Effect of alkaline earth dopant on density, mechanical, and electrical properties of $\text{Cu}_{0.97}\text{AE}_{0.03}\text{CrO}_2$ (AE=Mg, Ca, Sr, and Ba) delafossite oxide

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Abstract

CuCrO_2 and $\text{Cu}_{0.97}\text{AE}_{0.03}\text{CrO}_x$ (AE=Mg, Ca, Sr, and Ba) polycrystalline materials have been prepared through the classical solid state route. CuCrO_2 is the major phase in all cases, with larger grain sizes when the alkaline earth dopant is larger. Doping also promotes the formation of secondary phases, which appear in the grain boundaries in the Ca, Sr, and Ba doped samples. Density has been drastically improved through doping, reflected in lower electrical resistivities and higher mechanical properties than the measured in undoped samples. In spite of a relatively high decrease of Seebeck coefficient, all doped samples reached higher power factor values than the undoped ones in the whole measured temperature range. The highest power factor has been reached in Mg doped samples, $0.32\text{mW/K}^2\text{m}$ at 800°C , which is among the highest obtained so far in randomly oriented polycrystalline CuCrO_2 materials.

Keywords: Ceramics; Delafossites; Doping; Hardness; Electrical properties

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1. Introduction

Nowadays, much effort is being performed to reach sustainability in many different fields, eg. agriculture, mobility, etc. Among these fields, one of the most influencing the environment is energy, due to the fact that most of the energy consumed in the world comes from non renewable sources (oil, natural gas, etc.). It is well known that fossil fuels transformation into energy is very unefficient and releases large amounts of heat and greenhouse gases to the atmosphere. Consequently, harvesting some part of this wasted heat can increase the efficiency of these energy transforming processes, decreasing the fossil fuels consumption and the CO₂ release. For this purpose, thermoelectric (TE) materials can directly transform wasted heat into electrical energy without any mobile part, noise, or maintenance, being at the same time very reliable, simple, compact, and long working life. All these characteristics make the thermoelectric generators the ideal candidates for harvesting heat in remote or mobile applications [1]. In order to produce high efficiency thermoelectric generation systems, it is necessary to use high performances TE materials, quantified using the figure of merit, $ZT = TS^2/\rho\kappa$, being T , S , ρ , and κ , absolute temperature, Seebeck coefficient, electrical resistivity, and thermal conductivity, respectively [2]. At present, the practical applications are using intermetallic compounds with high thermoelectric performances at relatively low temperatures [3]. On the other hand, these compounds can include heavy and/or toxic elements, which are rather scatter in nature and, consequently, their massive application is very difficult.

These drawbacks were avoided with the discovery of high thermoelectric performances in a ceramic oxide [4], which can, additionally, work at higher temperatures. These results started a race to find new ceramic materials with high

thermoelectric properties leading to the discovery of new oxide compounds. Among them, some showed *p*-type conduction, as the cobalt oxide-based [5-7] or delafossite-type materials [8-10], while others possessed *n*-type one, as the manganese oxide- [11,12], or TiO- based ceramics [13,14]. In spite of the high chemical and thermal stability of these oxide compounds, they still show an important inconvenient, associated to their relatively low performances when compared to the intermetallic ones. Consequently, in the related literature shows a constant effort in raising the thermoelectric characteristics of these oxide materials through different approaches [14-17]. One of the most used strategies is aliovalent cation substitution, which modifies the charge carrier concentration and can form defects for enhanced phonon scattering [11,18-20].

On the other hand, among published works are dealing with the different delafossite-type materials [21,22], few of them are centered on CuCrO₂. Moreover, most of these works are centered in aliovalent substitutions of Cr³⁺ by M²⁺ (M=Zn, Ca, or Mg) [23-25].

The goal of this work is producing high performance CuCrO₂ *p*-type thermoelectric materials through alkaline earth (Mg, Ca, Sr, and Ba) substitutions for Cu⁺. The microstructural evolution of samples with the alkaline earth size has been determined in sintered specimens and related with their thermoelectric properties.

2. Experimental

The initial CuCrO₂, and Cu_{0.97}AE_{0.03}CrO₂ mixtures (AE = Mg, Ca, Sr, and Ba) were prepared from commercial Cu₂O (PS, Panreac), Cr₂O₃ (98 + %, Aldrich), MgO (QP, Panreac), CaCO₃ (PRS, Panreac), SrCO₃ (PRS, Panreac), and BaCO₃ (PRS, Panreac) powders. Appropriate amounts of each compound were weighed, mixed,

and milled 30min at 300rpm in water media in an agate ball mill. These milling conditions produce homogeneous powder suspensions which should be dried before thermal treatments. Consequently, these suspensions were kept under infrared radiation to totally dry the milled products, followed by a thermal treatment at 900°C for 12h to decompose the alkaline earth carbonates. This process has been performed in all samples, independently of the presence of alkaline earth carbonates, in order to obtain them in the same conditions. The resulting powders were subsequently pressed in form of pellets (3mm x 3mm x 12mm) at 400MPa and sintered at 1200°C for 12h with a final furnace cooling.

