Electronic structure and thermoelectric properties of nanostructured $\text{EuTi}_{1-x}\text{Nb}_x\text{O}_{3-\delta}$ ($x = 0.00; 0.02$)

L. Sagarna, A. Shkabko, S. Populoh, L. Karvonen, and A. Weidenkaff

Swiss Federal Laboratories for Materials Sciences and Technology (Empa), Solid State Chemistry and Catalysis, Überlandstrasse 129, 8600 Dübendorf, Switzerland

(Received 3 April 2012; accepted 5 July 2012; published online 19 July 2012)

The thermoelectric properties of polycrystalline nanostructured $\text{EuTiO}_{3-\delta}$ samples are improved by a substitution of 2% Nb for Ti. The figure of merit (ZT) was measured to reach $ZT(\text{EuTi}_{0.98}\text{Nb}_{0.02}\text{O}_{3-\delta}) \approx 0.4$ at $T = 1040$ K while $ZT(\text{EuTiO}_{3-\delta}) \approx 0.3$ at the same temperature. X-ray photoelectron spectra reveal that the in-gap states at the Fermi level are more pronounced for the Nb-substituted samples, resulting in an improved power factor. The valence band peak below the Fermi level is sharply shaped, therefore fulfilling the condition for a large Seebeck coefficient. The specific porosity of the samples reduces the lattice thermal conductivity with a minor effect on the electron transport. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4737872>]

It is known from theoretical studies that correlation effects in oxides can enhance thermoelectric properties.^{1,2} Predictions about the thermoelectric performance and the Seebeck coefficient of strongly correlated electron systems were presented by Rüegg *et al.*³ Among the perovskite-type oxides, SrTiO_3 has shown a particularly high thermoelectric figure of merit ($ZT = (S^2T)/(\kappa\rho)$, where S = Seebeck coefficient, ρ = electrical resistivity, κ = thermal conductivity, and T = absolute temperature) in the high-temperature region.^{4,5} In order to enhance ZT , ρ and κ have to be minimized and S has to be maximized. The lattice thermal conductivity is often decreased by substituting heavy atoms into the crystal structure, which enhance the phonon scattering.⁶ A recent approach to decrease the κ of Ti containing perovskite systems (ATiO_3 ; where A = rare earth or alkaline earth metal) have focused on substitutions of the A-site cation with heavier elements. A 20% substitution of Sr^{2+} by Eu^{2+} in SrTiO_3 was found to effectively reduce the mean free phonon path by 12% at room temperature.⁷ Based on this observation and taking into account the similarities between SrTiO_3 and EuTiO_3 ,^{8,9} a lower phonon mean free path is expected in EuTiO_3 due to the higher atomic mass of Eu as compared with Sr.

EuTiO_3 has been widely studied because of its interesting magnetic properties: it is one of the few antiferromagnetic materials with a positive Curie-Weiss constant (θ)¹⁰ and reveals a strong coupling between magnetic ordering and soft phonon modes.¹¹ Electronic band structure calculations of EuTiO_3 by Ranjan *et al.*¹² have predicted a sharp peak in the density of states (DOS) below the Fermi level (E_F), which is beneficial to increase the S ($\propto (\partial \ln f(E)/\partial E)_{E=E_F}$). A broad band dispersion near E_F would further enhance the electronic conductivity.¹³ The electrical conductivity of EuTiO_3 has been studied at low temperatures,¹⁴ and different methods have been applied for its synthesis.^{15,16}

