Modulation of magnetic properties and enhanced magnetoelectric effects in $MnW_{1-x}Mo_xO_4$ compounds*

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In this letter, we investigate the magnetic and ferroelectric properties of polycrystalline $MnW_{1-x}Mo_xO_4$ ($x = 0$, 0.05, 0.10, 0.20) compounds. The substitution of nonmagnetic Mo^{6+} ions for W^{6+} ions modifies the magnetic transition temperatures of $MnW_{1-x}Mo_xO_4$ by changing the Mn–O–Mn bond. As a result, distinct ferroelectric properties and enhanced magnetoelectric effects are observed in Mo^{6+}-doped $MnWO_4$ compounds. The effects of substitution of Mo^{6+} ions on magnetic properties and magnetoelectric coupling are discussed.

Keywords: magnetism, ferroelectricity, magnetoelectric effects, multiferroic properties

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1. Introduction

Magnetoelectric multiferroics have attracted renewed interest due to the cross coupling between magnetic and ferroelectric orders as well as potential applications in magnetic sensors, multi-state memories, and spintronic devices, etc.[1–4] Recently, large magnetoelectric effects have been observed in so-called type-II multiferroics, in which ferroelectric polarization is induced by noncentrosymmetric magnetic order.[5,6] One of the common features in this type of multiferroics is that ferroelectric polarization arises from specific spin orders via spin-correlated mechanisms, in particular in noncollinear cycloidal spin order through the inverse Dzyaloshinskii–Mariya (DM) interaction mechanism or *E*-type antiferromagnetic order through the symmetric exchange striction.[6–10] In order to deeply understand the coupling mechanism and optimize magnetoelectric effects, the multiferroic properties of type-II multiferroics have been extensively studied by modifying their exchange interaction, since the magnetic structure plays a key role in determining the ferroelectric properties.[11–16]

Among these type-II multiferroics, $MnWO_4$ is a representative and well-studied compound.[14–20] The schematic structure of this compound is shown in Fig. 1(a). It is monoclinic with space group $P2/c$ and each unit cell includes two Mn^{2+} ions that are interconnected by edges of distorted MnO_6 octahedra, forming zigzag chains along the *c* axis. The W^{6+} ions stacking alternately along the *a* axis are also coordinated by oxygen octahedral, corners sharing with MnO_6 octahedral.[14–20] Besides, this compound shows a complicated magnetic structure, which is established out of competition and subtle balance among complicated multiple magnetic interactions. Upon cooling, $MnWO_4$ experiences three magnetic phase transitions (AF1, AF2, and AF3).[14–20] Below the Néel temperature of 13.5 K (T_{N3}), it shows a sinusoidal spin order with an incommensurate modulation and propagation vector $\boldsymbol{q}_3 = (-0.214,\ 0.5, 0.457)$, which is schematically plotted in Fig. 1(b). Further decreasing the temperature leads to the appearance of another AF2 phase with a spiral magnetic order at 12.6 K (T_{N2}). As shown in Fig. 1(c), the spins of AF2 tilt toward the *b* axis, forming a helix structure, while the propagation vector remains unchanged ($\boldsymbol{q}_2 = \boldsymbol{q}_3$). According to the model of spin-current or inverse DM interaction, ferroelectric polarization along the *b* axis can be obtained in this antiferromagnetic phase, which well demonstrates the strong correlation between the spiral magnetism and the ferroelectricity in $MnWO_4$.[6,20] At a lower temperature, about 7.8 K (T_{N1}), the collinear AF1 phase, which is characterized by a frustrated ↑↑↓↓ spin structure with the commensurate modulation vector $\boldsymbol{q}_1 = (\pm 0.25, 0.5, 0.5)$ is observed. In this phase, the Mn spins form an angle of about 35° with an axis lying in the *a*–*c* plane, as presented in Fig. 1(d). Since this spin configuration preserves the spatial inversion symmetry, the ground state of $MnWO_4$ below 7.8 K is paraelectric.[20] According to the earlier report, the exchange coupling of this material can be effectively altered by various approaches, leading to the modification of its multiferroic properties.[14–19,21–26] It is known that the helical AF2 phase of $MnWO_4$ is the origin of ferroelectricity.[20] Therefore, many efforts have been devoted to modulate the stability of the AF2 phase by substituting magnetic Mn ions.[23–25] For example, in $Mn_{1-x}Fe_xWO_4$, the multiferroic AF2 phase is gradually suppressed and the low-temperature AF1 phase is stabilized with the Fe content increasing. As a result, $Mn_{0.9}Fe_{0.1}WO_4$ shows paraelectric

