Investigation of Rb substitution on the thermoelectric parameters of BSCO Ceramic Materials

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Abstract: This study will address the main themes of today, such as reliability, sustainable and clean energy. Within this objective, Bi2Sr2-xRbxCo20y materials with x=0.0, 0.025, 0.050, 0.075, 0.100 and 0.125 have been fabricated as powder by solid state technique. From the resistivity graphic, we can reach that pure and 0.025 Rb samples exhibit a semiconducting-like behavior (dp/dT<0) and the other samples exhibit a metallic-like behavior (dp/dT>0). The Seebeck coefficients of all samples are determined as positive values for all temperature ranges evidencing the conduction mechanism mainly governed by holes. The maximum power factor values have been obtained in Rb=0.10 sample as 0.19 Mw/K2 at around 650 °C.

1. Introduction

Thermoelectricity (TE) represents the direct solid-state conversion between thermal and electrical energy due to the Seebeck effect. In the current scenario, where more than half of the energy produced end up wasted in form of heat, TE energy conversion constitutes an alternative solution to improve energy efficiency of current industrial and domestic processes. Additionally, TE modules have non-moving parts, which make them silent, reliable and light. TE modules also represent an attractive alternative to power wireless sensors and systems, replacing batteries or expensive wiring. The efficiency of these materials is determined through the figure of merit, ZT (=S2Tσ/κS: Seebeck coefficient, T: absolute temperature; σ: electrical conductivity; and κ: thermal conductivity). Consequently, good thermoelectric materials should possess high S, σ, and working T, together with low κ. Nowadays, it is possible to find many works in the literature working on the improvement of ZT mostly by raising their electrical performances [1]. Thermoelectric materials involve a huge family, from semimetals and semiconductors to ceramics obtaining in different crystalline forms, from single crystals and polycrystals to nano-composites [2]. Recently, the best performances were observed in Bi2Te3 [3]. However, it is impossible to use them for the technological applications at high temperatures above room temperature in air-condition. On the other hand after the discovery of NaCoO [4], many experimental studies have been performed in order to find out thermoelectric CoO-based ceramics having a high-performance for using in energy transferred systems [5-8]. The oxide thermoelectric materials can be used at very high temperatures under oxygen media without degradation, due to their good thermal stability. In addition, oxide thermoelectric materials have less toxicity, less costs and relatively low performance comparison to the intermetallic ones. As a result, the main objective of this research is to investigate the effect of Rb substitution for Sr in Bi2Sr2Co20y system, by measuring the structural and microstructural modifications.

2. Experimental

The Bi2Sr2-xRbxCo20y ceramics, (x=0.0, 0.025, 0.050, 0.075, 0.100 and 0.125) were fabricated from...
commercial powders of Bi2O3, SrCO3, Rb2O, and Co2O3 through the well-know solid state technique. The powders were weighed, mixed, and ball milled at 300 rpm approximately 30 minutes in acetone. The suspension was dried under infrared radiation and manually milled to avoid the agglomerations. The homogeneous suspension was calcined twice: at 750 and 800 °C for 12 h, with an intermediate grinding to degrade the metallic carbonates. Then, the dried powders were uniaxially pressed in form of pellets under an applied pressure of 400 Mpa for 1 minute. Then, these pellets were sintered at 810 °C for 24 h with a final furnace cooling.

Electrical resistivity and Seebeck coefficient were measured with a standard dc four-probe technique in a LSR-3 system in between 50 and 650 °C under Helyum atmosphere.

3. Results and Discussions

In Fig. 1, as a function of Rb-substitutions, the variation of electrical resistivity with respect to the temperature is exhibited. As seen in figure, the electrical resistivities of materials are obviously varied by Rb substitution. While pure and x=0.025 samples show semiconducting one (dρ/dT<0), the others exhibit a metallic behaviour (dρ/dT>0). In addition, the values of resistivity slightly reduce up to 0.10Rb, then start to increasing for higher Rb values. This variation can be clarified by the raising of the charge carrier concentration since Rb+ substitution for Sr2+ promotes the oxidation of Co3+ to Co4+ in the conducting layer. In addition, the increasing of electrical resistivity above 0.10Rb may be related to an enhancement of the charge carrier mobility due to the high amount of defects procured by Rubidium substitution. The lowest electrical resistivity value at room temperature is found as 13.7 mΩcm in the 0.10Rb sample. This value is lower than the previously announced in materials produced with different methods which is 19-20 mΩcm [17,18].

The decreasing of resistivity up to x=0.10Rb content indicates an improvement of electrical conduction arising from Rb substitution. These facts show a lower thermoelectric phase content and a significant increase in the number of grain boundaries in the bulk material. As a result, the charge carriers motion is hampered by these surface detections and reveals a significant electrical resistance.

![Fig.1. Electrical resistivity versus temperature for Bi2Sr2-xRbxCo2Oy samples](image1)

![Fig.2. Seebeck coefficient versus temperature for Bi2Sr2-xRbxCo2Oy samples](image2)

As a function of Rb-content, in Fig. 2, the change of Seebeck coefficients with respect to temperature are shown. Since the sign of the Seebeck coefficient is always positive in the whole measured temperature range, one can be said that the conduction mechanism in the thermoelectric materials predominantly is controlled by holes. Moreover, for all the samples, the values of Seebeck coefficient are linearly increased with temperature. This tendency is
due to a metal or degenerated semiconductor behavior, if the variation of effective mass, Fermi level and carrier concentration with temperature are negligible. Moreover, all Rb-substituted samples have lower Seebeck coefficient comparison to the pure sample which is in agreement with the resistivity results.

**Fig.3.** Power factor versus temperature for Bi2Sr2-xRbxCa2Oy samples

From the resistivity and Seebeck data, the thermoelectric performances of samples, known as power factor (PF), as a function of temperature were calculated by using PF= S²/ρ formula. The results are presented in Fig. 3. As can be observed that all Rb substituted materials have higher power factor values comparison to the pure sample resulting of the drastic decrease in the electrical resistivity caused by Rb. The maximum value at room temperature is found as 0.095 mW/K²m for 0.10Rb substituted material which is higher than the previously reported studies [17,18].

**4. Conclusions**

In this study, Bi2Sr2-xRbxCa2Oy samples (x = 0, 0.025, 0.05, 0.075, 0.10, and 0.125) have been produced via the solid-state technique. A drastic decline in resistivity comparison to the pure sample has been found in Rb substituted materials due to the increment of their density. No significant variation of Seebeck coefficient was observed, causing of higher PF values in all the Rb substituted materials. For x=0.10Rb, the maximum PF value was calculated as 0.192 mW/K²m at 650 ºC. This clearly indicates that Rb inclusion is a feasible technique in order to obtain the thermoelectric ceramic materials having high performances.

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**References**


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