Cite this: *RSC Advances*, 2012, **2**, 6023–6027

www.rsc.org/advances

PAPER

Achieving chemical stability in thermoelectric Na_xCoO_2 thin films

P. Brinks, H. Heijmerikx, T. A. Hendriks, G. Rijnders and M. Huijben*

Received 20th April 2012, Accepted 26th April 2012

DOI: 10.1039/c2ra20734f

Stability issues in thermoelectric Na_xCoO_2 thin films have been solved by the addition of an *in situ* amorphous AlO_x capping layer, which prevents previously reported degradation when exposed to air. These chemically stable thin films enable detailed analysis of the intrinsic thermoelectric properties and form a significant progress towards applications. Single phase Na_xCoO_2 thin films with a low surface roughness are grown by pulsed laser deposition with either an epitaxial or textured crystal structure on $\text{Al}_2\text{O}_3(001)$ or $\text{LaAlO}_3(001)$ single crystal substrates, respectively. For textured thin films a resistivity and thermopower of $0.99 \text{ m}\Omega \text{ cm}$ and $69 \mu\text{V K}^{-1}$ are observed at room temperature, respectively. Based on an estimated thermal conductivity for thin films, the dimensionless figure of merit is very comparable to Na_xCoO_2 single crystals, demonstrating the effectiveness of the developed capping layer.

1 Introduction

A large rise in research on thermoelectric power generation is currently occurring because of the improved properties of various nanostructured thermoelectric materials.¹ These improved materials make the recovery of the waste heat emitted by vehicles and factories, but also electronic processors, more attractive and economically feasible. Due to a difference of several orders of magnitude in the surface to volume ratio for nanostructured materials compared to their bulk counterparts, the reactivity and high temperature stability is significantly different and a detailed knowledge about the long-term stability of these new thermoelectric materials is required. The observation of a high thermopower and low resistivity in Na_xCoO_2 single crystals² opened up the interest in them as promising thermoelectric candidate materials^{3–7} and figure of merit (ZT) values exceeding unity have already been achieved. The efficiency of a material for thermoelectric power generation is given by the dimensionless figure of merit ZT :

$$ZT = \frac{S^2 \sigma}{\kappa} T \quad (1)$$

in which S , σ and κ are the thermopower, electrical conductivity and thermal conductivity, respectively, at a specific temperature T . For Na_xCoO_2 crystals power factor ($S^2\sigma$) values of $\sim 50 \mu\text{W K}^{-2} \text{ cm}^{-1}$ have been obtained,² which are comparable to values for Bi_2Te_3 crystals.⁸ However, currently the ZT value of Na_xCoO_2 crystals is limited due to the relatively high thermal conductivity ($8\text{--}19 \text{ W mK}^{-1}$),^{9–11} which is significantly higher than that of Bi_2Te_3 crystals ($\sim 1 \text{ W mK}^{-1}$).⁸

The improvement achieved by using nanostructured materials is caused by the enhanced phonon scattering within these nano

structures. This leads to a reduction of the thermal conductivity, without affecting the electronic properties, and thereby results in an improved ZT value. One of the approaches towards these nanostructured materials is to design superlattice structures in thermoelectric thin films, which will enhance the phonon scattering because of the low-dimensional confinement between the interfaces. This approach has been theoretically predicted¹² and experimentally demonstrated¹³ for Bi_2Te_3 -based materials. In oxide thermoelectric materials the initial thermal conductivity is even larger, and therefore the enhancement of phonon scattering by superlattice design could lead to an even stronger reduction of the thermal conductivity. Thin films of Na_xCoO_2 could serve as the building blocks for such superlattice structures and have already been investigated in previous studies.^{14–19} However, no detailed analysis of the thermoelectric properties of these thin films has been performed to date, due to chemical instability of the thin films at ambient conditions.¹⁴

Here, we present a method to obtain single phase thin films of Na_xCoO_2 , which are chemically stable in ambient conditions. By the *in situ* deposition of an AlO_x capping layer on top of the thin films direct contact to moisture and CO_2 is prevented and the reactive nature of the Na_xCoO_2 layer can be suppressed. This enables us to study for the first time in detail the relationship between structural and thermoelectric properties, *i.e.* electrical transport and room temperature thermopower in chemically stable Na_xCoO_2 thin films on different single crystal substrates. We will demonstrate that Na_xCoO_2 thin films possess comparable thermoelectric behavior to their single crystal analogues.

