

LSCuO ceramics as possible material for thermoelectric energy conversion

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Abstract

Oxide ceramics of $La_{1.85}Sr_{0.15}CuO_{4-\delta}$ (LSCuO) were grown by using the solid-state reaction method. The oxygen stoichiometry was modified by submitting the obtained samples to a post-growth thermal process at $900^{\circ}C$ under an inert atmosphere. Powder X-ray diffraction analysis shows all samples are single-phase with K_2NiF_4 -type structure. The thermoelectric properties were studied from Seebeck coefficient $S(T)$ and electrical resistivity $\rho(T)$ measurements in the temperature range from 90 to 290K. The magnitude of $S(T)$ and $\rho(T)$ increases with the processing time reaching maximum values, at room temperature, close $150\mu V/K$ and $0.8m\Omega - cm$, respectively. From $S(T)$ and $\rho(T)$ data it was possible to calculate the thermoelectric power factor PF, which reaches maximum values close to $38\mu W/K^2cm$ in the temperature range between 90 and 160K. The behavior of the transport properties and PF becomes these ceramics promissory thermoelectric materials, which could be used in low temperature thermoelectric applications.

Keywords: Thermoelectric materials, Transport properties, LSCuO compounds, Figure of merit.

Resumen

Utilizando el método de reacción sólida fué posible preparar muestras policristalinas de $La_{1.85}Sr_{0.15}CuO_{4-\delta}$ (LSCuO). La estequiometría del oxígeno fué alterada sometiendo las

muestras a un proceso térmico a 900°C en una atmósfera inerte. La difracción de rayos-X mostró la presencia de compuestos monofásicos con una estructura del tipo K_2NiF_4 . Las propiedades termoeléctricas fueron estudiadas a partir de mediciones de coeficiente Seebeck $S(T)$ y resistividad eléctrica $\rho(T)$ en el rango de temperatura entre 90 y 290K. La magnitud de $S(T)$ y $\rho(T)$ se incrementa con el tiempo de desoxigenación alcanzando valores máximos cercanos a $150\mu\text{V/K}$ y $0.8\text{m}\Omega - \text{cm}$, respectivamente. A partir de las mediciones de $S(T)$ y $\rho(T)$ se determinó el factor de potencia termoeléctrico, el cual alcanza valores máximos cercanos a $38\mu\text{W/K}^2 - \text{cm}$, en el rango de temperatura entre 90 y 160K. El comportamiento de las propiedades de transporte y los valores alcanzados por el factor de potencia convierten estas cerámicas en materiales promisorios para ser utilizados en aplicaciones termoeléctricas.

Palabras clave: Materiales termoeléctricos, Propiedades de transporte, Compuestos de LSCuO, Figura de mérito.

1 Introduction

An important application of the thermoelectricity is the generation of electricity from heat and its inverse process, the solid state refrigeration. In both cases, the efficiency with which the energy conversion is achieved is expressed in terms of the temperature difference between the hot and cold junctions of the thermocouple and the thermoelectric quality of its materials, which is determined by the thermoelectric figure of merit, ZT . This performance coefficient is defined in terms of three transport parameters: electrical conductivity $\sigma(T)$, thermal conductivity and Seebeck coefficient $S(T)$ as follows:

$$ZT = \frac{(S_p - S_n)^2 T}{\left[\sqrt{\kappa_p/\sigma} + \sqrt{\kappa_n/\sigma} \right]^2} \quad (1)$$

where the subscripts p and n correspond to the polarity of majority charge carriers of the branches that are forming the thermoelectric device [1, 2, 3].

The challenge of thermoelectric material research is to find compounds with high ZT values which can be reached, according to the equation 1 by the decrease of thermal conductivity and/or through the enhancement of thermoelectric power factor, PF . This is a parameter that describes the electrical properties of a specific material, which is given by the expression:

$$PF = \frac{S^2}{\rho} \quad (2)$$

Thus, high values for PF is an essential feature of a thermoelectric material.

At low temperature the best thermoelectric materials are monocrystalline Bi-Sb alloys which are n-type semiconductors. However, their use in practical thermoelectric devices is limited by both their poor mechanical properties and because no suitable p-type material has been found with compatible properties.