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behavior in zero magnetic fields at all temperature ranges and its ferroelectricity could be induced by a magnetic field above 4.0 T.[23] However, in the case of Zn-doped $MnWO_4$, the AF1 transition temperature quickly shifts to lower temperature with increasing the doping content and only 5% of Zn ions is sufficient to suppress the collinear AF1 phase and stabilize the multiferroic AF2 phase as the ground state.[24] Interestingly, when Mn is replaced by Co, the AF2 phase would be stabilized by suppressing the AF1 phase at the proper substitution level. While at a higher Co doping level ($x \geq 0.05$), the magnetic phases would include several coexisting commensurate and incommensurate phases, leading to more complex multiferroic properties.[26] Up to now, there have been few reports about the investigation of multiferroic properties for the $MnWO_4$-based system in which W^{6+} ions are substituted.[17] In this letter, we synthesize a series of $MnW_{1-x}Mo_xO_4$ ($x = 0$, 0.05, 0.1, 0.2) compounds and study their magnetic, ferroelectric, and magnetoelectric coupling properties. Since the AF2 structure can be easily affected by an external magnetic field, a pronounced magnetoelectric effect is observed in $MnW_{1-x}Mo_xO_4$ compounds.

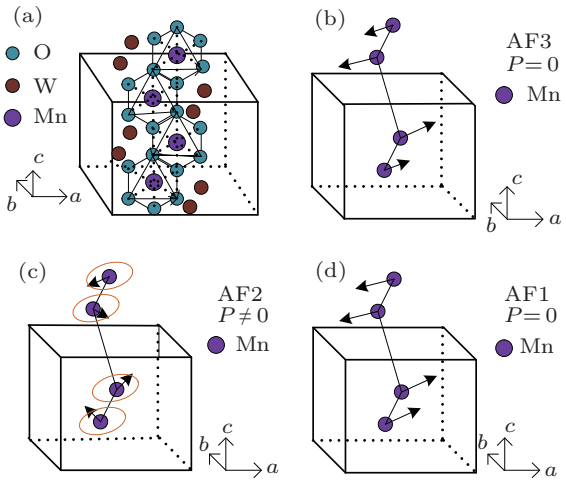


Fig. 1. (color online) Schematic images of crystal and magnetic structures of $MnWO_4$; (a) the crystal structure of $MnWO_4$; (b) spin structure of the AF3 phase with a sinusoidal spin order; (c) spin structure of the AF2 phase with a helical structure; (d) spin structure of the AF1 phase with a frustrated ↑↑↓↓ spin structure.

2. Experiments

The polycrystalline compounds $MnW_{1-x}Mo_xO_4$ were prepared by conventional solid state reactions. Stoichiometric amounts of high-purity WO_3, MoO_3, and MnO were chosen as the raw materials and thoroughly ball-milled for 24 h. Then the mixture was carefully grounded and then annealed in air at 873 K for 12 h. After intermediate grinding and sintering at 873 K for 12 h again, the powder was compressed to pellets and annealed at 1223 K for 20 h in air followed by cooling down to room temperature. The structures of the as-prepared samples were checked using X-ray diffraction equipped with Cu $K\alpha$ radiation at room temperature. The temperature dependence of the magnetization (M–T) was measured by a superconducting quantum interference device (SQUID, Quantum Design). The ferroelectric polarization as a function of the temperature was obtained by integrating the pyroelectric current, which was recorded with a Keithley 6514 connected to a physical property measurement system (PPMS, Quantum Design).

