Electronic Structure and Polarization of NaMgF$_3$/NaCaF$_3$ Superlattices: Insight from First-Principles

Xuewei Sun$^1$, Guiqiu Wang$^{1, a}$ and Kun Yang$^{1, b}$

$^1$ School of Science, Dalian Maritime University, Dalian 116026, P.R. China
$^2$ Merchant Marine College, Shanghai Maritime University, Shanghai 201306, P.R. China
Email: gqwang@dlmu.edu.cn; yangk@shmtu.edu.cn

Abstract. Employing First-principles calculations, we have studied the electronic structure and polarization properties of the fluoroperovskite NaMgF$_3$/NaCaF$_3$ superlattices. The in-plane lattice constants of the superlattices are found to lie between those of the bulks. The Berry phase calculations show that the polarization of the NaCaF$_3$ bulk is much larger than that of the NaMgF$_3$, and the polarization of the NaMgF$_3$/NaCaF$_3$ superlattices can be tuned by altering the stacking periodicity. The band structure dependence of the stacking period is also investigated.

1. Introduction

Recently, the ABF$_3$ fluoroperovskites have received great attention due to their diverse properties ranging from magnetic [1], solid electrolyte [2] to luminescence [3] behaviours. Due to the stable cubic structure and wide band gaps, some fluoride perovskites are candidates for vacuum ultraviolet (VUV) optical materials [4]. Two compounds, NaMgF$_3$ and NaCaF$_3$, are particularly interesting. NaMgF$_3$ was found to be very attractive for radiotherapy applications [5] and NaCaF$_3$ has been theoretically suggested to be ferroelectric perovskite with polarization of 0.27 C/m$^2$ [6].

The perovskite superlattice system that combines two or more perovskite compounds could produce desirable properties that superior to the constituent materials. However, most of the perovskite superlattices investigations focus on the perovskite oxides and very few fluoroperovskites superlattice researches have been reported in literature [7]. In view of the technological importance of NaMgF$_3$ and NaCaF$_3$, together with the polarization possibility in NaCaF$_3$, we construct short-period NaMgF$_3$/NaCaF$_3$ superlattices to study the polarization property and electronic structures by first-principles calculations. The influence of the stacking periodicity on the superlattice properties is also explored.

2. Computational Details

Our first-principles calculations are performed using the VASP code [8, 9] with the projector-augmented wave (PAW) pseudo-potentials [10]. The generalized gradient approximation (GGA) with the PW91 functional [11] is applied for the exchange-correlation potential treatment. For bulks and superlattices calculations, the Monkhorst-Pack [12] k-point meshes of 8×8×8 and 8×8×2 are used, respectively. The plane-wave cutoff energy is 500 eV and the electronic convergence criterion is set at 10$^{-7}$ eV throughout the calculations. To calculate the polarizations, the Berry phase method is carried out. The structure of the (NaMgF$_3$)$_m$(NaCaF$_3$)$_n$ superlattices with different stacking periodicities are constructed and denoted as $mln$. This means that $m$ unit NaMgF$_3$ layers and $n$ unit NaCaF$_3$ layers stack...
alternately along the $c$ axis. In our calculations, short-period superlattices $m+n = 2$ and $3$ are investigated. During the structural optimization of the superlattices, both the lattice and the atomic positions are fully relaxed within the tetragonal $P4mm$ space group, which allows the polarization directing along the $c$ axis.

3. Results and Discussion

For both NaMgF$_3$ and NaCaF$_3$ bulks, we computed the geometric structure with the tetragonal $P4mm$ symmetry first. The obtained lattice constants $a$ and $c$ for NaMgF$_3$ are almost the same, which are 3.928 and 3.929 Å, respectively. For NaCaF$_3$, the calculated lattice constants $a$ and $c$ are relatively larger than those of the NaMgF$_3$, which are 4.316 and 4.388 Å, respectively. The calculated in-plane lattice constants, $a$, for all the superlattices as a function of the NaMgF$_3$ ratio are plotted in figure 1.

To make a comparison, the lattice constants, $a$, of bulk NaMgF$_3$ and NaCaF$_3$ are also given in figure 1. All the in-plane lattice constants of the superlattices lie between those of the NaMgF$_3$ and NaCaF$_3$ bulk. It is obvious that the values of the in-plane lattice constant of the superlattices decrease with the increasing NaMgF$_3$ ratio, where a linear scaling relationship exists.

![Figure 1. In-plane lattice constant as a function of the NaMgF$_3$ ratio for (NaMgF$_3$)$_m$(NaCaF$_3$)$_n$ superlattices.](image)

For the polarization calculations, we determine the polarization of the bulk NaCaF$_3$ first to compare the Berry phase results to previous computational result. The obtained value is 0.30 C/m$^2$, which agrees well with previous calculated 0.27 C/m$^2$ by Boyer et al. [6]. This indicates that Berry phase method could produce the polarization of the fluoroperovskites and their superlattices well. We then calculated the polarizations of all the (NaMgF$_3$)$_m$(NaCaF$_3$)$_n$ superlattices and the tetragonal NaMgF$_3$ bulk.

