PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

PCCP RSCPublishing

COMMUNICATION

Zero Thermal Expansion in $NaZn_{13}$-Type $La(Fe, Si)_{13}$ Compounds

Cite this: DOI: 10.1039/x0xx00000x

Wei Wang,[a] Rongjin Huang, [*a] Wen Li, [a,b] Jie Tan, [a,b] Yuqiang Zhao, [a,b] Shaopeng Li, [a,b] Chuanjun Huang, [a] and Laifeng Li[*a]

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/pccp

A zero thermal expansion material in a pure form of $NaZn_{13}$-type $La(Fe, Si)_{13}$ was fabricated. Through optimizing the chemical composition, isotropic zero thermal expansion is achieved. The obtained materials exhibit a low expansion of $|\alpha| < 1.0\times10^{-6}$ K^{-1} (α is the coefficient of linear thermal expansion) over a broad temperature range(15-150 K). The present study indicated that the thermal expansion behavior of the $NaZn_{13}$-Type $La(Fe, Si)_{13}$ Compounds depended mainly on content of Si element. This new material is desirable for many fields of industry as reliable and low-cost zero thermal expansion material.

As a particular type of functional materials, zero thermal expansion (ZTE) materials have attracted considerable interest because of their very low coefficient of thermal expansion (CTE). Thus, ZTE materials are desired in many fields of precision engineering, including machining and processing, optics, electronics and so on, which need the CTE can be as low as possible. [1]

One method to achieve ZTE materials is to combine normal materials showing a positive thermal expansion (PTE) with special materials displaying a negative thermal expansion (NTE). Therefore, NTE materials have significant practical value as thermal-expansion compensators.[2, 3] Nevertheless, in such ZTE composites, one ingredient expands while the other contracts when the temperature changes. In consequence, the induced thermal stress at interfaces or grain boundaries can cause micro-fracture, which would impact the mechanical properties more or less. However, this micro-cracking problem can be overcome if the material is formed by one homogeneous material. Definitely, such an ideal pure-form ZTE material is highly desired.[2, 4, 5]

Up to now, besides several materials such as Invar alloys,[6] Fe[Co(CN)6],[7] YbGaGe,[8] $(Al_{2x}(HfMg)_{1-x})(WO_4)$,[3,5] $PbTio_3$-based compounds,[9-12,] ScF_3-based compounds,[13] fused silica, $LiAlSiO_4$,[1] TaO_2F[14,15] and antiperovskite manganese nitride,[4, 16] very few materials exhibit the novel ZTE. Moreover, the ZTE behavior of most materials generally appears in a narrow temperature range. And there are few reports on ZTE for low-temperature applications. In fact, low-temperature NTE materials have wide potential applications in micro-electromechanical systems in space and superconducting magnets such as low heat leak cryogenic valve, piston/piston sleeve of refrigerator, and carrying construction of superconducting magnet. So the new material with ZTE behavior over a wider temperature range would be very useful for the applications.

The $La(Fe,Si)_{13}$-based compounds have been studied extensively for exploring excellent magnetocaloric effect (MCE)[17-19] and attempting to realize the potential applications in magnetic refrigeration. Recently, the $La(Fe, Si)_{13}$-based compound have been considered as new NTE materials due to the large, isotropic and non-hysteretic NTE properties as well as relatively high electrical and thermal conductivity.[20]

The NTE property of the $La(Fe,Si)_{13}$-based compounds is triggered by the large magnetovolume effect (MVE). In the $La(Fe,Si)_{13}$-based compounds with the $NaZn_{13}$-type crystal structure, as shown in the Figure 1, Fe atoms occupy two nonequivalent sites,

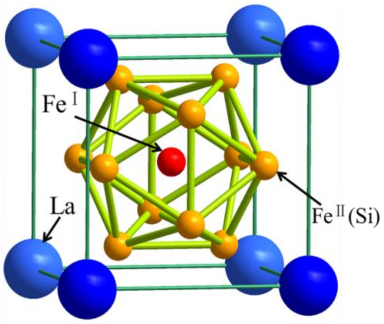

Fig. 1. $NaZn_{13}$-type structure (space group Fm3c) of the $La(Fe, Si)_{13}$-based compounds.

