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Structural incommensurate modulation rule in hexagonal $\text{Ba}(\text{Ti}_{1-x}\text{M}_x)\text{O}_{3-\delta}$ ($\text{M} = \text{Mn}, \text{Fe}$) multiferroics

X. K. Wei,^{1,2,3} Q. H. Zhang,¹ C. Q. Jin,¹ and R. C. Yu^{1,a}

¹Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, P. R. China

²Ceramics Laboratory, EPFL-Swiss Federal Institute of Technology, Lausanne, 1015, Switzerland

³Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons (ER-C), Research Centre Jülich, Jülich, 52425, Germany

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The structural incommensurate modulation (SIM) rule in hexagonal $\text{Ba}(\text{Ti}_{1-x}\text{M}_x)\text{O}_{3-\delta}$ ($1/18 \leq x \leq 1/3$, $\text{M} = \text{Mn}, \text{Fe}$) multiferroic ceramics is investigated using transmission electron microscope (TEM). Our systematic analysis on the modulation characteristics in the electron diffraction patterns, especially along [001] direction, reveals that three types of anti-phase domain boundaries (APBs) dominate the SIMs. According to the derived APB models, the calculated oxygen vacancies at both O1 (face sharing) and O2 (corner sharing) sites qualitatively agree quite well with our previous results. Analysis on the high-resolution TEM images reveals that complex dislocation structures also play important roles in the formation of the SIMs. *Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License.* [<http://dx.doi.org/10.1063/1.4766181>]

I. INTRODUCTION

Exploration of novel multiferroic materials, which have coupled magnetic and electric order parameters has attracted a great deal of interest in recent years.¹ Among the widely concerned systems, magnetic ion doped ferroelectrics such as BaTiO_3 and PbTiO_3 was paid much attention lately.²⁻⁸ For example, coexistence of ferromagnetism (FM) and ferroelectricity (FE) was observed in either Fe- or Mn-doped tetragonal BaTiO_3 samples at room temperature.²⁻⁴ However, the coupling interaction between FM and FE was not observed in this doped system. Comparatively, combined FM and FE were also observed at room temperature in Fe-doped hexagonal BaTiO_3 ,^{9,10} and cross-controlled magnetoelectric effects were realized because of the oxygen-vacancy ordering at O1 site.⁹ In addition, the magnetoelectric coupling effect also exists in Mn-, Fe- or Ni-doped PbTiO_3 ceramics.⁶⁻⁸

Besides the physical property, the structure of the doped system is another important issue worthy of being concerned. Investigations such as X-ray diffraction (XRD), electron paramagnetic resonance (EPR), and Mössbauer spectra have revealed that oxygen vacancies (Vos) prefer to occupy the O1 site and partial Ti^{4+} ions will be reduced into Ti^{3+} ions in the hexagonal matrix.⁹⁻¹⁴ The conductivity almost increases linearly with the increase of the oxygen vacancy content since more compensated electrons are introduced at the same time. However, positive contribution of more vacancy to FM only works as the doping content of Fe is less than 12 mol%,^{11,15} further doping would weaken the ferromagnetic interaction. Such a behavior can mainly be ascribed to the crystal and electronic structure changes because of doping, e.g., occupancy ratio change of the dopants at Ti1 and Ti2 sites, the coordination number change of the transition metals and the introduction of defect structures.^{10,16}

^aAuthor to whom correspondence should be addressed: Electronic mail: rcyu@aphy.iphy.ac.cn.



Our previous study on dense Fe-doped hexagonal BaTiO₃ reported the multiferroic behavior of the incommensurately modulated system.¹⁰ In this letter, the structural incommensurate modulations (SIMs) are systematically investigated in Mn- and Fe-doped hexagonal BaTiO₃ series samples. Through analyzing the characteristics of the electron diffractions, we find that the anti-phase domain boundaries (APBs), which take place along [001] direction and can be categorized into different groups, dominate the SIMs behavior. Associated with the defect structures caused by the Vos, the physical property of the doped system can be well understood.

II. EXPERIMENTAL DETAILS

The hexagonal Ba(Ti_{1-x}M_x)O_{3-δ} (as M = Mn, $x = 1/18, 1/9, 1/6$; as M = Fe, $x = 1/6, 1/3$) ceramic samples, which are named as BTM05, BTM11 and BTM17, BTF17 and BTF33, respectively, were prepared using solid state reaction method.¹⁷ After the twice preliminary sintering, the as-grown (AG) and post-annealed (PA) samples were thirdly sintered at 1300 °C (20 h) in air and at 1100 °C (20 h) in air, respectively. Our experiments reveal that preliminary sintering in oxygen atmosphere is favorable for purifying Mn-doped samples. The TEM specimen was prepared by crushing the sample in ethanol and then supporting the fragments on the carbon-film coated cooper grid. Our TEM observations were performed on a Tecnai F20 electron microscope.

