

## Fabrication and thermoelectric properties of layered cobaltite, $\gamma$ -Sr<sub>0.32</sub>Na<sub>0.21</sub>CoO<sub>2</sub> epitaxial films

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(Received 25 October 2005; accepted 13 January 2006; published online 23 February 2006)

Thermoelectric properties of  $\gamma$ -Sr<sub>0.32</sub>Na<sub>0.21</sub>CoO<sub>2</sub> epitaxial films, which were fabricated on the (0001)-face of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrates by ion exchange processes between Na<sup>+</sup> and Sr<sup>2+</sup> ions with  $\gamma$ -Na<sub>0.8</sub>CoO<sub>2</sub> epitaxial films, were measured to clarify the effect of Sr<sup>2+</sup>-ion exchange of  $\gamma$ -Na<sub>0.8</sub>CoO<sub>2</sub> on the thermoelectric properties. Electrical conductivity ( $\sigma$ ), Seebeck coefficient ( $S$ ), and thermoelectric power factor ( $PF=S^2\sigma$ ) of the  $\gamma$ -Sr<sub>0.32</sub>Na<sub>0.21</sub>CoO<sub>2</sub> film (300 K) were  $8.9 \times 10^2$  S cm<sup>-1</sup>, +120  $\mu$ V K<sup>-1</sup>, and  $1.2 \times 10^{-3}$  W m<sup>-1</sup> K<sup>-2</sup>, respectively. These values were relatively large compared to those of  $\gamma$ -Na<sub>0.8</sub>CoO<sub>2</sub> epitaxial films ( $\sigma=1.2 \times 10^3$  S cm<sup>-1</sup>,  $S=+95$   $\mu$ V K<sup>-1</sup>, and  $PF=1.1 \times 10^{-3}$  W m<sup>-1</sup> K<sup>-2</sup>). The  $\gamma$ -Sr<sub>0.32</sub>Na<sub>0.21</sub>CoO<sub>2</sub> epitaxial film exhibited much improved chemical stability against moisture compared to the  $\gamma$ -Na<sub>0.8</sub>CoO<sub>2</sub> epitaxial film. The Sr<sup>2+</sup>-ion exchange of  $\gamma$ -Na<sub>0.8</sub>CoO<sub>2</sub> is vital for practical thermoelectric applications. © 2006 American Institute of Physics. [DOI: 10.1063/1.2178768]

Thermoelectric energy conversion (TE) is considered to be a promising technology for power generation in the next generation, because one can utilize waste heat from many sources, e.g., various industries, transportation systems, etc. The performance of TE materials is generally characterized by the dimensionless figure of merit  $ZT (=S^2\sigma T/\kappa$ , where  $S$ ,  $\sigma$ ,  $T$ , and  $\kappa$  are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively).

Recently, several oxides having good TE performance have been reported one after another.<sup>1-4</sup> Among these, the layered sodium cobaltite  $\gamma$ -Na<sub>x</sub>CoO<sub>2</sub> ( $0.5 \leq x \leq 0.8$ )<sup>4-9</sup> has attracted much attention as a  $p$ -type thermoelectric energy conversion material, because it exhibits a fairly large Seebeck coefficient due to strong electron correlation effects, even though it exhibits metallic behavior. However, its chemical durability is clearly insufficient, i.e.,  $\gamma$ -Na<sub>x</sub>CoO<sub>2</sub> is easily decomposed into insulating Co(OH)<sub>2</sub> under high humidity conditions (temperature, 80 °C; humidity, ~80%) due to the fact that Na<sup>+</sup> ions can easily dissolve in water. This is a fatal drawback of  $\gamma$ -Na<sub>x</sub>CoO<sub>2</sub> for practical TE applications.