3. Results and discussion

Figure 2(a) shows the room-temperature powder X-ray diffraction pattern and Rietveld refinement for $MnWO_4$. The structural refinement data (Table 1) indicate that the polycrystalline $MnWO_4$ is crystallized in a wolframite-type monoclinic structure with a space group ($P2/c$). The XRD patterns of $MnW_{1-x}Mo_xO_4$ compounds are shown in Fig. 2(b), indicating that the samples are well crystallized and no impurity phase can be detected within the apparatus resolution. Due to the slight difference of ionic radius between Mo^{6+} (0.59 Å) and W^{6+} (0.60 Å),[27] there are no obvious peaks shifting shown in the inset of Fig. 2, suggesting that the pristine crystal structure is almost unchanged with the substitution of Mo^{6+} ions.

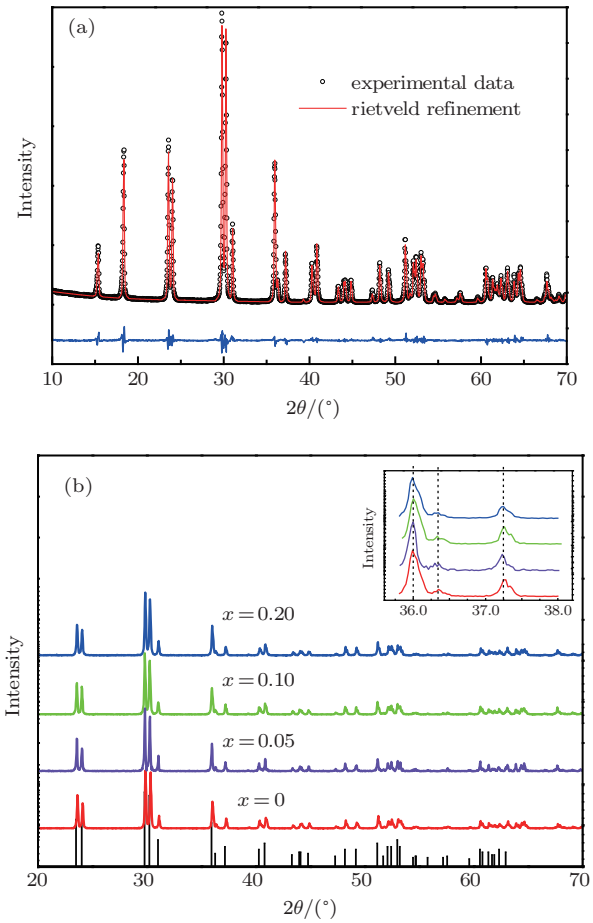


Fig. 2. (color online) (a) The room-temperature powder X-ray diffraction pattern and Rietveld refinement for $MnWO_4$; (b) XRD patterns for $MnW_{1-x}Mo_xO_4$ compounds measured at room temperature. The inset shows the amplified local data for (002) and (200) reflections.

Table 1. Lattice parameters, unit cell volume, atomic coordinates, and site occupation obtained by Rietveld refinement data for the polycrystalline $MnWO_4$. Here, $a = 4.82535(7)$, $b = 5.75353(8)$, $c = 4.99285(7)$, $\alpha = 90°$, $\beta = 91.1561(13)°$, $\gamma = 90°$, $V = 138.5772(32)$, $W_{wp} = 7.85\%$, and $R_p = 6.19\%$.

Atom	Wyckoff	Site	x	y	z
Mn	2f	2	0.500000	0.6870(4)	0.250000
W	2e	2	0.000000	0.18016(16)	0.250000
O1	4g	1	0.2107(11)	0.1045(10)	0.9517(14)
O2	4g	1	0.2526(11)	0.3537(11)	0.3844(14)