---

[a] *Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, P.R. China.*
E-mail: huangrongjin@mail.ipc.ac.cn
E-mail: laifengli@mail.ipc.ac.cn
[b] *University of Chinese Academy of Sciences, Beijing, P.R. China.*

i.e., 8 b (Fe_I) and 9 6i (Fe_{II}), respecitively. The Fe_I atom is surrounded by an icosahedron with 12 Fe_{II} atoms, and the Fe_{II} atom has 1 Fe_I atom and 9 Fe_{II} atoms as the nearest neighbors.[21] Previous report had indicated that the Fe_I - Fe_{II} distance plays a critical role in exchanging energy. So the change of the Fe_I - Fe_{II} distance owing to substitutional or interstitial addition will affect the magnetic exchange interaction and finally, alter thermal expansion property. Moreover, it has been reported that the NTE operation-temperature window can be tuned by varying the magnetic transition temperature when the Fe is partially subsitituted by other element,[17] which absolutely enhances the practical applications of this NTE material.

Seldom work, however, has been reported that the La(Fe, $Si)_{13}$-based compounds can be further improved to be ZTE materials by appropriate substitution of elements. Herein we control the thermal expansion by optimizing the chemical composition to achieve La(Fe, $Si)_{13}$-based compounds with ZTE over a broad temperature range as well as large NTE coefficients.

Polycrystalline samples of $LaFe_{13\text{-}x}Si_x$ (x=1.5, 1.8, 2.1 and 2.4) were prepared in an arc melting furnace under a high purity argon atmosphere. The raw materials of Fe, Si and La were at least 99.9% pure. Button samples were melted four times and each time the buttons were turned over to ensure homogeneity during melting. The arc-melted ingots wrapped by Ta foils were sealed in a quartz tube filled with high purity argon gas, subsequently homogenized at 1050 ℃ for 30 days, and finally quenched quickly into ice water.

XRD measurements at ambient temperature were performed on the BRUKER D8-discover diffractometer with Cu Kα radiation (λ = 1.5406 Å, operation voltage 40 kV, current 40 mA).Data were collected within the range $20\,° < 2\theta < 80\,°$ with a 0.01 step size, with a counting time of 1 s per point in all cases. The Variable temperature XRD data were also collected on the BRUKER D8. The specimen was measured with the temperature range from 15K to 300K. At first, the specimen was cooled to 15K with 2K/min. And then it was heated to the definite temperature with 0.5K/min and keep the temperature for 10 minutes before testing to make it stable. The lattice constant was carefully calculated by JADE, using a cubic (Fm3c) model.[22] The error bar was smaller than 0.0001 Å, which is much smaller than 10^{-7} K^{-1} in α.

The specific heat and magnetic properties were measured with a Physical Property Measurement System (PPMS-14T, Quantum Design) equipped with AC Magnetometer System (ACMS) option and Heat Capacity (HC) option.

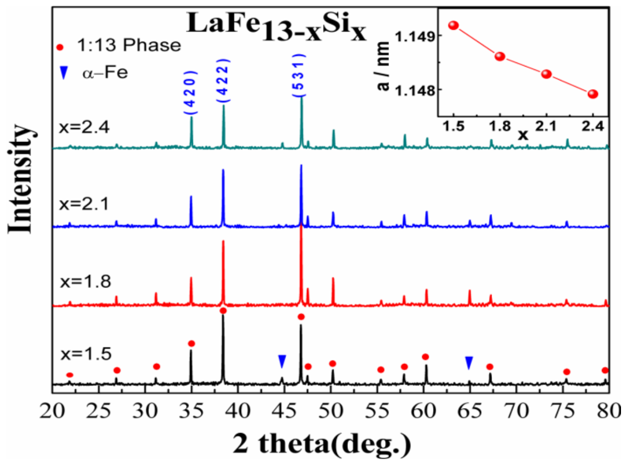

Fig. 2. X-ray diffraction patterns for samples of $LaFe_{13\text{-}x}Si_x$ (x=1.5, 1.8, 2.1 and 2.4) at room temperature. (Insert) Crystal lattice parameters as a function of Si concentration for samples of $LaFe_{13\text{-}x}Si_x$ (x=1.5, 1.8, 2.1, and 2.4) at room temperature.