The research for efficient thermoelectric materials that work at room temperature and below has often involved non-conventional semiconductors [1]. In this sense, oxide ceramics as: $LaCoO_3$, $La_{1-x}Sr_xCoO_3$, $Bi_2Ca_2Co_2O_x$, $NaCo_2O_4$, $Ca_3Co_4O_9$, $Ca_3Co_2O_6$ are promissory candidates to become thermoelectric materials because of their transport properties and their physical-chemical stability [4, 5, 6, 7].

Particularly, the $La_{2-x}Sr_xCuO_{4-\delta}$ compounds are members of perovskites-family, they adopt a tetragonal-symmetry and K_2NiF_4 -type structure. These compounds are receiving considerable attention owing to their potential application as mixed conductors in a wide temperature range. The crystal lattice of K_2NiF_4 structures can be described as a stack of perovskite layers alternating with LaO rock salt layers. These compounds have shown to exhibit a wide range of oxygen stoichiometry, which involves a considerable improvement of the transport properties. This is due to their capability to accommodate interstitial oxygen in the LaO rock salt layers. In these ceramics the majority of the transport phenomena takes place throughout the CuO_2 planes, which causes a marked asymmetry of their transport properties and a metallic or semicon-

ducting behavior, which depend on the *Sr* content and critically on the oxygen stoichiometry [8, 9].

Taking into account the versatility of their transport properties, these LSCuO ceramics can be considered as candidates for thermoelectric materials. In this sense, a study of thermoelectric properties of LSCuO compounds is presented, in which their transport properties were modified by submitting the obtained samples to a thermal process in order to change the oxygen stoichiometry.

2 Experimental

From high purity powders of La_2O_3 , SrO and CuO (Merck 99.99%), samples with nominal composition $La_{1.85}Sr_{0.15}CuO_{4-\delta}$ were prepared by using conventional solid-state reaction method. The oxygen content present in the obtained samples was modified by submitting them to a thermal process at $900^{\circ}C$ under an argon atmosphere, the duration of the thermal process took values from 0 to 50 hours. Seebeck coefficient data were obtained by differential technique, with an accuracy about $0.5\mu V/K$. On the other hand, the electrical resistivity was measured by the standard DC four probe method. The transport measurements were carried out in the temperature range between 100 and 290K. In addition, the structural and morphological properties of the samples were studied by powder X-ray diffraction analysis (XRD) and Scanning Electron Microscopy (SEM), respectively.

3 Results and Discussion

The x-ray diffraction analysis shows a compound with tetragonal crystalline structure and space group $I4/mmm$. No evidence of impurities or secondary phases were found in the XRD profiles, as can be seen in figure 1. Significantly changes were not observed in lattice parameters with the increasing the annealing time (see table 1).

Figure 2 shows the morphology of LSCuO compounds obtained by scanning electron microscopy. The short time annealed samples

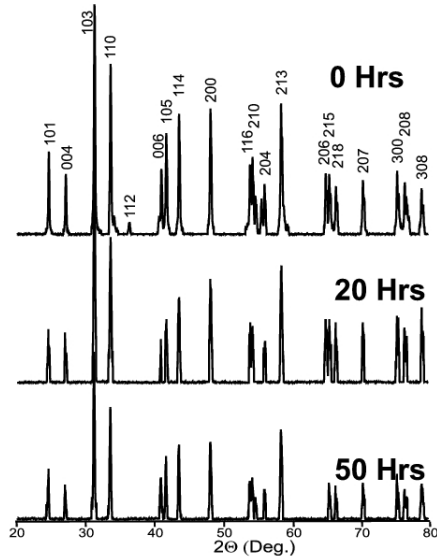


FIGURE 1. Powder XRD profiles, at room temperature, of oxygen deficient $La_{1.85}Sr_{0.15}CuO_{4-\delta}$ polycrystalline samples.

TABLE 1. Typical lattice parameters of LSCuO ceramics obtained from powder x-ray diffraction analysis.

