

# Overview of thermoelectric sodium cobaltite: $\text{Na}_x\text{Co}_2\text{O}_4$

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An overview of the crystal structure, synthesis techniques for single crystal and polycrystalline  $\text{Na}_x\text{Co}_2\text{O}_4$  and their thermoelectric properties are presented. The study on the strong electron correlation in this oxide which is believed to be the likely source of the enhanced thermopower is reviewed. The recently discovered superconducting behavior for the Na-deficient hydrated compound  $\text{Na}_x\text{Co}_2\text{O}_4 \cdot y\text{H}_2\text{O}$  is also discussed.

## 1. Introduction

Thermoelectric (TE) technology for energy conversion between heat and electricity via Seebeck and Peltier effects provides a viable method for solid state cooling and remote power supply. In view of global environmental and energy problems, TE is becoming an increasing important field for power generation utilizing vast amount of waste heat emitted from various industrial factories, automobiles and homes. The performance of TE materials is generally evaluated by the dimensionless figure-of-merit which is defined as  $ZT = s^2T / \rho(\kappa_L + \kappa_e)$ , here  $s$  is the Seebeck coefficient (also called thermopower),  $\rho$  is the resistivity,  $\kappa_L$  and  $\kappa_e$  is lattice and electronic thermal conductivity, respectively.

Due to their high thermal and chemical stability and non-toxicity, ceramic oxide materials have the potential for high temperature power generation application. But traditional TE theory considers them which usually possess low mobility dirty TE materials. The appearance of a new transition-metal oxide,  $\text{NaCo}_2\text{O}_4$  with unexpected good TE properties reported by Terasaki in 1997 [1] challenges the traditional guiding principle. As shown in Fig. 1,  $\text{NaCo}_2\text{O}_4$  single crystal synthesized by NaCl flux method was found to be potential as a good p-type TE with low metallic in-

plane resistivity  $\rho_a \sim 0.2 \text{ m}\Omega\text{-cm}$  and large  $\alpha \sim 100 \mu\text{V/K}$  (symbol  $S$  is used in the plot), even though the mobility is quite low,  $\mu \sim 13 \text{ cm}^2/\text{V-s}$ . Its power factor ( $\text{PF} = \alpha^2 T / \rho$ ) value of  $1.5 \text{ W/m-K}$  is even larger than that of  $\text{Bi}_2\text{Te}_3$ ,  $1.2 \text{ W/m-K}$  at  $300\text{K}$ . In 2001, Fujita reported [2] the  $ZT$  of  $\text{Na}_x\text{Co}_2\text{O}_4$  single crystal could reach 1.2 at  $800\text{K}$ , quite comparable to conventional TE materials. This high  $ZT$  value suggests this oxide a promising p-type TE for high temperature applications. In 2003, Takada discovered [3] that Na-deficient hydrated compound  $\text{Na}_{0.35}\text{Co}_2 \cdot 1.3\text{H}_2\text{O}$  displayed superconducting behavior at a critical temperature ( $T_C$ ) below  $5 \text{ K}$ . The investigation on the role of intercalating thick  $\text{H}_2\text{O}$  layer may provide valuable information to fully understand the high  $T_C$  superconducting cuprates. To the best of our knowledge  $\text{Na}_x\text{Co}_2\text{O}_4$  is to date the most promising p-type TE oxide and currently have been one of the highlights in TE research area.

## 2. Structure, synthesis and TE properties of single crystal and polycrystalline $\text{Na}_x\text{Co}_2\text{O}_4$

As a member of the alkali ternary oxide group  $\text{A}_x\text{MO}_2$  ( $\text{A} = \text{Na, K; M} = \text{Cr, Mn, Co etc.}$ ),  $\text{NaCo}_2\text{O}_4$  was first reported by Fouassier *et al.* in 1973 for its interesting structural and transport properties [4]. This ceramic oxide has a hexagonal layered structure with edge-sharing 2D triangle  $\text{CoO}_2$  sheets and Na layers alternately stacked along c-axis. The electrons in  $\text{CoO}_2$  layer are localized and confined due to the strong electron interaction, which is the likely source of low metallic  $\rho$  and enhanced  $\alpha$ . The Na layer, acting as the charge reservoir and donating electrons distributed among Co ions is insulating and highly disordered like an amorphous solid. The Na atoms are thought to randomly occupy part of positions and the resulting phonon-point defect (Na vacancies) scattering leads to low  $\kappa$ . Depending on the ratio of Na/Co, this compound has four bronze type phases having different oxygen packing orders in hexagonal sheets, i.e.,  $\alpha\text{-Na}_x\text{CoO}_2$  ( $0.9 \leq x \leq 1$ , O3 phase),  $\alpha'\text{-Na}_{0.75}\text{CoO}_2$  (O'3 phase),  $\beta\text{-Na}_x\text{CoO}_2$  ( $0.55 \leq x \leq 0.6$ , P3 phase), and  $\gamma\text{-Na}_x\text{Co}_y\text{O}_2$  ( $0.55 \leq x/y \leq 0.74$ , P2 phase) [4].