Another approach to reduce the lattice thermal conductivity is based on nanostructuring.¹⁷ When the grain size decreases and approaches a scale comparable to the mean free path, the phonons are scattered by the grain boundaries. Moreover, nanostructuring can enhance the Seebeck coefficient by the quantum confinement, which modifies the DOS,

and by the filtering of low energy electrons.^{17,18} The research carried out by Yu *et al.* proved the reduction of κ and preservation of ρ in nanomesh structures by the alteration of the phonon band structure of a semiconductor thin film.¹⁹ Studies on electrical conductivity of metallic foams²⁰ and nanocomposites²¹ proved that porous materials lead to a high electrical resistivity. However, foams have very different effective properties compared to their bulk counterparts. Finding a suitable porous morphology with a better ratio of the electrical to thermal conductivities could result in increasing the ZT values.^{22,23} Mesoporous samples have been prepared by different methods like *Chimie douce* synthesis²⁴ or citric acid-assisted soft chemistry synthesis.²⁵ In this work, a nanostructuring approach producing porous samples has been applied on $\text{EuTi}_{1-x}\text{Nb}_x\text{O}_{3-\delta}$ ($x = 0.00; 0.02$).

$\text{EuTi}_{1-x}\text{Nb}_x\text{O}_{3-\delta}$ ($x = 0.00; 0.02$) samples were prepared in two steps. First, a stoichiometric mixture of Eu_2O_3 , TiO_2 , and Nb_2O_5 powder was ball-milled and reacted in air for 10 h at 1273 K, resulting in a pyrochlore-type phase ($\text{A}_2\text{B}_2\text{O}_7$).¹⁶ Then, the powder was reground and pressed into bars ($10 \times 2 \times 2 \text{ mm}^3$) using $2 \cdot 10^4$ Pa uniaxial pressure. In order to perform thermal diffusivity measurements at high temperature, another set of samples was pressed into 10 mm diameter and 1.5 mm thick disk shaped pellets. Finally, all the samples were sintered for further 10 h at 1273 K under reducing atmosphere (flowing mixture of 5% H_2 in Ar). The resulting phase is a cubic-perovskite $Pm\bar{3}m$ with $a = 3.905 \text{ \AA}$ for $\text{EuTiO}_{3-\delta}$ (Fig. 1(b)) and $a > 3.905 \text{ \AA}$ for $x = 0.02$ samples. The grains form porous sintered bodies with well interconnected crystallites of 150 nm size (Fig. 1(a)). The relative densities of the sintered bars were 54% and 49% for $x = 0.00$ and $x = 0.02$, respectively, and 42% ($x = 0.00$) and 45% ($x = 0.02$) for the disk shaped pellets. In order to investigate the influence of the density on the thermoelectric properties, a 100% dense sample of EuTiO_3 was produced by floating zone technique.

The electrical resistivities of the samples as a function of temperature are shown in Figure 2. The decrease of ρ with T is observed for both samples, reaching $\rho_{(x=0.00)} = 1.2 \times 10^{-3} \Omega\text{m}$ (Fig. 2(a)) and $\rho_{(x=0.02)} = 6.7 \times 10^{-4} \Omega\text{m}$ (Fig. 2(b)) at

FIG. 1. (a) Low magnification transmission electron micrograph (TEM) of dispersed $\text{EuTiO}_{3-\delta}$ particles from a ground sintered pellet, prepared through a solid-state route as described in the text. (b) Electron diffraction micrograph of a EuTiO_3 crystalline particle indexed according to the $Pm\bar{3}m$ space group.

$T = 1040$ K. Nb-substitution provides a significant lowering of ρ in the temperature range of $8 \text{ K} < T < 1040 \text{ K}$, indicating additional charge carriers (electrons) being introduced in the Ti $3d$ band of $\text{EuTi}_{1-x}\text{Nb}_x\text{O}_{3-\delta}$ ($x > 0.00$).

