A first-principle study on the electronic properties of substitutionally Cu (I, II)-doped LiNbO₃

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The electronic properties of Cu-doped lithium niobate (LiNbO₃) systems are investigated by first-principles calculations. In this work, we focus on substitutionally Cu→Li-doped LiNbO₃ system with cuprous and cupric doping, which corresponds to the Li_{5/6}Cu_{1/6}NbO₃ and Li_{4/6}Cu_{1/6}NbO₃ [abbreviated as (Li, Cu I)NbO₃ and (Li, Cu II)NbO₃]. The density functional theory (DFT) calculations show that the electronic property of LiNbO₃ is completely different from (Li, Cu I)NbO₃ and (Li, Cu II)NbO₃. The calculated band structure and density of state (DOS) of (Li, Cu I)NbO₃ show a small band gap of 1.34 eV and the top of valance band (VB) is completely composed of a doping energy level originating from Cu 3d filled orbital. However, the calculated band structure and DOS of (Li, Cu II)NbO₃ show a relatively large band gap of 2.22 eV and the top of VB is mainly composed of Cu 3d unfilled orbital and O 2p orbital.

Keywords: Band structure; copper doping; LiNbO₃; first-principle calculation.

1. Introduction

Lithium niobate (LiNbO₃, LN) has been extensively researched for its excellent ferroelectric, piezoelectric, dielectric, pyroelectric, electro-optical and nonlinear optical properties.^{1–3} Due to its excellent properties, it has been intensely studied for applications in holographic memories, second harmonic generation and electro-optics.

As we know, nanomaterials have been the subject of enormous interest because of their extremely small feature size and potential for wide-ranging industrial, biomedical and electronic applications.⁴ Therefore, in our previous report,⁵ we prepared copper-doped LiNbO₃ nanocrystals by adopting a facile method, including the use of low-cost raw materials Li₂CO₃, Nb₂O₅ and Cu(NO₃)₂·3H₂O. Importantly, the copper-doped LiNbO₃ nanocrystals obtained visible light absorption property (benefit for higher utilization efficiency of sunlight in photocatalysis application), compared with a pure LiNbO₃ sample. However, it is still not clear for the origin of visible light absorption property, although the valance of

doped Cu in the copper-doped LiNbO₃ nanocrystals prepared in our previous work was determined to be +2 by XPS technology. Hence, it is necessary to investigate the band structure and electronic properties of pure LiNbO₃ crystal and copper-doped LiNbO₃ crystal, which are closely related to their photo-absorption characteristic. In the last decade, a first-principles study has been carried out to evaluate the electronic properties of LiNbO₃ based on DFT calculation.^{6–10} Therefore, based on the first-principles, the electronic properties of substitutionally Cu (I, II)-doped LiNbO₃ and pure LiNbO₃ crystal were investigated in this work.

2. Computational Details

All calculations are carried out within plane-wave density functional theory by employing the Vienna *ab initio* simulation package (VASP).^{11–13} The generalized gradient approximation (GGA) with Perdew, Burke and Ernzerhof (PBE) functional scheme is used for the exchange correlation

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potential. The convergence tests of total energy with respect to electron wave function expanded using plane waves with a cut-off energy of 500 eV have been examined. The ionic position, cell volume and lattice parameters of the system are fully relaxed with conjugate gradient method until Hellmann–Feynman forces are smaller than 0.02 eV/Å and energy convergence criteria is fulfilled at 1×10^{-5} eV. A popular scheme for k -point sampling is Monkhorst Pack (MP).^{14,15} The MP grid is chosen to be $9 \times 9 \times 5$ for the calculations of pure LiNbO₃ crystal and copper-doped LiNbO₃ crystal.

3. Structural Optimization

In this work, two doped model structures are built based on the cuprous and cupric doping corresponding to Cu (I) substituting Li-site and Cu (II) substituting double Li-sites, which are shown in Fig. 1, respectively. All atoms are allowed to move freely and also to change the position in order to minimize the energy and hence to achieve a stable