Figure. 2 shows the X-ray diffraction patterns of the tested family of $LaFe_{13\text{-}x}Si_x$ (x=1.5, 1.8, 2.1 and 2.4) at ambient temperature and normal pressure. All the samples have a dominating phase with the $NaZn_{13}$-type structure (space group, (Fm3c). There are no visible diffraction peaks of pure elements and other second phases in the XRD diffraction patterns, except for the small amount of α-Fe detected as marked by the symbol ▼. The variation in lattice parameters with the increasing Si content is shown in Fig. 2(insert). It is obvious that the lattice parameter (a=1.1492, 1.1486, 1.1483 and 1.1479 nm severally) decreases with increasing Si content, i.e. the partly substitution of Si for Fe leads to a contraction of the lattice due to the smaller radius of Si than Fe atoms.

In order to determine the variation in the lattice parameter with temperature, i.e. the thermal expansion properties, in situ variable-temperature X-ray diffraction was performed. Figure 3 gives the linear thermal expansion data (Δa/a (300 K)) as a function of temperature for the $LaFe_{13-x}Si_x$ (x = 1.5, 1.8, 2.1, and 2.4). From this figure we can see that the values of Δa/a (300 K) increase with decreasing temperature at a certain temperature range, i.e., NTE occurs. It is noteworthy that the NTE properties are strongly affected by partial substitution of Si for Fe. And the temperature range of NTE behavior turns to broader and moves to lower temperature region with increasing the amount of Si from 1.5 to 2.4. For example, the width of pronounced NTE property for the $LaFe_{11.5}Si_{1.5}$ is about 100 K (150-250 K), while as the Si content increase to 2.4, the width of pronounced NTE property reaches as large as 150 K (150-300 K), which is about 50% larger than that of the $LaFe_{11.5}Si_{1.5}$. The average coefficient of thermal expansion is calculated to be -14.2×10^{-6} K^{-1} (150-300 K). The broadened NTE operation-temperature window indicates the significant effect of the partial substitution of Si for Fe.

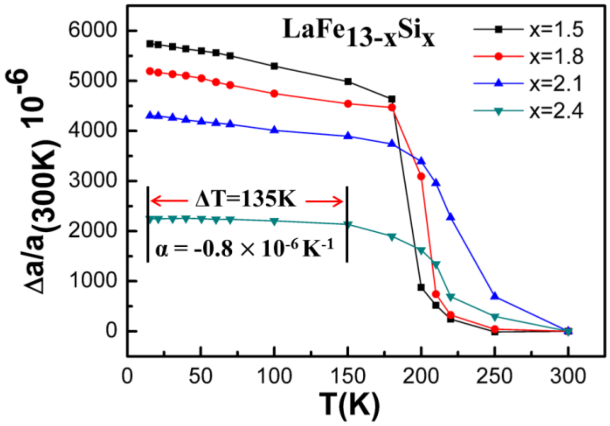

Fig. 3. Temperature dependence of linear thermal expansion Δa/a (reference temperature: 300K) for samples $LaFe_{13\text{-}x}Si_x$ (x=1.5, 1.8, 2.1 and 2.4).

