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Review Article

Structure and Properties of Barium and Strontium Cobaltites Synthesized in a Solar Furnace

Paizullakhanov MS[1]*, Rajamatov OT[1], Nodirmatov EZ[1], Holmatov AA[2] and Karshieva NH[3]

[1]Material Sciences Institute
[2]Fergana Politechnik Institute
[3]Tashkent Stat Technical University

***Corresponding author:** Mukhammad-Sultanxan Payzullakhanov, Material Sciences Institute

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Abstract

Perovskite cobaltites of strontium $SrCoO_{3-\delta}$ and barium $BaCoO_{3-\delta}$ have been studied. It is shown that the technological route, which includes melting a stoichiometric mixture of cobalt oxide with barium or strontium carbonates in a solar furnace, quenching the melt into water, grinding the casting and molding, followed by sintering at 1100°C, makes it possible to obtain a material based on hexagonal barium and strontium cobaltites with a developed fine microstructure and semiconductor properties, the nature of the electrical conductivity.

Keywords: *Barium cobaltites, Strontium, Solar furnace, Melting, Hardening, Sintering, Ceramics*

Introduction

It is known that perovskite cobaltites of strontium $SrCoO_{3-\delta}$ and barium $BaCoO_{3-\delta}$ exhibit a wide range of electronic and magnetic characteristics and are of great interest. A feature of such compounds is the possibility of influencing their transport properties by varying the concentration of anionic vacancies [1]. At the same time, synthesis at high pressures makes it possible to obtain an ideal oxygen stoichiometry ($\delta = 0$). For example, $SrCoO_3$ obtained at 6 GPa [2,3] is a simple cubic perovskite structure.

When $SrCoO_{3-\delta}$ oxides are produced at ambient pressure in air, they exhibit the approximate stoichiometry of $Sr_2Co_2O_5$ (or $SrCoO_{2.5}$). The observed high-temperature brownmillerite-like structures, the so-called "high-temperature phases", and the hexagonal structures, called "low-temperature phases" are stabilized due to order-disorder transitions of oxygen vacancies. The complete ordering of vacancies with the formation of the brownmillerite phase is established within a few seconds during quenching after high-temperature (usually 1000°C) solid-phase synthesis [4,5].

Recently, more and more attention has been paid to barium cobaltite oxide due to its semiconductor characteristics [6-9]. Materials based on $BaCoO_{3-\delta}$ doped with some other elements have low resistivity at low temperatures and can be used as thermistors.

Technological Approaches

In this work, we studied perovskite structures based on barium and strontium cobaltites obtained by melt synthesis in a solar furnace of the corresponding mixture of barium and/or strontium carbonates with cobalt oxide: $BCO_3 + Co_2O_3$; $SrCO_3+Co_2O_3$. From the mixture after grinding (63 μm) and molding by semi-dry pressing (P = 1t), samples were made in the form of a cylinder ∅ 20 mm, which were installed on a water-cooled melting unit located on the focal plane of the solar furnace.

A concentrated flux of solar radiation with a density of the order of Q = 150 W/cm² was directed to the sample. Such a value of the flux density according to the law of Stefan Boltzmann $T = \sqrt[4]{\frac{Q}{\sigma}}$, where $\sigma = 5.67 \times 10^{-8}$ W/m²K is the Stefan Boltzmann constant, corresponded to the temperature of the heated body 1900°C. At this temperature, the sample melted. Melt droplets fell into water and cooled at a rate of 10^3 deg/s. Such cooling conditions made it possible to fix the high-temperature structural states of the material.

Drops of the melt loaded into water cracked into small glassy particles of arbitrary shape. To study such a material, it was ground to a fineness of 60 μm, dried at 400°C, and samples were molded in the form of cylinders ∅8 mm and 15 mm high for firing at a temperature of 1000°C followed by arbitrary cooling.

The obtained samples were subjected to X-ray phase analysis using a DRON-3M setup with a copper anode with K-α radiation in the Bragg-Brentano reflection geometry with CuKα radiation (λ = 1.5418˚A). The data were obtained between $20 \leq 2\theta \leq 60°$. The slit system was chosen to ensure that the X-ray beam was completely within the sample over the entire 2θ range.

