CHIN. PHYS. LETT. Vol. 34, No. 1 (2017) 016101

Optimal Bandgap of Double Perovskite La-Substituted Bi_2FeCrO_6 for Solar Cells: an *ab initio* GGA+U Study

B. Merabet[1,2**], H. Alamri[3], M. Djermouni[2,4], A. Zaoui[2], S. Kacimi[2], A. Boukortt[5], M. Bejar[6]

[1]*Electrotechnics Department, Faculty of Technology, Mustapha Stambouli University, Mascara 29000, Algeria*
[2]*Computational Materials Physics Laboratory, UDL-SBA 22000, Algeria*
[3]*Physics Department-University College, Umm Al-Qura University, Makkah, Saudi Arabia*
[4]*Centre Universitaire Ahmed Zabana, Relizane 48000, Algeria*
[5]*Elaboration Characterization Physico-Mechanics of Materials and Metallurgical Laboratory ECP3M, Faculty of Sciences and Technology, Abdelhamid Ibn Badis University of Mostaganem, Mostaganem 27000, Algeria*
[6]*Laboratoire de Physique Appliquée, Faculté des Sciences, Université de Sfax, Sfax 3000, Tunisie*

(Received 26 August 2016)

The ab initio generalized gradient approximation (GGA)+U study of multiferroic $(La_{0.5}Bi_{0.5})_2FeCrO_6$ in pnma structure and ferri-magnetic order, including Hubbard corrections ($U = 4.1$ eV) for transition metal/rare earth d-electrons with 20 atoms cell, shows optimum local magnetic moments of (Cr^{3+}, Fe^{3+}) equal to (-2.56, 4.14) μB and an ideal spin-down band gap of 1.54 eV. Tuned-band gap La-substituted double oxide perovskites BFCO should exhibit enhanced visible-light absorption and carrier mobility, thus could be convenient light absorbers and then efficient alternatives to wide-gap chalcopyrite absorber-based solar cells failing to achieve highest power conversion efficiencies, and even compete with their metal-organic halide perovskites counterparts.

PACS: 61.50.Ah, 72.40.+w, 73.22.Pr, 78.56.−a, 78.67.Wj DOI: 10.1088/0256-307X/34/1/016101

Unlike traditional semiconductor-photovoltaic (SC-PV) devices, ferroelectrics (FEs) display spontaneous polarization (centrosymmetry breaking of crystallographic unit cells), built-in depolarization field to separate photoexcited electron-hole pairs.[1] Since FE response/other properties coupling is possible, FEs are applied in memory storage media,[2] field-effect transistors and random-access memories.[3] In hetero p–n and Schottky-junctions, the charge separation is realized by a built-in potential near interface and output photovoltage is limited by band gap energy (E_g of 1.34 eV as an ideal value[4]) of SC absorbers. However, most FEs are perovskite oxides with E_g above 3.3 eV. Wide E_g and small optical absorption coefficient are critical shortcomings of FE oxide perovskites (FEOPs) for PV applications. In terms of PV efficiency, poor visible light absorption and weak bulk conductivity negatively affecting the performance limit FE-PVs for such applications, though power conversion efficiencies (PCEs) that such based devices have are potentially beyond Shockley–Queisser limits[5] estimated in single junction devices. To reduce E_g of FEOPs (ABO_3) for absorbing more visible light, researchers have developed effective approaches such as cation (B) doping,[6] thus modifying B–O bonding could tune E_g in the range of 1.4–2.7 eV by tailoring the Fe/Cr cationic ordering and domain size.[7] However, Bi-substitution that reduces E_g of FEOPs also produces structural disorder, nonstoichiometric defects or oxygen vacancies into systems, usually lowering carrier mobility and weakening transport properties in cation-doped FE oxides, thus most cation-doped semiconducting FE oxide solid-solutions still have low output photocurrent densities and PCE.[8] In multiferroic Bi_2FeCrO_6 (BFCO) materials with $A_2BB'O_6$ double perovskite (DP) structure in which ferromagnetism and ferroelectricity coexist,[9] a PCE of ∼8.1% was achieved through E_g engineering.[7] In bismuth-based multiferroics where Bi^{3+} ions occupy the perovskite A site, stereo-chemically active $6s^2$ lone pair induces in magnetic oxides a symmetry-lowering structural distortion that can lead to ferroelectricity,[10] due to the fact that non-centrosymmetric crystal structure Bi-multiferroics exhibit strong inversion symmetry and then are promising for PVs via spontaneous electric polarizations that promote required separation of photo-excited carriers and permit photo-voltage that can exceed E_g of such materials.[11] Also, large dielectric constant and polarization magnitude are innate advantages of such FEOPs for separating photo-excited charge carriers.[4] To enhance dielectric response in Bi-multiferroics, Bi could be substituted by lanthanum,[12] as the spin cycloid characterizing bulk Bi-based materials disappears upon La doping.[13] Since the photovoltage achievable from simple SC devices is mainly limited by E_g of the light absorber, we propose here to focus on $(La_xBi_{1-x})_2FeCrO_6$ (LBFCO) DPs, with La-concentration of $x = 0.5$ as a representative example, trying to achieve possible conspicuous success in E_g engineering. Vijayanandhini *et al.*[14] investigated the orthorhombic (*Pnma* space group) perovskite LBFCO, reporting suscepti-

