New solution method to produce high performance thermoelectric ceramics: a case study of Bi-Sr-Co-O

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Abstract

$Bi_2Sr_2Co_{1.8}O_x$ ceramics have been synthesized through a solution method involving the addition of polyethyleneimine as coordinating agent for the metallic cations. From these powders, bulk sintered materials have been prepared. Microstructure has been studied by means of scanning electronic microscopy (SEM) and it has shown that samples are mainly composed by the thermoelectric phase, with very small amounts of secondary phases. Electrical resistivity measurements showed very small values (around 21mΩ.cm at room temperature), nearly constant with temperature, while thermopower increases rapidly to values higher than 200μV/K at 650ºC. Power factor value at 50ºC is about 0.08mW/K^2.m and 0.20 at 650ºC, which makes this ceramic a potential material for power generation applications.

Keywords: Synthesis, Ceramics, Thermopower, Electrical resistivity, Power factor.

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1. Introduction

From the discovery of ceramic oxides with high thermoelectrical properties [1], cobaltite ceramics have attracted attention due to their performances [2,3]. Many different conformation techniques have been used in order to obtain bulk thermoelectrical properties close to those obtained in single crystals, as reactive templated grain growth (RTGG) [4, 5], templated grain growth (TGG) [6], hot pressing (HP) [7], and spark plasma sintering [8]. Most of these processes use powders prepared by the classical solid state reaction method which is characterized by several mixing, milling and calcination processes. In spite of these repeated processes, typical materials show incomplete reaction and compositional inhomogeneities that influence their final properties. In this context, solution syntheses appear as a solution to improve the precursor homogeneity, together with smaller particle size, which result on the increase of the precursors reactivity. These changes on the precursors can help improving the thermoelectrical performances of those polycrystalline cobaltites which is of the main importance in order to be used in power generation devices reaching high thermal-to-electrical energy conversion.

In this contribution it is presented a solution method, used for the first time on the cobaltite materials, involving a polymer addition to produce high performance bulk thermoelectric Bi-Sr-Co-O ceramics.

2. Experimental

2.1. Precursors preparation

Synthesis of Bi-Sr-Co-O precursors was made in several steps. Firstly, adequate amounts of metallic acetates (analytical grade) were dissolved in a mixture of glacial acetic acid and distilled water (~ 40:60vol.%, respectively). Polyethyleneimine (PEI, 50wt.% water) was added (~ 1 mol PEI:2 moles $Bi_2Sr_2Co_{1.8}O_x$) to the solution which turned darker immediately indicating the cation-nitrogen coordination. Solvent evaporation was produced in a rotary evaporator reducing the initial volume to about 20%. Total solvent evaporation is performed on a hot plate at about 50ºC until a dark pink thermoplastic paste is obtained. Further heating turned this paste to violet color, followed by a partial decomposition and, finally, producing a self propagated combustion at about 300-350ºC which raises immediately the temperature inside the crucible to about 750ºC measured with an IR optical pyrometer.

The obtained powders were manually milled, thermally treated at 750 and 810ºC for 6 hours, with an intermediate milling, uniaxially pressed at 400MPa in form of prisms (~ 3x3x14mm^3) and then sintered at 870ºC for 24 hours under air, with furnace cooling.

Sintered materials were characterized by powder X-ray diffraction (XRD, Rigaku D/max-B). The platelet thickness was estimated from X-ray line broadening measurements, the calculation was done using the (006) and (008) diffraction peaks, according to the Scherrer formula [9]. Microstructural characterization was performed by scanning electron microscopy (SEM, JEOL 6000) provided with an energy dispersive spectroscopy (EDS) system. Micrographs of transversal fractured and longitudinal polished sections of the samples have been recorded to

analyze the grain sizes and shapes as well as the different phases and their distribution.

2.2. Thermoelectrical characterization

Electrical resistivity (ρ) and thermopower (S), were simultaneously determined by the standard dc four-probe technique in a LSR-3 measurement system (Linseis GMBh). They were measured in the steady state mode at temperatures ranging from 50 to 650ºC under He atmosphere. With the electrical resistivity and thermopower data, the power factor ($PF=S^2/\rho$) has been calculated in order to determine the samples performances.