The activation energy of the $x = 0.00$ was calculated with the Arrhenius formula

$$\rho = \rho_0 \exp(E_a/2k_B T), \quad (1)$$

FIG. 2. (a) Temperature dependence of electrical resistivity of $\text{EuTiO}_{3-\delta}$ (inset: $\ln \rho$ vs. $1/T$ and the activation energies, $E_a = 2k_B \cdot d(\ln \rho)/d(1/T)$, below and above $T = 560$ K). The resistivity values at $T < 170$ K were out of the instrumental measurement range ($> 500 \text{ } \Omega\text{m}$) and, therefore, not recorded. (b) $\rho(T)$ of $\text{EuTi}_{0.98}\text{Nb}_{0.02}\text{O}_{3-\delta}$ (inset: $\ln \rho$ vs. $1/T^{0.5}$ at $T < 65$ K fitted to the ES VRH model).

where E_a = activation energy and k_B = Boltzmann constant. The linear dependency of $\ln(\rho)$ vs. $(1/T)$ (inset of Fig. 2(a)) shows a change in the E_a from $E_a = 0.384 \text{ eV}$ at low temperature to $E_a = 0.996 \text{ eV}$ at high temperature. The ρ values of the polycrystalline $x = 0.00$ samples (54% density) were compared with the values for the 100% dense EuTiO_3 : $\rho = 5.5 \text{ } \Omega\text{m}$ for the porous samples and $\rho = 3.9 \text{ } \Omega\text{m}$ for the dense sample at room temperature, which indicates an increase of the ρ by 41% due to the porosity.

The $x = 0.02$ samples show considerably lower electrical resistivity (Fig. 2(b)). At low temperatures, the low energy electrons are localized in electronic potentials (“electronic droplets”) and the conduction is realized by hops near the Fermi level between the droplets.²⁶ The transport behavior of the $x = 0.02$ sample up to 65 K can be fitted with the Efros-Shklovskii (ES) variable-range hopping (VRH) [Eq. (2)], where the responsible conduction mechanism is the Coulomb interaction in the hopping regime which produces a gap in the density of states²⁷

$$\rho = \rho_0 \exp(T_0/T)^{1/2}, \quad (2)$$

where ρ_0 and T_0 are material parameters (see inset Fig. 2(b)). At $T = 65$ K, the electronic transport turns into metallic conduction within $65 \text{ K} < T < 120 \text{ K}$. This is understood as a transition from localized electronic states to nonlocalized states. When the energy of the electrons increases, the “electronic droplets” merge reaching the percolation level and the electrons can move through the entire system.²⁶ The difference in electronic transport properties compared to the $x = 0.00$ sample is due to higher concentration of “electronic droplets” caused by charge-carrier doping, which reduces the hopping lengths. The activation energy calculated for the $x = 0.02$ sample is 0.24 eV above 343 K.

The porous structure, formed by well-fused particles, provides the low overall densities of the samples. The high porosity has a significant effect on the thermal conductivity. Figures 3(a) and 3(b) show the total thermal conductivity (κ) of the $x = 0.00$ and $x = 0.02$ porous sample pellets. Thermal conductivity values of $\kappa_{(x=0.00)} = 2.5 \text{ W K}^{-1} \text{ m}^{-1}$ and $\kappa_{(x=0.02)} = 2.2 \text{ W K}^{-1} \text{ m}^{-1}$ are reached at $T = 330$ K. The values are significantly lower than the $\kappa = 7 \text{ W K}^{-1} \text{ m}^{-1}$ measured for the 100% dense EuTiO_3 sample, indicating the influence of the porosity. The lowered crystallite size also affects κ since the theoretical calculation of the thermal conductivity with Maxwell formula²⁸ would predict a value of $\kappa = 5.7 \text{ W K}^{-1} \text{ m}^{-1}$ for the 100% dense sample. In this case, the change in κ is a decrease by 56% from the dense sample to the porous one.

The total thermal conductivity κ consists of the electronic (κ_{el}) and the lattice (κ_{lat}) contributions. The electronic contribution can be approximated using the Wiedemann-Franz law: $\kappa_{\text{el}} = L_0 T / \rho$, where $L_0 = 2.443 \times 10^{-8} \text{ W S}^{-1} \text{ K}^{-2}$ is the Lorenz number for the free electron gas. Using this approximation, it is possible to reveal that κ is strongly dominated by the lattice contribution, presenting more than 95% of the total thermal conductivity. Therefore, the results of κ measurements are highly affected by the relative densities of the samples, and the effect of 2% Nb-substitution on κ can be considered negligible.

