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Mechanical properties of Ag-doped $Na_{1.5}Co_2O_4$

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Abstract

The polycrystalline samples of $Na_{1.5}Co_{2-x}Ag_xO_4$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) were synthesized from powder precursors prepared by the polymerized complex (PC) method. Various mechanical properties of the samples, including the elastic modulus, Debye temperature and Vickers hardness, were evaluated. The elastic moduli and Debye temperature increase with increasing Ag content. The relationship between the Vickers hardness and Young's modulus indicates a metallic characteristic. The microstructure of the non-doped sample shows coarse grains of about 10–20 μm. On the other hand, the Ag-doped samples show fine grains with Ag particles around 10 μm.

Keywords: Sodium cobalt oxide; Mechanical properties; Young's modulus; Debye temperature; Heat capacity; Thermal barrier coating

1. Introduction

Sodium cobalt oxide ($Na_xCo_2O_4$) was first synthesized in 1974 by Von Jansen and Hoppe [1]. The crystal structure of the γ-phase of this material is hexagonal, which can be pictured as a layer structure comprising CoO_2 conducting layers which are made of edge-shared CoO_6 octahedra and inter-layers of Na^+ ions alternatively stacked along the c-axis. The sodium ions are intercalated in trigonal prismatic or octahedral coordination of oxygen atoms [2]. An important feature in this structure is that sodium ions randomly occupy the available sites by 50%. In this sense, $NaCo_2O_4$ should be written as Na_xCoO_2 (x = 0.5). Nevertheless, we will call it $NaCo_2O_4$, because the best thermoelectric properties are realized near the 50% Na occupancy [3]. The γ-phase $Na_xCo_2O_4$ shows a large Seebeck coefficient despite its metallic conductivity. Recently, Terasaki et al. [4] reported the outstanding thermoelectric properties of a single crystal of this oxide, i.e., an unusual Seebeck coefficient of 0.1 mV K^{-1} accompanied by a low resistivity of 0.2 mΩ cm, at 300 K. To improve the thermoelectric efficiency of $Na_xCo_2O_4$, Na or Co is substituted by other metals. For instance, the Seebeck coefficient of 100–150 μV K^{-1} and the dimensionless figure of merit (ZT) of 0.03–0.05 have been obtained for $NaCo_{2-x}T_xO_4$ (T = Mn, Ru, Pb, Cu, Pd, Rh), at 300 K [5–9].

In the present study, the thermoelectric materials of $Na_{1.5}Co_{2-x}Ag_xO_4$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) were prepared from the powder precursors obtained from the polymerized complex (PC) method. The mechanical properties of these materials were measured and calculated. The relationship between the hardness and Young's modulus of the materials was studied.

2. Experimental procedure

Polycrystalline samples of $Na_{1.5}Co_{2-x}Ag_xO_4$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) were synthesized from powder precursors prepared by the PC method [10]. Firstly, citric acid (99.7%) was dissolved in ethylene glycol (99.5%) by heating and stirring at 473 K for 1 h. Secondly, $Co(NO_3)_2{\cdot}6H_2O$ (99.95%), $NaNO_3$ (99%) and $AgNO_3$ (99.9%) corresponding to the nominal composition of $NaCo_{2-x}Ag_xO_4$ were added to this

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Table 1
Starting materials for the PC method

Sample composition	Citric acid (g)	Ethylene glycol (ml)	$NaNO_3$ (g)	$Co(NO_3)_2{\cdot}6H_2O$ (g)	$AgNO_3$ (g)
Non-doped	42.0280	503.7241	7.2242	29.1030	0
Ag-doped (0.1)	42.0280	503.7241	7.2242	27.6479	0.8494
Ag-doped (0.2)	42.0280	503.7241	7.2242	26.1927	1.6987
Ag-doped (0.3)	42.0280	503.7241	7.2242	24.7376	2.5481
Ag-doped (0.4)	42.0280	503.7241	7.2242	23.2824	3.3974
Ag-doped (0.5)	42.0280	503.7241	7.2242	21.8273	4.2468

Note: The ratio of citric acid:ethylene glycol:metals was 0.2:9:0.05 by molarity.

solution. The actual amounts of the starting materials are given in Table 1. Finally, the mixture was stirred and heated at 573 K for 6 h. The colloidal solution became highly viscous, and this viscous polymeric product was decomposed to a dark-mass precursor at 723 K for 1 h. The mass precursor was ground and calcined at 1073 K for 5 h in order to obtain the powder of the γ-$Na_xCo_2O_4$ phase. The calcined powder was compacted into a pellet of 10 mm diameter and 2 mm thickness under a pressure of 150 MPa and then annealed at 1173 K for 24 h in air. The crystal structure of the samples was analyzed by a powder X-ray diffraction (XRD) at room temperature using Cu Kα radiation, λ = 0.15406 nm. The microstructures of these samples were determined by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). For the mechanical property measurements, the density of the samples was calculated from the mass and dimension. The longitudinal and shear sound velocities were measured by an ultrasonic pulse-echo method at room temperature to evaluate the shear modulus, Young's modulus and Debye temperature. The hardness was measured by a micro-Vickers hardness tester at room temperature.