3. Results and discussion

Fig. 1 shows the XRD plot for the $Bi_2Sr_2Co_{1.8}O_x$ samples. Most of the peaks correspond to the thermoelectric phase, with minor peaks associated to non-thermoelectrical secondary phases. The highest peaks (marked with a *) belong to the misfit cobaltite phase and are in agreement with previously reported data [4,10]. The other peaks correspond to the minor $Bi_{0.75}Sr_{0.25}O_y$ phase, with $R\bar{3}m(\#166)$ space group (marked with a •) [11] and to the Si (111) peak (indicated by a #) used as reference. The XRD results indicate that nearly pure $Bi_2Sr_2Co_{1.8}O_x$ phase was obtained in a relatively short sintering time.

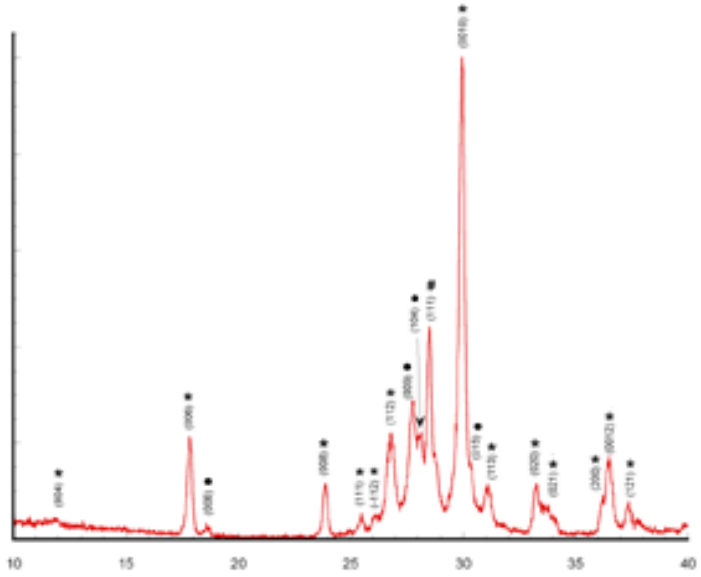

Fig. 1. XRD plot of the $Bi_2Sr_2Co_{1.8}O_x$ samples. Peaks are marked with a * for the thermoelectric $Bi_2Sr_2Co_{1.8}O_x$ phase, • $Bi_{0.75}Sr_{0.25}O_y$ non thermoelectric phase ($R\bar{3}m$ H'), and # for Si (used as reference).

Typical transversal fractured section of the sintered specimens is represented in Fig.2a. It is clear that samples are composed of randomly oriented plate-like grains, most of them exceeding 10μm in the ab planes. On the other hand, thickness is difficult to be measured as they are, in turn, formed by many thin grains well stacked along the ab planes. In order to overcome this problem, the individual plate-like grain thickness has been estimated from the X-ray line broadening measurements using the (006) and (008) diffraction lines of the $Bi_2Sr_2Co_{1.8}O_x$ phase, according to the Scherrer formula. The obtained mean value for the grain thickness is about 35nm which clearly indicates that the crystal preferential growth is produced along the ab plain (coincident with the conduction CoO planes).

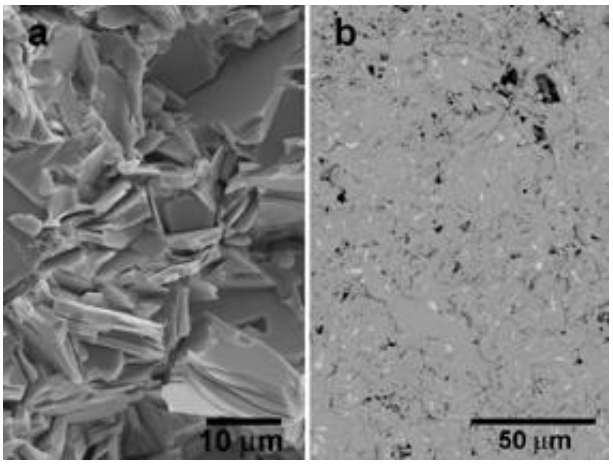

Fig. 2. Representative SEM micrographs of $Bi_2Sr_2Co_{1.8}O_x$ ceramics. a) transversal fractured surface, and b) longitudinal polished surface. Different contrasts correspond to $Bi_2Sr_2Co_{1.8}O_x$ (grey), SrO (dark grey), and $Bi_{0.75}Sr_{0.22}O_y$ (white).