III. RESULTS AND DISCUSSION

In Fe-doped samples, we discovered a structural phase separation in AG BTF17, a non-modulated phase exhibiting the similar structural feature to hexagonal BaTiO₃ and a modulated phase, in which Vos appear only at O1 site and simultaneous O1 and O2 sites, respectively.¹⁷ The structural phase separation is also observed in AG BTM05, but the doping content decreases to $x = 1/18$. As is known, the SIMs in the doped system are characterized by the satellite spots appearing around the fundamental reflections. Figure 1(a) shows the ED pattern of PA BTM11 along [001] direction, and typical reflection spots along this direction for AG BTM05, AG BTM11, AG BTM17, PA BTM17, AG BTF17, PA BTF17, AG BTF33 and PA BTF33 are presented in Figs. 1(b)–1(i), respectively. We can see clearly from these reflection spots that the SIMs have two features: (a) the direction where the satellite spots locate deviates from the reciprocal vector of $\mathbf{g}_{(100)}$; (b) the satellite spots around the fundamental reflections split into two parts. For some samples, their splitting angle is evident and the modulation wavelengths can be defined as λ_1 and λ_2 , e.g., in AG BTM11, AG BTM17 and PA BTF33; while for other samples, the satellite spots almost overlap and the corresponding modulation wavelengths are almost the same ($\lambda_1 \approx \lambda_2$). Meanwhile, similar modulation characters can also be observed along $[20\bar{1}]$ or other directions, and deviation of the modulation direction from the adjacent reciprocal vector and splitting of the satellite spots prevails in the doped system.¹⁰ Figs. 1(j) and 1(k) are the ED patterns of PA BTM11 and AG BTM11 along $[20\bar{1}]$ direction and the variation of the modulation characters caused by post annealing can be clearly seen. What worth noting is that such modulation characters were not observed along $\langle 100 \rangle$ directions in all the Mn- and Fe-doped samples, except for the additional reflections appearing between two fundamental reflection rows in PA BTM17 (see Fig. 1(m)).¹⁶

With respect to the origin of the satellite spots, planar defects such as stacking faults, linear defects such as dislocations and regular arrays of crystal defects such as APBs are possible reasons for their presence in a matrix.¹⁸ The diffraction characteristics of the doped system indicates that the APBs mainly account for the SIMs.¹⁰ Through calculating the multiple of the modulation wavelength (λ) observed along [001] direction with respect to the crystal planar spacing $d_{(100)}$, three types of APBs are outlined here (see Table I). For the first type, λ is about integral multiple of $d_{(100)}$ and most samples such as AG BTM05, AG BTM17, PA BTF17 and PA BTF33 belong to this group. For the second type, λ is about integral plus a half multiple of $d_{(100)}$ and only partial modulations in AG BTM11 and PA BTM17 belong to this category. For the third type, λ is about integral plus one third or two thirds multiple of $d_{(100)}$, the modulations in PA BTM11, AG BTF17 and AG BTF33 show such features. In addition, Fe-doped samples tend to show one type of modulations, while Mn-doped