FIG. 3. Temperature dependence of the total thermal conductivity (κ) at low and high temperature ranges for (a) $\text{EuTiO}_{3-\delta}$ and (b) $\text{EuTi}_{0.98}\text{Nb}_{0.02}\text{O}_{3-\delta}$ (error bars according to Populoh *et al.*³⁸).

At low temperatures, κ_{lat} is limited by scattering processes induced by the lattice defects and grain boundaries. The small peaks at $T_{(x=0.00)} = 268$ K and $T_{(x=0.02)} = 273$ K can be related to the specific heat anomaly caused by a structural phase transition predicted by Bussmann-Holder *et al.*²⁹ At higher temperatures, the mean free path of the phonons becomes shorter, as the Umklapp processes turn out to be the dominating scattering scheme over the lattice-defect related scattering. At high temperature range, κ_{lat} decreases proportional to $1/T$, reflecting the increasing amount of phonons available to participate in the Umklapp scattering. In our case, the calculated 56% decrease of κ —compared to 100% dense unsubstituted sample—by the enhanced porosity outweighs the simultaneous decrease of 41% in ρ , which is considered beneficial for the ZT value in line with the results of Ref. 22.

The Seebeck coefficient (S) of both samples (Fig. 4) is negative over the whole temperature range confirming n -type conductivity. Large negative values of $S_{(x=0.00, T=268\text{ K})} = -1084 \mu\text{V K}^{-1}$ and $S_{(x=0.02, T=691\text{ K})} = -421 \mu\text{V K}^{-1}$ are reached. The origin of the pronounced peak in the S values of $\text{EuTiO}_{3-\delta}$ can be associated with a phonon drag effect,³⁰ taking place in the low-temperature regime where phonon-electron interactions dominate. In such a condition, the phonons tend to deflect the electrons towards one end of the material, giving rise to an enhanced $|S|$.³¹ This peak can also be

FIG. 4. Temperature dependence of the Seebeck coefficient (S) of the samples.

related to the structural transition reported in Ref. 29, since the maximum in the $S_{(x=0.00)}$ occurs at the same temperature ($T = 268$ K) as the small change in thermal conductivity (Fig. 3). A structural transition influences the DOS near the Fermi level (E_F) and thus the Seebeck coefficient.

At high temperature, the $S(T)$ values of both samples converge, reaching $S_{(x=0.00)} = -389 \mu\text{V K}^{-1}$ and $S_{(x=0.02)} = -360 \mu\text{V K}^{-1}$ by 1040 K. The behavior of the Seebeck coefficient at the high temperatures limit, where the kinetic terms of S can be neglected, can be described by Heikes formula.³² In the case of highly correlated electron system with large electron-electron repulsion (U) and forbidden double occupancy (as it is assumed in this system³³), the following modified Heikes formula can be considered to estimate the expected S :³⁴

$$S(T \rightarrow \infty) = -(k_B/e) \ln[(2 - 2n)/n], \quad (3)$$

where n = charge carrier concentration per unit cell. The calculated value for $\text{EuTi}_{0.98}\text{Nb}_{0.02}\text{O}_{3-\delta}$ is $S_{(T \rightarrow \infty)} = -395 \mu\text{V/K}$ (with $n = 0.02$) and has a small deviation from the measured value. However, we cannot apply the formula for the unsubstituted sample since an appropriate value of n for $\text{EuTiO}_{3-\delta}$ ($n \sim 10^{-6}$) would give a $|S|$ value above 1000 $\mu\text{V/K}$, which is in disagreement with the measurement. The measured S of both samples tends to similar values at high temperature. This behavior could be explained by Heikes formula if we consider that the extra electrons induced by oxygen vacancies in the $x = 0.00$ sample raise the charge carrier density to $n \sim 0.02$. Another possible explanation is given by Kobayashi,³⁵ who postulates that the electric conduction occurs in a highly localized way and the exchange of entropy and charge occurs via the neighboring Ti^{3+} and Ti^{4+} ions.