**Corresponding author. Email: boualem19985@yahoo.fr
© 2017 Chinese Physical Society and IOP Publishing Ltd

bility versus temperature measurement, a ferrimagnetic (FiM) or weak ferromagnetic (WFM) order for these systems, and WFM paramagnetic transition above 400 K. On the other hand, it is worth noting that magnetic properties of LBFCO are influenced by the strain effect and crystallographic orientation that such effect induces, thus $(Bi_{0.9}La_{0.1})_2FeCrO_6$ epitaxial films exhibit large coherent compressive strains for inducing a substantial magnetic moment, and strain engineering of oxide perovskites may also be somehow employed for E_g tuning.[9] Providing that via a control of the cation ratio and distribution in $(Bi, La)_2FeCrO_6$ DPs E_g of these BLFCOs can be tuned to enhance the PCE, our density functional theory (DFT) study within the generalized gradient approximation (GGA) ($+U$: Hubbard parameter), mainly focuses on electronic properties of $(La_{0.5}Bi_{0.5})_2FeCrO_6$ in the *pnma* structure/FiM phase and La substituting effects on PCE via E_g tuning, which is crucial for optimizing performance characteristics of LBFCOs applied for solar cells.[7] Figure 1 shows our structure with the lattice parameters $a = 55393$ Å, $b = 78171$ Å and $c = 55246$ Å.[14]

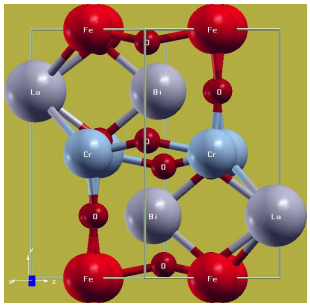

Fig. 1. The *pnma* (#62) crystal structure of DP La-substituted BFCO (50% La-substitution into the Bi site): an ideal ordered DP structure $La_2BB'O_6$ (B=Fe, B′=Cr). For the FiM state, the spin state of (B, B′) is (+ or ↑, − or ↓).