Furthermore, as shown in Fig. 3, the most interesting feature is that the variation of Δa/a become smaller and smaller in the temperature range from 15 to 150 K with content of Si from 1.5 to 2.4. Apparently, further Si doping weakens the anomaly of the thermal expansion and eventually may restore a positive thermal expansion. Therefore, we assumed that optimizing the chemical composition may achieve ZTE behavior in a pure-form $LaFe_{13-x}Si_x$. Indeed the average CTEs of the $LaFe_{11.5}Si_{1.5}$ are -5.6×10^{-6} K^{-1} (15-150 K), while specifically, as the Si content reaches to 2.4, the volume nearly does not depend on a wide temperature fluctuation. From 150 to 15 K, the $LaFe_{10.6}Si_{2.4}$ exhibits a negligible volume change with an average CTEs of -0.8×10^{-6} K^{-1}. These values are smaller than that of Fe[Co(CN)$_6$] (-0.44 × 10^{-5} K^{-1})[7] and $PbTiO_3$-based compounds (-0.31 × 10^{-5} K^{-1})[10]. Obviously, it could be found that the Si dopant can successfully obtain ZTE materials. Compared with the previous La(Fe, Si)$_{13}$-based compounds with typical NTE property, there are two evident characteristics for the $LaFe_{10.6}Si_{2.4}$: (i) Near ZTE property appears; and (ii) the working temperature range of ZTE is large(15-150 K). Additionally, considering relatively high electrical, thermal conductivity as well as the low-cost of the raw materials, the $LaFe_{10.6}Si_{2.4}$ may be a promising candidate for low-temperature ZTE materials.

It is well known that the specific heat and the CTE, in thermodynamics, are connected by the Grüneisen parameter, which determines the change of the system dimension with the variation of thermal energy.[23] So investigating the specific heat is definitely important to analyze the thermal expansion property. Generally, the specific heat $C_p(T)$ can be expressed as $C_p(T)/T = \gamma + \beta T^2 + \delta T^4$, where the parameters γ, β, and δ represent electronic contribution, phonon contribution, and the deviations term, respectively.[24, 25] As mentioned above, the crystal lattice parameter of La(Fe, Si)$_{13}$-based compounds undergoes a change due to the magnetovolume effect, which is associated with the increased kinetic energy of the electron system. To break the magnetic order in FM state at low temperature, the itinerant electron system needs to absorb energy and when the amount of energy is larger than that originates from thermal fluctuation, the crystal lattice will contract to compensate for an extra energy. So abnormal behavior of the specific heat indicates the large lattice expansion or contraction because the evolution of lattice is correlated with the phonon and electron closely.

Figure 4 shows the curves of specific heat as a function of temperature under zero fields. It is observed that all samples show peaks in $C_p(T)$ around the temperatures where the magnetic transition occurs. A pronounced peak at 200 K is noticed for the $LaFe_{11.5}Si_{1.5}$. With increasing Si content, the peaks broaden gradually and move to higher temperature. The peak width will reflect on the corresponding temperature range of lattice contraction. It is noticed that the $LaFe_{10.6}Si_{2.4}$ does not show a λ-type peak but an arch over a wide temperature range, which is corresponding to the broadened NTE operation-temperature window. The broadened specific heat curves with increased Si content indicates that the Si dopant can availably broaden the discontinuous lattice contraction and is beneficial to the arising of the ZTE behavior.

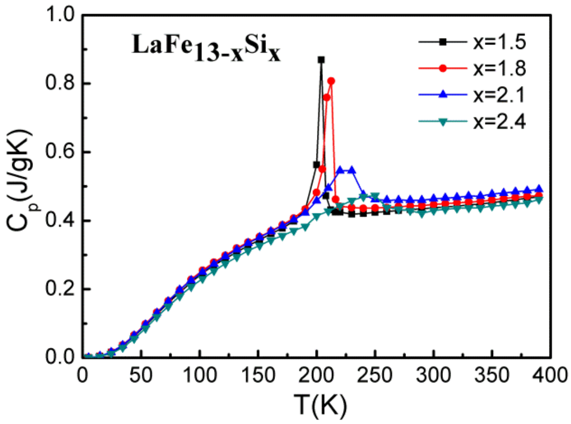

Fig. 4. Specific heat under zero field in the temperature range of 5-390K for samples of $LaFe_{13-x}Si_x$ (x=1.5, 1.8, 2.1 and 2.4).