2 Experimental methods

Thin film samples of Na_xCoO_2 were fabricated by pulsed laser deposition (PLD) on single crystal (001)-oriented Al_2O_3 and (001)-oriented LaAlO_3 substrates, which are promising substrate candidates.^{14–19} Before deposition, the substrates were annealed

Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE, Enschede, The Netherlands. E-mail: m.huijben@utwente.nl

for 1 h at 1050 °C (Al_2O_3) and at 950 °C with an oxygen flow of 150 ml min^{-1} (LaAlO_3), exhibiting smooth surfaces with clear unit-cell-height steps with atomic force microscopy (AFM). The low level of surface roughness after annealing can be seen in Fig. 1a and Fig. 1d for a typical annealed Al_2O_3 and LaAlO_3 substrate, respectively. A sintered target with the composition $\text{Na}_{0.9}\text{CoO}_2$ was chosen as it is predicted to have the best thermoelectric properties,²⁰ which were also demonstrated experimentally in single crystals.¹¹

Thin Na_xCoO_2 films were deposited with a laser fluence of $\sim 4 \text{ J cm}^{-2}$, a spotsize of $\sim 1.08 \text{ mm}^2$ and a repetition rate of 1 Hz. These laser settings resulted in single phase thin films, whereas at higher laser repetition rates impurity phases were formed. During growth the oxygen environment was kept at $\sim 0.4 \text{ mbar}$. After the growth the samples were slowly cooled to room temperature in 1 atm of oxygen at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ to optimize the oxidation level. In order to improve the chemical stability of the thin films, we added an amorphous AlO_x capping layer *in situ* to several Na_xCoO_2 thin films. These amorphous AlO_x layers were grown at room temperature in $\sim 5 \times 10^{-3} \text{ mbar}$ of oxygen, from a polycrystalline Al_2O_3 target. AFM analysis demonstrates a surface topography of the thin films with low roughness (RMS: $\sim 4 \text{ nm}$) independent of the presence of the amorphous (AlO_x) capping layer, see Fig. 1. Gold contacts were deposited to establish good ohmic contact to the Na_xCoO_2 layer for thermoelectric characterization.

3 Results and discussion

3.1 Structural characterization

The structural properties of the thin films were determined by X-ray diffraction. A typical $2\theta/\omega$ scan for a 60 nm thin Na_xCoO_2 film, deposited at 430 °C, is shown in Fig. 2 when grown on an Al_2O_3 and a LaAlO_3 substrate. Both thin films exhibit only (00l) peaks of Na_xCoO_2 indicating a preferred growth orientation with the c-axis of the thin film and the substrate aligned parallel to each other. The c-axis lattice parameters are $10.95 \pm 0.05 \text{ \AA}$ and $11.05 \pm 0.05 \text{ \AA}$ for samples deposited on Al_2O_3 and LaAlO_3 ,

Fig. 2 X-Ray diffraction spectra for 60 nm Na_xCoO_2 thin films deposited on single crystal Al_2O_3 (a) and LaAlO_3 (b) substrates. Only (00l) peaks of the thin films are observed, indicating that the films are single phase and exhibit a preferred growth orientation.

substrates, respectively. Since no impurity peaks are observed it is concluded that the films are single-phase.

Even though the growth orientation is similar for the thin films grown on these two different substrates, for the in-plane direction clear differences are observed. For thin films grown on Al_2O_3 substrates an in-plane epitaxial relationship is found between the substrate and the thin film. The hexagonal structure of the Na_xCoO_2 is rotated by 30° with respect to that of the substrate. This is demonstrated in Fig. 3 where it is shown that in a φ scan the peak positions of the (104) peak of the substrate are found to match that of the (112) film peak. The a-axis lattice parameter is $2.82 \text{ \AA}$ for these epitaxial thin films. For the LaAlO_3 substrate no in-plane epitaxial relationship between the substrate and the thin film was found, therefore indicating that the samples were textured. Although a large lattice mismatch exists for both substrate materials, the different crystal structure of these substrates, hexagonal²¹ (Al_2O_3) and cubic²² (LaAlO_3), enables the growth of either epitaxial or textured Na_xCoO_2 thin films.