Typically  $\text{Na}_x\text{Co}_2\text{O}_4$  single crystals were synthesized via a high temperature NaCl flux method using  $\text{Na}_2\text{CO}_3$  and  $\text{Co}_3\text{O}_4$  as starting materials and firing up to  $1050 \text{ }^\circ\text{C}$  followed by slow cooling at a rate of  $0.5\text{--}5 \text{ }^\circ\text{C/hr}$  [1, 2]. Typical size of as-grown crystals is  $\sim 1\text{--}2 \text{ mm}$  and it is difficult to grow bigger samples.

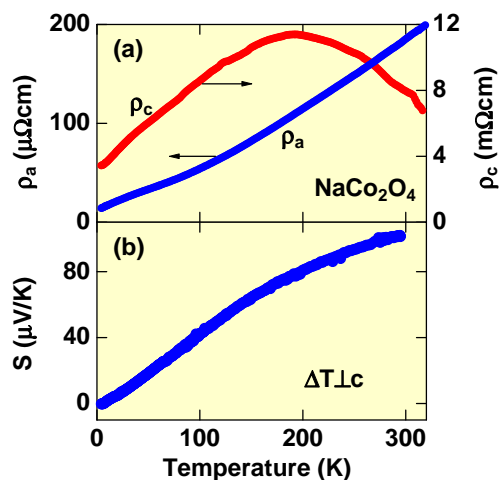
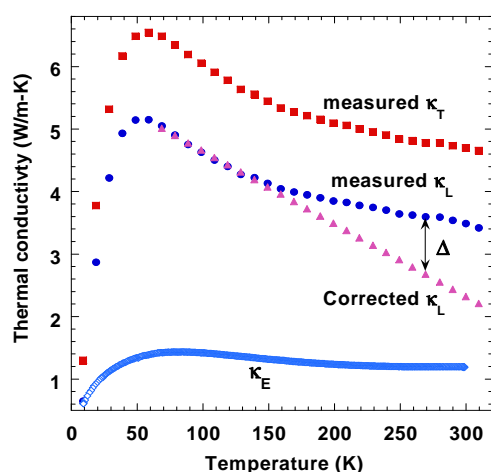


Fig. 1: In-plane  $\rho$  and  $\alpha$  of  $\text{NaCo}_2\text{O}_4$  single crystal (Ref. 1).

Via rotating the crucibles to increase the solution homogeneity and inserting a platinum wire, through which the current was sent into the surface of solution to reduce the nucleation, Mikami et al. [5] obtained plate-like crystals with size up to  $10 \times 10 \times 0.5 \text{ mm}^3$ . In 2003 Peleckis et al. [6] successfully grew  $\text{Na}_x\text{Co}_2\text{O}_4$  whiskers with size up to 1.6 mm in length, 15–40  $\mu\text{m}$  in width and 1.5–4.0  $\mu\text{m}$  in thickness through an unconventional method from potassium-containing compositions. Large single crystals required for inelastic neutron scattering experiments have also been grown by floating-zone technique utilizing optical furnace [7]. These crystals growths were performed in the high temperature regime, thus it's difficult to prevent the vaporization of large amount of Na during synthesis due to its high vapor pressure at elevated temperature. Recently we reported [8] a novel low temperature technique to successfully synthesize  $\text{Na}_x\text{Co}_2\text{O}_4$  plate-like single crystals with size up to 6 mm at low temperature 550 °C by using NaOH/NaCl as the flux and Co powders as the Co source.