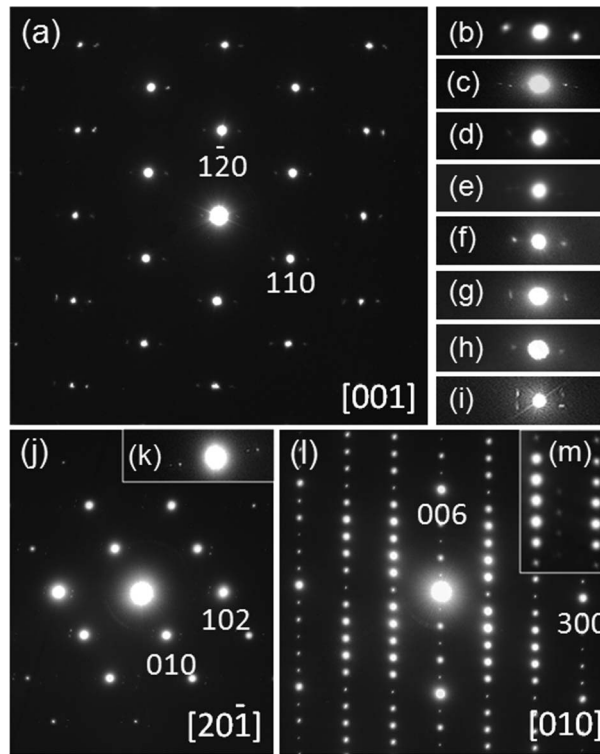


FIG. 1. (a) The ED pattern of PA BTM11 along [001] direction. (b)-(i) Typical reflection spots of AG BTM05, AG BTM11, AG BTM17, PA BTM17, AG BTF17, PA BTF17, AG BTF33 and PA BTF33, respectively, along [001] direction. (j) The ED pattern of PA BTM11 along [201] direction, the insert (k) is the typical reflection spots of AG BTM11 along [201]. (l) The ED pattern of PA BTM11 along [010] direction, the insert (m) is partial reflection spots of PA BTM17 along [010] direction.

TABLE I. The modulation parameters along [001] direction and calculated V_{os} based on the APB models in Mn- and Fe-doped hexagonal BaTiO₃.

Sample	Mn05 _A	Mn11 _A	Mn11 _P	Mn17 _A	Mn17 _P	Fe17 _A	Fe17 _P	Fe33 _A	Fe33 _P
λ_1/nm	1.05	1.30	1.37	1.55	1.23	1.66	2.94	1.64	3.06
λ_2/nm	1.05	1.00	1.37	1.04	1.68	1.66	2.94	1.64	3.06
Multiple	2.12	2.62	2.75	3.13	2.48	3.35	2.97	3.32	3.07
of $d_{(100)}$	2.12	2.02	2.75	2.10	3.39	3.35	2.97	3.32	3.07
V_{O1}	0.019	0.037	0.057	0.056	0.072	0.089	0.056	0.145	0.111
V_{O2}	0.157	0.104	0.040	0.133	0.031	0.017	0.112	0.017	0.109

Note: A and P are short for AG and PA, respectively.

samples tend to show mixed types. The differences in the modulation characters may attribute to different magnetic and electrical properties of the different dopant doped samples.

According to the different modulation relationships, corresponding APB models are proposed based on the ideal structure of hexagonal BaTiO₃ (see Fig. 2). For the first type, one domain vertically shifts $c/2$ relative to the other domain, but the horizontal shift is either none or $b/2$ (a , b and c are the lattice parameters). Thus, as Figs. 2(a)–2(c) show, the displacement vector is either $\mathbf{R}_{1-1} = \frac{1}{2}[\mathbf{001}]$ or $\mathbf{R}_{1-2} = \frac{1}{2}[\mathbf{011}]$ and their vacancy content at O2 site is $V_{O2} = m/6N$ per unit cell (m and N are respectively the numbers of boundary planes and unit cells in one domain). For these two cases, the Ti2-centered octahedra need a reconstruction (Fig. 2(b)) or they are edge-connected through an O2-O2edge (Fig. 2(c)). For the second type, the APB derives from a vertical shift of $c/3$ or $2c/3$ of one domain along [001] direction associated with a horizontal shift in a - b plane. Correspondingly, the Ti2-centered octahedra are corner-connected through the O2 atoms and their displacement vectors

