

Enhanced thermopower in an intergrowth cobalt oxide $\text{Li}_{0.48}\text{Na}_{0.35}\text{CoO}_2$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 L379

(<http://iopscience.iop.org/0953-8984/18/29/L01>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 12:21

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Enhanced thermopower in an intergrowth cobalt oxide $\text{Li}_{0.48}\text{Na}_{0.35}\text{CoO}_2$

Zhi Ren¹, Jingqin Shen¹, Shuai Jiang¹, Xiaoyang Chen¹, Chunmu Feng²,
Zhu'an Xu¹ and Guanghan Cao^{1,3}

¹ Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China

² Test and Analysis Center, Zhejiang University, Hangzhou 310027, People's Republic of China

E-mail: ghcao@zju.edu.cn

Received 6 April 2006, in final form 15 June 2006

Published 30 June 2006

Online at stacks.iop.org/JPhysCM/18/L379

Abstract

We report the measurements of thermopower, electrical resistivity and thermal conductivity in a complex cobalt oxide $\text{Li}_{0.48}\text{Na}_{0.35}\text{CoO}_2$, whose crystal structure can be viewed as an intergrowth of the O3 phase of Li_xCoO_2 and the P2 phase of Na_yCoO_2 along the c -axis. The compound shows a large room-temperature thermopower of $\sim 180 \mu\text{V K}^{-1}$, which is substantially higher than those of Li_xCoO_2 and Na_yCoO_2 . The figure of merit for the polycrystalline sample increases rapidly with increasing temperature, and achieves nearly 10^{-4} K^{-1} at 300 K, suggesting that the $\text{Li}_x\text{Na}_y\text{CoO}_2$ system is a promising candidate for thermoelectric applications.

1. Introduction

Thermoelectric material enables direct and reversible conversion of heat to electricity, which can be applied for clean power generation and refrigeration using only solid-state elements [1, 2]. Efficient and desirable thermoelectric materials need not only to have a high dimensionless figure of merit defined by $ZT = S^2T/\rho\kappa$, where S is the Seebeck coefficient or the thermopower, T the absolute temperature, ρ the electrical resistivity, and κ the thermal conductivity, but also to be stable in air at elevated temperatures. Conducting oxides have an advantage for the latter aspect, however they have long been ignored as potential thermoelectric materials until the discovery of large thermopower in NaCo_2O_4 by Terasaki *et al* [3]. This material exhibits a rather low ρ as well as a large S (one order of magnitude larger than in typical metals) at room temperature. The power factor S^2/ρ at 300 K is comparable to the well-known thermoelectric material $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ [4]. The ZT parameter at 800 K was reported to exceed the criterion value of 1.0, suggesting that cobaltite is a promising material for the application of high-temperature thermoelectric power generation [5].

After this discovery in the NaCo_2O_4 system [3], a number of lamellar cobalt oxides (e.g. $\text{Ca}_3\text{Co}_4\text{O}_9$ [6–8], $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ [9, 10], and $\text{TlSr}_2\text{Co}_2\text{O}_y$ [11]) containing CdI_2 -type CoO_2

³ Author to whom any correspondence should be addressed.