Figure 3 shows the M–T curves at 0.1 T for $MnW_{1-x}Mo_xO_4$ compounds in both zero-field-cooling (ZFC) and field-cooling (FC) modes. As shown in Fig. 3(a), there is little difference between the ZFC and FC curves of $MnWO_4$. However, in the case of Mo-doped compounds (Figs. 3(b)–3(d)), a remarkable magnetization separation between the ZFC and FC curves is observed below about 12 K, suggesting that the low-temperature spin structure becomes more flexible with the substitution of Mo^{6+} ions. Moreover, it is worth noting that not only the values of magnetization but also the transition temperatures of the AF phases vary with the increase of Mo content, which indicates that the magnetic interaction has been changed in $MnW_{1-x}Mo_xO_4$ compounds. As mentioned above, earlier reports about the doped $MnWO_4$ system mainly focuses on magnetic or nonmagnetic 3d-transition metal ions, which modify the magnetic interaction by different magnetic moments or ionic radius with respect to Mn ions.[14–16,21–24] In the present compounds, both W^{6+} and Mo^{6+} ions have the same nonmagnetic d^0 configuration and almost the same ionic radius, except that there is a certain difference of electronegativity between W^{6+} (2.36) and Mo^{6+} (2.16) ions due to the different charge distribution of 4d and 5d ions.[25,28] Since the Mo–O bond is more ionic than the W–O bond, the Mn–O bond would become more covalent according to the inductive effect.[17,29,30] Besides, the slight difference of the radius between the W^{6+} and Mo^{6+} ions would make a perturbation on the Mn–O–Mn bond and modify the magnetic properties. Therefore, the strength of the super-exchange interaction of Mn–O–Mn is modified with Mo doping, leading to the change of magnetic interaction in $MnW_{1-x}Mo_xO_4$ compounds.

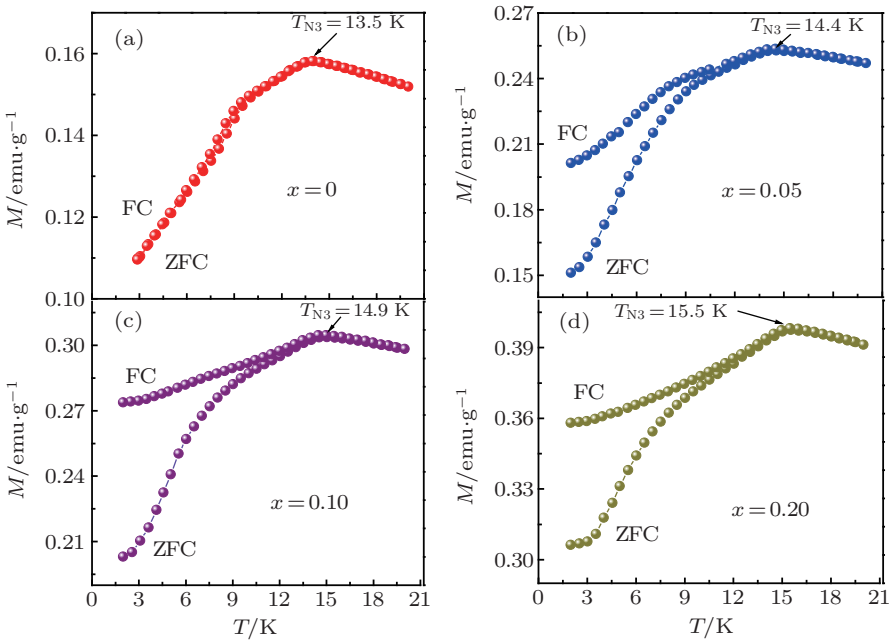


Fig. 3. (color online) The temperature dependence of magnetization for $MnW_{1-x}Mo_xO_4$ compounds in the ZFC and FC modes under 0.1 T. (a) $x = 0$; (b) $x = 0.05$; (c) $x = 0.10$; (d) $x = 0.20$.

Owing to intrinsic coupling between magnetic and ferroelectric properties in type-II multiferroics, the ferroelectric polarization of $MnW_{1-x}Mo_xO_4$ compounds would be changed with variation of magnetic structures. Figures 4(a)–4(d) plot the temperature dependence of the pyroelectric current (I–T) of the compounds for $x = 0$, 0.05, 0.1, 0.2, respectively. In order to show the inherent relation between magnetic and ferroelectric orders, the ZFC M–T curves for the compounds are also presented. Before measurement, the samples are cooled down to 2 K in a poling field of 1 MV/m. Then, the poling field is removed. After short-circuiting for a sufficiently long time, the pyroelectric current is collected upon heating from 2 K to 20 K with a warming rate of 3 K/min. Since the domain states in the ferroelectric phase are memorized even in the nonpolar phase with a collinear spin configuration,[31] we can cool down the sample to the AF1 paraelectric phase in an electric field and measure the pyroelectric current from 2 K. In the case of $MnWO_4$, the peak of the pyroelectric current is