Ti^{4+} is the predominating oxidation state of titanium in both samples, as demonstrated in Figure 5(a) with the Ti 2p x-ray photoelectron spectra (XPS) of the $x = 0.02$ sample. The most intense peak is centered at $E_b = 459.24$ eV, similarly to SrTiO_3 perovskite phases, indicating Ti^{4+} species.³⁶ The small low-energy shoulder can be explained by a less intensive feature centred at $E_b = 456.4$ eV, indicating

FIG. 5. (a) Deconvoluted x-ray photoemission spectrum of Ti 2p electrons of $\text{EuTi}_{0.98}\text{Nb}_{0.02}\text{O}_{3-\delta}$. (b) Eu 4d spectra of $\text{EuTi}_{0.98}\text{Nb}_{0.02}\text{O}_{3-\delta}$ with Eu^{2+} . $\text{Eu}_2\text{Ti}_2\text{O}_7$ with Eu^{3+} is also shown for comparison.

additional Ti^{3+} in a minor amount, likely due to oxygen vacancies. The main characteristic of the Nb $3d_{5/2}$ spectrum (not shown here), centred at $E_b = 207.82$ eV, supports the existence of Nb five-valent cation. The Eu 4d core-level structure (Fig. 5(b)) has two main peaks at 129.72 eV and 134.97 eV, which belong to the multiplet structure resulting from the $5d^0 4f^7$ ground-state configuration of Eu^{2+} , as was recently found.³⁷ The small hump at around 143 eV (indicated with an arrow) can be associated to additional Eu^{3+} . For comparison, the Eu 4d spectrum of $\text{Eu}_2\text{Ti}_2\text{O}_7$ was also recorded and the two peaks corresponding to Eu^{3+} were found at 136.51 eV and 142.51 eV (Fig. 5(b)).

The valence band (VB) spectra of the samples plotted in Figure 6 show a narrow peak centred at 2.50 eV below the E_f corresponding to Eu 4f, as theoretically predicted for EuTiO_3 .¹² The spectrum of $\text{Eu}_2\text{Ti}_2\text{O}_7$ was recorded for comparison (Fig. 6): the peak related to Eu^{2+} 4f states appears at a similar energy but with a lower intensity. It is, indeed, expected a higher intensity of this peak for the perovskite $\text{EuTiO}_{3-\delta}$ phase than for the pyrochlore $\text{Eu}_2\text{Ti}_2\text{O}_7$ phase. The three additional features below E_f in the data sets of Figure 6 correspond to O 2p (5.5 eV), indicated with the arrows, and Eu^{3+} (8 eV and 12 eV),³⁷ marked with the asterisks. However, the high spectral intensity from 4 eV up to 14 eV is characteristic only for the $\text{Eu}_2\text{Ti}_2\text{O}_7$ phase, due to the higher oxygen and Eu^{3+} contents.

It is known from theory,¹³ that a sharp DOS near the Fermi level results in a high Seebeck coefficient. In Figure 6, the VB spectra of $\text{EuTiO}_{3-\delta}$ and $\text{EuTi}_{0.98}\text{Nb}_{0.02}\text{O}_{3-\delta}$ are

FIG. 6. Valence band spectra of $\text{EuTi}_{0.98}\text{Nb}_{0.02}\text{O}_{3-\delta}$, $\text{Eu}_2\text{Ti}_2\text{O}_7$, and $\text{EuTiO}_{3-\delta}$.

compared. Both samples show a high and narrow peak below E_f , which reflects the large of S values of the samples at room temperature. Besides, tailing of the band-edges towards and beyond the zero-point energy manifests additional in-gap states at E_f affecting the electronic transport. The comparison of the VB spectra of both materials shows that the density of the in-gap states is higher in the Nb-substituted $x = 0.02$ sample than in the unsubstituted $x = 0.00$ sample, leading to a lower electrical resistivity by substitutions.