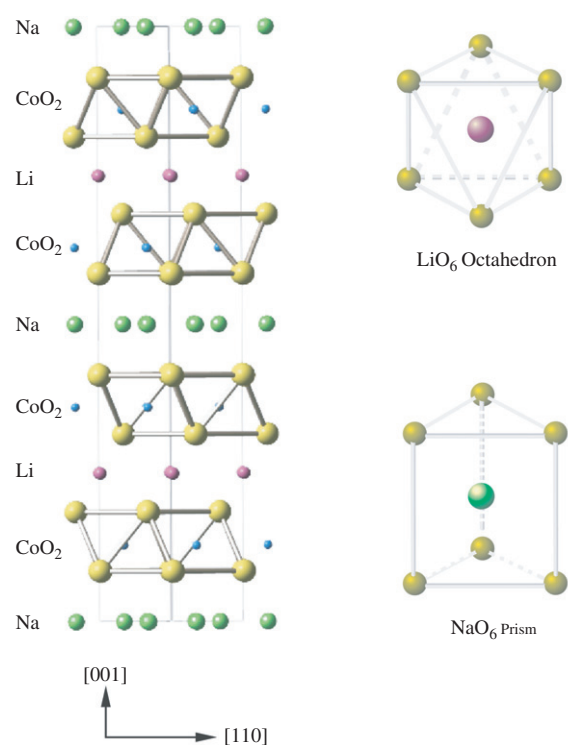


Figure 1. Crystal structure of $\text{Li}_x\text{Na}_y\text{CoO}_2$. The local oxygen environments of lithium and sodium are shown on the right.

(This figure is in colour only in the electronic version)

layers were found to display considerably high thermopower. Therefore, the triangular CoO_2 layers play a reasonably important role for the thermoelectric property. In other words, it is rational to look for new thermoelectric oxides in the system containing CoO_2 layers.

Balsys and Davis [12] first reported a new layered cobalt oxide $\text{Li}_{0.43}\text{Na}_{0.36}\text{CoO}_{1.96}$ in 1994. The crystal structure can be described as an intergrowth of the O3 phase of Li_xCoO_2 (LCO) [13] and the P2 phase of Na_yCoO_2 (NCO) [14] along the c -axis, as revealed by high-resolution neutron powder diffraction studies [12]. In between the edge-sharing CoO_6 octahedron layers, as seen in figure 1, the lithium ions are sited within an octahedral oxygen framework, whereas the sodium ions are within a trigonal prismatic oxygen environment. Accordingly, the structure of $\text{Li}_x\text{Na}_y\text{CoO}_2$ (LNCO) can be called OP4, where the letter O represents the octahedral coordination for lithium ions, the letter P represents the prismatic coordination for sodium ions, and the digit 4 denotes four CoO_2 layers per unit cell. Since the conductivity of Li_xCoO_2 is much lower than that of Na_yCoO_2 when $x \sim y$ [15], LNCO can be made and adjusted to be a natural quantum-well-like superlattice, which may possibly enhance the thermoelectric performance [16]. In this letter, we report the thermoelectric properties in this novel compound.

2. Experimental details

Balsys and Davis [12] prepared the LNCO sample by several steps. They prepared $\text{Na}_{0.7}\text{CoO}_2$ and LiCoO_2 in advance, then mixed the two compounds in an equal molar ratio. The mixture was finally fired at 1123 K for 4 days in an air atmosphere. The report implied that the resultant sample contained some LCO as a secondary phase. We also found that this preparation method led to some impurities of LCO and/or NCO. Alternatively, we synthesized the LNCO samples by direct solid-state reaction using high-purity Li_2CO_3 , Na_2CO_3 and Co_3O_4 as the starting

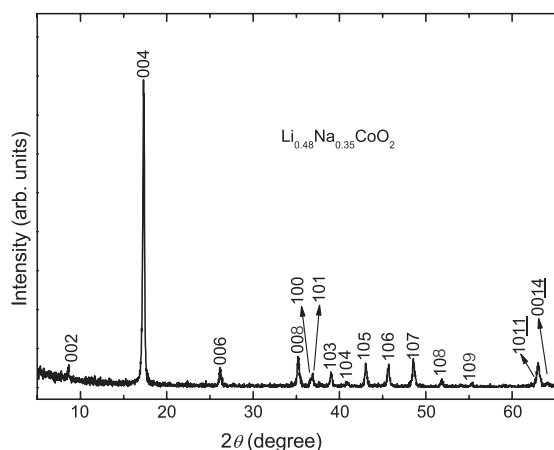


Figure 2. X-ray powder diffraction pattern for the as-quenched $\text{Li}_{0.48}\text{Na}_{0.35}\text{CoO}_2$ sample.

materials. The well-mixed powders with different stoichiometry were pressed into pellets under a pressure of 2000 kg cm^{-2} . The pellets were rapidly heated to 1173 K in flowing oxygen, held for 30 h, and then quenched. The as-quenched samples were finally annealed in an oxygen flow at 673 K for 24 h and allowed to cool down slowly to room temperature.

