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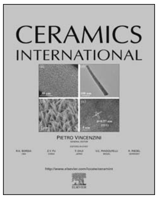

Antiferromagnetism and heat capacity of $NaCo_{2-x}Cu_xO_4$ ceramics

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ABSTRACT

Polycrystalline samples of $NaCo_{2-x}Cu_xO_4$ (x=0, 0.01, 0.03 and 0.05) were synthesized in two different ways: 1) by a mechanochemically assisted solid-state reaction method (MASSR) and 2) by a citric acid complex method (CAC). In this work we examined the influence of these synthesis routes and small Cu concentrations on magnetic properties and the heat capacity of sintered samples. The magnetic susceptibility (χ) of all samples followed the Curie-Weiss law in the temperature range between 50 K and 300 K, while a negative Weiss constant (θ) implied an antiferromagnetic interaction. According to the magnetic susceptibility data, a peak around 30 K indicating the presence of Co_3O_4 as a secondary phase appeared for all MASSR samples and CAC samples with Cu content above 1%. The effective magnetic moment (μ_{eff}) of CAC samples was lower than the theoretical, spin only value obtained for the Co^{4+} ion in the low spin state indicating the presence of low spin Co^{3+}(S =0). These values were also lower compared to the values obtained for MASSR samples. The highest μ_{eff} of 1.75 μ_B/atom Co was obtained for the undoped MASSR sample. The heat capacity of CAC samples at 2 K decreased with Cu concentration due to lowering of the electronic specific heat coefficient (γ). The highest γ of 63.9 mJ/molK^2 was obtained for the undoped CAC sample. This reduction in γ values was the result of the decrease of the density of state and/or mass enhancement factor.

1. Introduction

In the past few decades, there has been a growing interest in alternative energy sources and new methods for energy conversion. Thermoelectric materials belong to the group of materials that directly convert waste heat into electric energy. Among them, layered oxides attract great attention because of their interesting structural, physical and chemical properties, such as $NaCo_2O_4$ (NCO), which exhibits good thermoelectric properties [1–3]. Increase of the Seebeck coefficient (S), simultaneously with the decrease of thermal conductivity (κ) and electrical resistivity (ρ) are the main requests for high thermoelectric performance [4]. High S (also called thermopower) as a consequence of a strong electron correlation and low ρ make $NaCo_2O_4$ a promising material for potential use in thermoelectric devices [5,6].

$NaCo_2O_4$ belongs to compounds with a bronze-type crystal structure of the A_xBO_2 ($0.5 \le x \le 1$) general formula [7]. This layered oxide consists of Na and CoO_2 layers alternately stacked along the c-direction. The stoichiometry of Na in this compound is variable, and depending on the sodium content, there are three types of crystal structure: P3: β–$Na_xCo_2O_4$ ($1.1 \le x \le 1.2$), P2: γ–$Na_xCo_2O_4$ ($1.0 \le x \le 1.4$), O3: α–$Na_xCo_2O_4$ ($1.8 \le x \le 2.0$), whereby the P2 structure possesses the highest thermopower [8]. As arrangement of sodium ions in the crystal lattice depends on the temperature and Na content [9], diversity of $Na_xCo_2O_4$ properties comes from the different sodium content, accordingly [10].

In general, cobalt oxides are systems with a strong electron correlation, where 3d orbitals have a specific degeneration, due to the spin and orbital degrees of freedom. Two competitive processes are responsible for degeneration of electronic states of Co^{3+} and Co^{4+} ions: crystalline field and Hund's rule coupling [11]. Interactions between 3d electrons largely affect the transport properties of all cobaltites and they are expected to affect magnetic properties of these materials, as well [12]. In the octahedral crystal field, as is the case in the CoO_2 layer, the 3d orbitals split into two e_g and three t_{2g} orbitals, which in the rhombohedral crystal field further split into e'_g and a_{1g} orbitals [13–15]. Hybridization between these orbitals causes the formation of two

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Fermi surfaces [13]. Basically, the magnetic susceptibility and the electronic specific heat coefficient are proportional to the density of states, which is determined by a large Fermi surface [13].

