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Thermoelectric response of oxygen nonstoichiometric YBaCo$_2$O$_{5+\delta}$ cobaltites synthesized via non-ion selective EDTA-citrate-metal complexing

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ABSTRACT

The physical transport properties of layered 112-type YBaCo$_2$O$_{5+\delta}$ cobaltites, synthesized via non-ion selective EDTA-citrate-metal complexing, were systematically investigated by means of electrical and thermal conductivity as well as through thermopower measurements. The transport properties were shown to be markedly dependent on the oxygen content δ. The temperature dependence of the thermopower, $S(T)$, exhibits p-type conductivity in the temperature range 60–320 K. In the low-temperature antiferromagnetic region, $S(T)$ exhibits an unusual behavior (broad peak), which can be explained by the electron magnon scattering mechanism. The temperature dependence of the thermal conductivity exhibits a glass-like behavior, and no thermal conductivity peak can be seen at low temperatures for any of the samples. The absence of the phonon peak at low temperatures is associated with the oxygen non-stoichiometry, which brings about strong lattice disorder. The calculated figure of merit (ZT) shows values ($\sim 10^{-5}$ at room temperature) too small for applications, as expected from 112-type cobaltite systems.

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1. Introduction

Recently, Co-based compounds have been intensively investigated due to the existence of fascinating magnetic, electrical, and magnetotransport properties, such as an exceptionally high magnetoresistance in the ordered oxygen-deficient 112-phase double perovskites LnBaCo$_2$O$_{5+\delta}$ (Ln=Eu, Gd) [1]. The rich phase diagram exhibited by these oxides is linked to the variations of the oxygen content δ. Indeed, the electronic states of Co and the surrounding oxygen are notably changed upon varying this parameter [2]. Currently, the crystal structure of these oxides is described as an ordered sequence of [CoO$_2$]-[BaO]-[CoO$_2$]-[LnO$_\delta$] layers along the c-axis, where oxygen vacancies exist in the lanthanide layer [3]. So the structure of the LnBaCo$_2$O$_{5+\delta}$ cobaltates is very flexible and sensitive to both tiny variations of the oxygen content and the size of the Ln^{3+} cation. This, in turn, leads to strong variations of the magnetic properties [2]. The oxygen content δ controls the mixed valence state and the coordination (pyramidal or octahedral) of the cobalt ions. The valence of Co ions varies from +2.5 at δ=0 (pyramidal environment of Co ions) to +3.5 at δ=1

(octahedral environment of Co ions). At δ=0.5 (O$_{5.5}$), one might expect that only Co^{3+} ions will be present (alternating pyramidal and octahedral environments). Although the oxygen content δ and the Ln size lead to strong variations in the physical properties, the various possible spin states of cobalt ions also dramatically influence the magnetic behavior of the 112 cobaltites. Certainly the existence of several possible spin states in a given oxidation state makes the cobaltites a rich but also challenging system to study. Co^{3+} has three possible spin states: the low spin state (LS, t$_{2g}^6$ε$_g^\circ$, $S=0$), the intermediate spin state (IS, t$_{2g}^5$ε$_g^1$, $S=1$), and the high spin state (HS, t$_{2g}^4$ε$_g^2$, $S=2$), which arise from the competition between the crystal field (CF), the on-site Coulomb correlations, and the intra-atomic exchange energy [4]. LnBaCo$_2$O$_{5+\delta}$ compounds feature successive paramagnetic-ferromagnetic-antiferromagnetic (PM-FM-AFM) transitions within a range of 200–300 K and an insulator-metal transition between 300 and 400 K [5]. There exists a strong debate with respect to the cause of these magnetic and electrical phases. Among the cobalt oxides synthesized in the last few years, the compound with Y^{3+}, which is a non-magnetic ion, is a good candidate for isolating the intrinsic properties of Co in the layered perovskites. Moreover, Y is among the smallest cations that can form this compound. Interestingly, LnBaCo$_2$O$_{5+\delta}$ cobaltites, which belong to the so-called strongly correlated electron systems, have received considerable attention

in the last few years, and deservedly so, since they are a promising alternative to conventional semiconductors in the field of thermoelectric power generation [6]. Since spin and orbital degrees of freedom play an important role in the transport properties of strongly correlated systems, the thermoelectric response could be enhanced by a large spin-orbital degeneracy of charge carriers [7]. Apart from the variability of oxygen content in $LnBaCo_2O_{5+\delta}$ cobaltites, the role of band structure parameters in determining the thermoelectric power in these oxides can be confidently studied by using lanthanides with different ionic radii [8]. Therefore, $LnBaCo_2O_{5+\delta}$ compounds can provide a suitable basis for elucidating the relation between the spin-orbital degeneracy and the thermoelectric properties in strongly-correlated electronic materials.

In the present paper, the electron transport properties of $YBaCo_2O_{5+\delta}$ cobaltites synthesized via the wet-chemistry route are investigated. Resistivity, $\rho(T)$, thermopower (Seebeck coefficient), $S(T)$, and thermal conductivity, $\kappa(T)$, measurements were employed as experimental methods for this purpose. The latter two are sensitive to the magnetic and electrical nature of charge carriers (hole/electron) and can supply information besides that given by standard characterizations like magnetotransport measurements. Given that the presence of grain boundaries does not affect the $S(T)$ data extensively, complications in their interpretation for polycrystalline samples are avoided. Nevertheless, grain boundaries decidedly can influence the thermal conductivity of the material. The relatively large positive values of the thermoelectric power ($\sim 50\ \mu V\,K^{-1}$ at 300 K) and the measured resistivities ($\sim 2.3 \times 10^{-1}\ \Omega$ cm at 300 K) allow one to calculate the power factor $S^2\sigma$ as well as the figure of merit $ZT = S^2\sigma T/\kappa$, which are parameters that characterize thermoelectric materials [9]. In these last-named expressions, S, $\sigma(\sim 1/\rho)$, κ, and T represent the thermopower, electrical conductivity, thermal conductivity, and absolute temperature, respectively.