Sample	a=b(Å)	c(Å)	Volume (Å ³)
0Hrs	3.775(1)	13.245(6)	188.42(1)
20Hrs	3.771(1)	13.246(6)	189.07(2)
50Hrs	3.781(6)	13.236(2)	189.18(1)

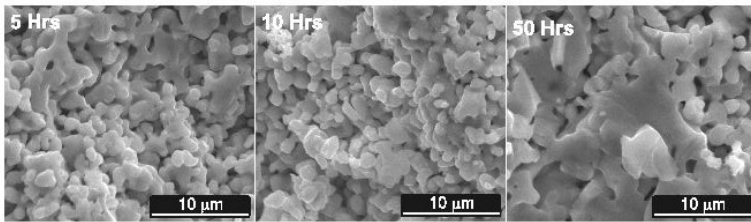


FIGURE 2. SEM micrographs of sintered LSCuO polycrystalline samples submitted to different post-growth annealing processes.

exhibit the grain structure and the porosity typical of well oxygenated LSCuO compounds. However, it is clearly seen that with increasing the post-growth annealing time the porosity decreases and the grains get together each other, which have effects on the transport properties and specially on the heat flow across the samples.

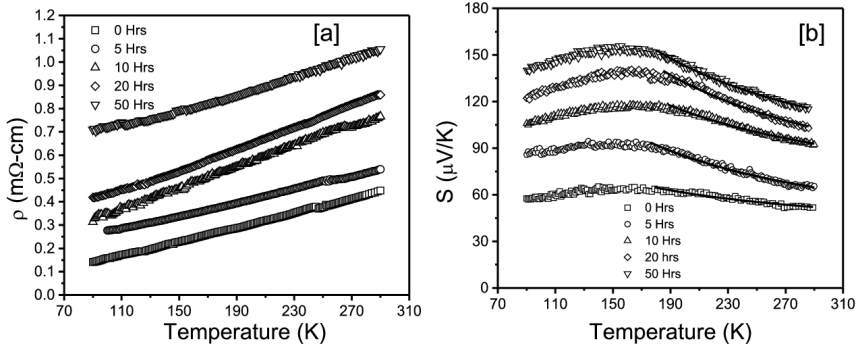


FIGURE 3. Temperature behavior of electrical resistivity [a] and [b] Seebeck coefficient of LSCuO ceramics submitted to different post-growth thermal processes.

The electrical resistivity increases with increasing temperature showing a metallic-like behavior (see figure 3a). The magnitude of $\rho(T)$ increases with the annealing time, at room temperature, from $0.3m\Omega - cm$ to $1m\Omega - cm$. This trend agrees with the observed behavior in the Seebeck coefficient of these LSCuO ceramics, which is perhaps related to the decrease of carrier concentration as the annealing time increases.

The behavior of Seebeck coefficient is shown in figure 3b, $S(T)$ is positive over the measured temperature range, suggesting a hole-type conduction. Its magnitude increases monotonically with the annealing time reaching maximum values close to $150\mu V/K$, at temperatures around 150K.

Two contributions to the Seebeck coefficient can be identified, the first one is given by carrier diffusion, which according to the Mott-Jones model is proportional to temperature, $S = -\pi^2\kappa_B^2T/3e\xi_F$, and the second one is proportional to $1/T$, which in these correlated

compounds is ascribed to hopping of small pollarons. According to this model, $S(T)$ can be expressed as [10, 11, 12]:

$$S - S_0 = \frac{\kappa_B}{|e|} \ln \frac{1-p}{p} \approx \frac{E_g}{|e|T} \quad (3)$$

where κ_B , p , S_0 and E_g are the Boltzmann constant, the electronic (hole) concentration, the high temperature extrapolated Seebeck coefficient and the energy gap, respectively. Therefore, $S(T)$ can be described by a expression of the form:

$$S(T) = \alpha T + \frac{\beta}{T} \quad (4)$$

where α and β are fitting parameters. Plotting ST vs. T^2 (see figure 3a), the least-squares fit in the temperature range between 180 and 290K gives the α and β parameters. From β parameter the energy gap, according to equation 2, was calculated, it increases with the processing time, from 13 to 32 meV, which are typical values presented by this kind of perovskites. In the same way, the α parameter increases too, which suggest that the diffusion contribution to $S(T)$ is increasing as the oxygen level decreases. This result implies that the Fermi energy decreases as can be seen in table 2.