DFT band structure calculation[15] for bulk crystalline $(La_{0.5}Bi_{0.5})_2FeCrO_6$ DP is carried out within Wien2K, implementing the FP-LAPW[16] and GGA-PBE approximations,[17] full relativistic effects are calculated with the Dirac equations for core states, and the scalar relativistic approximation is used for the other states.[18] The spin-orbit coupling is ignored because it only has a slight effect. The on-site Coulomb interaction is included in the GGA+U approach[19] with $U = 4.1$ eV for both Fe and Cr $3d$ electrons[20] (exchange and correlation potential to treat such electrons). For simplicity, the same U was used on both the Fe and Cr sites in La-substituted Bi_2FeCrO_6.[21] Our DFT calculations are performed by using the highly accurate full-potential projector augmented wave method,[22] whose potentials are used to describe the electron–ion interaction with 15, 14, 12 and 6 valence electrons for Bi($5d^{10}6s^26p^3$), Fe($3p^63d^64s^2$), Cr($3p^63d^54s^1$) and O($2s^2p^4$), respectively, representing ionic cores. Brillouin zone (BZ) integrations are performed with the tetrahedron method in a $7 \times 11 \times 7$ Monkhorst–Pack k point mesh centered at high symmetry point Γ, inside the BZ.[23] We adopted an orthorhombic *Pnma* (#62) structure with 20 atoms in a primitive unit cell and an FiM phase[14] with Fe spin orienting up and Cr down. The muffin tin (MT) radii of La/Bi, Fe, Cr, O equal to 2.6, 1.95, 2.0, 1.6 Bohr, respectively. The parameter $R_{MT} \times k_{MAX}$ and separation energy between valence and core states are respectively set to 7 and -7 Ry. Thus ordered $(La_{0.5}Bi_{0.5})_2FeCrO_6$ with Fe^{3+}/Cr^{+3} lattice planes has a spin-down E_g of 1.54 eV near the ideal Shockley–Queissier limit,[5] known equal to 1.34 eV. The La substitution in LBFCO-DP could be a powerful tool to engineer the band structure and then impact optical properties.

Motivated by the ordered La_2FeCrO_6 (LFCO) as an artificial superlattice of $LaFeO_3/LaCrO_3$ synthesized by Ueda *et al.*,[24] predicted to be FiM from GGA Bandstructure calculations,[25] Baettig *et al.*[20] proposed the analogous Bibased compound Bi_2FeCrO_6 (BFCO) exhibiting an FiM order,[26] although the magnetic coupling between Fe^{3+} and Cr^{3+} was predicted in terms of super-exchange to be either FiM or FM.[27] To further improve FM moments and significantly reduce leakage currents in bulk BFCO materials, Bi has been substituted in highly distorted BFCODP[28] structure by the rare earth metal La,[13] since La^{3+} prefers to substitute for Bi^{3+} due to valence and ion radius similarities, though with La-substitution many phase transitions may occur in Bi-based FEOPs as La content (x) increases,[29] like $R3c$ to *pnma* occurring in the range 0.1–0.3 of x for $Bi_{1-x}La_xFeO_3$.[30] Since the magnetic order of $(La_xBi_{1-x})_2FeCrO_6$ (for $x = 0$), with Fe spin orienting up and Cr spin down, turns out to be FiM[31–33] (as proved by experiment for $(La_{1-x/2}Bi_{x/2})(Fe_{0.5}Cr_{0.5})O_3$ samples[14]), and even the ground state of La_2FeCrO_6 ($x = 1$) from band structure calculations might be FiM,[25] we adopted it throughout our calculations. So far, the ground state magnetic ordering of $(La_{0.5}Bi_{0.5})_2FeCrO_6$ is FiM exhibiting optimum local magnetic moments of $(Cr^{3+}, Fe^{3+}) = (-2.56, 4.14)$ μB and a spin-down gap of 1.54 eV, compared with those of the FM order-based structure of (2.63, 4.14) μB and 2.01 eV, and those of the FiM pnma symmetry with 25% La-substitution into the Bi site of (−2.59, 4.09) μB and 1.53 eV. Though the lowest energy structure of $(La_{0.5}Bi_{0.5})_2FeCrO_6$ reveals the structure to be $R3$ (like BFCO[20]), within the FiM *pnma* symmetry an SC character has been obtained contrary to the metallic behavior of $R3$ structure may be related to Goldschmidt's tolerance factor.[33] For solar cell