observed just at 12.6 K (T_{N2}), which is consistent with the earlier reports.[20] As for $MnW_{0.95}Mo_{0.05}O_4$, a similar I–T curve is observed except at a higher transition temperature of the ferroelectric phase (13.0 K), suggesting that the AF2 phase is stabilized with the substitution of Mo^{6+} ions. As shown in Fig. 4(c), the pyroelectric current of $MnW_{0.9}Mo_{0.1}O_4$ peaks at 14.4 K and does not disappear until 2 K, indicating that the ferroelectric phase regime has been greatly extended. It is obvious that the magnitude of the pyroelectric current decreases sharply with $x = 0.1$ and reduces to almost zero when twenty percent of Mo^{6+} ions are introduced. Therefore, due to the limit of apparatus resolution, the corresponding relationship between the magnetic and the ferroelectric phases cannot be observed from Fig. 4(d).

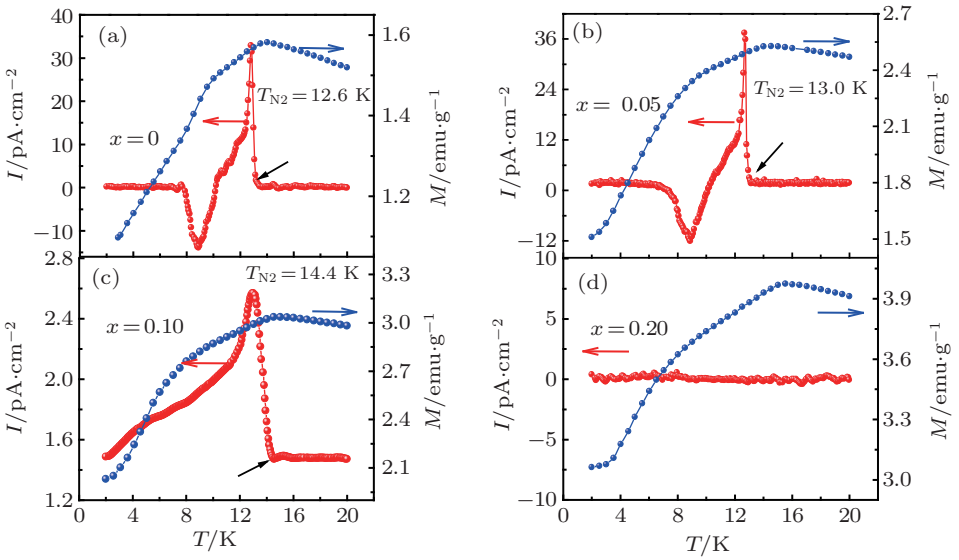


Fig. 4. (color online) The temperature dependence of pyroelectric current for $MnW_{1-x}Mo_xO_4$ compounds. (a) $x = 0$; (b) $x = 0.05$; (c) $x = 0.10$; (d) $x = 0.20$.