Powder x-ray diffraction (XRD) experiments were carried out using a D/Max- γ A diffractometer with Cu $K\alpha$ radiation. It was found that single-phase LNCO samples could be formed only in a narrow range of compositions. One of our best samples was obtained with the initial composition $\text{Li}_{0.47}\text{Na}_{0.44}\text{CoO}_2$. By inductively coupled plasma atomic-emission spectrometry (ICP-AES) measurement, the final composition was determined to be $\text{Li}_{0.48(1)}\text{Na}_{0.35(1)}\text{CoO}_2$, assuming no oxygen deficiencies. The variation in composition arises from the loss of sodium during the solid-state reaction.

The measurements of electrical resistivity, thermal conductivity and thermopower were performed on rectangular bars ($1.5 \times 2 \times 6 \text{ mm}^3$) cut from the annealed LNCO pellets. The resistivity was obtained using a standard four-probe technique with a dc current of 0.5 mA. The thermopower and thermal conduction were measured by a steady-state method with a temperature difference of $\sim 1 \text{ K}$. All the electrodes were carefully made using well-conducting silver paste.

3. Results and discussion

Figure 2 shows the XRD pattern of the as-quenched LNCO sample. All the XRD peaks can be well indexed using a hexagonal cell with the $P6_3/mmc$ space group. The lattice parameters refined by a least-squares fit are $a = 2.824 \text{ \AA}$ and $c = 20.293 \text{ \AA}$. It can be seen that the c -axis is taken as the expected value of $2(c_1/3 + c_2/2)$, where c_1 and c_2 are the c -axes of the LCO O3 phase [15] and of the NCO P2 phase [14], respectively. One may also note that the value of the a -axis is larger than that of LCO ($a = 2.816 \text{ \AA}$) [15] but smaller than that of NCO ($a = 2.830\text{--}2.843 \text{ \AA}$) [14, 17]. This implies that the oxygen sheets close to the lithium layers are under some compression, while those neighbouring the sodium layers bear some tension. Such asymmetric interactions on the conducting CoO_2 layers might bring about some additional effects on physical properties.

Figure 3 shows the temperature dependence of resistivity and thermal conductivity for the annealed LNCO sample. The resistivity basically exhibits semiconducting behaviour (i.e. $d\rho/dT < 0$) in the whole temperature range. The room-temperature resistivity is $\sim 20 \text{ m}\Omega \text{ cm}$.

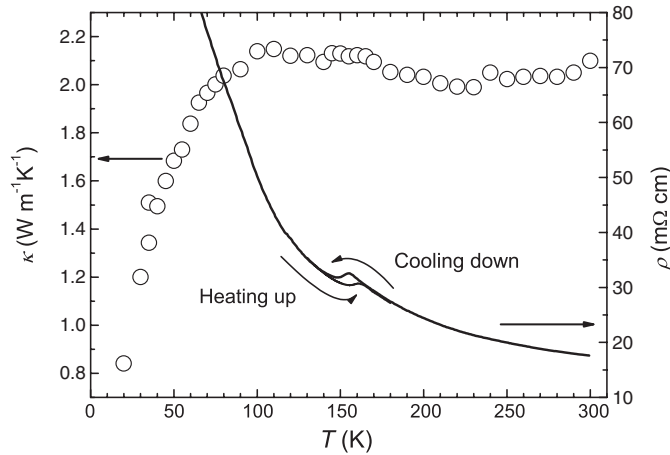


Figure 3. Temperature dependence of electrical resistivity and thermal conductivity for the as-annealed $\text{Li}_{0.48}\text{Na}_{0.35}\text{CoO}_2$ polycrystalline sample.

