A novel method to control oxygen stoichiometry and thermoelectric properties in (RE)BaCo$_2$O$_{5+\delta}$

T DASGUPTA, S SUMITHRA and A M UMARJI*

Materials Research Centre, Indian Institute of Science, Bangalore 560 012, India

Abstract. Rare earth cobaltites of the type (RE)BaCo$_2$O$_{5+\delta}$ (RE = Y, Gd, Eu and Nd) were synthesized by solid state technique. A novel, fast quenching technique was used to tune the oxygen content in these compounds. Room temperature Seebeck and electrical resistivity measurements were used to infer the oxygen content. A maximum in the S and ρ was observed for all the compositions when δ value was close to 0·5.

Keywords. Oxides; chemical synthesis; X-ray diffraction; thermogravimetric analysis; electrical properties.

1. Introduction

Oxygen content plays an important role in determining the physical properties of perovskite related oxides. Such an effect of oxygen stoichiometry on physical properties is possible when the compositions have variable valence transition metals like Fe, Mn, Co, Cu etc. Vacancy ordering in these types of structures has lead to novel structural families. Classical example of such oxides is 123 superconductors where the oxygen is non-stoichiometric and T_C correlates with the non-stoichiometry of oxygen.

Layered cobalt oxide materials like Na$_x$CoO$_2$ and La$_{1-x}$Sr$_x$CoO$_3$ have been studied for their thermoelectric properties and are seen to exhibit high ZT values (Terasaki *et al* 1997; Kurosaki *et al* 2001; Terasaki 2003; Zhou *et al* 2006). Another potential layered material for thermoelectric applications are the rare earth cobaltites of the type, REBaCo$_2$O$_{5+\delta}$. These materials have recently caught attention due to their unusual transport properties and are being extensively studied for GMR applications (Barbey *et al* 1994; Martin *et al* 1997; Maignan *et al* 1999). The crystal structure of these oxides is made up of alternate layers of RE and Ba separated by a Co layer. The oxygen content can be tuned to lie between 5 and 6 ($0 \leq \delta \leq 1$) by changing the synthesis parameters. Depending on the oxygen content, the crystal structure can be either tetragonal (for $\delta < 0\cdot4$ and $>0\cdot6$) or orthorhombic (Maignan *et al* 1999). To maintain charge neutrality the valence states of Co changes according to the oxygen content. For $\delta < 0\cdot5$, Co ions are in a mixed valence of either +2 or +3 while for $\delta > 0\cdot5$, the Co ions are either in a +3 or +4 state. For exactly $\delta = 0\cdot5$, all the Co ions are in +3 state. Apart from the synthesis parameters the oxygen content

is also seen to depend on the rare earth cation size. Based on TGA and iodometric titration data, δ (as synthesized) is seen to vary from 0·7 to 0·4 as the size of the rare earth decreases. A $\delta \cong 0\cdot7$ is observed for RE = Pr and Nd, $\delta \cong 0\cdot4$ for RE = Sm, Eu, Gd and Tb, and $\delta \cong 0\cdot3$ for Dy and Ho (Maignan *et al* 1999). For the Y compound, as synthesized δ is reported to be close to zero (Barbey *et al* 1994).

The ability to change the oxygen content also leads to tunability of S and ρ values. Large thermoelectric power has been observed in these materials when $\delta = 0\cdot5$ (Martin *et al* 1997; Taskin *et al* 2003, 2005). Controlling the oxygen stoichiometry in these materials is very important. General methods employed are to equilibrate the material at elevated temperatures for several hours under controlled oxygen partial pressures (Taskin *et al* 2005). But further work is necessary to understand the effect of the RE cation size on the crystal structure and hence the transport properties.

In this work, we synthesize different (RE)BaCo$_2$O$_{5+\delta}$ (RE = Gd, Eu, Nd, Y) by solid state method and study the room temperature S and ρ values. We report an easy and novel method for tuning the oxygen content in these types of materials. Diffraction studies and iodometric titration are employed to infer the oxygen content. Seebeck coefficient and resistivity data are used as supplementary information.

2. Experimental

The cobaltites of general formula, REBaCo$_2$O$_{5\pm\delta}$ (RE = Gd, Eu, Nd, Y), were synthesized by the regular solid-state synthesis technique. The rare earth oxides were preheated to above 800°C to remove any adsorbed volatilities. Stoichiometric amounts of the rare earth oxides were mixed with BaCO$_3$ and Co(NO$_3$)$_2$·6H$_2$O. The initial

composition was ground for 2 h in ethanol medium and heat treated at 850°C for 24 h. It was further reground, pelletized and heat treated again at 1100°C for 24 h. The final composition was confirmed for its phase formation from X-ray diffraction (XRD) studies (Philips, Model PW 1050/37). Lattice constant refinement program PROSZKI (Lasocha and Lewinsky 1994) was used for calculating the lattice constants.