3. Results and discussion

The powder XRD pattern at room temperature of the non-doped sample shows the single γ-$NaCo_2O_4$ phase. On the other hand, the Ag-doped (x = 0.1, 0.2) samples are composed of the γ-$NaCo_2O_4$ and Ag_2O phases and the Ag-doped (x = 0.3, 0.4, 0.5) samples are composed of the γ-$NaCo_2O_4$, Na_2O_2 and Ag_2O phases as shown in Fig. 1. The intensity of the peaks corresponds to the peak data on the JCPDS card, No. 30-1182 (γ-$Na_{0.71}Co_{0.96}O_2$), No. 15-0068 (Na_2O_2) and No. 72-2108 (Ag_2O).

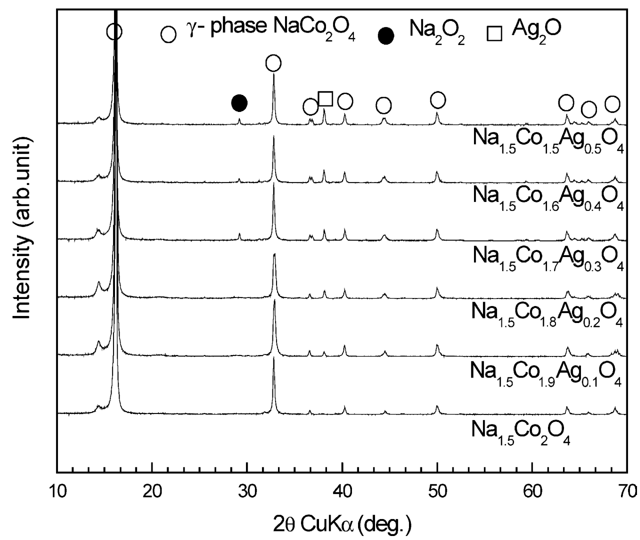

Fig. 1. X-ray diffraction patterns of the powder $Na_{1.5}Co_{2-x}Ag_xO_4$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) annealed at 1173 K for 24 h in air.

The hexagonal lattice parameters of the γ-$NaCo_2O_4$ phase and characteristics of the samples are summarized in Table 2. The lattice parameters are also shown in Fig. 2 as a function of x. As seen in Fig. 2, the lattice parameters a and c are not changed by Ag doping, indicating that the Ag is present as precipitates or inclusions (as shown in Fig. 4(b and c)).

The shear modulus, Young's modulus and Debye temperature were evaluated as shown in Table 2. For isotopic media, the shear modulus (G), Young's modulus (E), compressibility (β) and Debye temperature (θ_D) can be written in terms of the longitudinal sound velocity V_L and shear velocity V_S as [11–13]:

$$G = \rho V_S^2, \quad (1)$$

Table 2
Sample characteristics of $Na_{1.5}Co_{2-x}Ag_xO_4$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5)

Sample composition	Lattice parameter of γ-$NaCo_2O_4$ phase		Bulk density (g/cm^3)	Shear modulus (GPa)	Young's modulus (GPa)	Vickers hardness (GPa)	Debye temperature (K)
	a (nm)	c (nm)					
$Na_{1.3}Co_2O_4$ [9]	0.2834	1.0899	3.88	43.4	109	0.90	476
$Na_{1.5}Co_2O_4$	0.2839	1.0990	3.64	19.9	49.8	0.17	359
$Na_{1.5}Co_{1.9}Ag_{0.1}O_4$	0.2844	1.0907	3.87	27.0	67.4	0.26	406
$Na_{1.5}Co_{1.8}Ag_{0.2}O_4$	0.2845	1.0891	4.03	36.6	91.5	0.26	464
$Na_{1.5}Co_{1.8}Ag_{0.3}O_4$	0.2837	1.0805	4.04	32.7	81.7	0.14	440
$Na_{1.5}Co_{1.8}Ag_{0.4}O_4$	0.2844	1.0870	4.14	35.2	88.0	0.19	449
$Na_{1.5}Co_{1.8}Ag_{0.5}O_4$	0.2850	1.0817	4.25	45.4	113	0.23	503