To address this issue, the approach we made was to modify the chemical components without degrading TE performance. We focused our attention on layered strontium cobaltite,  $\gamma$ -Sr<sub>x</sub>CoO<sub>2</sub>. First, we hypothesized that  $\gamma$ -Sr<sub>x</sub>CoO<sub>2</sub> might exhibit high electrical conductivity and a large Seebeck coefficient, comparable to those of  $\gamma$ -Na<sub>x</sub>CoO<sub>2</sub>, because the crystal structure of  $\gamma$ -Sr<sub>x</sub>CoO<sub>2</sub> (Ref. 10) is basically simi-

lar to that of  $\gamma$ -Na<sub>x</sub>CoO<sub>2</sub>. We also hypothesized that  $\gamma$ -Sr<sub>x</sub>CoO<sub>2</sub> might exhibit better chemical stability against moisture than  $\gamma$ -Na<sub>x</sub>CoO<sub>2</sub> because the divalent metal cation Sr<sup>2+</sup> is less soluble than Na<sup>+</sup>.

The TE properties of the  $\gamma$ -Sr<sub>0.35</sub>CoO<sub>2</sub> ceramic reported by Ishikawa *et al.*,<sup>10</sup> who synthesized it by sintering at 400 °C, were quite low as compared to those of  $\gamma$ -Na<sub>x</sub>CoO<sub>2</sub>. Although a high-density ceramic or single crystal for  $\gamma$ -Sr<sub>x</sub>CoO<sub>2</sub> is preferable to clarify the intrinsic TE properties, this is considered to be extremely difficult, because the phase transition of  $\gamma$ -Sr<sub>x</sub>CoO<sub>2</sub> occurs at a relatively low temperature (~400 °C). In order to examine the intrinsic TE properties of  $\gamma$ -Sr<sub>x</sub>CoO<sub>2</sub>, we fabricated high-quality epitaxial films of  $\gamma$ -Sr<sub>0.32</sub>Na<sub>0.21</sub>CoO<sub>2</sub>, because, epitaxial films generally exhibit intrinsic carrier transport properties, such as bulk single crystal. The  $\gamma$ -Sr<sub>0.32</sub>Na<sub>0.21</sub>CoO<sub>2</sub> epitaxial films exhibited better chemical stability as compared to  $\gamma$ -Na<sub>0.8</sub>CoO<sub>2</sub>, while they retained good TE properties. Here, we report the preparation and TE properties of  $\gamma$ -Sr<sub>0.32</sub>Na<sub>0.21</sub>CoO<sub>2</sub> epitaxial films.

Epitaxial films of  $\gamma$ -Sr<sub>0.32</sub>Na<sub>0.21</sub>CoO<sub>2</sub> were prepared by Sr<sup>2+</sup>-ion exchange treatment of  $\gamma$ -Na<sub>0.8</sub>CoO<sub>2</sub> epitaxial films, which were grown by reactive solid-phase epitaxy (R-SPE) (Ref. 11) on the (0001)-face of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrates. The details of the R-SPE technique for the preparation of  $\gamma$ -Na<sub>0.8</sub>CoO<sub>2</sub> epitaxial films have been described elsewhere.<sup>12</sup> First, an appropriate amount of Sr(NO<sub>3</sub>)<sub>2</sub> powder was placed on the R-SPE-grown  $\gamma$ -Na<sub>0.8</sub>CoO<sub>2</sub> epitaxial film. Then, the film was heated at 300 °C for 5 h in air. After that, the film was cooled down to room temperature and was washed with distilled water several times to remove excess Sr(NO<sub>3</sub>)<sub>2</sub> powder attached to the film.

The crystalline quality, orientation and thickness of the films were evaluated by high-resolution x-ray diffraction