This value is about six times larger than that of NaCo_2O_4 [18] or $\text{Na}_{0.75}\text{CoO}_2$ [19], two orders of magnitude smaller than that of $\text{Li}_{0.96}\text{CoO}_2$ [15], and comparable to that of $\text{Ca}_3\text{Co}_4\text{O}_9$ [6, 7]. It is noted that the $\rho(T)$ curve shows an anomaly at ~ 150 K with a thermal hysteresis. No anomaly was found in the magnetic measurement (to be shown elsewhere). We speculate that this phenomenon could be related to the ordering of Na^+ ions (the ordering of Li^+ ions is ignored, because Li^+ almost fully occupies its lattice site). The disorder of sodium ions at high temperatures induces a strong Anderson localization effect. Upon the ordering of Na^+ , the Anderson localization becomes weak, which leads to a decrease in resistivity when cooling down to ~ 150 K. It is noted that the ordering of sodium ions has been identified by electron diffraction in the NCO system [20].

Like the NCO system, the thermal conductivity of the LNCO sample is very low. The value of κ at 300 K is $\sim 2 \text{ W m}^{-1} \text{ K}^{-1}$, close to that of the NCO polycrystalline sample [18]. However, in contrast to the NCO system, which shows that κ increases obviously with increasing temperature up to room temperature, $\kappa(T)$ of the LNCO sample is weakly temperature dependent from 100 to 300 K. Detailed analysis of the $\kappa(T)$ behaviour is beyond the scope of this letter. Nevertheless, we believe that the unusually low thermal conductivity is also due to a phonon glass effect, which has been proposed by Takahata *et al* [18] for explaining the thermal conductivity in the NCO system.

Figure 4 shows the thermopower as a function of temperature for the LNCO sample. The positive sign of S in the whole temperature range establishes the hole-like character of the prevailing charge carriers. Although the sample shows semiconducting behaviour in the resistivity measurement, the $S(T)$ curve exhibits a similar temperature dependence to the in-plane thermopower of the metallic NCO crystals [3]. Strikingly, the thermopower at 300 K is as high as $182 \mu\text{V K}^{-1}$, which is $\sim 60 \mu\text{V K}^{-1}$ larger than the S values of $\text{Na}_{0.75}\text{CoO}_2$ [19] and LiCoO_2 [15]. Therefore, the LNCO sample shows an enhanced thermopower.

The origin of large thermopower in NCO has been investigated both theoretically and experimentally for a few years. Koshibae *et al* [21] considered that the degeneracy of carriers, together with strong correlation of 3d electrons, brought about the large thermopower. Based on the LDA band calculation, on the other hand, it was also able to give a large thermopower, since the density of states $N(E)$ has a large slope at the Fermi level [22]. Wang *et al* [23] studied the magnetic field dependence of thermopower in NCO, and they concluded that the spin entropy was the likely origin of the enhanced thermopower. In a word, the large thermopower is not universally clarified yet.

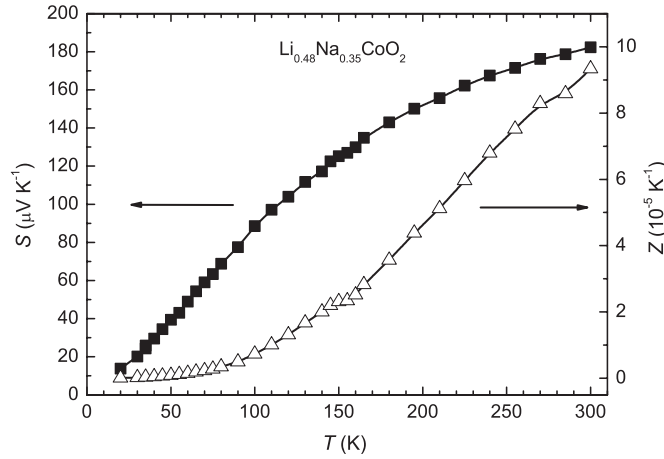


Figure 4. Temperature dependence of thermopower (S) and figure of merit (Z) for the as-annealed $\text{Li}_{0.48}\text{Na}_{0.35}\text{CoO}_2$ polycrystalline sample.