For the brittle and small size  $\text{Na}_x\text{Co}_2\text{O}_4$  single crystals, accurately measuring the thermal conductivity  $\kappa$  is always challenging [9]. For the flux-grown  $\text{Na}_x\text{Co}_2\text{O}_4$  crystals (typically small size), Fujita et al. [2] reported  $\sim 19 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at 300 K via the thermal diffusivity, heat capacity and density measurements (sample size  $\sim 1.5 \times 1.5 \times 0.03 \text{ mm}^3$ ), but Satake et al. reported [10] much smaller value  $\sim 3\text{--}8 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at 300 K via a revised “Harman” method (size  $\sim 2 \times 0.5 \times 0.05 \text{ mm}^3$ ). For crystals grown from floating-zone method, Sales et al. reported [11]  $\sim 7.0 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  for a large  $\text{Na}_{1.5}\text{Co}_2\text{O}_4$  crystal with typical size of  $5 \times 5 \times 1 \text{ cm}^3$ , and Foo et al. reported [12] an exceptionally high  $\kappa$  value ( $300 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ) for  $\text{Na}_{1.0}\text{Co}_2\text{O}_4$  crystal at 53 K, but much smaller  $\kappa$  values with much weaker temperature-dependence for other Na composition  $\text{Na}_x\text{Co}_2\text{O}_4$  crystals. In our lab, a direct thermal conductivity measurement technique called parallel thermal

Fig. 2: In-plane  $\kappa$  of  $\text{Na}_x\text{Co}_2\text{O}_4$  single crystals by “PTC”



technique [14].  $\kappa_T$ ,  $\kappa_L$ ,  $\kappa_E$  and  $\Delta$  are total, lattice and electronic thermal conductivity and thermal radiation, respectively.

conductance (“PTC”) was developed [13, 14] to measure the  $\kappa$  of flux-grown  $\text{Na}_x\text{Co}_2\text{O}_4$  crystals and the in-plane  $\kappa$  was found to be  $\sim 5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at 300 K, as shown in Fig. 2. The phonon mean free path (MFP) is estimated to be  $l_{\text{ph}} \sim 9 \text{ \AA}$  at 300 K, which is

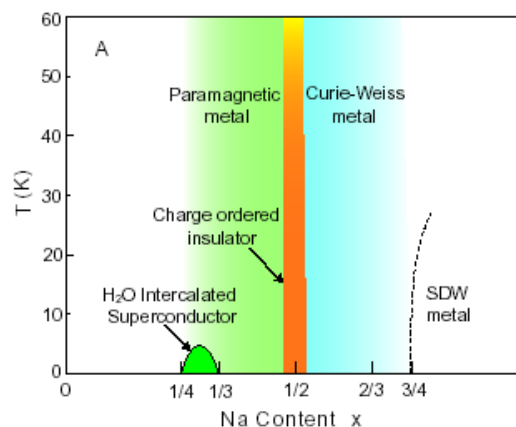
comparable to the lattice constant but much smaller than the reported MFP of conducting carriers [14].

Because of the structure anisotropy and grain boundaries, the TE properties of polycrystalline  $\text{Na}_x\text{Co}_2\text{O}_4$  is not as favorable as single crystals. The  $\rho$  of polycrystalline samples obtained by traditional solid state reaction is around ten times higher than the single crystals, and as a result, the power factor ( $\text{PF} = \alpha^2 T / \rho$ ) is much smaller. The value of ZT ( $\sim 0.2$  at 1000K) of polycrystalline sample is much smaller than the traditional TE semiconductors, but it is the highest among the p-type TE polycrystalline oxides.

Due to the volatile nature of sodium, precise control of the composition is very difficult, and the typical way is to add excess Na in the starting materials to compensate. Motohashi et al. [15] developed a technique called “rapid heat-up” to precisely control the Na content by avoiding Na evaporation. Ohtaki and his collaborators [16] used “double-step” sintering to get high  $\alpha \sim 190 \mu\text{V}/\text{K}$  and  $\text{ZT} \sim 0.78$  at 800°C. Tajima et al. [17] employed a reactive template grain growth (RTGG) technique to obtain highly textured polycrystalline samples with  $\text{PF} \approx 0.06\text{--}0.15 \text{ W}/\text{m}\cdot\text{K}$ . Nagira et al. [18] prepared high-quality  $\text{Na}_x\text{Co}_2\text{O}_4$  samples with ZT of 0.7 at 1000K by a polymerized complex (PC) method. Meanwhile, Terasaki et al. [19–21] extensively studied the doping effects of a large number of elements for both Na-site (like Ca, Sr) and Co-site (such as 3d elements: Mn, Fe, Cu, Zn and 4d elements: Ru, Rh, Pd etc.) and found out that partial substitution of Cu with Co can effectively enhance  $\alpha$  and ZT. We systematically studied [22] the effect of Na content on the TE and magnetic properties for polycrystalline  $\text{Na}_x\text{Co}_2\text{O}_4$  and found out that with increasing Na concentration x: (1)  $\alpha$  monotonously increases while magnetic susceptibility and effective moment monotonically decrease; (2) the  $\kappa$  and  $\rho$  and heat capacity are not appreciably affected.