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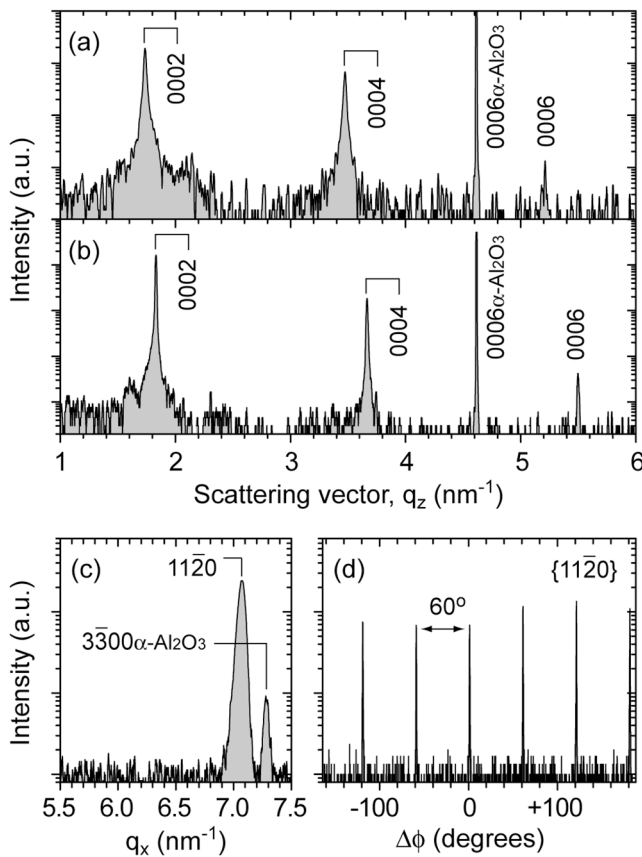


FIG. 1. Out-of-plane XRD patterns of (a)  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  epitaxial film, which was grown on the (0001)-face of an  $\alpha$ - $\text{Al}_2\text{O}_3$  substrate by  $\text{Sr}^{2+}$ -ion exchange treatment of a  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  epitaxial film, and (b) starting  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  epitaxial film, which was grown by R-SPE. (c) In-plane XRD pattern of the  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  film. (d) In-plane rocking curve ( $\phi$ -scan) of the  $\{11\bar{2}0\}$   $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$ .

(XRD) (ATX-G, Cu  $K\alpha_1$ , Rigaku Co.) measurements. The geometry of this x-ray diffractometer has been described in literature.<sup>11–16</sup> The surface morphology of the film was observed by atomic force microscopy (AFM) (SPI-3800N, S.I.I.) at room temperature. Electrical conductivity ( $\sigma$ ), carrier concentration ( $n$ ), and Hall mobility ( $\mu_{\text{Hall}}$ ) of the films were measured by the dc four-point probe method in the van der Pauw configuration. The Seebeck coefficient ( $S$ ) of the films was measured by a conventional steady-state method.

Figure 1 shows an out-of-plane XRD pattern of  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  epitaxial films, which were grown on an (0001)-oriented  $\alpha$ - $\text{Al}_2\text{O}_3$  substrate by R-SPE [(a) after the  $\text{Sr}^{2+}$ -ion exchange treatment; (b) as-grown  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  epitaxial film]. Only the intense Bragg diffraction peaks for  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  000 $l$  are seen, together with the  $\alpha$ - $\text{Al}_2\text{O}_3$  0006 peak, in Fig. 1(b), indicating the high crystal quality of the film. The lattice parameter,  $c=1.091$  nm, corresponded well with the literature value ( $c=1.0811$  nm).<sup>17–19</sup> After the  $\text{Sr}^{2+}$ -ion exchange treatment [Fig. 1(a)], the lattice parameter became 1.151 nm, which is close to that of  $\gamma$ - $\text{Sr}_{0.35}\text{CoO}_2$  powder ( $c=1.1525$  nm),<sup>10</sup> suggesting that  $\text{Sr}^{2+}$ -ion exchange occurred. The chemical composition of the resultant film, which was evaluated by x-ray fluorescence analysis, was  $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$ . This chemical composition remained essentially unchanged after the film was treated with  $\text{Sr}(\text{NO}_3)_2$  powder at 300 °C for 5 days. Thus, we concluded that the chemical composition is stable at 300 °C.

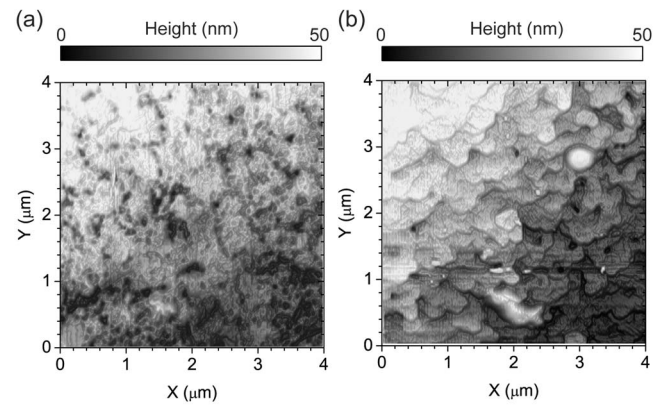


FIG. 2. Topographic AFM images of the epitaxial films of (a)  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  and (b) R-SPE-grown  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$ .