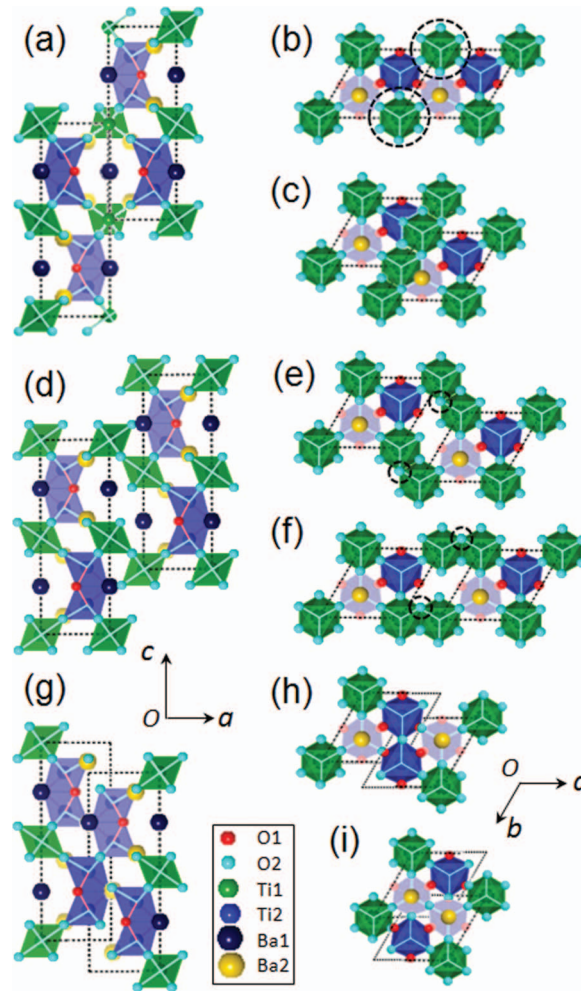


FIG. 2. The APB models illustrated along $[010]$ (the left side) and $[001]$ (the right side) directions. (a),(b) APB with displacement vector of $\mathbf{R}_{I-1} = 1/2[0\ 0\ 1]$, the dash black circles indicate the reconstructed octahedra. (c) The APB for $\mathbf{R}_{I-2} = 1/2[0\ 1\ 1]$. (d)-(f) The APB with displacement vectors of $\mathbf{R}_{II-1} = 1/6[3\ 3\ n]$ and $\mathbf{R}_{II-2} = 1/6[3\ 0\ n]$ (integer $n = 2, 4$), the corner sharing O2 atoms are marked out by the dash black circle. (g),(h) The APB with displacement vector of $\mathbf{R}_{III-1} = 1/6[\bar{2}2\bar{1}]$, (i) the APB for $\mathbf{R}_{III-2} = 1/6[\bar{4}4\bar{1}]$.

are $\mathbf{R}_{II-1} = 1/6[3\ 3\ n]$ and $\mathbf{R}_{II-2} = 1/6[3\ 0\ n]$ (integer $n = 2, 4$), respectively. Their vacancy content at O2 site is $V_{O2} = m/18N$ per unit cell, which is one third of the above-mentioned type (see Figs. 2(d)–2(f)). For the last type, formation of the APB is the most complex since partial O1 and O2 atoms need to share some atomic sites. For the integral plus two thirds multiple, the displacement vector of $\mathbf{R}_{III-1} = 1/6[\bar{2}2\bar{1}]$ is formed through a vertical shift of $c/6$ along $[00\bar{1}]$ combining with horizontal shifts of $-a/3$ and $b/3$; while for the integral plus one third multiple, the displacement vector $\mathbf{R}_{III-2} = 1/6[\bar{4}4\bar{1}]$ is formed in a similar way. Their corresponding vacancy contents are $V_{O1} = m/36N$, $V_{O2} = m/18N$ for the former and $V_{O1} = m/18N$, $V_{O2} = m/36N$ for the latter.

Before calculating the vacancy content resulting from the introduction of the dopants, two assumptions are reasonably made: (i) since Vos prefer to occupy O1 site in the doped system,^{13,14} all doped elements are assumed to occupy the Ti2 site. (ii) According to the reported results on Fe-doped samples,^{9,12} equivalent amounts of Ti2 ions to the dopants are assumed to be reduced into trivalent state. We find that the vacancy content derived from our APB models qualitatively agrees quite well with our previous XRD refinement results based on the two assumptions (see Table I and Ref. 17). Considering the modulation characteristics of the doped system, the splitting or none splitting satellite spots generally locate along one direction in the reciprocal