The oxygen stoichiometry of the synthesized compounds was varied by a novel technique. The samples were initially annealed in air at a desired temperature for 2 h followed by rapid air quenching. The quenching was carried out by pressing the pellets between pads of aluminum foils. The oxygen content in the samples depended on the annealing temperature. This was verified by iodometric titrations carried out on select compositions (Karppinen *et al* 2002). The oxygen uptake by the quenched samples was studied by thermogravimetric analysis (TGA) (TA Instruments-SDT Q600).

The electrical conductivity on the quenched samples was measured in a home built setup based on the Van der Pauw four-probe technique (Van der Pauw 1958). The sheet resistance values were measured by making spring loaded platinum contacts and the resistivity values calculated using an efficient algorithm (Chan 2000). The Seebeck coefficient was also measured on a home built setup (Dasgupta and Umarji 2005). The values were measured with respect to copper.

3. Results

3.1 *X-ray diffraction studies*

The XRD of the different $REBaCo_2O_{5+\delta}$ samples indicate the monophasic nature of the compositions synthesized.
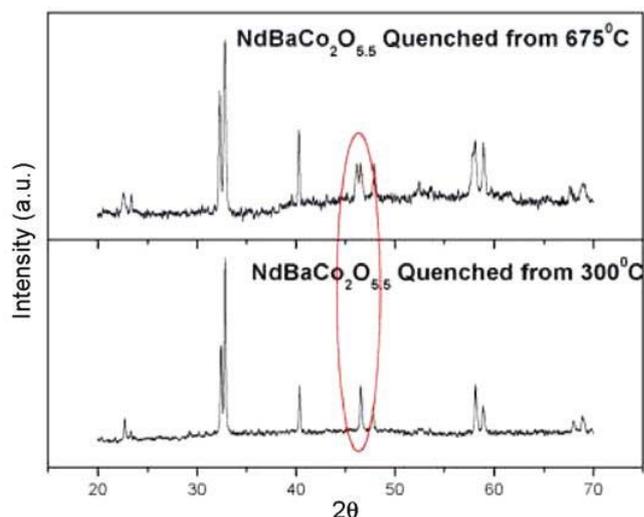
The refined lattice parameters of the as synthesized compounds agreed with the reported values for the respective compositions (Maignan *et al* 1999). In figure 1 the XRD of the $NdBaCo_2O_{5+\delta}$ composition quenched from two different temperatures is shown. The sample quenched from 675°C is orthorhombic while that from 300°C is tetragonal. This is evident from the splitting of the (040) peak encircled in the figure. TGA data on the 675°C quenched sample is shown in figure 2. It is seen that there is an initial weight gain of around 250°C followed by a monotonous loss above 330°C. The change in oxygen concentration calculated from the weight gain comes to $\Delta\delta \sim 0.15$. Thus the low temperature oxygen concentration in $NdBaCo_2O_{5+\delta}$ is $\delta \sim 0.65$, which is close to the reported as synthesized value (Maignan *et al* 1999).
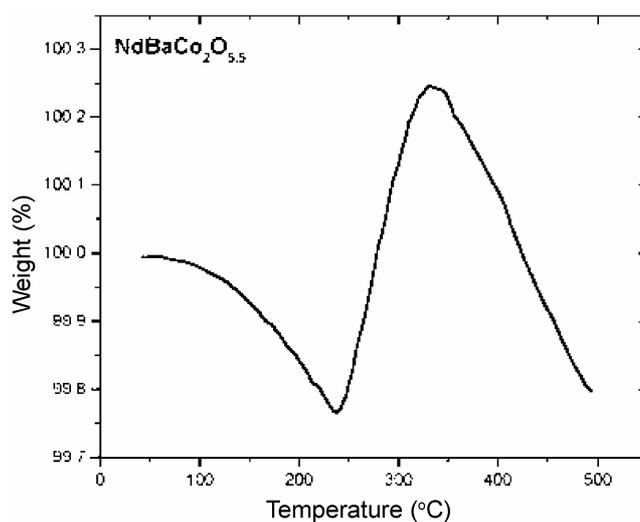
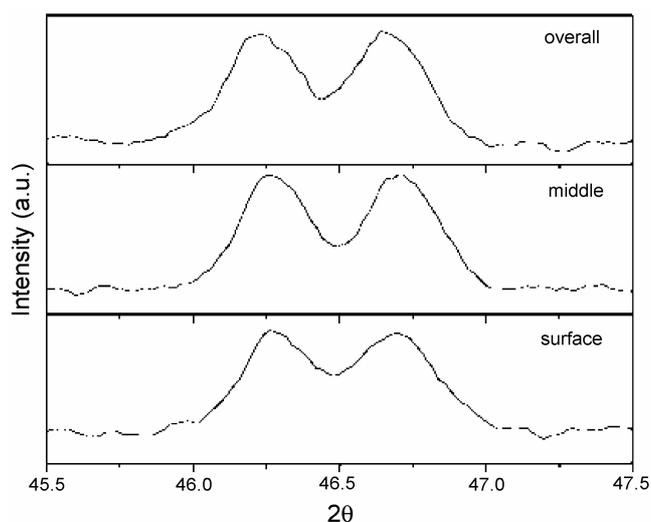**Figure 2.** TGA plot of $NdBaCo_2O_{5+\delta}$ quenched from 675°C.