Phases in the sintered bodies were identified through powder X-ray diffraction (XRD) in a Rigaku D/max-B X-ray powder diffractometer (CuK α radiation) between 15 and 60°. Microstructural observations were made on the samples surfaces using a Field Emission Scanning Electron Microscope (FESEM, Zeiss Merlin) with energy dispersive spectrometer (EDS). Apparent density was measured using Archimedes' principle in, at least, four samples for each composition, taking 5.09g/cm³ as the theoretical one [26]. Mechanical characterization has been made through microhardness using a Vickers indentation system (Matsuzawa MXT70). Several samples have been characterized under different applied loads, between 4.905 and 9.810N, and a dwell time of 15s. Vickers hardness of samples has been calculated using the formula:

$$HV = 1.8544 \frac{F}{d^2}$$

where HV is microhardness in MPa, F is the applied load in N, and d is the vertical and horizontal diagonals mean value of each indentation, in mm.

Charge carrier concentration has been determined at room temperature in each composition using a L79/HCS system (Linseis GmbH). Electrical resistivity and

Seebeck coefficient were measured in the steady state mode, using the standard dc four-probe configuration between 50 and 800°C in a LSR-3 system (Linseis GmbH). The samples performances have been evaluated through their PF values, calculated using Seebeck coefficient and electrical resistivity data.

3. Results and discussion

Powder XRD patterns for all samples are displayed in Fig. 1, between 15 and 50° for clarity. At a first sight it is clear that all samples present very similar patterns, and most of the peaks (identified by their diffraction planes) correspond to the CuCrO_2 thermoelectric phase [27,28]. On the other hand, the relative intensity of peaks does not correspond to the obtained in randomly oriented samples, pointing out to a preferential grain orientation during the samples preparation for the XRD characterization, as observed in similar anisotropic systems [29]. Moreover, some very small peaks could not be associated to any secondary phase composition due to their very low intensity.

FESEM observations performed on the surfaces of all samples are shown in Fig. 2. In Fig. 2a, corresponding to the undoped CuCrO_2 samples, the microstructure can be described as a mixture of small and large grains of CuCrO_2 phase, in agreement with the XRD data. Moreover, a large porosity can be also easily noticed. On the other hand, drastic changes in the microstructure are produced by doping (see Figs. 2b-e). In the case of Mg doping (Fig. 2b), all grains are larger than the observed in undoped samples, even if the dual grain size distribution is still maintained. In these samples, EDS analysis has shown that large grains correspond to $(\text{Mg,Cu})\text{CrO}_2$ phase, while the small ones have been associated to $(\text{Mg,Cu})\text{Cr}_2\text{O}_x$ secondary phase. Other interesting observation in this micrograph is that the porosity content

seems to be lower than in the former samples. When observing the Ca, Sr, and Ba doped samples (Figs. 2c-e), it is evident that their microstructure is very similar; the sintered materials are formed by very large grains and show lower porosity than the undoped and Mg-doped samples. EDS analysis performed in Ca, Sr, and Ba doped samples has shown that large grains composition is CuCrO_2 with lower alkaline earth content when its radius is larger, while there are very small white grains (clearly observed in Fig. 2e) with $\text{AE}(\text{Cu})\text{CrO}_x$ composition (AE = Ca, Sr, or Ba). The secondary phases found in all the doped samples have not been identified in the XRD patterns, probably due to their low proportion, and their relatively small grain sizes.

In order to assess the evolution of porosity observed in the micrographs, the density of all samples has been measured, and the obtained results are displayed in Table I. These data are in a clear agreement with the microstructural observations, which showed that porosity seemed to decrease when the alkaline earth atomic weight was increased. Moreover, doped samples improve density values between 29 and 50%, when compared with the undoped ones. These density modifications are reflected in the mechanical properties of samples, evaluated through the Vickers microhardness, presented in Fig. 3 as a function of the applied load. As it can be seen in the graph, hardness values are drastically improved with the doping process, when compared with the obtained in the undoped CuCrO_2 samples. Moreover, the standard error is very small, being, in some cases, lower than the symbols sizes. On the other hand, the hardness is clearly depending on the applied load, decreasing when the load is increased, in agreement with the typical behaviour reported in other TE or related ceramic materials [30-32].