The temperature coefficient of thermal expansion was measured on a cathetometer in the temperature range 25-950°C. The electrical resistance was measured by the four-contact method in the temperature range 25-1000°.

The density of the samples was determined pycnometrically $\rho_{ef} = m/V_{ef}$, the value of which was 4.87 g/cm³ for $BaCoO_3$ and 4.64 g/cm³ for $SrCoO_3$

Experimental Results and Their Discussion

Figure 1 shows X-ray patterns of barium and strontium perovskite cobaltites. The analysis of X-ray patterns showed that for the case of $BaCoO_3$ the diffraction pattern is described by a hexagonal lattice of space group P63/mmc with lattice parameters a = 5.652 A, c = 4.763 A. In the case of strontium cobaltite $SrCoO_3$, a hexagonal structure is also observed with lattice parameters a = 9.511 A, c = 12.287 A.

Figure 2 shows SEM micrographs of barium and strontium cobaltites obtained by melt quenchin. SEM analysis of $BaCoO_{3-\delta}$ micrographs shows that the grains have a fine and uniform microstructure. The average ceramic grain size is 3 µm. The relative density of the samples was 94%. The dense microstructure made it possible to obtain good reproducibility of the electrical characteristics of the ceramic.

The temperature coefficient of thermal expansion of the samples in the temperature range 25-950°C was $\alpha = 11.7 \times 10^{-6}\ K^{-1}$ for $SrCoO_3$ and $\alpha = 14.1 \times 10^{-6}\ K^{-1}$ for $BaCoO_3$.

The temperature dependence of resistivity (ρ) and samples are shown in Figure 3. As can be seen from Figure 3, the resistivity decreases exponentially with increasing temperature. Resistivity depends on temperature and can be expressed by the Arrhenius equation

$$\rho = \rho_0 \exp\left(-\frac{E_a}{kT}\right)$$

where ρ and ρ_0 are electrical resistivity at a certain temperature and room temperature, respectively. E_a is the activation energy of electrical conductivity.

The analysis of the obtained results made it possible to determine the activation energy equal to 0.01 eV. The obtained results indicate that $BaCoO_3$ and $CaCoO_3$ cobaltites, demonstrating high electrical conductivity and low thermal expansion coefficient, can be used as a promising thermoelectric material [10].

Conclusion

Thus, the technological route, which includes melting a stoichiometric mixture of cobalt oxide with barium or strontium carbonates in a solar furnace, quenching the melt into water, grinding

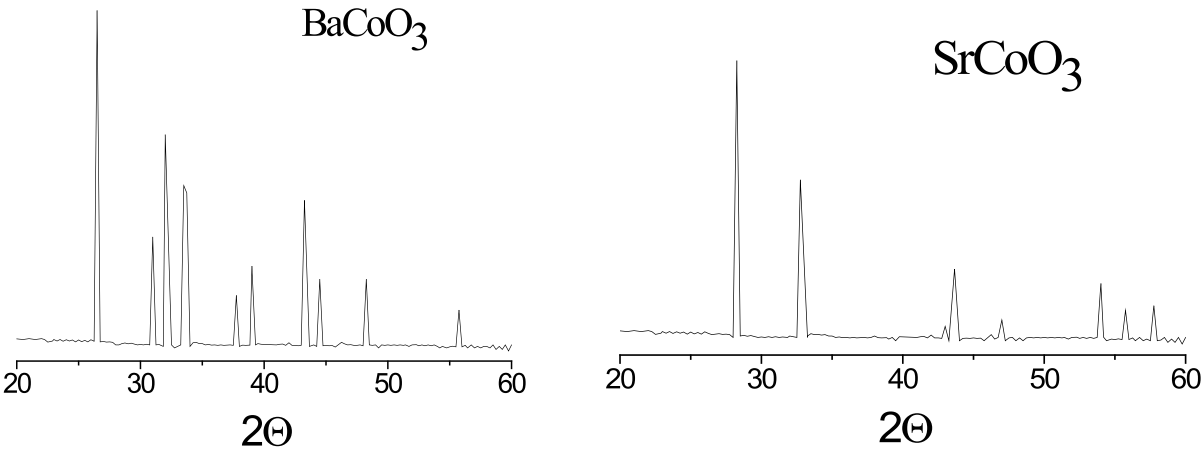

Figure 1: X-ray patterns of perovskite structures of barium cobaltites BaCoO3 and strontium SrCoO3 obtained from a melt in a solar furnace.