and most probable configuration. As a result, the optimized structures are obtained for the optimized structure with global minimum. The optimized LiNbO₃, Li_{5/6}Cu_{1/6}NbO₃ and Li_{4/6}Cu_{1/6}NbO₃ structures are shown in Fig. 2, respectively. As shown in Table 1, the lattice parameters of pure LiNbO₃ structure are $a = b = 5.22061$ Å, $c = 14.09363$ Å, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. The lattice parameters of Li_{5/6}Cu_{1/6}NbO₃ structure are $a = b = 5.23326$ Å, $c = 14.18521$ Å, $\alpha = \beta = 90^\circ$ and $\gamma = 120.0001^\circ$. The lattice parameters of Li_{4/6}Cu_{1/6}NbO₃ structure are $a = b = 5.22207$ Å, $c = 14.14371$ Å, $\alpha = 90.0012^\circ$, $\beta = 90.0014^\circ$ and $\gamma = 119.9983^\circ$. As a result, the lattice parameters of LiNbO₃ structure slightly increased when Cu (I) substitute Li-site of LiNbO₃, which can be attributed to that small difference in ionic radius between Cu (I) ($r = 0.77$ Å, CN = 6) and Li ($r = 0.76$ Å, CN = 6) ions.¹⁶ In addition, when Cu (II) substituting double Li-sites of LiNbO₃, the lattice of LiNbO₃ structure presents small distortion, which is related to the relatively large

Fig. 1. Structure models of (a) (Li, Cu I)NbO₃ and (b) (Li, Cu II)NbO₃.

Fig. 2. Optimized crystal structures of (a) LiNbO₃, (b) (Li, Cu I)NbO₃ and (c) (Li, Cu II)NbO₃.

Table 1. Lattice parameters of optimized crystal structures.

Lattice parameters	a (Å)	b (Å)	c (Å)	Alpha	Beta	Gamma
LiNbO ₃	5.22061	5.22061	14.09363	90.0000	90.0000	120.0000
(Li, Cu I)NbO ₃	5.23326	5.23326	14.18521	90.0000	90.0000	120.0001
(Li, Cu II)NbO ₃	5.22207	5.22222	14.14371	90.0012	90.0014	119.9983

Table 2. Octahedron parameters of optimized crystal structures.

	LiNbO ₃ Li–O octahedron	Li _{5/6} Cu _{1/6} NbO ₃ Cu(I)–O octahedron	Li _{4/6} Cu _{1/6} NbO ₃ Cu(II)–O octahedron
Bond length (Å)	(Li–O ₄) = 2.08842(0) (Li–O ₅) = 2.08842(0) (Li–O ₁₃) = 2.27755(0) (Li–O ₁₄) = 2.27755(0) (Li–O ₁₅) = 2.27755(0) (Li–O ₆) = 2.08842(0)	(Cu–O ₅) = 2.09299(0) (Cu–O ₁₃) = 2.36675(0) (Cu–O ₁₄) = 2.36676(0) (Cu–O ₁₅) = 2.36674(0) (Cu–O ₄) = 2.09301(0) (Cu–O ₆) = 2.09299(0)	(Cu–O ₃) = 2.21653(0) (Cu–O ₆) = 2.21707(0) (Cu–O ₉) = 2.21725(0) (Cu–O ₁₃) = 2.02796(0) (Cu–O ₁₀) = 2.02787(0) (Cu–O ₁₆) = 2.02713(0)
Average bond length (Å)	2.1830	2.2299	2.1223
Octahedron volume (Å ³)	12.8310	13.5254	11.9629

difference in ionic radius between Cu (II) ($r = 0.73 \text{ \AA}$, CN = 6) and Li ($r = 0.76 \text{ \AA}$, CN = 6) ions.¹⁶ In Fig. 2, three kinds of octahedrons (Li–O₆, Cu(I)–O and Cu(II)–O) are highlighted. Their bond length, average bond length and octahedron volume are shown in Table 2. It can be illustrated that the place of the intermediate atoms (Li and Cu) is different because of their variant bond length values. In addition, the average bond length (Å) and volume (Å³) of Li–O octahedron is smaller than that of Cu(I)–O octahedron but larger than that of Cu(II)–O octahedron. The results illustrate that when Cu (I) substitute Li-sites of LiNbO₃, the corresponding octahedron expanded. In contrast, the octahedron shrunk when Cu (II) substitute Li-sites of LiNbO₃. The trends are consistent with the change in the lattice parameters.

4. Results and Discussions

4.1. XRD patterns of optimized LiNbO₃, Li_{5/6}Cu_{1/6}NbO₃ and Li_{4/6}Cu_{1/6}NbO₃ structures

Figure 3(a)–3(c) show calculated XRD patterns of optimized LiNbO₃, Li_{5/6}Cu_{1/6}NbO₃ and Li_{4/6}Cu_{1/6}NbO₃ structures, respectively, and the inset is enlarged image (2θ from 21° to 27°). It can be seen that their XRD patterns are similar apart from the small difference of diffraction peak intensity, which illustrates that the Cu-doped solution can be formed at the concentration of Cu doping and the origin crystal structure of LiNbO₃ is not destroyed. In addition, the enlarged XRD patterns clearly show the position of diffraction peak (012) is different (marked with a dotted box). Compared to the pure LiNbO₃, the (012) diffraction peak of Li_{5/6}Cu_{1/6}NbO₃ and Li_{4/6}Cu_{1/6}NbO₃ crystal shifts to lower diffraction angel, which illustrates the increase of the lattice plane distance.