The temperature evolution of electrical resistivity, as a function of the dopant, is displayed in Fig. 4. In the figure, the first data of undoped and Ba-doped samples have not been represented for clarity due to their high resistivity values. All samples present a semiconducting-like behaviour ($dp/dT < 0$) in the whole measured temperature range (see insert for the Mg-doped samples). In spite of the differences observed among these samples, the variation of resistivity is relatively low, when compared with the large decrease obtained through Mg-doping (around one order of magnitude lower). This evolution with doping cannot be easily explained from the microstructural features previously discussed, as the resistivity should decrease when the dopant cation size is increased, due to the enhancement of the grain sizes. On the other hand, the identification of AE(Cu)CrO_x grains (AE = Ca, Sr, and Ba) between the CuCrO₂ ones, with larger sizes when the atomic weight of the alkaline earth is raised, indicates a degradation of the electrical connectivity of the thermoelectric grains, explaining their higher resistivity, when compared with the Mg-doped samples. The lowest resistivity values achieved in these Mg-doped samples at 50°C (110 mΩ.cm) are much lower than the measured in Mg-doped nanocrystals (68000 mΩ.cm) [33], or bulk polycrystalline materials (200-3000 mΩ.cm) [9,24]. Moreover, they are drastically lower than the reported for Mn, Zn, Ca, Ni, Co, Fe, and V-doped ceramics (33300-5000 mΩ.cm) [23]. On the other hand, they are comparable to the reported for Mg doped materials prepared through sol-gel (100 mΩ.cm) [8], or using very long (>700 h) thermal treatments (60 mΩ.cm) [34]. When comparing the values at 650°C, the resistivity in the Mg-doped materials presented in this work (45 mΩ.cm) is lower than the reported in the previously mentioned literature.

Hall measurements of the different samples were performed in order to explain this behaviour using charge carrier concentration (n). The obtained results are shown in Fig. 5, where it can be observed that charge carrier concentration is drastically increased for the Mg doped samples, compared with the undoped ones, decreasing when the alkaline earth cation size is increased. This effect can be associated to the decrease on the solubility limit when the difference in sizes between Cu^{2+} and alkaline earth is larger. Moreover, the lower solubility of these cations in the structure may decrease the interstitial oxygen content in the samples, when compared with the Mg doped ones [35-37]. Furthermore, this lower solubility is responsible of precipitation of secondary phases between the thermoelectric grains (higher amount when the alkaline earth cation is larger), as discussed in the microstructural observations.

Fig. 6 displays the variation of the Seebeck coefficient as a function of temperature for the pure and doped CuCrO_2 samples. All of them exhibit positive values in the whole measured temperature range, indicating predominant hole conduction mechanism. S values clearly agree with the electrical resistivity values, at room temperature, the samples presenting higher S also possess higher resistivity. Consequently, the highest S values are found in the undoped samples. Moreover, S is decreased when the temperature is raised, except in the Mg doped samples, where it slightly increases with temperature as previously reported [34]. Due to the fact that Mg doped samples present the lowest resistivity, their S values will be compared with the available literature. The highest S values in these samples at room temperature ($285\mu\text{V/K}$) are lower than the reported ($125\text{-}1100\mu\text{V/K}$) in materials with higher electrical resistivity (see above) [9,23,24,33], but higher than the previously mentioned ceramics with lower resistivity ($125\text{-}275\mu\text{V/K}$) [8,34]. On

the other hand, the raise of S with temperature observed in these Mg-doped materials, leads to S values at 650°C ($400\mu\text{V/K}$) which are comparable to the obtained in higher resistivity samples ($350\text{--}650\mu\text{V/K}$)

Using the electrical resistivity and the Seebeck coefficient data, PF has been calculated, as a function of temperature, and presented in Fig. 7, to determine the samples performances. As it can be easily observed, all doped samples display higher PF than the undoped ones in the whole measured temperature range. The highest PF values have been achieved in the Mg doped samples, while the other doped samples show very similar values at all temperatures being, all of them, much higher than the determined in the undoped ones. The maximum PF values at room temperature measured in Mg doped materials ($0.07\text{mW/K}^2\text{m}$) are around the measured in typical CuCrO_2 doped delafossite materials ($0.001\text{--}0.09\text{mW/K}^2\text{m}$) [8,9,23,24,33,34]. On the other hand, at high temperatures (650°C) the highest value ($0.32\text{mW/K}^2\text{m}$) is much higher than the reported in several doped materials ($0.013\text{--}0.21\text{mW/K}^2\text{m}$) [23,24]. In addition to the raise of thermoelectric performances, it should be noted that the best reported results have been obtained through sol-gel preparation of by very long thermal treatments ($>700\text{ h}$).