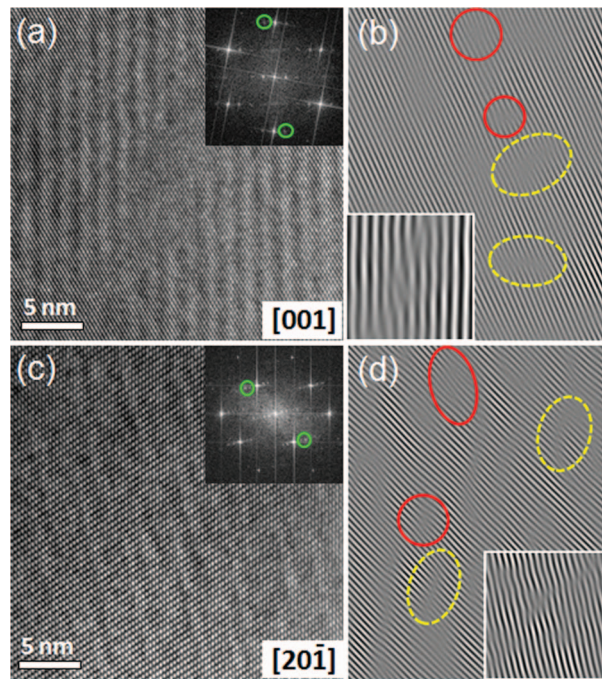


FIG. 3. (a) (c) The HRTEM images of PA BTM11 along $[001]$ and $[20\bar{1}]$ directions, their inserts are the corresponding FFT images, respectively. (b)(d) The filtered images of (a) and (c) using the satellite spots around (120) and (010) reflections as indicated by the solid green circles in the inserts of (a) and (c), respectively. The inserts show their filtered images using the satellite spots around the transmitted beam, respectively. The solid red circles and the yellow dash circles indicate the dislocation and extended dislocation structures, respectively.

space, it is reasonable to assume that $m = 2$. Taking PA BTM17 as an example, the multiple of 2.48 from one modulation suggests that $V_{O2-1} = 1/9N$, while the multiple of 3.39 from the other modulation yields that $V_{O1-2} = 1/9N$ and $V_{O2-2} = 1/18N$. Supposing that the two modulations contribute equivalently to the vacancy content, therefore, the calculated results are $V_{O1} = 1/18 + V_{O1-2}/2 = 0.072$, $V_{O2} = V_{O2-2}/2 = 0.031$. The XRD refinement results yield that $V_{O1} = 0.102$ and $V_{O2} = 0.050$.¹⁷

With respect to the relationship between the modulation wavelength and crystal spacing $d_{(102)}$, the same modulation rule is also observed along $[20\bar{1}]$ direction in both Mn- and Fe-doped samples, e.g., the multiple in AG BTM11 is $N_1 = 5.03$ and $N_2 = 3.99$, in PA BTF17 $N = 4.39$ and in PA BTF17 $N = 4.66$.¹⁰ The differences in the multiples along $[001]$ and $[20\bar{1}]$ directions suggest that the defect structures may possibly break the hexagonal lattice in the incommensurately modulated system, which is verified by our high-resolution transmission electron microscopy (HRTEM) results. Figure 3(a) shows the HRTEM image of PA BTM11 collected along $[001]$ direction, the APBs can clearly be seen both from the HRTEM image and the filtered image shown in the insert of Fig. 3(b). The image collected along $[20\bar{1}]$ direction shows similar characters (see Figs. 3(c) and 3(d)). Furthermore, as possible ends of the APBs, dislocations such as edge dislocation and extended dislocation are clearly seen from the filtered images which are obtained using the satellite spots around the fundamental reflections. In addition, distortion of the hexagonal matrix can also be identified through measuring the angles between $\{110\}$ reflections along $[001]$ direction. Therefore, our results point out that the SIMs result from a combination of APBs and dislocation structures. With respect to the deviation of the calculated vacancy content from the refinement results, this is mainly because of the imponderable vacancy content from the dislocation structures. In addition, the content ratios of Ti^{3+}/Ti^{4+} , Mn^{3+}/Mn^{4+} and Fe^{3+}/Fe^{4+} as well as their actual distribution at Ti1 and Ti2 sites also influence greatly to the vacancy concentration.

As for the purpose of post annealing in our experiments, previous studies have shown that physical properties of the doped system are very sensitive to thermal treatment conditions,^{17,19}

e.g., in 90% mol of Fe-doped BaTiO₃, different sintering routes lead to the formation of either hexagonal or monoclinic phase;¹⁷ compared with AG hexagonal Ba(Ti_{0.3}Fe_{0.7})O_{3-δ}, post annealing in oxygen atmosphere results in the transformation from near-paramagnetism to FM owing to the presence of Fe⁴⁺ ions.^{16,19} Generally, changes of the physical property of the doped system is determined by the concentration and distribution changes of Vos and valence state changes of the transition metals. First-principles calculation on hexagonal BaTiO₃ has predicted that O1 vacancy is more stable than O2 vacancy,²⁰ this is consistent with our experimental result, i.e., the vacancy content at O1 site is more than that at O2 site in AG Fe-doped samples. However, along with the changes of modulation type, such a distribution law is reversed as the samples are post annealed (see Table I). Subsequently, magnetization of samples with displacement vectors of R_{1-1} and R_{1-2} is greatly reduced; while weak ferroelectricity comes into being owing to spatial inversion symmetry breaking of the hexagonal matrix.^{9,10} Concerning the structure changes in Mn-doped samples, our results reveal that the vacancy content at O1 site is less than that at O2 site in the AG samples, but post annealing results in the reversal of the distribution law. More interesting results about the magnetic and electrical property of both AG and PA Mn-doped samples and the influence of SIM on their physical property will be elaborated elsewhere.