Fig. 3. Calculated XRD patterns of (a) LiNbO₃, (b) (Li, Cu I)NbO₃ and (c) (Li, Cu II)NbO₃.

4.2. Band structure and density of states of LiNbO₃, Li_{5/6}Cu_{1/6}NbO₃ and Li_{4/6}Cu_{1/6}NbO₃

Band structures and density of states of LiNbO₃, Li_{5/6}Cu_{1/6}NbO₃ and Li_{4/6}Cu_{1/6}NbO₃ have been determined to elaborate their electronic properties. Just for comparison, Figs. 4(a)–4(c) show the calculated band structures and density of states of LiNbO₃, Li_{5/6}Cu_{1/6}NbO₃ and Li_{4/6}Cu_{1/6}NbO₃, respectively. The valence and conduction bands (VB, CB) are formed by packs of several bands. The origin of the energy is set as E-fermi energy (E_f). As shown in Fig. 3(a), the calculated band gap value of pure LiNbO₃ is about 3.45 eV. This result is close to our previous report values (direct band value of 3.3 eV),⁵ which is obtained by

Fig. 4. Band structure and partial density of states (PDOS) of (a) LiNbO_3 , (b) $(\text{Li}, \text{Cu I})\text{NbO}_3$ and (c) $(\text{Li}, \text{Cu II})\text{NbO}_3$.

Tauc plots.¹⁷ Furthermore, the DOS of LiNbO_3 illustrates that the CB is composed of Nb 4d empty orbital and the VB is mainly composed of O 2p orbital. In addition, it also illustrates that the Li element has no contribution on the CB and VB. Figure 3(b) shows the calculated band gap value of $\text{Li}_{5/6}\text{Cu}_{1/6}\text{NbO}_3$ is 1.34 eV, which is much smaller than that of pure LiNbO_3 . As illustrated in the DOS curve of Fig. 3(b), the smaller band gap value is resulted from the appearance of Cu 3d orbital in the forbidden band, compared with the pure LiNbO_3 . Furthermore, the CB of $\text{Li}_{5/6}\text{Cu}_{1/6}\text{NbO}_3$ is composed of Nb 4d empty orbital and the VB is mainly composed of Cu 3d filled orbital. In addition, Fig. 3(c) shows the calculated band gap value of $\text{Li}_{4/6}\text{Cu}_{1/6}\text{NbO}_3$ is 2.22 eV. In our previous report,⁵ the Cu-doped LiNbO_3 nanocrystals with lower Cu doping concentration ($\sim 0.39\%$) show a band gap of 2.95 eV. The relatively large difference between the calculated and experimental band gap value may be attributed to the difference of Cu doping concentration. In addition, as illustrated in the DOS of Fig. 3(c), the CB of $\text{Li}_{4/6}\text{Cu}_{1/6}\text{NbO}_3$

is also composed of Nb 4d orbital and the VB is composed of Cu 3d unfilled and O 2p orbitals.

5. Conclusion

In this work, the Cu $\rightarrow$ Li doped LiNbO_3 system with cuprous and cupric doping, which correspond to the $(\text{Li}, \text{Cu I})\text{NbO}_3$ and $(\text{Li}, \text{Cu II})\text{NbO}_3$, respectively, was focused. The electronic properties of the Cu-doped LiNbO_3 systems are investigated by first-principles calculations, compared with pure LiNbO_3 . The DFT calculations show that an obvious difference of the electronic properties can be found for LiNbO_3 , $(\text{Li}, \text{Cu I})\text{NbO}_3$ and $(\text{Li}, \text{Cu II})\text{NbO}_3$. Their calculated band structures show $(\text{Li}, \text{Cu I})\text{NbO}_3$ has the smallest band gap of 1.34 eV and $(\text{Li}, \text{Cu II})\text{NbO}_3$ has a relatively large band gap of 2.22 eV, which is smaller than that of pure LiNbO_3 (a band gap of 3.45 eV). In addition, their calculated density of state (DOS) illustrate that the top of valance band

of (Li, Cu I)NbO₃ is completely composed of a doping energy level originating from Cu 3d filled orbital. However, the top of VB of (Li, Cu II)NbO₃ is mainly composed of Cu 3d unfilled orbital and O 2p orbital.

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