Figure 3. The XRD patterns of $NdBaCo_2O_{5+\delta}$ sample quenched from 675°C taken from different regions of a pellet demonstrating the compositional homogeneity in the sample.

Figure 1. The effect of quenching temperature on the XRD pattern in $NdBaCo_2O_{5+\delta}$.

Table 1. Lattice parameters for REBaCo$_2$O$_{5.5}$.

Rare earth	Space group	a (Å)	b (Å)	c (Å)	Volume (Å)^3	Quench temperature (°C)
Y*	*P4/mmm*	3·876 (1)	3·876 (1)	7·503 (2)	112·84 (3)	–
Gd	*Pmmm*	3·878 (2)	3·911 (5)	7·537 (5)	114·36 (1)	450
Eu	*Pmmm*	3·882 (1)	3·921 (2)	7·553 (2)	115·00 (1)	475
Nd	*Pmmm*	3·901 (1)	3·930 (4)	7·590 (4)	116·39 (6)	675

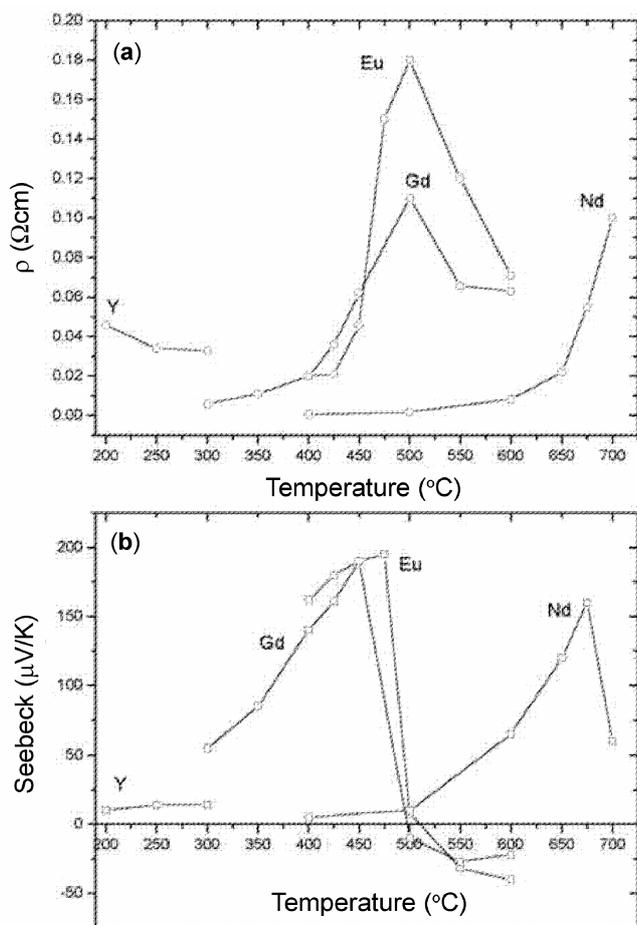*The oxygen content of Y composition is reported to be close to 5 and hence this method cannot be employed for it.

Figure 4. The room temperature (**a**) electrical resistivity and (**b**) Seebeck coefficient values as a function of the annealing temperature for REBaCo$_2$O$_{5+\delta}$ (RE-Y, Gd, Eu and Nd) compounds.

To confirm the homogeneity of the oxygen stoichiometry in the quenched samples XRD was carried out on various sections of the pellet i.e. from the top, middle and overall part of a pellet. The characteristic peak (040) that is the signature of orthorhombicity in the structure has been chosen for comparison, as it is sensitive to the oxygen stoichiometry. In figure 3 it is observed that the X-ray diffraction pattern of the sample did not show any varia-

tion for different sections of the pellet. The peak splitting in the different specimens were 0·43 ± 0·01° (in 2θ) in all the specimens.