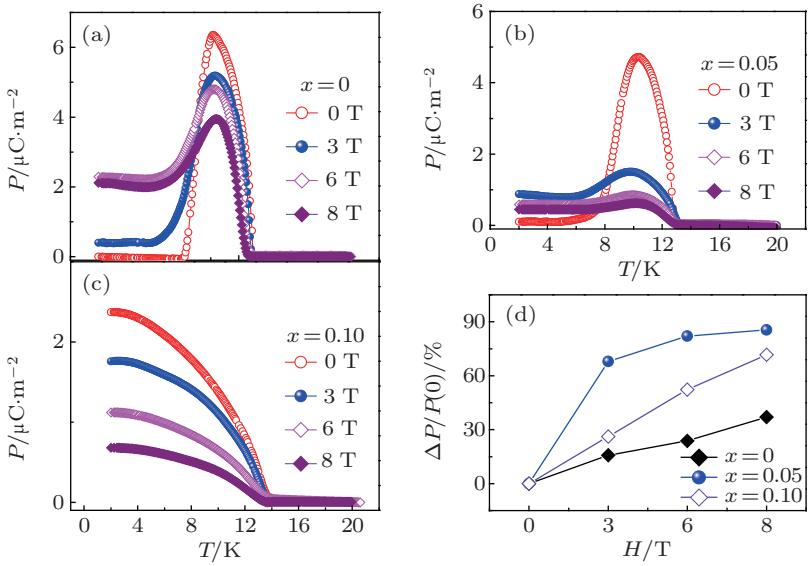


Fig. 5. (color online) (a)–(c) Ferroelectric polarization as a function of temperature under various magnetic fields for the samples with $x = 0$, 0.05, 0.10, respectively; (d) the magnetic field dependence of magnetoelectric susceptibility for $MnW_{1-x}Mo_xO_4$ compounds at the ferroelectric polarization peak temperature.

Figures 5(a)–5(c) show the temperature dependence of ferroelectric polarization (P–T) under various magnetic fields, where the ferroelectric polarization is calculated by integrating the pyroelectric current. Consistent with the earlier report, in parent phase $MnWO_4$, ferroelectric polarization can be observed only within the AF2 phase between T_{N1} and T_{N2}.[20] By applying an external magnetic field, the magnetic and ferroelectric behaviors vary correspondingly. As shown in

Fig. 5(a), T_{N1} decreases with the increase of the magnetic field and the ferroelectric polarization around it increases, which suggest that the ferroelectric AF2 phase begins to extend to the paraelectric AF1 phase.[25] On the other hand, the ferroelectric polarization in the vicinity of T_{N2} decreases with the magnetic field increasing. This phenomenon could be understood by the spin-current model ($P \propto r_{ij} \times (S_i \times S_j)$, where S_i and S_j are two adjacent spins along the propagation direction r_{ij}) in which the magnitude of ferroelectric polarization is related to the angle between the two adjacent spins.[6,7] For the AF2 phase, an applied magnetic field would modify the angle between the two neighboring spins, leading to the change of ferroelectric polarization. As for $MnW_{0.95}Mo_{0.05}O_4$, a similar P–T curve is observed but the value of ferroelectric polarization decreases more sharply with applying the magnetic field, which is shown in Fig. 5(b). However, in the case of $x = 0.1$, the substitution of Mo ions has led to the replacement of the AF2 phase for the AF1 phase in the measured temperature range (2 K–14 K) and the suppression of ferroelectric polarization by the external magnetic field is observed as well. Figure 5(d) shows the magnetic field dependence of magnetoelectric susceptibility α ($\alpha = \Delta P/\Delta H$, $\Delta P = P(0) - P(H)$) for $MnW_{1-x}Mo_xO_4$ compounds at the ferroelectric polarization peak temperature. It is evident that the values of α under each field are obviously enhanced in Mo-doped $MnWO_4$ with respect to the pristine phase. As mentioned before, the ferroelectric polarization in Mo-doped $MnWO_4$ compounds originates from its special spin configuration, which is more sensitive to the applied magnetic field due to the modification of the Mn–O–Mn bond. Since the intimate coupling between the magnetism and the ferroelectricity, the ferroelectric polarization can be more easily modified by a magnetic field for the compounds with $x = 0.05$ and 0.1, showing an enhanced magnetoelectric effect.

4. Conclusion

In summary, the magnetic and magnetoelectric properties are investigated in a series of doped $MnWO_4$ compounds. With substitution of Mo^{6+} ions for W^{6+} ions, the AF2 phase tends to extend to the AF1 phase and T_{N2} increases as well. Due to the inherent coupling between ferroelectricity and magnetism, the ferroelectric properties of Mo-doped $MnWO_4$ compounds change correspondingly. Since the modified spin structure in the $MnW_{1-x}Mo_xO_4$ compound is more sensitive with the external magnetic field, an enhanced magnetoelectric effect is observed in these multiferroics.