Structural, thermoelectrical, and x-ray photoemission characterization was carried out on porous polycrystalline samples of $\text{EuTi}_{1-x}\text{Nb}_x\text{O}_{3-\delta}$ ($x = 0.00; 0.02$). The porosity decreased the thermal conductivity by 56% compared with the dense sample, while the electrical conductivity was lowered by only 41%. The VB spectra revealed a sharp DOS near the Fermi level due to Eu 4f electrons in both samples. This caused the measured high Seebeck coefficient,¹³ which reached $S_{(x=0.00)} = -1053$ $\mu\text{V/K}$ and $S_{(x=0.02)} = -267$ $\mu\text{V/K}$ at room temperature. The additional in-gap states observed in the VB spectra justified the high electronic conductivity, especially in the case of the Nb-substituted samples. The ZT values obtained at 1040 K, $ZT_{(x=0.00)} \sim 0.3$ and $ZT_{(x=0.02)} \sim 0.4$, are among the highest within the family of thermoelectric oxides.

We would like to thank the SNF (Swiss National Science Foundation) for financial support within the National Centre of Competence in Research (NCCR) “MaNEP—Materials with Novel Electronic Properties.” We also appreciate Myriam H. Aguirre’s and Sylvie Hébert’s collaboration with helpful discussions and language corrections by James Eilertsen.

¹I. Terasaki, Y. Sasago, and K. Uchinokura, *Phys. Rev. B* **56**, R12685 (1997).

²M. H. Aguirre, D. Logvinovich, L. Bocher, R. Robert, S. G. Ebbinghaus, and A. Weidenkaff, *Acta Mater.* **57**, 108 (2009).

³A. Rüegg, S. Pilgram, and M. Sigrist, *Phys. Rev. B* **77**, 245118 (2008).

⁴S. Ohta, T. Nomura, H. Ohta, M. Hirano, H. Hosono, and K. Koumoto, *Appl. Phys. Lett.* **87**, 092108 (2005).

⁵Y. Wang and H. J. Fan, *Scr. Mater.* **65**, 190 (2011).

⁶G. J. Snyder and E. S. Toberer, *Nature Mater.* **7**, 105 (2008).

⁷K. Kato, M. Yamamoto, S. Ohta, H. Muta, K. Kurosaki, S. Yamanaka, H. Iwasaki, H. Ohta, and K. Koumoto, *J. Appl. Phys.* **102**, 116107 (2007).