3.2 *Transport properties*

The oxide pellets were annealed at various temperatures and quenched in order to vary the oxygen stoichiometry. The resistivity and Seebeck coefficients for the different rare earth cobaltites as a function of the quenching temperature is shown in figures 4(a) and (b), respectively. For the intermediate rare earths i.e. Eu and Gd, a peak in the resistivity value is observed. In Y the resistivity value monotonously decreases while that in Nd increases in the temperature range scanned. The Seebeck data for Eu and Gd goes from *p* type to *n* type behaviour with increasing annealing temperature. Also before the *p* to *n* transition the *S* value goes through a maximum. In case of Y and Nd, the *S* values are always positive (*p* type) in the temperature range scanned.

4. Discussion

The ability to tune the oxygen stoichiometry in the RE-BaCo$_2$O$_{5+\delta}$ compounds and maintain compositional homogeneity by quenching is proven from figures 1–3. Thus the rapid air quenching technique can be a fast and more effective way compared to the earlier reported method which required prolonged annealing at the desired temperature in controlled oxygen partial pressure. The lattice parameters of REBaCo$_2$O$_{5+\delta}$ compositions obtained by this method are listed in table 1. Except for RE-Y, the oxygen stoichiometry is adjusted close to 5·5 ($\delta = 0.5$). It can be noted that higher quenching temperature is necessary as the RE^{3+} ion size increases. For GdBaCo$_2$O$_{5.0+\delta}$, the resistivity and Seebeck data are similar to that reported in literature (Taskin *et al* 2005). Electrical conduction in these materials is driven by hopping of electrons between the different valence states of cobalt. Thus the maxima in the resistivity corresponds to the $\delta = 0.5$ composition with only Co^{3+} ions present. This was confirmed from the iodometric titration data for Eu and Gd samples with the calculated δ being 0·51 and 0·505, respectively.

The optimum quenching temperature to achieve this $\delta = 0\cdot5$ composition is seen to increase with the size of the rare earth cations. This can be explained from the reported data of the as synthesized δ in these materials (Maignan *et al* 1999). Larger rare earths like Nd, having an as synthesized $\delta = 0\cdot7$ will require higher annealing temperatures to reach the $\delta = 0\cdot5$ composition. The compositions of Eu and Gd are seen to retain the $\delta = 0\cdot5$ composition by quenching from intermediate temperatures. Thus it is possible in Eu and Gd compositions to scan a wide range of δ in the temperature range studied. The Seebeck data of the compounds also match with that reported in literature. At lower annealing temperatures with $\delta > 0\cdot5$, the behaviour is **p** type. A crossover to the **n** type takes place below δ of 0·5. The Seebeck value is seen to be maximum at $\delta \sim 0\cdot5$ for all the rare earths.

5. Conclusions

In the present work a novel technique for tuning the oxygen content of $REBaCo_2O_{5+\delta}$ is demonstrated. The oxygen tuning is carried out by annealing the pellets at various temperatures followed by subsequent quenching. The change in δ is shown to be homogenous throughout the pellet. The room temperature S and ρ values were measured as a function of oxygen content. A maxima in both S and ρ values is observed in all the compositions near $\delta = 0\cdot5$.

References

Barbey L, Nguyen N, Caignaert V, Studer F and Raveau B 1994 *J. Solid State Chem.* **112** 148

Chan W K 2000 *Rev. Sci. Instrum.* **71** 3964

Dasgupta T and Umarji A M 2005 *Rev. Sci. Instrum.* **76** 094901

Karppinen M, Matvejeff M, Salomaki K and Yamauchi H 2002 *J. Mater. Chem.* **12** 1761

Kurosaki K, Muta H, Uno M and Yamanaka S 2001 *J. Alloys & Compd.* **315** 234

Lasocha W and Lewinski K 1994 *J. Appl. Cryst.* **27** 437

Maignan A, Martin C, Pelloquin D, Nguyen N and Raveau B 1999 *J. Solid State Chem.* **142** 247

Martin C, Maignan A, Pelloquin D, Nguyen N and Raveau B 1997 *Appl. Phys. Lett.* **71** 1421

Terasaki I 2003 *Physica* **B328** 63

Terasaki I, Sasago Y and Uchinokura K 1997 *Phys. Rev.* **B56** R12685

Taskin A A, Lavrov A N and Ando Y 2003 *22nd International conf. on thermoelectrics* p. 196

Taskin A A, Lavrov A N and Ando Y 2005 *Phys. Rev.* **B71** 134414

Van der Pauw L J 1958 *Phillips Tech. Rev.* **20** 220

Zhou A J, Zhu T J and Zhao X B 2006 *Mater. Sci. Eng.* **B128** 174