When observing the longitudinal polished section of $Bi_2Sr_2Co_{1.8}O_x$ (Fig. 2b) it is found that major phase is the grey one with very small amounts of secondary phases (white and dark grey contrasts). EDS analysis performed on different points for each contrast showed that the grey one correspond to the thermoelectric $Bi_2Sr_2Co_{1.8}O_x$ phase, dark grey to SrO, and white to $Bi_{0.75}Sr_{0.22}O_y$ (very close to the $Bi_{0.75}Sr_{0.25}O_y$ composition, determined by XRD). The amount of the different phases has been performed on several micrographs using Digital Micrograph software. The determined phase amounts have been around 5vol% for the $Bi_{0.75}Sr_{0.22}O_y$ phase, 2vol.% SrO, and 93vol.% thermoelectric $Bi_2Sr_2Co_{1.8}O_x$ phase. On the other hand, SrO phase found on the polished samples has not been found in the XRD due to its small proportion in the samples.

The evaluation of the porosity has been performed using the apparent density of the samples. In all cases, it has been shown to be 91±2 % of the theoretical density.

The temperature dependence of the resistivity is shown in Fig. 3. As it can be easily seen, the ρ(T) curve shows a very small variation with temperature, with a semiconducting-like behaviour from room temperature to about 350ºC, changing to metallic-like behaviour from 350 to about 600ºC and remaining practically constant at higher temperatures. The very low resistivity values found in these samples are due to the small content of secondary phases and porosity. As a consequence, these values are close to the values obtained for textured materials (~ 15mΩ.cm at 275ºC) [5] or single crystals (~ 18mΩ.cm at room temperature) [4].

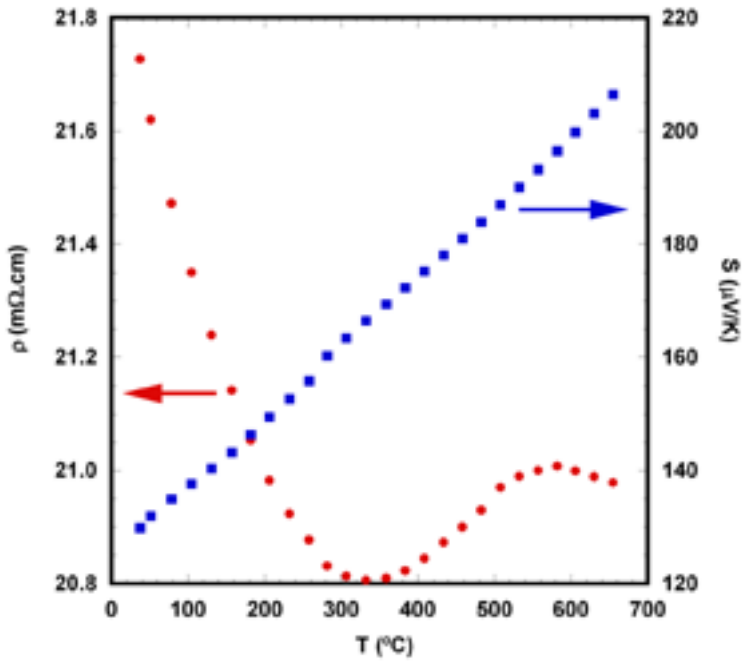

Fig. 3. Temperature dependence of ρ (●) and S (■) for polycrystalline $Bi_2Sr_2Co_{1.8}O_x$ materials.

As it can be also seen in Fig. 3, where S vs. T is represented, the values are positive in the entire temperature range, indicating a hole conduction mechanism. On the other hand, they increase almost linearly with temperature, with values of about 130μV/K at ~50ºC which are higher than those obtained for textured materials (125μV/K at 275ºC) [5] or single crystals (110μV/K at 25ºC) [4]. This high value is due to the reduction of the cobalt oxidation state in the CoO_2 layer, calculated from Koshibae's relation [12]. These values are about 3.57 for the measured samples (instead 3.63 for the stoichiometric ones [13]), clearly indicating that the synthetic method generates higher amount of oxygen vacancies than the usual methods.

In order to estimate the samples performances, PF values were calculated as a function of temperature and represented in Fig. 4. Comparing the graphics from S (Fig. 3) and PF (Fig. 4), they follow a parallel evolution with temperature due to the small variations of ρ with temperature. At room temperature, the PF value of about 0.075mW/K^2.m is higher than the obtained for single crystals (0.06mW/K^2.m) [4] and very close to textured materials (0.1mW/K^2.m) [5].