Only the intense Bragg diffraction peak for  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  11 $\bar{2}0$  is seen, together with that for  $\alpha$ - $\text{Al}_2\text{O}_3$  3300, in Fig. 1(c). The six-fold symmetry of  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  {11 $\bar{2}0$ } was clearly seen in the in-plane rocking curve [Fig. 1(d)], indicating that  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  epitaxial film was successfully converted to an  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  epitaxial film, keeping the relationship of  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  (0001)[11 $\bar{2}0$ ] $\parallel$  $\alpha$ - $\text{Al}_2\text{O}_3$ (0001)[1100] by the  $\text{Sr}^{2+}$ -ion exchange treatment at 300 °C.

Figure 2 shows topographic atomic force microscopy (AFM) images of the epitaxial films of (a) the resultant  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  and (b) the starting  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$ . Although steplike structures composed of several flakelike domains are clearly seen in Fig. 2(b), a fairly rough surface is observed in Fig. 2(a), which is most likely due to fact that the ion exchange reaction occurred from the film top surface.

Figure 3 shows the temperature dependence of  $\sigma$  for the resultant  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  epitaxial films (178 nm thick) and the starting  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  films (110 nm thick).<sup>20</sup> The  $\sigma$  value of the  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  epitaxial film was

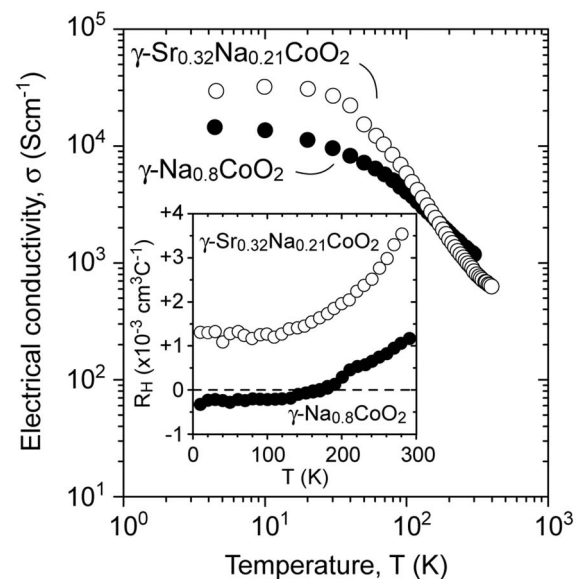


FIG. 3. Temperature dependence of the electrical conductivity ( $\sigma$ ) for the epitaxial films of the  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  (178 nm thick) and the R-SPE-grown  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  (110 nm thick). The Hall coefficient ( $R_H$ ) of the films is also shown in the inset.

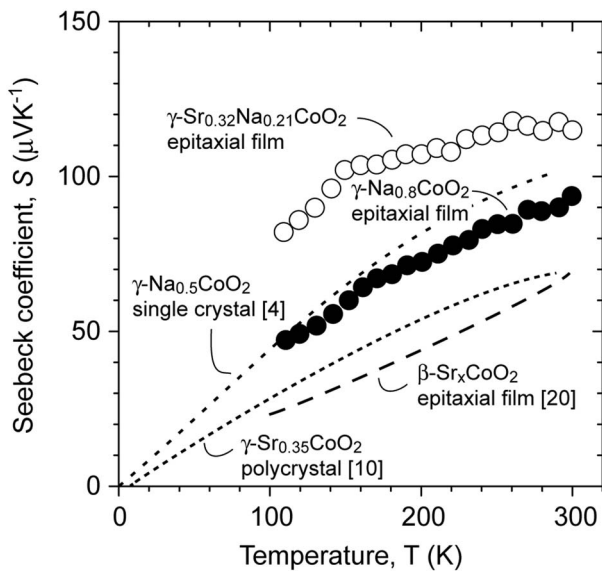


FIG. 4. Temperature dependence of the Seebeck coefficient ( $S$ ) for the  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  (178 nm thick) and R-SPE-grown  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  (110 nm thick) epitaxial films. The  $S$  values of several layered cobaltites (Refs. 4, 10, and 20) are also shown.