2. Experimental details

Polycrystalline samples of $YBaCo_2O_{5+\delta}$ were prepared based on the non-ion selective EDTA–citrate–metal complexing method [10]. Here, $Y(NO_3)_3 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $Ba(NO_3)_2$ were used as starting precursors. Initially, citric acid and ethylenediaminetetraacetic acid were added to distilled and deionized water in a molar ratio of 2:1 and dissolved at 60 °C under magnetic stirring. Next, the precursors were added in a molar ratio of 1:2 with respect to the total moles of acid. The final solution was heated to 80 °C under strong stirring until a homogeneous, translucent (violet color) solution was obtained. At this point, pH ~ 6 was obtained by dropping ammonium hydroxide into the solution. When this mixture was completely homogenous, ethylene glycol (EG) was added. The polymerization process was carried out at 110 °C until a gel was formed. This gel was then heated to 120 °C in order to form a resin and remove the excess water. A second set of polycrystalline samples of $YBaCo_2O_{5+\delta}$ was prepared, based on the Pechini method. Here, $Y(NO_3)_3 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $Ba(NO_3)_2$ were used as starting precursors. First the precursors were dissolved in a stoichiometric proportion in distilled and deionized water at 60° C under magnetic stirring. Next, citric acid was dissolved into this solution in a molar relation of 1:4 with respect to total cations from nitrates. When this mixture was completely homogenous, it was mixed with ethylene glycol. The final solution was heated to 110 °C under strong stirring. In the following step, the resins obtained by the two synthesis methods were heated to 250 °C, 350 °C, and 450 °C for a period of 5 h at each temperature. The solid obtained was ground in an agate mortar and then annealed in air at 1000 °C for 15 h in a tubular

electric oven, followed by furnace-cooling down to room temperature. After regrinding the powder, the annealing process was repeated. Then the final product was reground, obtaining a very fine powder. The oxygen stoichiometry of the synthesized compounds was varied by using a novel technique. The powders were heated to 350 °C and 700 °C in pure oxygen gas for 5 h, followed by a rapid quenching. This annealing process produced samples with $\delta = 0.37$ and $\delta = 0.17$, respectively. The oxygen content of the samples was determined by means of iodometric titration. In doing so, 20 mg of the prepared oxides were dissolved in 10 ml of HCl solution, and potassium iodide was added. The iodine generated was titrated with thiosulfate (0.025 M) and then was measured using an Ag/AgCl electrode. Thermal behavior of the samples at high temperatures was studied by means of differential scanning calorimetry and thermogravimetric analysis (DSC/TGA), using a NETZSCH STA 409CD thermal analyzer. X-ray powder diffraction patterns of the compounds were registered with a Panalytical X'Pert Pro diffractometer using Cu-Kα radiation ($\lambda = 0.15418$ nm) in the standard θ–2θ configuration. The diffraction data were collected by step scanning (0.013° per step) over the angular range $10° \leq 2\theta \leq 90°$ and analyzed with Fullprof software. The morphological properties and the elemental analysis were studied by means of scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (EDS), respectively. The observation via transmission electron microscopy (TEM) was performed using a Philips CM200 microscope operating at 200 kV. For sample preparation, the powders were mixed separately with ethanol and then treated in an ultrasound bath for a few minutes. 5 μL of the thus prepared dispersion was then pipetted onto a carbon-coated copper TEM grid and left to dry in air. Gatan digital micrograph software was used to acquire images and perform further image processing. Infrared (IR) spectra were recorded in the range 4000–400 cm^{-1} using an FTIR-Perkin-Elmer spectrophotometer. Careful magnetic measurements were performed via vibrating sample magnetometry (VSM) (Quantum Design) over the temperature range 50–320 K and magnetic fields as high as 3 T. Resistivity, thermopower, and thermal conductivity measurements were carried out with a Quantum Design physical property measurement system (PPMS). The thermopower and thermal conductivity data were recorded using the continuous scanning mode with a 0.2 K/min cooling rate. The measurements were performed on black, single-phase $YBaCo_2O_{5+\delta}$ powders were ground and pressed into the form of ceramic disks (2 mm thick and 6 mm in diameter), using pressure as high as 4500 psi. The disks were sintered in air at 1050 °C for 36 h, followed by slow cooling down to room temperature. The sintered disks were attached to heaters and a heat sink with silver paste. The temperature variations were registered by means of cernox thermometers.

3. Results and discussion

Fig. 1(a) shows the thermal analysis of the resin obtained using the non-selective method. Four mass losses can clearly be seen in this plot. The first one occurs from room temperature up to ~ 193 °C with a mass loss of 3.67%. In this temperature range, the DSC curve shows an endothermic peak at 114.3 °C. This peak is associated with the removal of humidity and other volatile substances [11]. The second notable mass loss (22%) is evident from 230 °C to 420 °C. The mass loss in this temperature range is accompanied by energetic variations, with the exothermic band at 314.1 °C and the endothermic peak at 388.8 °C being most prominent, which is typical for the first decomposition stage of the resin. The third mass loss (26.94%) begins directly after the second one and is accompanied by an exothermic band at ~ 600 °C. This band could be associated with the second decomposition stage of