- ⁸B. Ravel and E. A. Stern, *Physica B* **208–209**, 316 (1995).
- ⁹J. Brous, I. Fankuchen, and E. Banks, *Acta Crystallogr.* **6**, 67 (1953).
- ¹⁰T. R. McGuire, M. W. Shafer, R. J. Joenk, H. A. Alperin, and S. J. Pickart, *J. Appl. Phys.* **37**, 981 (1966).
- ¹¹T. Katsufuji and H. Takagi, *Phys. Rev. B* **64**, 054415 (2001).
- ¹²R. Ranjan, H. Sadat Nabi, and R. Pentcheva, *J. Phys.: Condens. Matter* **19**, 406217 (2007).
- ¹³D. M. Rowe, *Thermoelectrics Handbook Macro to Nano-structured Materials* (Taylor & Francis, Boca Raton, FL, 2005).
- ¹⁴K. Ishikawa, G. Adachi, and J. Shiokawa, *Mater. Res. Bull.* **18**, 257 (1983).
- ¹⁵M. Kachlik, K. Maca, V. Goian, and S. Kamba, *Mater. Lett.* **74**, 16 (2012).
- ¹⁶N. L. Henderson, J. Baek, P. S. Halasyamani, and R. E. Schaak, *Chem. Mater.* **19**, 1883 (2007).
- ¹⁷M. S. Dresselhaus, G. Chen, M. Y. Tang, R. G. Yang, H. Lee, D. Z. Wang, Z. F. Ren, J.-P. Fleurial, and P. Gogna, *Adv. Mater.* **19**, 1043 (2007).
- ¹⁸J.-F. Li, W.-S. Liu, L.-D. Zhao, and M. Zhou, *NPG Asia Mater.* **2**, 152 (2010).
- ¹⁹J.-K. Yu, S. Mitrovic, D. Tham, J. Varghese, and J. R. Heath, *Nat. Nanotechnol.* **5**, 718 (2010).
- ²⁰K. P. Dharmasena and H. N. G. Wadley, *J. Mater. Res.* **13**, 625 (2002).
- ²¹C. J. Vineis, A. Shakouri, A. Majumdar, and M. G. Kanatzidis, *Adv. Mater.* **22**, 3970 (2010).
- ²²J.G. Noudem, S. Lemonnier, M. Prevel, E. S. Reddy, E. Guilmeau, and C. Goupil, *J. Eur. Ceram. Soc.* **28**, 41 (2008).
- ²³S. Populoh, M. Trottmann, M. H. Aguirre, and A. Weidenkaff, *J. Mater. Res.* **26**, 1947 (2011).
- ²⁴L. Bocher, M. H. Aguirre, R. Robert, M. Trottmann, D. Logvinovich, P. Hug, and A. Weidenkaff, *Thermochim. Acta* **457**, 11 (2007).
- ²⁵R. Robert, D. Logvinovich, M. H. Aguirre, S. G. Ebbinghaus, L. Bocher, P. Tomeš, and A. Weidenkaff, *Acta Mater.* **58**, 680 (2010).
- ²⁶H. Böttger and V. V. Bryksin, *Phys. Status Solidi B* **78**, 9 (1976).
- ²⁷S. Shekhar, V. Prasad, and S. V. Subramanyam, *Phys. Lett. A* **360**, 390 (2006).
- ²⁸T.-H. Tsai, L.-S. Kuo, P.-H. Chen, and C.-T. Yang, *PIERS Online* **5**, 231 (2009).
- ²⁹A. Bussmann-Holder, J. Köhler, R. Kremer, and J. Law, *Phys. Rev. B* **83**, 212102 (2011).
- ³⁰D. G. Cantrell and P. N. Butcher, *J. Phys. C* **20**, 1985 (1987).
- ³¹H. Ohta, S. Kim, Y. Mune, T. Mizoguchi, K. Nomura, S. Ohta, T. Nomura, Y. Nakanishi, Y. Ikumura, M. Hirano, H. Hosono, and K. Koumoto, *Nature Mater.* **6**, 129 (2007).
- ³²J. Kwak and G. Beni, *Phys. Rev. B* **13**, 652 (1976).
- ³³K. Z. Rushchanskii, S. Kamba, V. Goian, P. Vaněk, M. Savinov, J. Prokleška, D. Nuzhnyy, K. Knížek, F. Laufek, S. Eckel, S. K. Lamoreaux, A. O. Sushkov, M. Ležaić, and N. A. Spaldin, *Nature Mater.* **9**, 649 (2010).
- ³⁴P. M. Chaikin and G. Beni, *Phys. Rev. B* **13**, 647 (1976).
- ³⁵W. Kobayashi, *J. Appl. Phys.* **95**, 6825 (2004).
- ³⁶K. J. Kim, D. W. Moon, S. H. Nam, W. J. Lee, and H. G. Kim, *Surf. Interface Anal.* **23**, 851 (1995).
- ³⁷E.-J. Cho and S.-J. Oh, *Phys. Rev. B* **59**, R15613 (1999).
- ³⁸S. Populoh, M. H. Aguirre, O. C. Brunko, K. Galazka, Y. Lu, and A. Weidenkaff, *Scr. Mater.* **66**, 1073 (2012).