$\sim 10^3 \text{ S cm}^{-1}$  at 300 K, which is one order of magnitude larger than that of the ceramic (Ref. 10), and it gradually increased, almost proportionally to  $T^{-2}$ , with decreasing temperature. The values of  $n$  and  $\mu_{\text{Hall}}$  of the  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  epitaxial film were  $1.8 \times 10^{21} \text{ cm}^{-3}$  and  $3.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively, at 300 K, which were slightly different from those of the R-SPE-grown  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  ( $n = 4.9 \times 10^{21} \text{ cm}^{-3}$ ,  $\mu_{\text{Hall}} = 1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ). The  $\sigma$  value of the  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  epitaxial film was slightly larger than that of the R-SPE-grown  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  below 200 K, most likely due to the fact that the contribution of ionized and/or neutral impurities in the  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  epitaxial film is much smaller than that in the R-SPE-grown  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$ . It should be noted that the Hall coefficient ( $R_H$ ) of the  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  epitaxial film was always positive, even at very low temperature ( $\sim 4 \text{ K}$ ), even though the sign of the R-SPE-grown  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  changed at  $\sim 180 \text{ K}$ , as shown in the inset. This difference suggests that the electronic state of the valence band ( $\text{Co } 3d_{t_2g}$ ) is perturbed by replacement of  $\text{Na}^+$  with the  $\text{Sr}^{2+}$  ion.

Figure 4 shows the temperature dependence of  $S$  for the resultant  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  epitaxial films (178 nm thick) and the starting  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  films (110 nm thick). The  $S$  values of several layered cobaltites<sup>4,10,18</sup> are also shown for comparison. The  $S$  value of the R-SPE-grown  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  epitaxial film was comparable to that of  $\gamma$ - $\text{Na}_{0.5}\text{CoO}_2$  single crystal,<sup>4</sup> indicating high crystal quality of the film. The overall  $S$  values of the  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  epitaxial film are much larger than those of the polycrystalline  $\gamma$ - $\text{Sr}_{0.35}\text{CoO}_2$  (Ref. 10) and the  $\beta$ - $\text{Sr}_x\text{CoO}_2$  epitaxial film (Ref. 20), most likely due to the difference in the carrier concentration. The thermoelectric power factor ( $PF = S^2\sigma$ ) of the  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  epitaxial film was calculated to be  $1.2 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$  at 300 K, a value that is large, comparable to that of the  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  epitaxial film ( $PF = 1.1 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ ).

We then examined the chemical stability of the  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  epitaxial film against moisture. Although a  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  epitaxial film (86 nm thick) was completely decomposed into electrically insulating  $\text{Co}(\text{OH})_2$  when the film was heated at  $80 \text{ }^\circ\text{C}$  under high humidity conditions ( $\sim 80\%$ ) for 5 days, no significant change was observed for the crystal structure and the thermoelectric properties of the  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  epitaxial film (80 nm thick). These results led us to the conclusion that the  $\text{Sr}^{2+}$ -ion exchange treatment improves the chemical stability of  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$ , while it retains the good TE properties.

In summary, we have demonstrated herein the preparation and thermoelectric properties of  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  epitaxial films, which were prepared by  $\text{Sr}^{2+}$ -ion exchange treatment of  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  epitaxial films. The epitaxial relationship was  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  (0001)[11 $\bar{2}$ 0] ||  $\alpha$ - $\text{Al}_2\text{O}_3$ (0001)[1 $\bar{1}$ 00]. The electrical conductivity ( $\sigma$ ), Seebeck coefficient ( $S$ ) and thermoelectric power factor ( $PF = S^2\sigma$ ) of the  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  film (300 K) were  $8.9 \times 10^2 \text{ S cm}^{-1}$ ,  $+120 \text{ } \mu\text{V K}^{-1}$  and  $1.2 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ , respectively, values which compare favorably with those of the  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  epitaxial film ( $PF = 1.1 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ ). The  $\text{Sr}^{2+}$ -ion exchange treatment enhances the chemical stability of  $\gamma$ - $\text{Na}_{0.8}\text{CoO}_2$  while it maintains the good TE properties. The  $\gamma$ - $\text{Sr}_{0.32}\text{Na}_{0.21}\text{CoO}_2$  epitaxial film can be a promising candidate to develop thin film thermoelectric energy conversion devices.