Considering that the NTE behavior is triggered by magnetic transition, an understanding of the magnetic properties would be very useful for illustrating the mechanisms of the NTE and ZTE properties. The temperature dependence (5−300 K) of the magnetization M(T) of all samples measured in a magnetic field of 500 Oe is shown in Figure 5(a). The M(T) curve exhibits a sharp ferromagnetic−paramagnetic (FM−PM) phase transition. The Curie temperatures (T_c) were determined from dM/dT curves, leading to the values of 208, 216, 238 and 254 K for $LaFe_{13-x}Si_x$ (x = 1.5, 1.8, 2.1, and 2.4), respectively. It is obvious that the Tc depended linearly on the Si content (Fig. 5 insert). This small increase of Tc could be attributed to the a change in the density of 3d states (Nd) at Fermi level (EF) due to the different number of electrons contributed from the Si to the conduction band compared with that of Fe.[20, 26] Furthermore, the Fe_I−Fe_{II} distance plays the critical role in the exchange interaction.[20, 21] With increasing Si content, the Fe_I−Fe_{II} distance increases because of the smaller atomic size of Si compared with that of Fe, which promotes the positive exchange interaction and may break the long-range magnetic order in Fe and help to form local magnetic domains. As a result, the magnetic phase transition takes place gradually rather than a sharp change. This slow change is very helpful to achieve continuous ZTE, which need lattice contraction induced by the magnetic moment counteracts with the thermal expansion upon heating exactly.

To better understand the origin of the magnetic transition and ZTE properties, a further analysis was performed. The isothermal magnetization versus applied field M(H) was measured at different temperature. Fig. 5(b) exemplifies the typical Arrott plot derived from M(H) within a broad temperature range around T_c for Si=2.4.

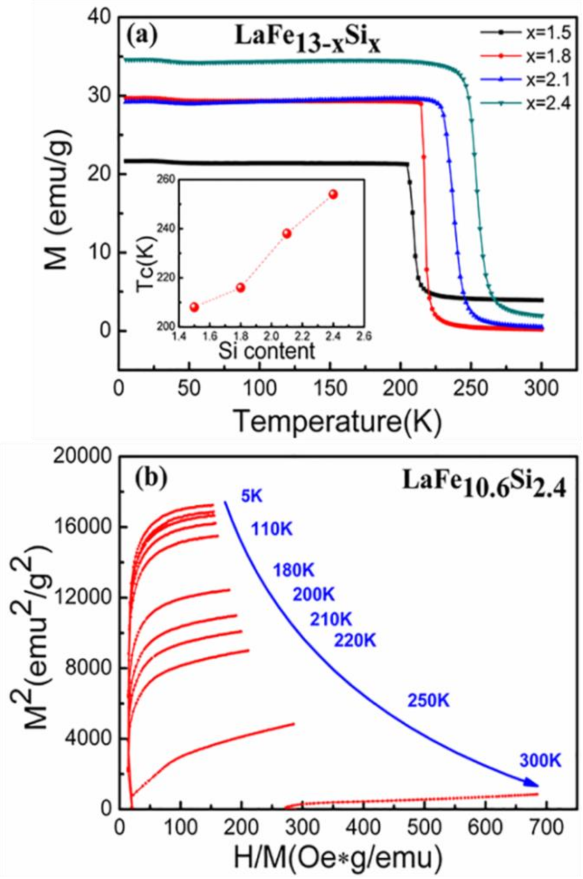

Fig. 5. (a) Temperature dependence of magnetization in a magnetic field of 0.05 T for samples of $LaFe_{13-x}Si_x$ (x=1.5, 1.8, 2.1 and 2.4). (b) Arrott plots of $LaFe_{13-x}Si_x$ with x=2.4. (Inset) Curie temperatures of $LaFe_{13-x}Si_x$ (x=1.5, 1.8, 2.1 and 2.4).

