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New environmentally friendly Ba-Fe-O thermoelectric material by flexible laser floating zone processing

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ABSTRACT

Ceramics with nominal $BaFe_{12}O_x$ composition were processed through laser floating zone technique from 25 to 200 mm/h growth rates. These processing conditions were found to promote microstructural differences between the outer and inner parts of the rods, being more pronounced at higher growth rates. Along with the higher microstructural inhomogeneity, the samples grown at 100 and 200 mm/h display reasonable n-type thermoelectric properties provided by $BaFe_{18}O_x$ phase formation. Their highest power factor measured at 800 °C is comparable to the best observed so far in oxide ceramic materials, with additional advantage of high abundance and low costs of Fe_2O_3, and $BaCO_3$ precursors.

Thermoelectric (TE) power generation is a promising technology to harvest heat, especially if combined with other energy conversion systems. In this regard, it can decrease the concomitant CO_2 emissions, helping to fight against global warming. Highly efficient and environmentally friendly TE materials are desired for using in commercial devices. Their thermoelectric performances are quantified by the dimensionless figure-of-merit, ZT ($=TS^2/\rho\kappa$, where S, T, ρ, and κ are Seebeck coefficient, absolute temperature, electrical resistivity, and thermal conductivity, respectively). Therefore, high performances TE materials should possess high S, with low ρ and κ [1]. On the other hand, it is also common to use the power factor, PF ($=S^2/\rho$) for comparative analysis of the TE properties.

In practical applications, intermetallic materials with high ZT are used, e.g. automobile industry. In spite of their high efficiency, these materials show some drawbacks, as their relatively low working temperatures, high costs, and the presence of heavy and toxic elements in their composition. The discovery of high TE properties in Na_xCoO_2 [2] allowed to surpass the working temperature limitation, provided by the higher thermal stability of the oxide ceramics. Since that, many research efforts have been focused on oxides, such as MnO-, TiO-, and CoO-based materials [3–5]. Still, the research on more abundant and environmentally friendly iron oxide-based materials is rather scarce [6,7]. In 2015, Cao et al. [8] have reported the growth of $BaCO_3$ and Fe_2O_3 powders by high pressure floating zone growth technique, mainly obtaining a mixture of $BaFe_{12}O_{19}$ and $BaFe_{18}O_{27}$ phases. However, when growing under pressures below 50 atm the presence of iron and barium oxide secondary phases has been reported [8]. These ferrites are members of hexagonal ferrites (hexaferrites), discovered in 1950s, and characterized by their high magnetic fields and Curie temperatures above 720 K. Due to these characteristics, they have been widely used as permanent magnets, in magnetic recording media, in microwave devices, and for fabricating multiferroic devices [8,9]. The electrical and magnetic results obtained by Cao et al. [8] are comparable to the obtained in Ca-Co-O and Sr-Ti-O systems.

Taking into account these previously published data, the present work focuses on structural, microstructural, and thermoelectric properties of $BaFe_{12}O_x$ ceramics, processed through the laser floating zone technique (LFZ). Moreover, the effects of different solidification rates on the relevant properties are also presented and discussed.

Polycrystalline samples with nominal $BaFe_{12}O_x$ composition were prepared by mixing stoichiometric amounts of Fe_2O_3 (Sigma Aldrich, >99%) and $BaCO_3$ (Fluka, >99%). The powders were subjected to planetary ball milling for obtain more homogeneous mixture. A binder (PVA - Polyvinyl alcohol) was added to the powder mixture to allow cold extrusion of the precursor mixture in the form of rods. These green ceramic samples (designated as-prepared samples) were subsequently used as feed and seed rods in an LFZ device equipped with a continuous power CO_2 laser ($\lambda = 10.6$ µm, Spectron SLC) described elsewhere [10].

All the LFZ grown samples were processed at 25, 50, 100, and 200 mm/h under air, with a seed rotation of 5 rpm counterclockwise to maintain the cylindrical geometry, while the feed was rotated at 15 rpm, in the opposite direction, in order to assure the molten zone

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compositional homogeneity. After the growth process, long (~100 mm) and geometrically uniform (~3 mm diameter) textured cylindrical rods have been produced. Finally, the textured bars were cut into pieces with the adequate dimensions for their characterization (~15 mm long).

The phases in the samples have been identified through X-ray diffraction (XRD) analysis performed at room temperature on powders obtained by crushing as-grown fibers, using a Rigaku D/Max-B diffractometer system (CuKα radiation). Samples were measured between 10 and 80° 2θ range with a step of 0.02° and 2 s dwell time.

Microstructures have been observed on longitudinal polished sections of samples in a field emission scanning electron microscope (FESEM, Zeiss Merlin), equipped with an energy X-ray dispersive spectroscopy (EDS) system. Different contrasts have been analysed using EDS to determine their qualitative composition for comparative purpose. Electrical resistivity and Seebeck coefficient have been simultaneously measured by the standard dc four-probe technique in a LSR-3 measurement system (Linseis GmbH) under He atmosphere, in the steady state mode, at temperatures ranging from 50 (~ room temperature) to 800 °C. Samples performances have been compared using the power factor, calculated from the previously measured electrical resistivity and Seebeck coefficient data.