In contrast to previous reports on the narrow range of deposition temperatures for the growth of single-phase thin films,¹⁴ we observed a much wider range ($330 \text{ }^\circ\text{C}$ – $650 \text{ }^\circ\text{C}$) for our deposition conditions. Fig. 4 shows a clear difference in the

Fig. 1 Atomic force microscopy images ($3 \times 3 \mu\text{m}^2$) of annealed Al_2O_3 and LaAlO_3 substrates (a and d), after growth of a 60 nm Na_xCoO_2 thin film (b and e) and after growth of an additional 80 nm amorphous AlO_x capping layer (c and f).

Fig. 3 X-Ray diffraction measurements demonstrating the epitaxial relationship between the Al_2O_3 substrate and the Na_xCoO_2 thin film. The ϕ positions of the (112) and (104) peaks of the thin film and substrate, respectively, indicate the rotation of the a-axis of the film by 30° compared to the substrate as schematically shown.

crystallinity for Na_xCoO_2 thin films grown on LaAlO_3 substrates at various deposition temperatures. Due to the volatility of sodium, it is expected that the sodium concentration within the sample is dependent on the deposition temperature.¹⁵ Therefore, a change in sodium concentration as a function of deposition temperature could lead to a corresponding change in the c-axis length of the Na_xCoO_2 unit cell.^{23,24} However, the observed peak shift is relatively small, as can be seen in Fig. 4, and a c-axis lattice parameter of $11.05 \pm 0.05 \text{ \AA}$ was determined for these samples. Based on these results it is concluded that the sample stoichiometry is constant for this range of deposition temperatures.

3.2 Chemical stability

The electrical transport properties of thin Na_xCoO_2 films are known to degrade with time in ambient conditions.¹⁴ We indeed observed a strong increase in resistance for Na_xCoO_2 thin films, see Fig. 5. For the epitaxial and textured films an increase of

Fig. 4 X-Ray diffraction measurements of the (002) peak of the Na_xCoO_2 thin film on LaAlO_3 substrates at varying deposition temperatures. Only small peak shifts are observed, indicating minimal variation in the sample stoichiometry.

Fig. 5 Time-dependent resistance measurements of Na_xCoO_2 thin films on Al_2O_3 (blue) and LaAlO_3 (red) single crystal substrates at 300 K. Measurements are shown for samples with (solid lines) and without (dashed lines) an AlO_x capping layer.

resistance by a factor of 2.2 and 50, respectively, is observed over a period of two days, after which it stabilizes. The degradation can be interrupted by placing the sample in a vacuum environment (10^{-5} mbar), while subsequent exposure to ambient conditions continues the degradation process. These stability issues have previously hampered accurate analysis of the thermoelectric properties of Na_xCoO_2 thin films.

A reaction of sodium from the sample with moisture and carbon dioxide from the air has been suggested to occur,¹⁴ which leads to the formation of sodium carbonate (Na_2CO_3). However, after exposing the samples to ambient conditions for several days, no significant change in the XRD spectra is observed, indicating that a large volume fraction is not influenced by these reactions. From these observations it is concluded that only the surface layer and the grain boundaries are sensitive to the exposure to ambient conditions. To verify the formation of Na_2CO_3 at the surface, X-ray photoelectron spectroscopy (XPS) measurements were performed on a thin film, which had been transferred into the XPS chamber immediately after deposition. During the sample transfer from PLD to XPS the sample was exposed to ambient conditions for a short time, during which some Na_2CO_3 had already been formed. This was indeed confirmed by XPS analysis, where for carbon 1s a double peak was observed. One of these peaks was identified as a carbonate peak. No change in the XPS spectrum was observed after storage in an ultra-high vacuum for one week. However, after exposure to ambient conditions for several days, a clear increase in the carbon 1s peak, originating from the carbonate impurity phase, was measured. Indicating that the formation of carbonate at the surface and grain boundaries is indeed a process taking place due to the exposure to ambient conditions. This has a dramatic effect on the electrical transport going through the degrading grain boundaries as shown in Fig. 5. The degradation process is significantly stronger for textured films, which can be explained by the misalignment of the grains for the in-plane direction.