References

[1] Scott J F 2007 *Science* **315** 954
[2] Spaldin N A and Fiebig M 2005 *Science* **309** 391
[3] Eerenstein W, Mathur N D and Scott J F 2006 *Nature* **442** 759
[4] Béa H, Gajek M, Bibes M and Barthélémy A 2008 *J. Phys.: Condens. Matter* **20** 434221
[5] Khomskii D 2009 *Physics* **2** 20
[6] Tokura Y and Seki S 2010 *Adv. Mater.* **22** 1554
[7] Katsura H, Nagaosa N and Balatsky A V 2005 *Phys. Rev. Lett.* **95** 057205
[8] Mostovoy M 2006 *Phys. Rev. Lett.* **96** 067601
[9] Sergienko I A, Sen C and Dagotto E 2006 *Phys. Rev. Lett.* **97** 227204
[10] Picozzi S, Yamauchi K, Sanyal B, Sergienko I A and Dagotto E 2007 *Phys. Rev. Lett.* **99** 227201
[11] Liu R D, Liu Y T, Chen D F, He L H, Yan L Q, Wang Z C, Sun Y and Wang F W 2013 *Chin. Phys. B* **22** 027507
[12] Hayashi K, Fukatsu R, Nozaki T, Miyazaki Y and Kajitani T 2013 *Phys. Rev. B* **87** 064418
[13] Magesh J, Murugavel P, Mangalam R V K, Singh K, Simon C and Prellier W 2012 *Appl. Phys. Lett.* **101** 022902
[14] Chaudhury R P, Lorenz B, Wang Y Q, Sun Y Y and Chu C W 2008 *J. Appl. Phys.* **103** 07E312
[15] Liang K C, Wang Y Q, Sun Y Y, Lorenz B, Ye F, Fernandez-Baca J A, Mook H A and Chu C W 2012 *New J. Phys.* **14** 073028
[16] Yan L Q, Lee B, Chun S H, Kim I, Chung J H, Kim S B, Park J Y, Lee S H, Chai Y S and Kim K H 2013 *J. Phys. Soc. Jpn.* **82** 094708
[17] Meddar L, Josse M, Maglione M, Guiet A, La C, Deniard P, Decourt R, Lee C, Tian C, Jobic S, Whangbo M H and Payen C 2012 *Chem. Mater.* **24** 353
[18] Song Y S, Yan L Q, Lee B, Chun S H, Kim K H, Kim S B, Nogami A, Katsufuji T, Schefer J and Chung J H 2010 *Phys. Rev. B* **82** 214418
[19] Chaudhury R P, Yen F, dela Cruz C R, Lorenz B, Wang Y Q, Sun Y Y and Chu C W 2008 *Physica B* **403** 1428
[20] Arkenbout A H, Palstra T T M, Siegrist T and Kimura T 2006 *Phys. Rev. B* **74** 184431
[21] Chaudhury R P, Lorenz B, Wang Y Q, Sun Y Y, Chu C W, Ye F, Fernandez-Baca J, Mook H and Lynn J 2009 *J. Appl. Phys.* **105** 07D913
[22] Liang K C, Chaudhury R P, Wang Y Q, Sun Y Y, Lorenz B and Chu C W 2012 *J. Appl. Phys.* **111** 07D903
[23] Chaudhury R P, Lorenz B, Wang Y Q, Sun Y Y and Chu C W 2008 *Phys. Rev. B* **77** 104406
[24] Chaudhury R P, Ye F, Fernandez-Baca J A, Lorenz B, Wang Y Q, Sun Y Y, Mook H A and Chu C W 2011 *Phys. Rev. B* **83** 014401
[25] Yu H W, Liu M F, Li X, Li L, Lin L, Yan Z B and Liu J M 2013 *Phys. Rev. B* **87** 104404
[26] Song Y S, Chung J H, Park J M S and Choi Y N 2009 *Phys. Rev. B* **79** 224415
[27] Marrero-Lopez D, Canales-Vazquez J, Ruiz-Morales J C, Irvine J T S and Nunez P 2005 *Electrochim. Acta* **50** 4385
[28] Fang S S, Xiao X, Lei X, Li W H and Dong Y D 2003 *J. Non-Cryst. Solids* **321** 120
[29] Etourneau J, Portier J and Ménil F 1992 *J. Alloys Compd.* **188** 1
[30] Gauthier G, Jobic S, Boucher F, Macaudi'ere P, Huguenin D, Rouxel J and Brec R 1998 *Chem. Mater.* **10** 2341
[31] Taniguchi K, Abe N, Ohtani S and Arima T 2009 *Phys. Rev. Lett.* **102** 147201