It is obvious that the slope of H/M versus M^2 curves at high field is positive at all measured temperature, which indicates that the phase transition is second order according to the Banerjee criterion. Also, it is apparent that an inflection point in the Arrott plots at T_c is signature of the itinerant-electron metamagnetic (IEM) transition from PM to FM order above T_c.[27] Finally, we deduced the spontaneous magnetization from the Arrott plots below T_c by extrapolating the Arrott plots to H/M=0. Fig. 6 displays the spontaneous magnetization as a function of temperature for all the samples. It can be seen that the spontaneous magnetization increases with the decreases in temperature, and the rising rate became smaller with increasing Si content. Besides, below the temperature about 210 K, the spontaneous magnetizations of the $LaFe_{13-x}Si_x$ (x= 1.5, 1.8, 2.1 and 2.4) decrease with the increase of Si content. This is because the magnetic moments reduce with the increasing content of Si.[28] As discussed above, NTE in $LaFe_{13-x}Si_x$-based compounds is due to the magneto-volume effect accompanied by the change of magnetic ordering, which is responsible for the contraction of lattice upon heating. Then from the Fig. 3 and Fig. 6, we can see that the higher spontaneous magnetization corresponds to larger value of $\Delta a/a$ at the same temperature, which seems that the NTE arises from the spontaneous magnetization and the magnitude of NTE is proportional to the degree of magnetic ordering. Si-doping destructs more or less the degree of the magnetic ordering. Anharmonic lattice vibrations possibly give rise to a positive thermal expansion. So the ZTE property seems to be a result of the interplay of spontaneous magnetization and lattice vibration. When the lattice contraction induced by the magnetic moment counteracts with the thermal expansion due to the decrease of the temperature precisely, the ZTE behavior appears. Therefore, the ZTE of $La(Fe, Si)_{13}$-based compounds can be obtained by optimizing the chemical composition.

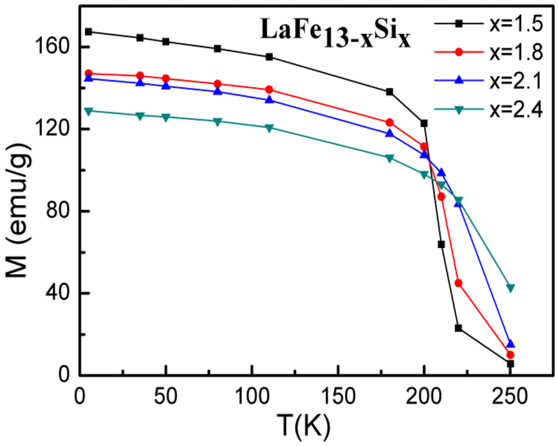

Fig. 6. The spontaneous magnetization as a function of temperature for samples of $LaFe_{13-x}Si_x$ (x=1.5, 1.8, 2.1 and 2.4).

In brief, the sharp change in the volume of the $La(Fe,Si)_{13}$-based compounds was successfully modified into continuous ZTE and by optimizing the chemical composition. The operation-temperature window of the NTE becomes broader with increasing the amount of Si dopant in the $LaFe_{13-x}Si_x$. Typically, a near ZTE coefficient of -0.8×10^{-6} K^{-1} in the temperature range from 15 to 150 K were obtained in the $LaFe_{10.6}Si_{2.4}$. Such ZTE materials with a broad ZTE temperature range will promote them highly potential in diversely practical applications.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51401224, 51232004, 51377156, 51322605, 51271192), the National Magnetic Confinement Fusion Science Program (Grant No. 2011GB112003), and the fund of the State Key Laboratory of Technologies in Space Cryogenic Propellants, SKLTSCP1204.