Consequently, the relatively high values reported in this work are very promising for practical applications, when considering the simple and short process used.

Moreover, these results could be easily improved using fabrication methods leading to better homogeneity and reactivity than the classical solid state method, producing more homogeneous microstructure and better electrical connectivity between the thermoelectric grains.

4. Conclusions

In this work, CuCrO_2 and $\text{Cu}_{0.97}\text{AE}_{0.03}\text{CrO}_x$ (AE=Mg, Ca, Sr, and Ba) polycrystalline materials have been successfully prepared using the classical solid state route. XRD data have shown that all samples are formed by nearly CuCrO_2 pure phase. SEM micrographs demonstrate that alkaline earth doping enhances the grain size of the thermoelectric phase. Moreover, when the atomic weight of the alkaline earth is higher, the final grain sizes are drastically increased. On the other hand, doping promotes the formation of secondary phases, which preferentially appear in the grain boundaries in the Ca, Sr, and Ba samples. Furthermore, these secondary phases are larger when with the higher atomic weight of the dopant due to the decrease of solubility in the CuCrO_2 matrix. These microstructural characteristics are reflected in a raise of density and hardness when the alkaline earth atomic weight is increased. Electrical resistivity is drastically diminished for the Mg doped samples, when compared with the undoped ones, increasing when the alkaline earth radius is larger. This behaviour is in agreement with the charge carrier concentration determined through Hall measurements, and the formation of secondary phases between thermoelectric grains observed in SEM images. In spite of a relatively high decrease of Seebeck coefficient, when related with the values obtained in undoped samples, doping leads to higher power factor values. The highest PF has been determined in Mg doped samples, with values around $0.32\text{mW/K}^2\text{m}$ at 800°C , which are among the best reported in CuCrO_2 family, and are promising for practical applications.

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Table I. Absolute and relative densities of Delafossite samples, taking 5.09g/cm³ as the theoretical density of CuCrO₂ [25].

Sample	Density (g/cm ³)	Relative density (%)
CuCrO ₂	3.18	62.5
Cu _{0.97} Mg _{0.03} CrO _x	4.10	80.6
Cu _{0.97} Ca _{0.03} CrO _x	4.26	83.7
Cu _{0.97} Sr _{0.03} CrO _x	4.41	86.6
Cu _{0.97} Ba _{0.03} CrO _x	4.75	93.3

Figure captions

Figure 1. Powder XRD patterns of delafossite samples, for: a) CuCrO_2 ; b) $\text{Cu}_{0.97}\text{Mg}_{0.03}\text{CrO}_x$; c) $\text{Cu}_{0.97}\text{Ca}_{0.03}\text{CrO}_x$; d) $\text{Cu}_{0.97}\text{Sr}_{0.03}\text{CrO}_x$; and e) $\text{Cu}_{0.97}\text{Ba}_{0.03}\text{CrO}_x$.

Figure 2. FESEM micrographs performed in representative surfaces of delafossite sintered samples, for: a) CuCrO_2 ; b) $\text{Cu}_{0.97}\text{Mg}_{0.03}\text{CrO}_x$; c) $\text{Cu}_{0.97}\text{Ca}_{0.03}\text{CrO}_x$; d) $\text{Cu}_{0.97}\text{Sr}_{0.03}\text{CrO}_x$; and e) $\text{Cu}_{0.97}\text{Ba}_{0.03}\text{CrO}_x$.

Figure 3. Vickers microhardness as a function of the alkaline earth dopant at different applied loads, (●) 4.91; and (■) 9.81N.

Figure 4. Evolution of electrical resistivity with temperature of CuCrO_2 samples as a function of the dopant cation, (●) undoped; (■) Mg; (◆) Ca, (▲) Sr; and (▼) Ba. The insert shows the semiconducting behaviour of the Mg-doped samples.

Figure 5. Charge carrier concentration (n), at room temperature as a function of the alkaline earth dopant in CuCrO_2 samples.

Figure 6. Seebeck coefficient evolution with temperature for CuCrO_2 samples, as a function of the dopant cation: (●) undoped; (■) Mg; (◆) Ca, (▲) Sr; and (▼) Ba.

Figure 7. PF evolution with temperature for CuCrO_2 samples, as a function of the dopant cation: (●) undoped; (■) Mg; (◆) Ca, (▲) Sr; and (▼) Ba.

Figure 1

Figure 2

Figure 3

Figure 4

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Figure 6

Figure 7