In 2004, Foo et al. [23] reported the phase diagram of  $\text{Na}_x\text{CoO}_2$  with varying Na content x, according to the magnetic susceptibility and in-plane resistivity results. As displayed in Fig. 3, when x increases from 0.3, the ground state goes from a Pauli paramagnetic metal to a charge-ordered insulator (at  $x=0.5$ ) to a “Curie-Weiss” metal ( $x \sim 0.65\text{--}0.75$ ), and finally to a weak-moment magnetically ordered state, SDW (spin-density-wave) state at  $x > 0.75$ .

Fig. 3: Phase diagram of  $\text{Na}_x\text{CoO}_2$  (Ref. 23).



### 3. Strong electron correlation and the source of enhanced thermopower

Like some other transition-metal oxides,  $\text{Na}_x\text{Co}_2\text{O}_4$  is also a correlated electron system, where the electrons are localized at the atomic sites and lose their mobility due to the strong Coulombic repulsion. A  $^{59}\text{Co}$  NMR study along with the susceptibility results revealed [24] that two distinct Co ions exist at low spin states, i.e., nonmagnetic  $\text{Co}^{3+}$  with spin  $s=0$  and magnetic  $\text{Co}^{4+}$  with  $s=1/2$ , as shown in Fig. 4. Due to the octahedral O environment, the 3d electron of Co ions are crystal field split into two distinct energy levels, the upper-lying two-fold level  $e_g$  and lower-lying three-fold level  $t_{2g}$  [25]. There are 0.5 holes per Co ion and 1 hole per unit cell (2 Co ions). The elementary charge-transport process is the hopping of a hole from  $\text{Co}^{4+}$  to  $\text{Co}^{3+}$  ions.

The evidence of existing strong electron correlation in this compound could be summarized as follows: 1) the bandwidth  $W$  is much smaller than the Coulomb on-site repulsion  $U$  [25]; 2) much larger electronic specific heat coefficient  $\gamma \sim 48 \text{ mJ/mol}\cdot\text{K}^2$  [26] than ordinary metals, possibly due to the low dimensionality and frustrated spin structure of triangle  $\text{CoO}_2$  sheet; 3) the continuing decrease of  $\rho$  down to low temperature of 4.2K [27].

The study at Princeton University showed [28] experimentally that the large  $\alpha$  for this metallic oxide comes from the electronic spin entropy. In the electron correlated system, the spin degrees are predicted to produce a large contribution to the  $\alpha$ . The spins are not fixed to specific atoms within the lattice, instead are free to move around. Therefore, if the applied magnetic field is strong enough to remove the spin degeneracy,  $\alpha$  should vanish to zero, only if the spin entropy really provides the main contribution. That's exactly what they found in their experiment.

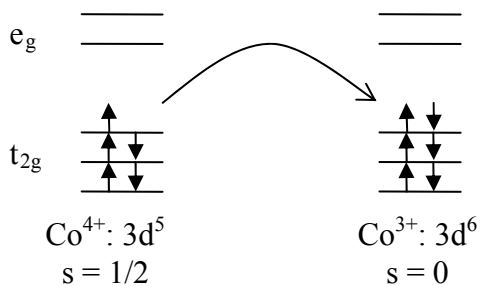


Fig. 4: Co ( $3d^74s^2$ ) electron configuration (at low spin state).

### 4. Superconductivity of hydrated sodium cobaltite $\text{Na}_x\text{Co}_2\text{O}_4 \cdot y\text{H}_2\text{O}$

In 2003 Takada et al. [3] first reported the superconductivity behavior ( $T_c \sim 5\text{K}$ ) in the hydrated form of sodium cobaltite  $\text{Na}_x\text{Co}_2\text{O}_4 \cdot y\text{H}_2\text{O}$ , as displayed in Fig. 5(a). The sudden drop to negative magnetic susceptibility  $\chi$  just below 5K was clearly observed. Such a strong diamagnetism, due to the expulsion of magnetic flux by a supercurrent, is a significant signal of the onset of superconductivity. Also the sharp decrease of  $\rho$  observed at around 4K (not shown here) also supports the superconducting transition. The thick insulating layer of water which is intercalated between the  $\text{CoO}_2$  sheet and Na layer, as shown in

Fig. 5(b), was thought to play an essential role to induce superconductivity.