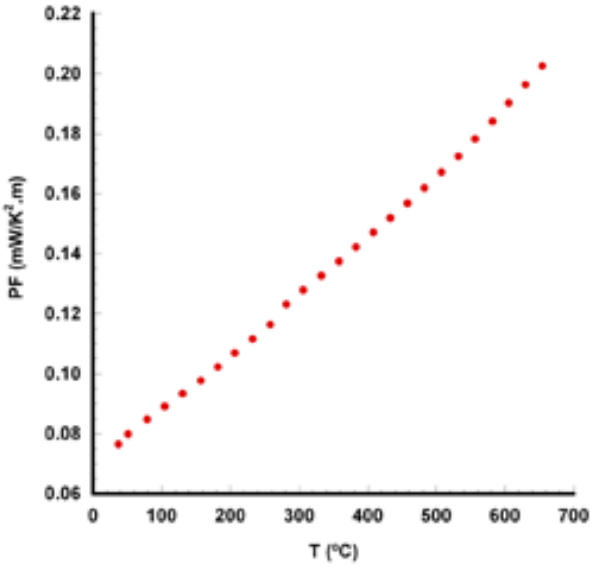

Fig. 4. Temperature dependence of PF for polycrystalline $Bi_2Sr_2Co_{1.8}O_x$ materials.

4. Conclusions

All the results indicate that the PEI method produces high quality and homogeneous polycristalline ceramic materials with low amounts of secondary phases and porosity, leading to compacts with improved thermoelectrical properties comparable to those obtained for single crystals and textured materials.

5. Acknowledgements

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Figure captions

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Figure(s)

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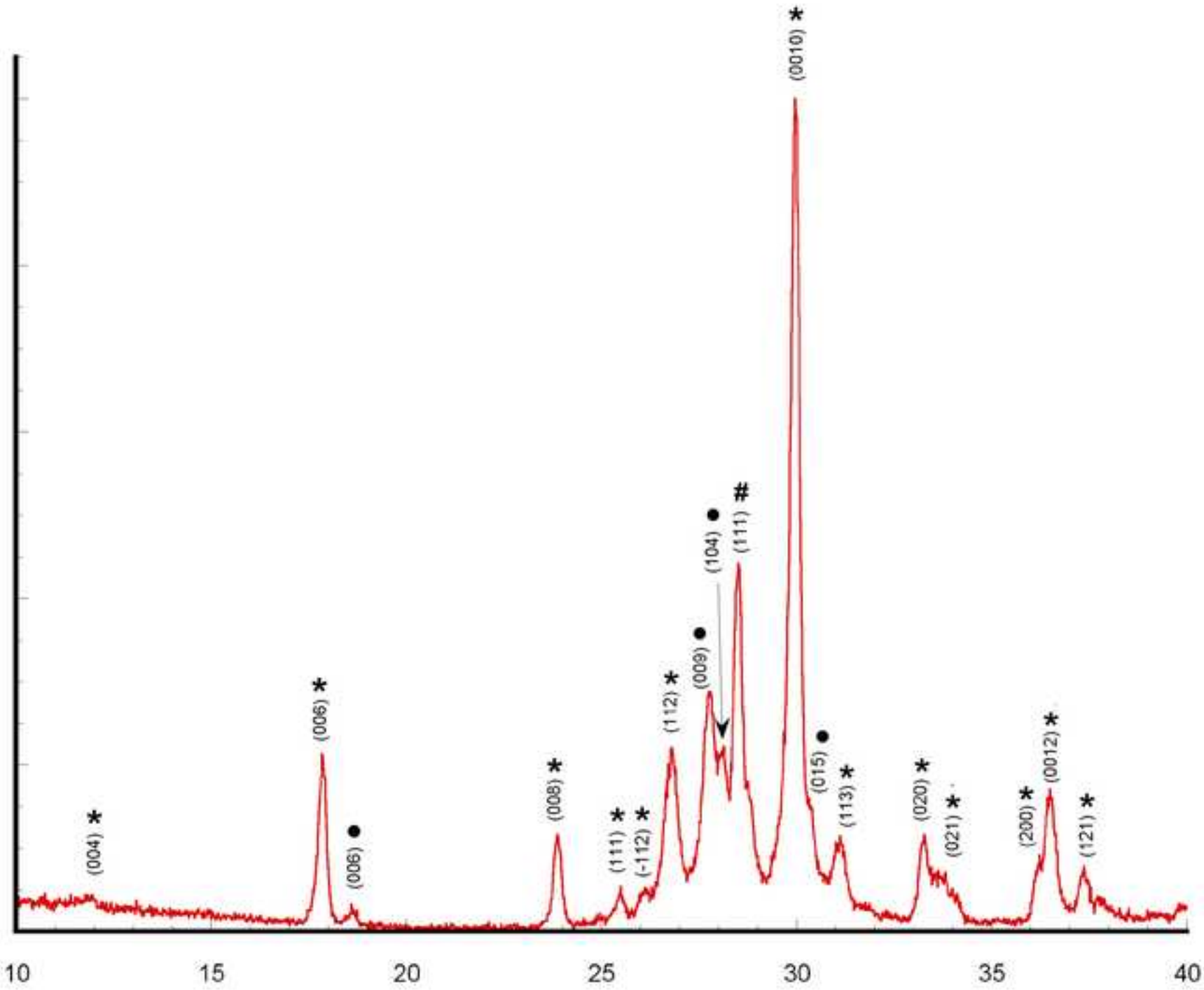