In order to prevent the formation of sodium carbonate at the surface and grain boundaries a capping layer was developed. The

in situ deposition of such a protective capping layer is a favorable solution to avoid any exposure to ambient conditions. A good candidate material is Al_2O_3 , since it has been used previously as a diffusion barrier²⁵ and it can be deposited by PLD in either polycrystalline or amorphous layers. For polycrystalline capping layers of Al_2O_3 only a small improvement in the stability was observed, which is most likely caused by an incomplete coverage due to island formation of the polycrystalline capping layer. However, a fully closed coverage of the surface can be expected for an amorphous AlO_x layer.²⁶ This was indeed confirmed by AFM for an AlO_x capping layer deposited at room temperature and at an oxygen pressure of 5×10^{-3} mbar. Deposition of AlO_x at higher oxygen pressures resulted in an increased surface roughness and, therefore, a reduced surface coverage. The surface topography of samples with an additional 80 nm amorphous AlO_x capping layer is shown in Fig. 1c and Fig. 1f for Na_xCoO_2 thin films on Al_2O_3 and LaAlO_3 substrates, respectively. This thickness was used to ensure a complete coverage of all the trenches and islands present at the Na_xCoO_2 surface. For both samples the RMS-value of the surface roughness is ~ 4 nm and is comparable to samples without a capping layer. Detailed analysis of the electrical transport properties showed that the implementation of an additional amorphous AlO_x capping layer completely prevented any degradation in ambient conditions for epitaxial and textured thin films, see Fig. 5. Reference samples where only the AlO_x capping layer was deposited were electrically insulating, ensuring that the measured behavior was only from the Na_xCoO_2 thin film. The AlO_x -capped samples remain stable over a period of several months and this enables us to study for the first time in detail the relationship between structural and thermoelectric properties in chemically stable Na_xCoO_2 thin films on different single crystal substrates.

3.3 Thermoelectric characterization

The thermoelectric properties of AlO_x -capped Na_xCoO_2 thin films are determined and compared to reported single crystal values. The temperature dependence of the electrical transport properties are measured in the range 4–300 K and shown in Fig. 6. The analysis is given for two samples which are deposited at 430 °C and 0.4 mbar on Al_2O_3 and LaAlO_3 substrates, respectively. These two samples represent typical results for thin films grown on these two substrates and show interesting

differences which can be explained by their crystallographic properties. A lower resistivity is observed for the sample deposited on Al_2O_3 , compared to the sample deposited on LaAlO_3 . Since the carrier densities are comparable, the change in resistivity is caused by variations in the carrier mobility. This difference in the carrier mobility can be explained by the crystallographic orientations of the grains within the thin films. Both samples have a parallel alignment of the c-axis in all grains. Additionally, the sample deposited on the Al_2O_3 substrate possesses grains, which are also in-plane aligned with respect to the substrate. This additional in-plane alignment leads to an enhanced carrier mobility, as electron scattering is reduced.

The observed metallic behavior down to low temperatures is in good agreement with previously reported single crystals. However, previous studies reported values for the room temperature resistivity of Na_xCoO_2 single crystals with a stoichiometry of $x = 0.8\text{--}0.95$ between 1.5 and 22 m Ω cm,^{6,11,27} while our thin films exhibit significantly lower values of 0.79 and 0.99 m Ω cm for growth on Al_2O_3 and LaAlO_3 substrates, respectively. Additionally, the measured carrier density at room temperature of $\sim 3 \times 10^{21}$ cm $^{-3}$ for our thin films is more than 2 orders of magnitude larger than the values observed for $\text{Na}_{0.9}\text{CoO}_2$ single crystals.⁶ Also a small increase in the carrier density at lower temperatures was reported for $\text{Na}_{0.9}\text{CoO}_2$ single crystals, in contrast to the strong observed enhancement for our thin films.

Comparing the transport properties of our thin films with Na_xCoO_2 single crystals with different compositions, a remarkable similarity is observed for $\text{Na}_{0.68}\text{CoO}_2$ single crystals.²⁸ For these single crystals a room temperature carrier density of $\sim 1.8 \times 10^{21}$ cm $^{-3}$ is measured, which strongly increases upon cooling. This is in good agreement with our observations. Additionally, the observed room temperature resistivity of ~ 0.8 m Ω cm is very similar to our thin films. It cannot be excluded that our thin films are composed of a sodium rich amorphous phase together with a crystalline phase with a stoichiometry close to $\text{Na}_{0.68}\text{CoO}_2$.