Recently Cava et al. [29] found that the superconductivity transition temperature  $T_c$  varied with Na content  $x$  and reached its highest value 5K near  $x=0.6$ . Kobayashi et al. [30] reported the temperature dependence of the Knight shift  $K_y$  in the superconducting  $\text{Na}_x\text{Co}_2\text{O}_4 \cdot y\text{H}_2\text{O}$  from the  $^{59}\text{Co}$  NMR study. A  $^{59}\text{Co}$  NQR study [31] also shows this hydrated oxide is a fully gapped superconductor and the superconductivity is thought to occur close to a ferromagnetic phase. Fujii and Terasaki recently proposed [32] a “block-layer” concept for the layered Co oxides, as is established in high temperature superconductors.

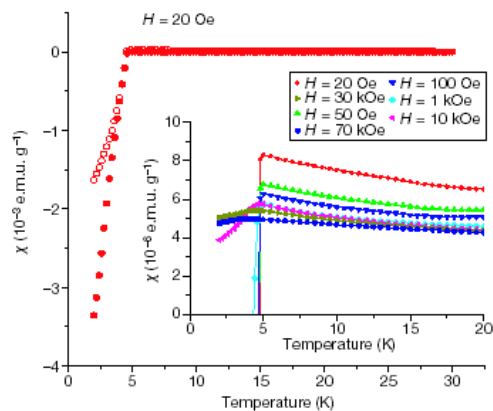


Fig. 5 (a): Magnetic susceptibility of  $\text{Na}_x\text{Co}_2\text{O}_4 \cdot y\text{H}_2\text{O}$  (Ref. 3).

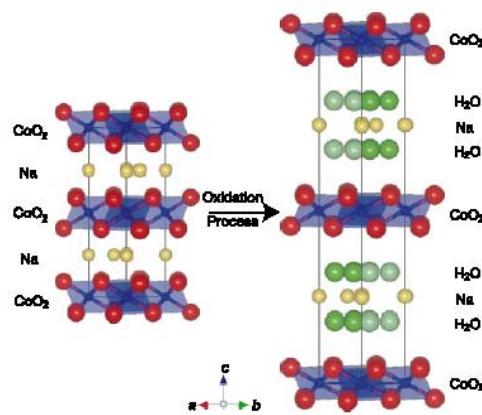


Fig. 5 (b): Crystal structure of  $\text{Na}_x\text{Co}_2\text{O}_4 \cdot y\text{H}_2\text{O}$  (Ref. 3).

Although the  $T_c$  of the hydrated sodium cobaltite is far below the  $T_c$  of superconducting copper oxides, the investigation of the mechanism behind it may give us some valuable hint to understand the source of superconductivity in the cuprates because of their resemblance in structure, such as 2D character of  $\text{CoO}_2$  layer and  $\text{CuO}_2$ . The main difference between these two layered oxide systems is that the Co ions form the triangle lattice with spins frustrated geometry, but  $\text{CuO}_2$  plane forms the square lattice of antiferromagnetic spins.

### Conclusions

A promising TE oxide material  $\text{Na}_x\text{Co}_2\text{O}_4$  is reviewed in terms of the crystal structure, synthesis techniques for single crystal and polycrystalline  $\text{Na}_x\text{Co}_2\text{O}_4$  and their TE properties. The reported high ZT values suggest this oxide a potential TE

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candidate for high temperature power generation applications. As a strongly correlated electron system, the spin entropy is believed to be the likely source of the enhanced  $\alpha$ . The study on the discovered superconducting behavior for the Na-deficient hydrated compound  $\text{Na}_x\text{Co}_2\text{O}_4 \cdot y\text{H}_2\text{O}$  may provide us useful clues to solve the mystery mechanisms in high  $T_c$  superconductor cuprates.