applications excellent photoelectronic properties for LBFCO such as optimal gap (≈1.5 eV) could be predicted. Like BFCO, $(La_{0.5}Bi_{0.5})_2FeCrO_6$ should also be an example of such a d^5–d^3 orbital combination, and the local magnetic moments are found to be (Cr^{3+}, Fe^{3+})=(−2.56, 4.14) μB, instead of (−2.18, 3.70) μB for BFCO,[33] as the magnetic order in such ordered DP structure could be controlled by the spin state of Fe^{3+} and Cr^{3+}. Here it is worth mentioning that $(La_{0.5}Bi_{0.5})_2FeCrO_6$ FiM could exhibit magnetic moments depending on the degree of Fe/Cr cation ordering in the films, an FiM SC phase should be more suitable for many applications mainly due to considering core electrons in our full-potential calculations, and substituting La at Bi sites could be related to a complicated magnetization. If ion spin states could be changed, applying GGA+U will be crucial for a meaningful result to be obtained.

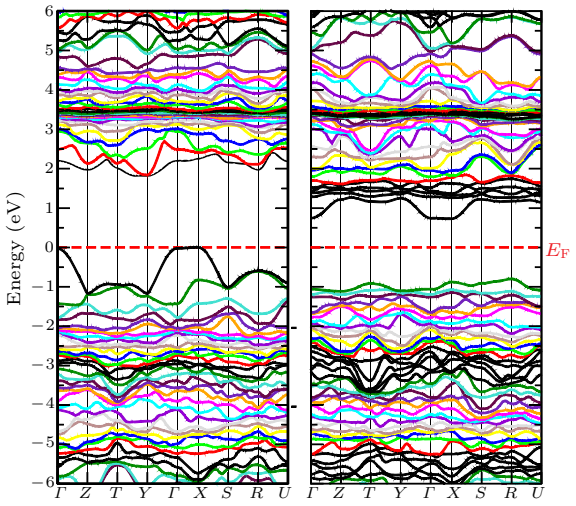

Fig. 2. Spin-resolved energy bands of DP La-substituted BFCO (with 50% of Ba substituted by La), calculated with GGA+U (4.1 eV). The left-side panel is for up-spin, and the right-side for down-spin.

Since E_g of most solid oxide FEs is of at least 3 eV, absorbing mainly in the ultraviolet region (8% of the solar spectrum only), new materials, such as Bi based FEOPs with a decreased E_g and large polarization would be highly desirable. Our DFT study with GGA+U shows that the ground-state FiM SC phase of DP La-substituted BFCO, with La substituted for Ba till 50%, has an optimal spin-down gap of 1.54 eV near the ideal value of 1.34 eV. Through a corresponding spin-dependent band structure shown in Fig. 2, one can clearly notice the FiM phase of DP La substituting BFCO, whose electronic structure could be studied. In the up-spin channel, the bands originate mainly from the O 2p and Cr 3dt_{2g} states, the empty bands are almost Fe 3dt_{2g} states, and the upper states are from Fe 3de_g, Cr 3de_g, and Bi 6p. In the down-spin channel, filled and empty bands are from the O 2p states and Fe 3d ones, and Cr 3d and Bi 6p states, respectively. Contrary to the up-spin channel, the Fe 3d states hybridize with O 2p and those of Cr 3d interact strongly with the Bi 6p, and the formed gap should be between the filled Cr 3d and the empty Fe 3d bands, which mainly originate from a crystal field splitting due to a deformation of the O octahedrons plus a spin exchange splitting of the 3d electrons. The principal spin interaction that an O atom between its nearest Fe and Cr atoms intermediates is as spins contribute opposite magnetic moments forming the ferrimagnetism. Such interaction becomes sensibly weaker from a nearest to next-nearest neighboring spin pairs.

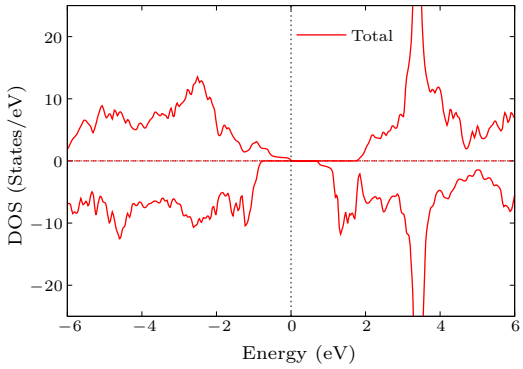

Fig. 3. Total spin-resolved DOS of DP La-substituted BFCO (with 50% of Ba substituted by La), calculated with GGA+U (equal to 4.1 eV). The upper part in each panel is the majority-spin DOS result, and lower the minority one. The Fermi level (E_F) has been taken as the energy zero.