Figure 2 shows the calculated polarization of all the (NaMgF$_3$)$_m$(NaCaF$_3$)$_n$ superlattices and the NaMgF$_3$ and NaCaF$_3$ bulks. The calculated polarization of the tetragonal NaMgF$_3$ is quite small, which is only 0.011 C/m$^2$. For the superlattices, it is determined that the polarizations lie in the range of the polarizations of the NaMgF$_3$ and NaCaF$_3$ bulk. It is worth noting that the main trend of the superlattice polarization as a function of the NaMgF$_3$ ratio is that the polarization decreases as the NaMgF$_3$ ratio increases. However, the polarization dependence of the NaMgF$_3$ ratio is not linear. The polarization of the 1/2 and 1/1 superlattices are 0.28 and 0.27 C/m$^2$, respectively, which are very close to that of the NaCaF$_3$ bulk. Whereas for superlattice 2/1 that has NaMgF$_3$ ratio of 66.7%, the polarization decreases to 0.17 C/m$^2$. This suggests that the polarization of the superlattices could be tuned by changing the stacking, and further studies with more stacking periodicities are needed to find the polarization tuning behaviour.
To further understand the electronic structures of the superlattices, we calculated the band structures of the superlattices and the bulks. The calculated band gap as a function of the NaMgF$_3$ ratio is displayed in Figure 3. The band gap for tetragonal $P4mm$ NaMgF$_3$ and NaCaF$_3$ bulk are 6.081 and 5.669 eV, respectively. Though there are no theoretical band gaps of the $P4mm$ bulk in literature, our results are in reasonable agreement with previous GGA band gaps of cubic NaMgF$_3$ (5.90 eV) [13] and NaCaF$_3$ (5.02 eV) [14]. It is clearly seen from Figure 3 that all the band gaps of the superlattices are lower than those of the NaMgF$_3$ and NaCaF$_3$ bulks. The gap values of the superlattices range from 5.023 to 5.345 eV, with superlattices 2/1 and 1/1 having the smallest and largest band gaps, respectively. Our band gap calculations suggest that the band gap can also be tuned by making NaMgF$_3$ and NaCaF$_3$ bulk into superlattice systems with different stacking.

4. Conclusions
Polarization is obtained for the short-period $(\text{NaMgF}_3)_m/(\text{NaCaF}_3)_n$ superlattices from first-principles calculations. The polarization of the superlattices increases with the increasing NaCaF$_3$ content in the superlattice, and the polarization of the tetragonal NaCaF$_3$ bulk (0.30 C/m$^2$) exceeds those of the superlattices. The dependence of the band structure on the NaCaF$_3$ ratio is also explored. The
calculated results indicate that polarization and band gap can be tuned by changing the stacking periodicity. Our results may be helpful to further investigations of electronic devices based on fluoroperovskites.

Acknowledgments
This work was supported by the National Natural Science Foundation of China (11875096 and 11304028).

References
[1] Oleaga A, Salazar A and Skrzypiec D 2015 J. Alloy. Compd. 629 178-183
[2] O’Keefe M and Bovin J O 1979 Science 206 599-600
[3] Seddik T, Khenata R, Merabiha O, Bouhemadou A, Bin-Omran S and Rached D 2012 Appl. Phys. A 106 645-653
[4] Yamanoi K, Nishi R, Takeda K, Shinzato Y, Tsuboi M, Luong M V, Nakazato T, Shimizu T, Sarukura N, Cadatal-Raduban M, Pham M H, Nguyen H D, Kurosawa S, Yokota Y, Yoshikawa A, Togashi T, Nagasono M and Ishikawa T 2014 Opt. Mater. 36 769-772
[5] Schuyt J J and Williams G V M 2017 J. Appl. Phys. 122 063107
[6] Boyer L L, Mehl M J, Mei W N, Duan C G, Flocken J W, Guenther R A, Hardy J R, Stokes H T and Edwardson P J 2000 AIP Conf. Proc. 535 364-371
[7] Yang X and Su H 2015 Sci. Rep. 5 15849
[8] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169-11186
[9] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758-1775
[10] Blöchl P E 1994 Phys. Rev. B 50 17953-17979
[11] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 Phys. Rev. B 46 6671-6687
[12] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188-5192
[13] Li Z-L, An X-Y, Cheng X-L, Wang X-M, Zhang H, Peng L-P and Wu W-D 2014 Chinese Physics B 23 037104
[14] Yang K, He Y, Cheng Y, Che L and Yao L 2017 Phys. Lett. A 381 890-895