<sup>1</sup>S. Ohta, T. Nomura, H. Ohta, M. Hirano, H. Hosono, and K. Koumoto, Appl. Phys. Lett. **87**, 1 (2005).

<sup>2</sup>M. Shikano and R. Funahashi, Appl. Phys. Lett. **82**, 1851 (2003).

<sup>3</sup>R. Funahashi, I. Matsubara, and S. Sodeoka, Appl. Phys. Lett. **76**, 2385 (2000).

<sup>4</sup>I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B **56**, 12685 (1997).

<sup>5</sup>K. Fujita, T. Mochida, and K. Nakamura, Jpn. J. Appl. Phys., Part 1 **40**, 4644 (2001).

<sup>6</sup>T. Motohashi, E. Naujalis, R. Ueda, K. Isawa, M. Karppinen, and H. Yamauchi, Appl. Phys. Lett. **79**, 1480 (2001).

<sup>7</sup>K. Takahata, Y. Iguchi, D. Tanaka, T. Itoh, and I. Terasaki, Phys. Rev. B **61**, 12551 (2000).

<sup>8</sup>M. L. Foo, Y. Wang, S. Watauchi, H. W. Zandbergen, T. He, R. J. Cava, and N. P. Ong, Phys. Rev. Lett. **92**, 247001 (2004).

<sup>9</sup>Y. Wang, N. S. Rogado, R. J. Cava, and N. P. Ong, Nature (London) **423**, 425 (2003).

<sup>10</sup>R. Ishikawa, Y. Ono, Y. Miyazaki, and T. Kajitani, Jpn. J. Appl. Phys., Part 2 **41**, L337 (2002); A topotactic route to obtain layered calcium cobalt oxides has been reported in B. L. Cushing and J. B. Wiley, J. Solid State Chem. **141**, 385 (1998).

<sup>11</sup>H. Ohta, K. Nomura, M. Orita, M. Hirano, K. Ueda, T. Suzuki, Y. Ikuhara, and H. Hosono, Adv. Funct. Mater. **13**, 139 (2003).

<sup>12</sup>H. Ohta, S.-W. Kim, S. Ohta, K. Koumoto, M. Hirano, and H. Hosono, Cryst. Growth Des. **5**, 25 (2005).

<sup>13</sup>H. Ohta, M. Orita, M. Hirano, and H. Hosono, J. Appl. Phys. **89**, 5720 (2001).

<sup>14</sup>H. Hiramatsu, K. Ueda, H. Ohta, M. Orita, M. Hirano, and H. Hosono, Appl. Phys. Lett. **81**, 598 (2002).

<sup>15</sup>H. Ohta, T. Kambayashi, M. Hirano, H. Hoshi, K. Ishikawa, H. Takezoe, and H. Hosono, Adv. Mater. (Weinheim, Ger.) **15**, 1258 (2003).

<sup>16</sup>H. Ohta, M. Hirano, K. Nakahara, H. Maruta, T. Tanabe, M. Kamiya, T. Kamiya, and H. Hosono, Appl. Phys. Lett. **83**, 1029 (2003).

<sup>17</sup>C. Fougassier, G. Matejka, J. M. Reau, and P. Hagenmuller, J. Solid State Chem. **6**, 532 (1973).

<sup>18</sup>V. M. Jansen and R. Hoppe, Z. Anorg. Allg. Chem. **408**, 104 (1974).

<sup>19</sup>R. J. Balsys and R. L. Davis, Solid State Ionics **93**, 279 (1996).

<sup>20</sup>T. Kanno, S. Yotsuhashi, and H. Adachi, Appl. Phys. Lett. **85**, 739 (2004).