The measured thermopower at room temperature is ~ 45 $\mu\text{V K}^{-1}$ and ~ 69 $\mu\text{V K}^{-1}$ for thin films grown on Al_2O_3 and LaAlO_3 substrates, respectively, which is very similar to single crystals with a composition close to $\text{Na}_{0.71}\text{CoO}_2$,¹¹ see Table 1. Since the carrier density for these thin films is comparable, the difference in the thermopower is dominated by the carrier mobility with the highest thermopower observed for the thin film with the lowest mobility. This is in good agreement with the initial observation of the unusual

Fig. 6 The temperature dependence of resistivity, carrier density and carrier mobility for AlO_x -capped Na_xCoO_2 thin films on Al_2O_3 (blue triangles) and LaAlO_3 (red squares) substrates.

Table 1 Thermoelectric properties of Na_xCoO_2 thin films and single crystals ($x = 0.71$) at 300 K

	Al_2O_3	LaAlO_3	Single crystal ¹¹
Resistivity ($\text{m}\Omega\text{ cm}$)	0.79	0.99	1
Thermopower ($\mu\text{V K}^{-1}$)	45	69	90
Power Factor ($\mu\text{W K}^{-2}\text{ cm}^{-1}$)	2.6	4.8	8.1
Thermal conductivity (W mK^{-1})	4	4	8
ZT	0.01	0.03	0.03

combination of a high carrier density, low carrier mobility and high thermopower for single crystal Na_xCoO_2 .²

A power factor of 2.6 and 4.8 $\mu\text{W K}^{-2}\text{ cm}^{-1}$ is determined at room temperature for thin films on Al_2O_3 and LaAlO_3 substrates, respectively. Even though the thermal conductivity of the thin films was not measured yet, a ZT value can be calculated based on an estimated value for the thermal conductivity. For single crystals a thermal conductivity between 8 and 19 W mK^{-1} is reported,^{9–11} which can only be obtained in the case of highly controlled growth with a very low defect density. Therefore, it can be expected that the thermal conductivity in thin films is substantially lower than for single crystal values. For an estimated thermal conductivity of 4 W mK^{-1} , ZT values of 0.01 and 0.03 are obtained at room temperature for thin films on Al_2O_3 and LaAlO_3 substrates, respectively, which are in very good agreement with reports on $\text{Na}_{0.71}\text{CoO}_2$ single crystals,¹¹ see Table 1.

4 Conclusions

In summary, we have developed a method to obtain single phase thin films of Na_xCoO_2 which are stable in ambient conditions, due to the *in situ* deposition of an amorphous AlO_x capping layer. Depending on the choice of the single crystal substrate, the thin films can be grown either epitaxial or textured. Although the power factor is lower than that of the Na_xCoO_2 single crystals, the thermal conductivity is also expected to be lower for these thin films. The ZT values of the Na_xCoO_2 thin films at room temperature are therefore comparable to that of the $\text{Na}_{0.71}\text{CoO}_2$ single crystals. These capped thin films enable the detailed study of the thermoelectric properties of Na_xCoO_2 and could open up new ways to maximize the ZT values. However, additional characterization of the thermoelectric properties at higher temperatures is required, since this is the most promising regime for future applications of thermoelectric oxide materials.

Acknowledgements

We acknowledge B. Kuiper for XPS measurements. This work was supported by the Netherlands Organization for Scientific Research (NWO) through a VENI grant (M.H.).