Nevertheless, the thermopower at the high-temperature limit is usually expressed by the generalized Heikes formula [24]. In the large electron–electron repulsion limit without considering the nearest-neighbour interaction, the Heikes formula can be separated into the spin part S_σ and the charge part S_c :

$$S = \frac{k_B}{e} \ln \left(2 \cdot \frac{1 - \xi}{\xi} \right) = \frac{k_B}{e} \ln 2 + \frac{k_B}{e} \ln \left(\frac{1 - \xi}{\xi} \right) = S_\sigma + S_c, \quad (1)$$

where ξ denotes the ratio of carriers to sites, i.e. the fraction of Co^{4+} . In the absence of oxygen vacancies, $\xi = 1 - x$. It was reported that the oxygen nonstoichiometry was remarkable only for $x < 0.5$, and the Na_xCoO_2 ($x > 0.7$) samples prepared by solid-state reaction had no detectable oxygen vacancy [25]. In applying equation (1) to the Na_xCoO_2 system, one can find that S is obviously overestimated. For example, the maximum S value reported for $\gamma\text{-Na}_{0.75}\text{CoO}_2$ was 110–120 $\mu\text{V K}^{-1}$ at 300 K [19, 26]. However, the calculated S value is 154 $\mu\text{V K}^{-1}$. Another example comes from $\alpha\text{-Na}_{0.9}\text{CoO}_2$ [27]. Although the room-temperature thermopower reached $\sim 150 \mu\text{V K}^{-1}$, the expected S value is as high as 250 $\mu\text{V K}^{-1}$.

In order to match the experimental data, here we propose an empirical expression for $S(\xi)$:

$$S(\xi) = S_0 + \frac{\beta k_B}{e} \ln \left(\frac{1 - \xi}{\xi} \right), \quad (2)$$

where S_0 and β are empirical parameters. Figure 5 shows the thermopower as a function of $\ln[(1 - \xi)/\xi]$ in the Na_xCoO_2 ($x \geq 0.67$) system. We dropped two data points of $x < 0.67$ because of the possible existence of oxygen nonstoichiometry. As can be seen, the data points from different authors lie basically on a straight line. The linear fit gives the intercept $S_0 = 55 \mu\text{V K}^{-1}$, close to the expected S_σ value (60 $\mu\text{V K}^{-1}$). However, the fitted β value is 0.52. It is stressed that the S value of $\text{Li}_{0.48}\text{Na}_{0.35}\text{CoO}_2$ is located far above the straight line. The thermopower enhancement is about 55 $\mu\text{V K}^{-1}$, which is possibly related to the particular intergrowth structure. Further investigations are needed for this issue.

Finally, let us discuss the potential applications. Using the data of $S(T)$, $\rho(T)$ and $\kappa(T)$, the figure of merit $Z (= S^2/\rho\kappa)$ can be obtained, as is also shown in figure 4. The Z value at room temperature reaches nearly 10^{-4}K^{-1} , which is higher than or comparable to those of other layered thermoelectric cobaltites [18, 7, 9]. Besides, the three factors of $S(T)$, $\rho(T)$ and $\kappa(T)$ cooperatively raise the Z value when further increasing the temperature. Therefore,

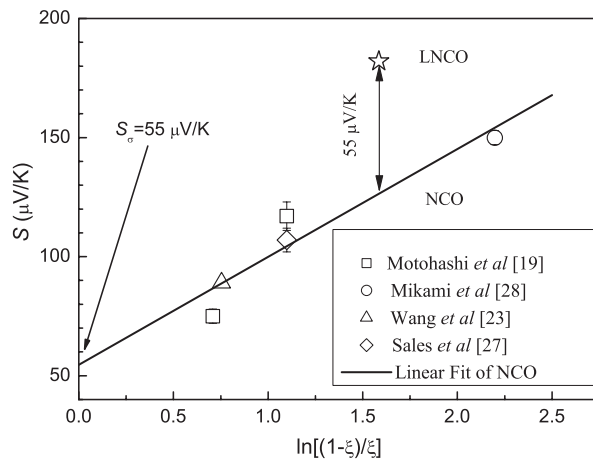


Figure 5. Thermopower S at 300 K as a function of $\ln[(1-\xi)/\xi]$ (where ξ denotes the concentration of Co^{4+}) in the Na_xCoO_2 ($x \geq 0.67$) system. The straight line is the linear-fit result. Data for $\text{Li}_{0.48}\text{Na}_{0.35}\text{CoO}_2$ is plotted for comparison.

the LNCO system should be another promising candidate for high-temperature thermoelectric applications.