In Fig. 1, the patterns of the as-grown fibers at different growth rates are shown. After LFZ processing, $BaFe_{18}O_{27}$ (ref card 01-075-0406), Fe_3O_4 (ref card 01-075-1609), $Ba_2Fe_{14}O_{22}$ (ref card 00-040-1047) and $BaFe_2O_4$ (ref card 00-025-1191) phases have been identified through their reflection peaks, clearly showing that all samples are multiphasic. Other interesting observation is that the amount of these phases is clearly influenced by the growth rate. At high pulling rates $BaFe_{18}O_{27}$ and Fe_3O_4 are the main phases, while at low speeds $BaFe_2O_4$ is the main one. All these phases are in agreement with the ones reported in the literature for this system [8,9].

The microstructures obtained at the different growth conditions are illustrated in Fig. 2. In these micrographs, it can be observed that the differences between the inner part of the rods (1) and the external one (2) are increasing with the growth rate (from a to d). The external part of the rods is composed of thinner grains than the inner one, and their orientation is more pronounced in the outer part, guided by the high radial thermal gradient. Moreover, the effect of solidification rate is more evident in the center part of the rods, where the misalignment of grains and the amount of secondary phases is larger when the growth rate is increased. EDS analysis performed on the different contrasts observed in the secondary electrons micrographs confirms that four different phases are present in these samples, identified by arrows and numbers in Fig. 2b1 for clarity. White contrast, #1, corresponds to a Ba-Fe-O solid solution with a cation proportion between 1:7 and 1:8. With the available data in the literature, it is possible to deduce that this solid solution is clearly out of equilibrium [11,12], typical for the materials with incongruent melting. This fact is further confirmed by the higher content of this phase when the growth rate is increased, due to even more non-equilibrium solidification conditions. Light grey contrast, #2, has been attributed to the $BaFe_{18}O_x$ phase (average composition through EDS $BaFe_{16.5}O_x$). Grey (#3), and dark grey (#4) contrasts have been identified as $BaFe_2O_4$ and iron oxide with composition close to Fe_3O_4, respectively. Furthermore, the amount of iron oxide in the rods is also increasing at higher growth rates due to the faster solidification that hinder the reaction to form the Ba-Fe-O-based stable phases, thus resulting in the mixture of $BaFe_{18}O_{27}$ with Fe_3O_4 phases. As it can be deduced from these data there is a slight difference between the phases identified through XRD and EDS due to the fact that EDS only displays qualitative compositions, and the results can be affected by the surrounding grains and topographic effects.

The electrical resistivity behavior of samples as a function of temperature is shown in Fig. 3. As it can be observed in the graph, samples grown at 25, and 50 mm/h are not presented due to their large electrical resistivity, fairly below the limits appropriate for 4-probes DC technique. Although their electrical characterization using impedance spectroscopy might be still of interest for assessing corresponding contribution to the charge transport, the expected performance is significantly below than that desired for TE material. The samples grown at 200 mm/h showed a large resistivity below 200 °C, apparently due to the high contact resistance, typical for oxides. Consequently, their performance is presented only at higher temperatures. The results clearly indicate a semiconducting-like behavior ($d\rho/dT < 0$) in the whole measured temperature range. In spite of the higher values measured at low temperatures (below 450 °C) in the 200 mm/h grown samples, at high temperatures they show slightly lower values than the

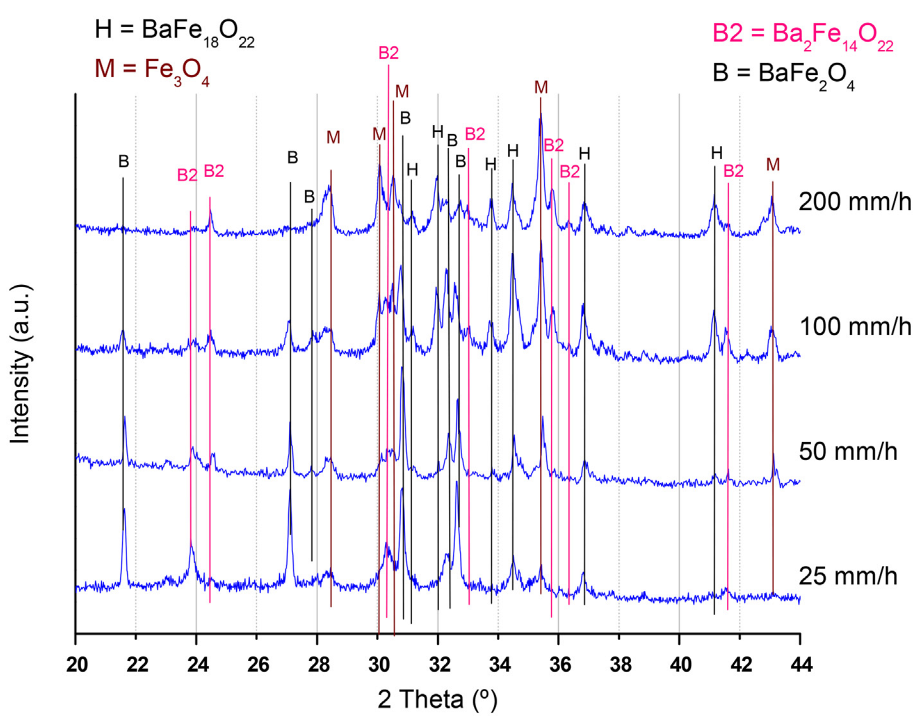

Fig. 1. Powder XRD patterns of the LFZ grown samples at different rates.