It is assumed that stoichiometric $NaCo_2O_4$ consists of equal amounts of Co^{4+} and Co^{3+} ions [16]. These ions can occupy one of the following spin states: low spin state, with electronic configurations ${t_{2g}}^5$ (${t_{2g}}^6$); intermediate, ${t_{2g}}^4{e_g}^1$ (${t_{2g}}^5{e_g}^1$); or high spin state ${t_{2g}}^3{e_g}^2$ (${t_{2g}}^4{e_g}^2$). The occupancy of spin states is dependent on the electron pairing energy and level splitting [15]. The low spin Co^{4+} ions are magnetic (with a spin quantum number of S=1/2) and the Co^{3+} ions are non magnetic (S=0) [11,16]. It is assumed that both Co^{4+} and Co^{3+} ions are in the low spin state in sodium cobaltite, and that is one of the reasons for high thermopower [11,14]. Mixed valence of Co ions in the low spin state is responsible for metallic conductivity of sodium cobaltite [17].

The magnetic properties of Na_xCoO_2 depend on the sodium content (x). For x=0.3, this material is Pauli paramagnetic, for x=0.5 it is a charge ordered insulator, for x~0.65–0.75 a Curie Weiss metal, and for x > 0.75 a spin density wave state was suggested [18]. Hydrated sodium cobaltite, $Na_{0.35}CoO_2{\cdot}1.3H_2O$, is a superconductor below approximately 5 K [19,20]. Neutron scattering experiments on $Na_{0.75}CoO_2$ and $Na_{0.82}CoO_2$ showed that magnetic ordering of these structures belongs to the A type of antiferromagnets, with two types of magnetic interactions: ferromagnetic, within a CoO_2 layer and antiferromagnetic, between two CoO_2 layers [21,22]. Long range antiferromagnetic ordering below 20 K was noticed for 0.75≤x≤0.9 [22].

In our previous work, we studied changes in the structural, microstructural and thermoelectric properties caused by Cu doping [23]. Taking into account all changes of these properties, the aim of this work was to examine the influence of small concentrations of the dopant on magnetic properties (magnetic susceptibility, Curie–Weiss constant and effective magnetic moment) and heat capacity of polycrystalline samples of $NaCo_{2-x}Cu_xO_4$ (x=0, 0.01, 0.03, 0.05) synthesized in two ways, by a mechanochemically assisted solid-state reaction and by the citric acid complex method.

2. Materials and methods

Polycrystalline samples of $NaCo_{2-x}Cu_xO_4$ (x=0, 0.01, 0.03, 0.05) were synthesized by a mechanochemically assisted solid-state reaction (MASSR) and a citric acid complex (CAC) method. The detailed procedure was described in our previous work [23]. The MASSR samples were denoted as NCO-MASSR, NCO1-MASSR, NCO3-MASSR, NCO5-MASSR and the CAC samples were denoted as NCO-CAC, NCO1-CAC, NCO3-CAC, and NCO5-CAC.

Sample magnetization was measured using a Quantum Design SQUID MPMS-XL-5 magnetometer in zero field cooled (ZFC) and field cooled (FC) regimes, between 2 K and 300 K and in applied field of 100 Oe. Heat capacity was measured by a Quantum Design Physical Property measurement system (PPMS 9 T), equipped with a 9 T magnet in the temperature range from 2 K to 300 K.

3. Results and discussion

The X-ray diffractograms of the MASSR sintered samples contained only peaks of pure γ–$NaCo_2O_4$ (JCPDF card no. 73-0133, space group C2/*c*) and no additional peaks corresponding to secondary phases were detected [23]. As for the XRD patterns of Cu doped MASSR and CAC samples, only the NCO5-CAC sample showed peaks of the secondary phase (CuO) as reported previously [23].