The power factor, $PF = S^2/\rho$, for thermoelectric conversion was

TABLE 2. Behavior of energy gap, α parameter and Fermi energy obtained from fitting Seebeck coefficient experimental data to the $S(T) = \alpha T + \beta/T$ model.

Sample	0 Hrs	5 Hrs	10 Hrs	20 Hrs	50 Hrs
$E_g(meV)$	13.0(2)	20.0(1)	25.3(3)	30.9(1)	32.8(2)
$\alpha(\mu V/K^2)$	0.043(2)	0.051(2)	0.056(1)	0.061(2)	0.102(1)
$\xi_F(eV)$	0.561(1)	0.486(2)	0.430(1)	0.393(1)	0.237(2)

calculated for these oxygen deficient LSCuO samples, the results are displayed in figure 4b. As can be seen, the power factor reaches maximum values, between 90 and 160K, about $38\mu V/K^2 - cm$.

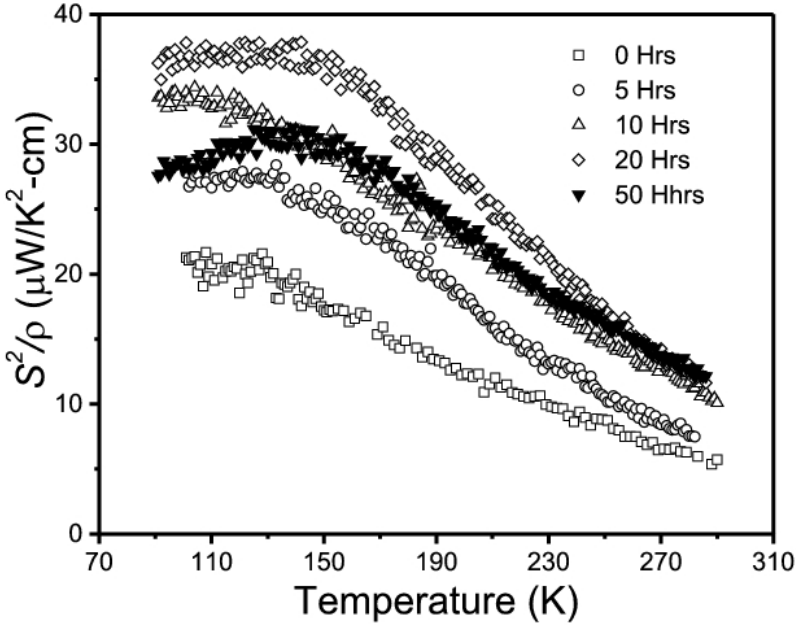


FIGURE 4. [a] ST vs. T^2 in the temperature range between 180 and 290 K. [b] Temperature behavior of thermoelectric power factor, S^2/ρ , of LSCuO-perovskites.

The values are comparable with the state-of-the-art of conventional semiconducting thermoelectric materials [1].

The magnitude and the temperature behavior exhibited by the transport properties and PF suggest that these oxygen deficient LSCuO ceramics could be promising thermoelectric materials if they are submitted to proper changes in their composition and oxygen content.

4 Conclusions

In summary, oxygen deficient polycrystalline $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-\delta}$ samples were prepared by solid-state reaction method. The obtained samples exhibit a tetragonal-like crystalline structure whose lattice parameters do not change significantly with the post-growth

thermal processes. These compounds exhibit high Seebeck coefficient values, which increase with the post-growth annealing time, their electrical resistivity exhibit a metallic behavior through the measured temperature range. The magnitude of $\rho(T)$ in all samples is less than $1m\Omega - cm$. The studied transport properties yield maximum values for PF close to $38\mu W/K^2 - cm$, which become these compounds promising thermoelectric material for low temperature technological applications in direct thermal-to-electrical energy conversion devices.

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