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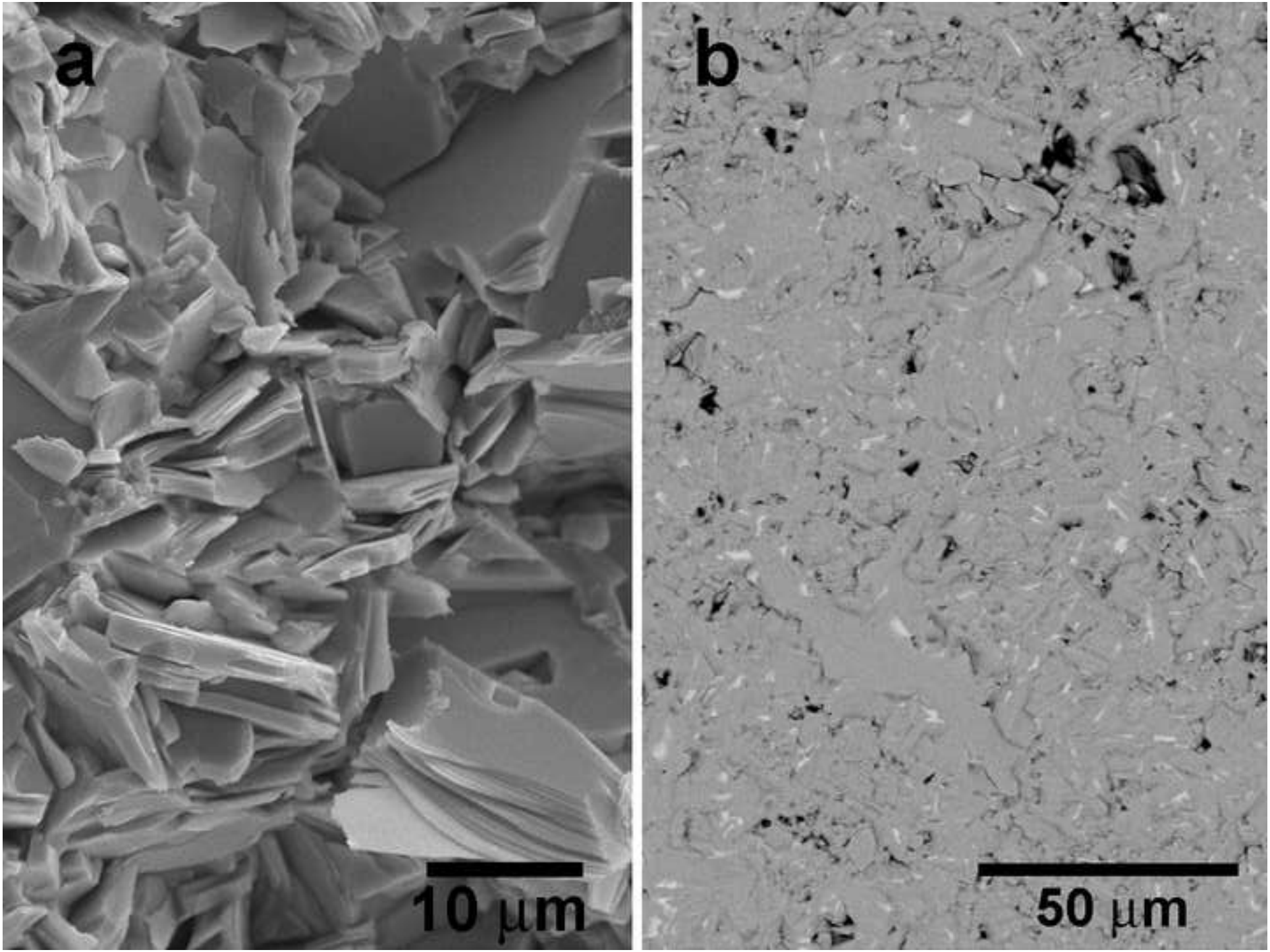