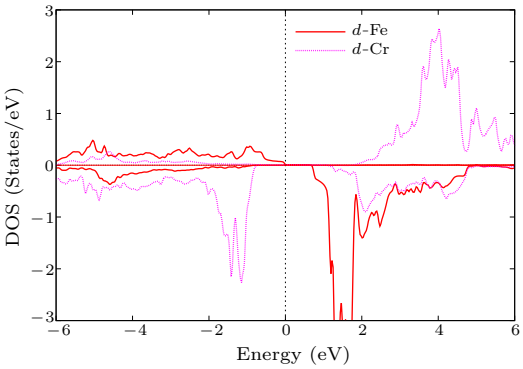

Fig. 4. Partial DOS projected in the atomic spheres of Fe d and Cr d of DP La-substituted BFCO (with 50% of Ba substituted by La).

In Figs. 3 and 4, we present the spin-resolved total density of states (DOS) and partial DOS in GGA calculations projected in the d states of Fe and Cr between −6 and 6 eV. La-substituted BFCO should undergo an octahedra tilting to optimize the local environment around the La/Bi site cation,[34] due to the crucial valance and size differences between the Fe^{3+} and Cr^{3+} cations for controlling the physical properties in such DPs,[35] octahedral tilts should change an overlap between Fe/Cr d states and O 2p states (Fig. 5) and significantly affect the FEOPs

properties.[36] The d states of Fe/Cr ion tend to split into three-fold lower in energy degenerate $3dt_{2g}$ states and two-fold degenerate $3de_g$ states, lying higher in energy pointing respectively away from/directly towards O atoms, causing the Fe/Cr–O bonds to distort. These so-called Jahn–Teller distortions have a significant impact on the electronic and magnetic properties of such DPs.[37] Our DP has its d-states close to the Fermi level (E_F), tending to form due to their small spatial narrow bands overlap with the O $2p$ states. However, the lone pair orbital of $Bi^{3+}(6s^2)$, namely outer orbital/energy level of Bi^{3+} has a $5d^{10}6s^2$ electron configuration, in which a lone pair exists. The stereochemical activity is responsible for a ferroelectric distortion that still occurs on substitution of Bi^{3+} with La^{3+}, and is more likely caused by the diminishing lone pair activity of Bi.[38] If we overlap Figs. 4 and 5, one can see that the O $2p$ orbital extending below E_F from -6 to -0.25 eV hybrids with the Fe $3dt_{2g}$ orbital mainly in the up-spin channel, and Cr $3dt_{2g}$ in the opposite one stretching from -6 to -0.75 eV also hybrids with O $2p$. A bangap appears at the down-spin channel centered by E_F, above which Fe $3dt_{2g}$ and Cr $3de_g$ orbitals act almost alternatively: 1–1.8 eV for Fe (down-channel) and 3–6 eV for Cr (up-channel).

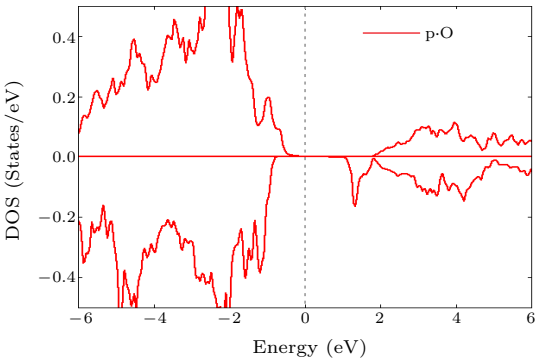

Fig. 5. Partial DOS projected in the atomic spheres of O p of DP La-substituted BFCO (with 50% of Ba substituted by La).

