994 *Ferroelectrics* **151** 215

[7] Vugmeister B E and Glinchuk M D 1990 *Rev. Mod. Phys.* **62** 993

[8] Wang Y G, Kleemann W, Zhong W L and Zhang L 1998 *Phys. Rev.* **57** 13343

[9] Sepliarsky M, Phillpot S R, Wolf D, Stachiotti M G and Migoni R L 2000 *Appl. Phys. Lett.* **76** 3986

[10] Peng Y P, Wang Y X, Zhang L, Wang C L, Zhang P L and Zhong W L 2000 *Phys. Lett.* A **269** 170

[11] Cohen R E 1992 *Nature* **358** 136

[12] Blaha P, Schwarz K and Luitz J, WIEN97 Vienna University of Technology 1997 (improved and updated Unix version of the original copyrighted WIEN-code, which was published by Blaha P, Schwarz K, Sorantin P, and Trickey S B 1990 *Comput. Phys. Commun.* 399)

[13] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Perdoson M R, Singh D J and Fiolhais C 1992 *Phys. Rev.* B **46** 6671

[14] Kendey B J, Howard C J and Choakoumakos B C 1999 *J. Phys.: Condens. Matter* **11** 1479

[15] Hewat A W, Rouse K D and Zaccai G 1972 *Ferroelectrics* **4** 153

[16] Fabricius G, Peltzer E L, Balcana Y, Rodriguez C O, Ayala A P, Presa P and Garcia A Lopez 1997 *Phys. Rev.* B **55** 164

[17] Postnikov A V, Neumann T, Borstel G and Methfessel M 1993 *Phys. Rev.* B **48** 5910

[18] Andrews S R 1985 *J. Phys: Condens. Matter* **18** 1357

[19] Singh D J 1996 *Phys. Rev.* B **53** 176