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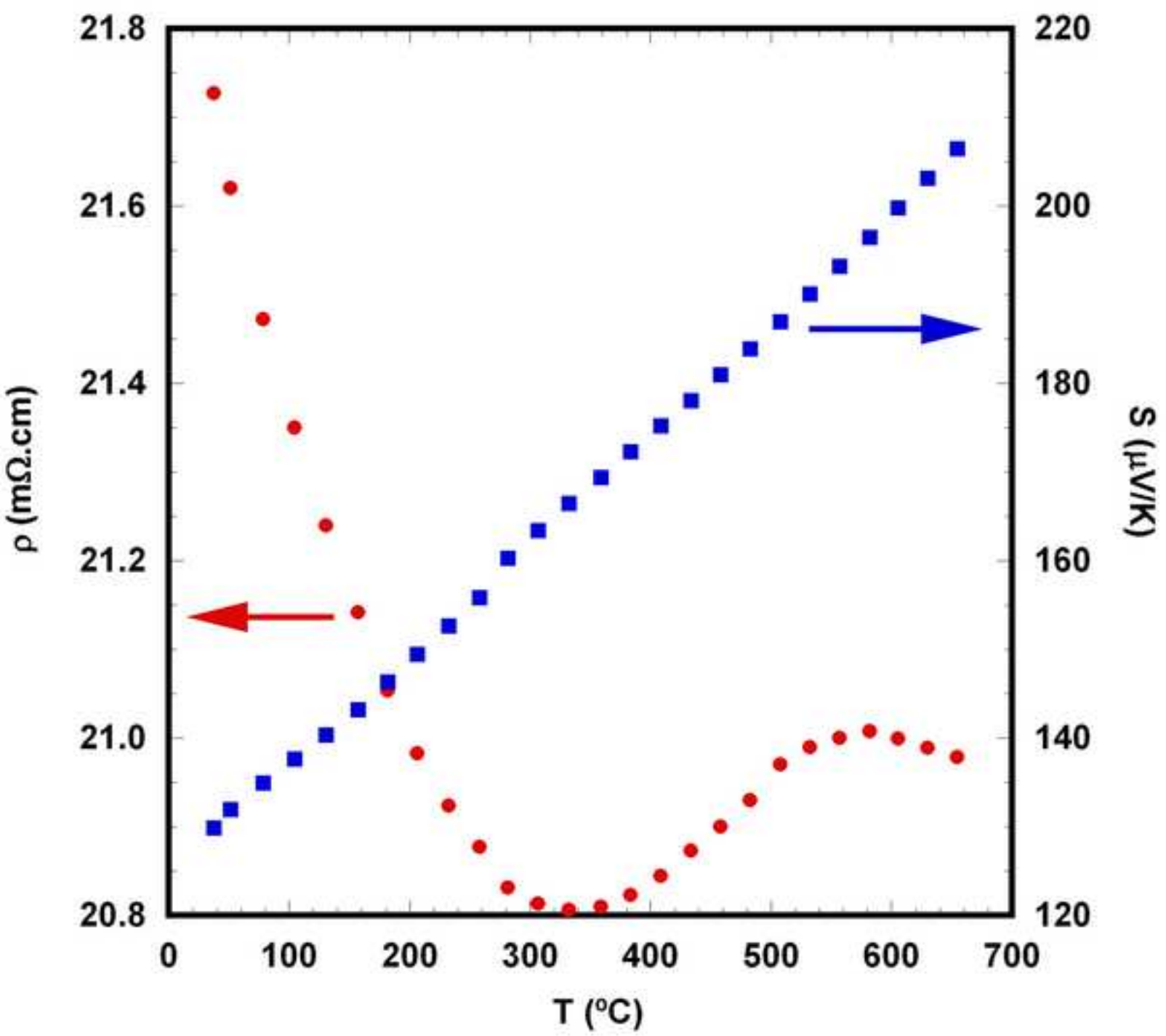

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