Figure 6 focuses on a typical polarized lone pair electron character due to La-substitution into the Bi site of $6s^2$ electrons that strongly affect the crystal structure and magnetic order of our $(La_{0.5}Bi_{0.5})_2FeCrO_6$ DP. Though Bi^{3+} and La^{3+} have close ionic radii, a prominent contribution is introduced by the highly polarizable Bi^{3+} $6s^2$ lone pair due (whose presence may play here an important role in lowing the symmetry) to its anisotropic local lattice distortion. In fact, as in Pb-based perovskites,[6] substituting the Bi site of BFCO-DP with elements (like La) whose bonds with oxygen are more covalent and less should reduce the band gap, and covalent/ionic characters are strongly related to the electronegativity difference between anion- and (Fe,Cr)-site with O. Figure 7 displays the charge density distribution of our DP La-substituted BFCO in the (110) plan showing that almost all atoms are covalently bonded.

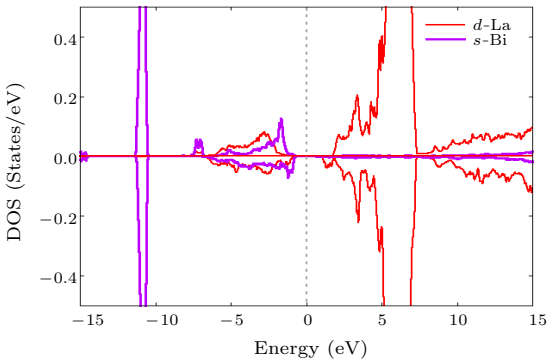

Fig. 6. Partial DOS projected in the atomic spheres of La d and Bi s of DP La-substituted BFCO (with 50% of Ba substituted by La).

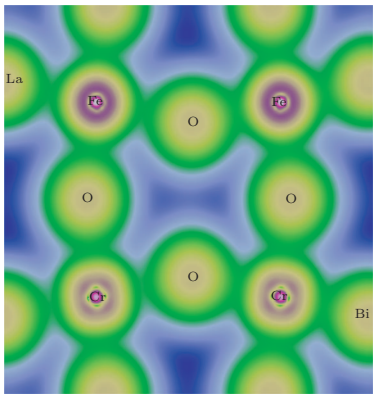

Fig. 7. Charge density of DP La-substituted BFCO, (with 50% of Ba substituted by La), at the (110) plane containing the five species.

In summary, we have studied the electronic structure and magnetic stability of La-substituted BFCO, La substituted for Ba till 50%, in the *pnma* phase and the FiM order. Our GGA+U results suggest La-substitution as a powerful tool to band gap engineer, thus impacting optical properties. La^{3+} tending to prefer O environments (contrasting with large off-centering and anisotropic O environments usual for Bi^{3+}) is explained in terms of a lone-pair mechanism. LBFCO, an SC with an optimal spin-down E_g of 1.54 eV and a magnetic moment $\sim$4 μB, should be a possible candidate for FE-PVs, while it remains to be verified if structure distortions in it are so large to originate a strong nearest neighbor super-exchange coupling in LBFCO containing $3d$ ions.

References

[1] Butler K T, Frost J M and Walsh A 2015 *Energy Environ. Sci.* **8** 838
Yuan Y, Xiao Z, Yang B and Huang J 2014 *J. Mater. Chem. A* **2** 6027
[2] Hu Z, Tian M, Nysten B and Jonas A M 2009 *Nat. Mater.* **8** 62