## Notes and references

- 1 Terasaki, Y. Sasago and K. Uchinokura. *Phys. Rev. B*, 1997, **56**, 12685.
- 2 K. Fujita, T. Mochida and K. Nakamura. *Jpn. J. Appl. Phys.*, part1, 2001, **40**, 4644.
- 3 K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian and T. Sasaki. *Nature*, 2003, **422**, 53.
- 4 C. Fouassier, G. Matejka, J-M. Reau, P. Hagenmuller, *J. Solid State Chem.*, 1973, **6**, 532.
- 5 M. Mikami, M. Yoshimura, Y. Mori et al. *Jpn. J. Appl. Phys.*, 2002, **41**, L777.
- 6 G. Peleckis, T. Motohashi, M. Karppinen and H. Yamauchi. *Appl. Phys. Lett.*, 2003, **83**, 5416.
- 7 F. C. Chou, J. H. Cho, P. A. Lee et al. *Phys. Rev. Lett.*, 2004, **92**, 157004.
- 8 X. Tang, J. He, K. Aaron, E. Abbott, J. Kolis, and T. Tritt, *J. Crystal Growth*, 2008, **310**, 665.
- 9 Thermal conductivity theory, properties and applications, edited by Terry Tritt, (Kluwer Academic/Plenum, 2004).
- 10 A. Satake, H. Tanaka, T. Ohkawa, T. Fujii, and I. Terasaki, *J. Appl. Phys.* 2004, **96**, 931.
- 11 B. C. Sales, R. Jin, K. A. Affholter, P. Khalifah, G. M. Veith, and D. Mandrus, *Phys. Rev. B*, 2004, **70**, 174419.
- 12 M. L. Foo, Y. Wang, S. Watauchi, H. W. Zandbergen, T. He, R. J. Cava, and N. P. Ong, *Phys. Rev. Lett.* 2004, **92**, 247001.
- 13 B. M. Zawilski, R. T. Littleton, and T. M. Tritt, *Rev. Sci. Instrum.* 2001, **72**, 1770.
- 14 X. Tang, K. Aaron, J. He, and T. Tritt, *Phys. stat. sol. (a)*, 2008, **205**, 1152.
- 15 T. Motohashi, E. Naujalis, R. Ueda et al. *Appl. Phys. Lett.*, 2001, **79**, 1480.
- 16 M. Ohtaki and E. Maeda, *J. Jpn. Soc. Powders and Powder Metallurgy*, 2000, **47**, 1159.
- 17 S. Tajima, T. Tani, S. Isobe et al. *Mater. Sci. & Eng. B*, 2001, **86**, 20-25.
- 18 T. Nagira, M. Ito, S. Katsuyama, K. Majima and H. Ngai. *J. Alloys and Compounds*, 2003, 348, 263.
- 19 T. Kawata, Y. Iguchi, T. Itoh et al. *Phys. Rev. B*, 1999, **60**, 10584.
- 20 I. Terasaki, Y. Ishii, D. Tanaka et al. *Jpn. J. Appl. Phys.*, 2001, **40**(1A), L65.
- 21 I. Terasaki, I. Tsukada and Y. Igucgi. *Phys. Rev. B*, 2002, **65**, 195106.
- 22 X. Tang, J. He, K. Aaron, E. Abbott, and T. Tritt, paper in preparation.
- 23 M. L. Foo, Y. Y. Wang, S. Watauchi et al. *Phys. Rev. Lett.*, 2004, **92**, 247001.
- 24 R. Ray, A. Ghoshray, K. Ghoshray et al. *Phys. Rev. B*, 1999, **59**, 9454.
- 25 D. J. Singh. *Phys. Rev. B*, 2000, **61**, 13397.
- 26 Y. Ando, N. Miyamoto, K. Segawa, T. Kawata and I. Terasaki. *Phys. Rev. B*, 1999, **60**, 10580.
- 27 I. Terasaki. *Proceedings of 18<sup>th</sup> ICT*, Baltimore, 1999, p 569.
- 28 Y. Wang, N. S. Rogado, R. J. Cava and N. P. Ong. *Nature*, 2003, **423**, 425.
- 29 R. E. Schaak, T. Klimczuk, M. L. Foo, R. J. Cava. *Nature*, 2003, **424**, 527.
- 30 Y. Kobayashi, M. Yokoi and M. Sato. *J. Phys. Soc. Jpn.* 2003, **72**, 2453.
- 31 Y. Kobayashi, M. Yokoi and M. Sato. *J. Phys. Soc. Jpn.* 2003, **72**, 2161.
- 32 T. Fujii, I. Terasaki, *Proc. New Thermoelectric Materilas*