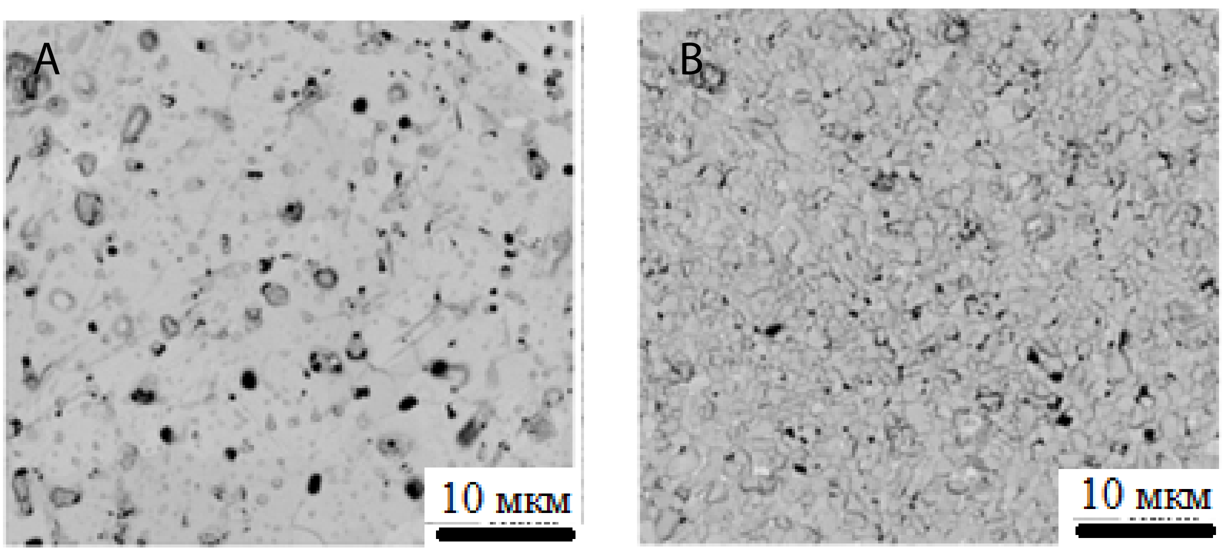

Figure 2: SEM micrographs of barium (a) and strontium (b) cobaltites obtained by melt quenching in a solar furnace.

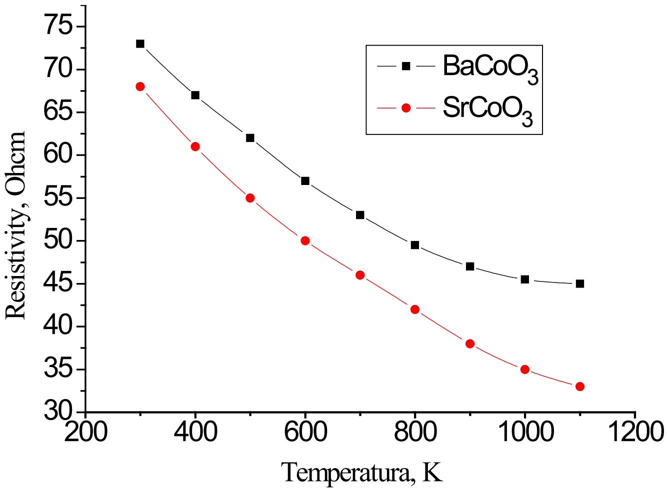

Figure 3: Temperature dependences of the electrical resistance of barium and strontium cobaltites in the temperature range 300-1200 K.

the casting and molding, followed by sintering at 1100°C, makes it possible to obtain a material based on hexagonal barium and strontium cobaltites with a developed fine microstructure and semiconductor properties. the nature of the electrical conductivity. The materials, exhibiting high values of electrical conductivity and low coefficient of thermal expansion, can be used as a promising thermoelectric material.

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