Scott J F 2007 *Science* **315** 954
[3] Garcia V and Bibes M 2012 *Nature* **483** 279
Lee D, Yang S M, Kim T H, Jeon B C, Kim Y S, Yoon J G, Lee H N, Baek S H, Eom C B and Noh T W 2012 *Adv. Mater.* **24** 402
[4] Fan Z, Sun K and Wang J 2015 *J. Mater. Chem.* A **3** 18809
[5] Shockley W 1961 *J. Appl. Phys.* **32** 510
[6] Bennett J W, Grinberg I and Rappe A M 2008 *J. Am. Chem. Soc.* **130** 17409
Berger R F and Neaton J B 2012 *Phys. Rev.* B **86** 165211
[7] Nechache R, Harnagea C, Li S, Cardenas L, Huang W, Chakrabartty J and Rosei F 2014 *Nat. Photon.* **9** 61
[8] Wang H, Gou G Y and Li J 2016 *Nano Energy* **22** 507
[9] Khare A, Singh A, Prabhu S S and Rana D S 2013 *Appl. Phys. Lett.* **102** 192911
[10] Seshadri R and Hill N A 2001 *Chem. Mater.* **13** 2892
[11] Alexe M and Hesse D 2011 *Nat. Commun.* **2** 256
[12] Gonzalez-V O E, WojdełJ C, Diéguez O and Íñiguez J 2012 *Phys. Rev.* B **85** 064119
[13] Zalesskii A V, Frolov A A, Khimich T A and Bush A A 2003 *Phys. Solid State* **45** 141
[14] Vijayanandhini K, Simon Ch, Pralong V, Bréard Y, Caignaert V, Raveau B, Mandal P, Sundaresan A and Rao C N R 2009 *J. Phys.: Condens. Matter* **21** 486002
Vijayanandhini K, Simon Ch, Pralong V, Caignaert V and Raveau B 2009 *Phys. Rev.* B **79** 224407
[15] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
[16] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D and Luitz J 2001 *Wien2k An Augmented Plane Wave Plus Local Orbitals Program For Calculating Cryst. Properties Vienna University Technol. Austria (ISBN* 3-9501031-1-2)
[17] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[18] Singh D 1994 *Plane Waves Pseudopotentials and the LAPW method* (Boston: Kluwer Academic)
[19] Liechtenstein A I, Anisimov V I and Zaane J 1995 *Phys. Rev.* B **52** R5467
[20] Baettig P, Ederer C and Spaldin N A 2005 *Phys. Rev.* B **72** 214105
[21] Dudarev S L 1998 *Phys. Rev.* B **57** 1505
[22] Blochl E, Jepsen O and Andersen O K 1994 *Phys. Rev.* B **49** 16223
[23] Blochl P E 1994 *Phys. Rev.* B **50** 17953
[24] Ueda K, Tabata H and Kawai T 1998 *Science* **280** 1064
[25] Miura K and Terakura K 2001 *Phys. Rev.* B **63** 104402
[26] Nechache R, Harnagea C, Carignan L P, Gautreau O, Pintilie L, Singh M P, Ménard D, Fournier P, Alexe M and Pignolet A 2009 *J. Appl. Phys.* **105** 061621
[27] Kanamori J 1959 *J. Phys. Chem. Solids* **10** 87
[28] Suchomel M R, Thomas C I, Allix M, Rosseinsky M J, Fogg A M and Thomas M F 2007 *Appl. Phys. Lett.* **90** 112909
[29] Garcia F G, Riccardi C S and Simoes A Z 2010 *J. Alloys Compd.* **501** 25
[30] Cheng Z X, Li A H, Wang X L, Dou S X, Ozawa K, Kimura H, Zhang S J and Shrout T R 2008 *J. Appl. Phys.* **103** 07E507
[31] Selbach S M, Einarsrud M A and Grande T 2009 *Chem. Mater.* **21** 169
Goldschmidt V M 1926 *Naturwissenschaften* **14** 477
[32] Ju S and Guo G Y 2008 *Appl. Phys. Lett.* **92** 202504
[33] Song Z W and Liu B G 2013 *Chin. Phys.* B **22** 047506
[34] Woodward P M 1997 *Acta Crystallograllogr. B: Struct. Sci.* **53** 32
[35] Nakamura T and Choy J H J 1977 *Solid State Chem.* **20** 233
[36] Rondinelli J M, May S J and Freeland J W 2012 *MRS Bull.* **37** 261
[37] Goodenough J B 1998 *Jahn-Teller Phenom. Solids Annu. Rev. Mater. Sci.* **28** 27
[38] Catalan G and Scott J F 2009 *Adv. Mater.* **21** 2463