References

- 1 B. C. Sales, *Science*, 2002, **295**, 1248–1249.
- 2 I. Terasaki, Y. Sasago and K. Uchinokura, *Phys. Rev. B*, 1997, **56**, R12685–R12687.
- 3 R. Funahashi, I. Matsubara, H. Ikuta, T. Takeuchi, U. Mizutani and S. Sodeoka, *Jpn. J. Appl. Phys.*, 2000, **39**, L1127–L1129.
- 4 K. Fujita, T. Mochida and K. Nakamura, *Jpn. J. Appl. Phys.*, 2001, **40**, 4644–4647.
- 5 T. Motohashi, E. Naujalis, R. Ueda, K. Isawa, M. Karppinen and H. Yamauchi, *Appl. Phys. Lett.*, 2001, **79**, 1480–1482.
- 6 M. Mikami, M. Yoshimura, Y. Mori, T. Sasaki, R. Funahashi and M. Shikano, *Jpn. J. Appl. Phys.*, 2003, **42**, 7383–7386.
- 7 M. Lee, L. Viciu, L. Li, Y. Wang, M. L. Foo, S. Watauchi, R. A. Pascal Jr., R. J. Cava and N. P. Ong, *Nat. Mater.*, 2006, **5**, 537–540.
- 8 T. Caillat, M. Carle, P. Pierrat and S. Scherrer, *J. Phys. Chem. Solids*, 1992, **53**, 1121–1129.
- 9 B. C. Sales, R. Jin, K. A. Affholter, P. Khalifah, G. M. Veith and D. Mandrus, *Phys. Rev. B*, 2004, **70**, 174419.
- 10 X. Tang and T. M. Tritt, *J. S. C. Acad. Sci.*, 2008, **6**, 10–13.
- 11 M. Lee, L. Viciu, L. Li, Y. Wang, M. L. Foo, S. Watauchi, R. A. Pascal Jr., R. J. Cava and N. P. Ong, *Phys. B*, 2008, **403**, 1564–1568.
- 12 L. D. Hicks and M. S. Dresselhaus, *Phys. Rev. B*, 1993, **47**, 12727–12731.
- 13 R. Venkatasubramanian, E. Siivola, T. Colpitts and B. O'Quinn, *Nature*, 2001, **413**, 597–602.
- 14 H. Zhou, X. P. Zhang, B. T. Xie, Y. S. Xiao, C. X. Yang, Y. J. He and Y. G. Zhao, *Thin Solid Films*, 2006, **497**, 338–340.
- 15 X. P. Zhang, Y. S. Xiao, H. Zhou, B. T. Xie, C. X. Yang and Y. G. Zhao, *Mater. Sci. Forum*, 2005, **3807**, 475–479.
- 16 J. Y. Son, B. G. Kim and J. H. Cho, *Appl. Phys. Lett.*, 2005, **86**, 221918.
- 17 Y. Krockenberger, I. Fritsch, G. Cristiani, A. Matveev, L. Alff, H. U. Habermeier and B. Keimer, *Appl. Phys. Lett.*, 2005, **86**, 191913.
- 18 A. Venimadhav, A. Soukiasian, D. A. Tenne, Q. Li, X. X. Xi, D. G. Schlom, R. Arroyave, Z. K. Liu, H. P. Sun, X. Pan, M. Lee and N. P. Ong, *Appl. Phys. Lett.*, 2005, **87**, 172104.
- 19 L. Yu, L. Gu, Y. Wang, P. X. Zhang and H. U. Habermeier, *J. Cryst. Growth*, 2011, **328**, 34–38.
- 20 S. Mukerjee and J. E. Moore, *Appl. Phys. Lett.*, 2007, **90**, 112107.
- 21 W. E. Lee and K. P. D. Lagerlof, *J. Electron Microsc. Tech.*, 1985, **2**, 247–258.
- 22 S. A. Hayward, F. D. Morrison, S. A. T. Redfern, E. K. H. Salje, J. F. Scott, K. S. Knight, S. Tarantino, A. M. Glazer, V. Shuvaeva, P. Daniel, M. Zhang and M. A. Carpenter, *Phys. Rev. B*, 2005, **72**, 054110.
- 23 Q. Huang, M. L. Foo, R. A. Pascal Jr., J. W. Lynn, B. H. Toby, H. Tao, H. W. Zandbergen and R. J. Cava, *Phys. Rev. B*, 2004, **70**, 134115.
- 24 Y. Krockenberger, I. Fritsch, G. Christiani, H. U. Habermeier, L. Yu, C. Bernhard, B. Keimer and L. Alff, *Appl. Phys. Lett.*, 2006, **88**, 162501.
- 25 S.-H. Kim, C.-E. Kim and Y.-J. Oh, *Thin Solid Films*, 1997, **305**, 312–326.
- 26 F. Di Fonzo, D. Tonini, A. Li Bassi, C. S. Casari, M. G. Beghi, C. E. Bottani, D. Gastaldi, P. Vena and R. Contro, *Appl. Phys. A*, 2008, **93**, 765–769.
- 27 T. Ikeda and M. Onoda, *J. Phys.: Condens. Matter*, 2006, **18**, 8673–8682.
- 28 M. Lin Foo, Y. Wang, S. Watauchi, H. W. Zandbergen, T. He, R. J. Cava and N. P. Ong, *Phys. Rev. Lett.*, 2004, **92**, 247001.