IV. CONCLUSIONS

In conclusion, our systematic analysis on the ED patterns of both Mn- and Fe-doped hexagonal BaTiO₃ samples reveals that the SIMs are dominated by three types of APBs, and appearance of the complex dislocation structures also plays an important role in the formation of the modulations. According to the proposed APB models, our calculated oxygen vacancy content qualitatively agrees quite well with our previous XRD refinement results. Our results may provide us an effective approach in understanding the physical property changes as a function of the content and category of the dopant in this doped system.

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- ¹ N. A. Hill, *J. Phys. Chem. B* **104**, 6694 (2000).
- ² B. Xu, K. Yin, J. Lin, Y. Xia, X. Wan, J. Yin, X. Bai, J. Du, and Z. Liu, *Phys. Rev. B* **79**, 134109 (2009).
- ³ R. Maier, J. L. Cohn, J. J. Neumeier, and L. A. Bendersky, *Appl. Phys. Lett.* **78**, 2536 (2001).
- ⁴ Y. H. Lin, J. C. Yuan, S. Y. Zhang, Y. Zhang, J. Liu, Y. Wang, and C. W. Nan, *Appl. Phys. Lett.* **95**, 033105 (2009).
- ⁵ Y. H. Lin, S. Y. Zhang, C. Y. Deng, Y. Zhang, X. H. Wang, and C. W. Nan, *Appl. Phys. Lett.* **92**, 112501 (2008).
- ⁶ V. R. Palkar and S. K. Malik, *Solid State Commun.* **134**, 783 (2005).
- ⁷ M. Kumar and K. L. Yadav, *J. Phys.: Condens. Matter* **19**, 242202 (2007).
- ⁸ M. Kumar and K. L. Yadav, *J. Appl. Phys.* **102**, 076107 (2007).
- ⁹ X. K. Wei, T. Zou, F. Wang, Q. H. Zhang, Y. Sun, L. Gu, A. Hirata, M. W. Chen, Y. Yao, C. Q. Jin, and R. C. Yu, *J. Appl. Phys.* **111**, 073904 (2012).
- ¹⁰ X. K. Wei, Y. T. Su, Y. Sui, Q. H. Zhang, Y. Yao, C. Q. Jin, and R. C. Yu, *J. Appl. Phys.* **110**, 114112 (2011).
- ¹¹ F. Lin, D. Jiang, X. Ma, and W. Shi, *J. Magn. Magn. Mater.* **320**, 691 (2008).
- ¹² T. Chakraborty, S. Ray, and M. Itoh, *Phys. Rev. B* **83**, 144407 (2011).
- ¹³ Ian E. Grey, Christina Li, Lachlan M. D. Cranswick, Robert S. Roth, and T. A. Vanderah, *J. Solid State Chem.* **315**, 312 (1998).
- ¹⁴ E. Mashkina, C. McCammon, and F. Seifert, *J. Solid State Chem.* **177**, 262 (2004).
- ¹⁵ N. V. Dang, H. M. Nguyen, P.-Y. Chuang, J.-H. Zhang, T. D. Thanh, C.-W. Hu, T.-Y. Chen, H.-D. Yang, V. D. Lam, C.-H. Lee, and L. V. Hong, *J. Appl. Phys.* **111**, 07D915 (2012).
- ¹⁶ X. K. Wei, L. D. Yao, X. Shen, Y. Yang, S. J. You, F. Y. Li, C. Q. Jin, and R. C. Yu, *Physica B: Condens. Matter* **405**, 4851 (2010).
- ¹⁷ X. K. Wei, Q. H. Zhang, F. Y. Li, C. Q. Jin, and R. C. Yu, *J. Alloys Compd.* **508**, 486 (2010).
- ¹⁸ J. W. Edington, *Electron Diffraction in the Electron Microscope* (Macmillan, 1975).
- ¹⁹ F. Lin, D. Jiang, X. Ma, and W. Shi, *Physica B: Condensed Matter* **403**, 2525 (2008).
- ²⁰ T. Colson, M. Spencer, and I. Yarovsky, *Comput. Mater. Sci.* **34**, 157 (2005).