Notes and references

1 A. W. Sleight, Inorg. Chem., 1998, **37**, 2854.
2. A. W. Sleight, Endeavour, 1995, **19,** 64.
3. A. E. Phillips, A. L. Goodwin, G. J. Halder, P. D. Southon, and a. C. J. Kepert, Angew. Chem., 2008, **47**, 1396.
4 K. Takenaka and H. Takagi, Appl. Phys. Lett., 2009, **94**, 131904.
5 T. Suzuki and A. Omote, J. Am. Ceram. Soc., 2006, **89**, 691.
6 M. van Schilfgaarde, I. A. Abrikosov and B. Johansson, Nature, 1999, **400**, 46.
7 S. Margadonna, K. Prassides and A. N. Fitch, J. Am. Ceram. Soc., 2004, **126**, 15390.
8 J. R. Salvador, F. Guo, T. Hogan and M. G. Kanatzidis, Nature, 2003, **425**, 702.
9 J. Chen, K. Nittala, J. S. Forrester, J. L. Jones, J. X. Deng, R. B. Yu and X. R. Xing, J. Am. Ceram. Soc., 2011, **133**, 11114.
10 J. Chen, X. R. Xing, C. Sun, P. G. Hu, R. B. Yu, X. W. Wang and L. H. Li, J. Am. Ceram. Soc., 2008, **130**, 1144.
11 P. H. Hu, J. Chen, X.Y. Sun, J. X. Deng, X. Chen, R. B. Yu, L.J. Qiao and X. R. Xing, J. Mater. Chem**.,** 2009,**19**, 1648-1652
12 P. H. Hu, H. J. Kang, J. Chen, J. X. Deng and X. R. Xing, J. Mater. Chem**.,** 2011, 2**1**, 16205-16209
13 L Hu, J. Chen, L. L. Fan, Y. Ren, Y. C. Rong, Z. Pan, J. X. Deng, R. B. Yu and X. R. Xing, J. Am. Chem. Soc., 2014, **136**, 13566–13569
14 S. Sawhill, E. Savrun, Ceram. International, 2012, **38** 1981–1989.
15 J.Z. Tao, A.W. Sleight, J. Solid State Chem., 2003, **173,** 45–48.
16 X. Y. Song, Z. H. Sun, Q. Z. Huang, M. Rettenmayr, X. M. Liu, M. Seyring, G. N. Li, G. H. Rao and F. X. Yin, Adv. Mater., 2011, **23**, 4690.
17 S. Fujieda, A. Fujita and K. Fukamichi, Appl. Phys. Lett., 2002, **81**, 1276.
18 F. Hu, B. Shen, J. Sun, Z. Cheng, G. Rao and X. Zhang, Appl. Phys. Lett., 2001, **78**, 3675.
19 J. D. Zou, B. G. Shen and J. R. Sun, J. Phys.: Condens. Matter., 2007, **19**, 196220.
20 R. Huang, Y. Liu, W. Fan, J. Tan, F. Xiao, L. Qian and L. Li, J. Am. Chem. Soc., 2013, **135**, 11469.
21 G. J. Wang, F. Wang, N. L. Di, B. G. Shen and Z. H. Cheng, J. Magn. Magn. Mater., 2006, **303**, 84.
22 T. Carey, C. C. Tang, J. A. Hriljac, P. A. Anderson. Chem. Mater. 2014, **26** 1561-1566.
23 X. Wang, S. H. Nie, J. J. Li, R. Clinite, M. Wartenbe, M. Martin, W. X. Liang and J. M. Cao, Appl. Phys. Lett., 2008, 92, 121918.
24 Y. Q. Zhang, Z. D. Zhang and J. Aarts, Phys Rev B., 2004, **70**, 132407.
25 B. Zhang, X. X. Zhang, S. Y. Yu, J. L. Chen, Z. X. Cao and G. H. Wu, Appl. Phys. Lett., 2007, **91**, 012510.
25 C. L. Wang and Y. Long, J. Appl. Phys., 2013, **113**, 143902.
27 J. Shen, Y. X. Li, J. Zhang, B. Gao, F. X. Hu, H. W. Zhang, Y. Z. Chen, C. B. Rong and J. R. Sun, J. Appl. Phys., 2008, **103**, 07B317.

28 L. Jia, J. R. Sun, J. Shen, Q. Y. Dong, J. D. Zou, B. Gao, T. Y. Zhao, H. W. Zhang, F. X. Hu and B. G. Shen, J. Appl. Phys., 2009, **105**, 07A924.