It is well known that magnetic measurements are highly sensitive to the presence of secondary phases with large magnetic moments. In order to investigate magnetic properties, as well as to verify the phase purity, we measured magnetization of samples in the ZFC and FC regime. Fig. 1 shows the temperature dependence of magnetization of undoped samples in the range between 2 K and 300 K. The NCO-MASSR sample showed a transition at 30 K that was attributed to Co_3O_4 (not detected in X-ray diffractograms), confirming the sensitivity of this characterization technique.

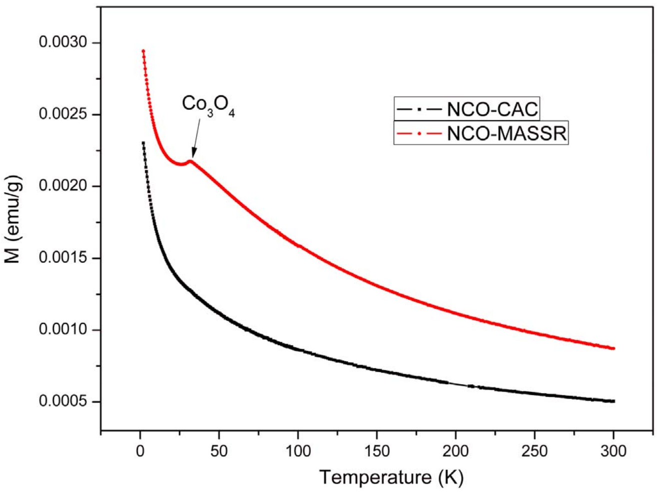

Fig. 1. Temperature dependence of the magnetization of undoped MASSR and CAC samples in the temperature range from 2 K to 300 K.

The temperature dependence of the inverse magnetic susceptibility of MASSR and CAC samples measured in the field of 100 Oe between 2 K and 300 K is shown in Fig. 2.

The inverse magnetic susceptibility obeys the Curie-Weiss law (Eq. (1)) in the temperature range between 50 K and 300 K:

$$\chi = \frac{C}{T - \theta}, \tag{1}$$

where C is the Curie and θ is the Weiss constant. It was noticed that the magnetic susceptibility of MASSR samples decreased with the increase in Cu concentration. This behavior is recognized and reported in literature and can be explained by lowering of the density of states and/or mass enhancement factor [13]. All MASSR samples showed an antiferromagnetic transition at approximately 30 K, which confirmed the presence of a small amount of the Co_3O_4 phase [24]. The CAC samples showed this transition only for x≥0.03.

The values of the effective magnetic moments, the Curie and Weiss constants of MASSR and CAC samples are presented in Table 1. All samples showed antiferromagnetic behavior with a negative Weiss constant. The values of μ_{eff} were calculated based on the Curie constant, which was obtained by linear fitting of the curve $\chi^{-1} = f(T)$ at temperatures above 50 K (Fig. 2). *The* μ_{eff} *value* was higher for MASSR samples compared to CAC samples, indicating a larger concentration of low spin Co^{3+} ions (S=0) in CAC samples. In a mean field approximation [25], if only one type of magnetic ions exists, the formula for calculating μ_{eff} is:

$$\mu_{eff}^2 = xg^2S(S+1)\mu_B^2, \tag{2}$$

where x is the fraction of magnetic ions per formula unit, g is the gyromagnetic factor and S is their spin. Sodium cobaltite contains Co^{3+} and Co^{4+} ions, and we can consider them as two different magnetic systems with the same ordering temperature. Then, the total μ_{eff} can be expressed as:

$$\mu_{eff}^2 = \mu_{eff1}^2 + \mu_{eff2}^2. \tag{3}$$

To calculate μ_{eff} of samples without secondary phases, NCO-CAC and NCO1-CAC, we determined the Co^{4+} content in them by inductively coupled plasma optical emission spectroscopy. The content of Co^{4+} ions was 46.5% in NCO-CAC and 48.4% in NCO1-CAC. To be more specific, the molar fraction of Co^{3+} ions is x_1=0.535, and x_2=0.465 for Co^{4+}(with S_1=0 and S_2=1/2 in the low spin state).

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