This work was supported by the Specialized Research Fund for the Doctoral Program of Higher Education (Grant No. 20040330563) and the National Science Foundation of China (Grant No. 10225417).

References

- [1] Mahan G, Sales B and Sharp J 1997 *Phys. Today* **50** 42
- [2] Tritt T M 1999 *Science* **283** 804
- [3] Terasaki I, Sasago Y and Uchinokura K 1997 *Phys. Rev. B* **56** R12685
- [4] Caillat T, Carle M, Pierrat P, Scherrer H and Scherrer S 1992 *J. Phys. Chem. Solids* **53** 1121
- [5] Fujita K, Mochida T and Nakamura K 2001 *Japan. J. Appl. Phys.* **40** 4644
- [6] Masset A C, Michel C, Maignan A, Hervieu M, Toulemonde O, Studer F, Raveau B and Hejtmanek J 2000 *Phys. Rev. B* **62** 166
- [7] Li S, Funahashi R, Matsubara I, Ueno K and Yamada H 1999 *J. Mater. Chem.* **9** 1659
- [8] Miyazaki Y, Kudo K, Akoshima M, Ono Y, Koike Y and Kajitani T 2000 *Japan. J. Appl. Phys.* **39** L531
- [9] Funahashi R, Matsubara I and Sodeoka S 2000 *Appl. Phys. Lett.* **76** 2385
- [10] Itoh T and Terasaki I 2000 *Japan. J. Appl. Phys.* **39** 6658
- [11] Hebert S, Lambert S, Pelloquin D and Maignan A 2001 *Phys. Rev. B* **64** 172101
- [12] Balsys R J and Davis R L 1994 *Solid State Ion.* **69** 69
- [13] Mizushima K, Jones P C, Wiseman P J and Goodenough J B 1980 *Mater. Res. Bull.* **15** 783
- [14] Fouassier C, Matejka G, Reau J M and Hagenmuller P 1973 *J. Solid State Chem.* **6** 532
- [15] Levasseur S, Menetrier M, Suard E and Delmas C 2000 *Solid State Ion.* **128** 11
- [16] Harman T C, Taylor P J, Walsh M P and LaForge B E 2002 *Science* **297** 2229
- [17] Bayrakci S P, Bernhard C, Chen D P, Keimer B, Kremer R K, Lemmens P, Lin C T, Niedermayer C and Strempler J 2004 *Phys. Rev. B* **69** 100410
- [18] Takahata K, Iguchi Y, Tanaka D, Itoh T and Terasaki I 2000 *Phys. Rev. B* **61** 12551
- [19] Motohashi T, Naujalis E, Ueda R, Isawa K, Karppinen M and Yamauchi H 2001 *Appl. Phys. Lett.* **79** 1480
- [20] Zandbergen H W, Foo M, Xu Q, Kumar V and Cava R J 2004 *Phys. Rev. B* **70** 024101
- [21] Koshibae W, Tsitsui K and Maekawa S 2000 *Phys. Rev. B* **62** 6869
- [22] Singh D J 2000 *Phys. Rev. B* **61** 13397
- [23] Wang Y, Rogado N S, Cava R J and Ong N P 2003 *Nature* **423** 425
- [24] Chaikin P M and Beni G 1976 *Phys. Rev. B* **13** 647
- [25] Karppinen M, Asako I, Motohashi T and Yamauchi H 2005 *Phys. Rev. B* **71** 092105
- [26] Sales B C, Jin R, Affholter A, Khalifah P, Veith G M and Mandrus D 2004 *Phys. Rev. B* **70** 174419
- [27] Mikami M, Yoshimura M, Mori Y, Sasaki T, Funahashi R and Shikana 2003 *Japan. J. Appl. Phys.* **42** 7383