Uncovered

Ceramics, squared

J. Carlos Diez and colleagues discuss thermoelectric ceramics and the challenge of optimizing their properties

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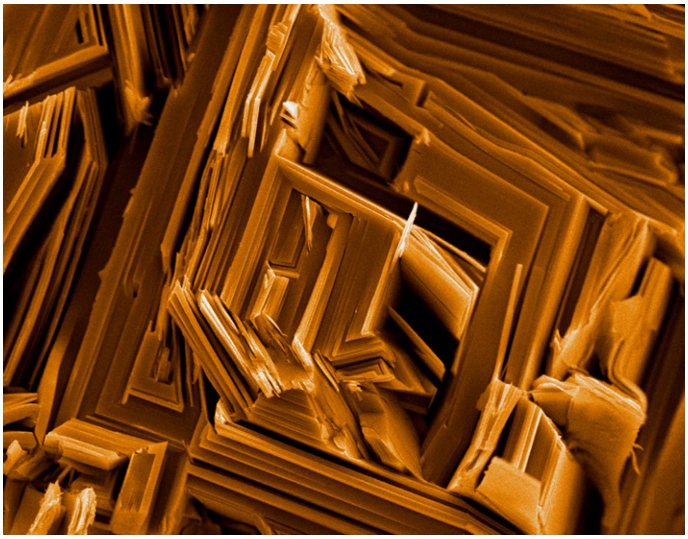

Thermoelectric materials can directly convert a temperature gradient into an electric voltage thanks to the Seebeck effect. Since its discovery in 1823, this characteristic has allowed the use of metallic junctions to control temperatures. These thermocouples possess a low electrical resistivity and Seebeck coefficient with high thermal conductivity. The thermoelectric performances of these materials are evaluated by the dimensionless figure-of-merit ($ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, T is the absolute temperature, σ is the electrical conductivity, and κ is the thermal conductivity) which is very small, indicating that metallic materials possess poor thermoelectric behavior. The introduction of intermetallic semiconductor materials, with higher thermoelectric performances than their metallic counterparts, has resulted in their practical application in thermoelectric modules. These modules can be found as Peltier devices, when used for refrigeration purposes, or Seebeck devices when used for electrical energy generation. Current applications of this kind of material include the environmentally friendly recovery of industrial and automobile waste heat, and in the production of electrical energy in radioisotope thermoelectric generators installed on spacecrafts, or in lighthouses located in isolated regions.

Nevertheless, the application of semiconductor materials for energy generation has been limited due to their relatively low thermal stability under air, which can result in the release of heavy and/or toxic elements, and degradation and/or oxidation processes at high temperatures which can diminish their performances. Nowadays, research effort is being focused on ceramic materials with relatively high thermoelectric performances which can work at higher temperatures than the intermetallic ones. Some of these ceramics are based on Co-oxides, with a high Seebeck coefficient and low electrical resistivity and thermal conductivity. Moreover, they are mostly composed of abundant, less expensive and more environmental friendly elements than the intermetallic compounds. Their main drawback can be found in their relatively low (compared with the intermetallic materials) ZT values, meaning that raising the figure-or merit is the most pressing task to be performed, so that they may be used in practical power generation applications. One of these Co-oxides is $[Bi_{0.87}SrO_2]_2[CoO_2]_{1.82}$, described as a misfit layer compound with monoclinic symmetry, composed – in turn – of two subsystems exhibiting incommensurate periodicities. The structure of the misfit layer crystal can be described as an alternation along the *c*-axis of distorted rock-salt-type slabs, formed from [BiO] and [SrO] layers (the first subsystem), and of $[CoO_2]$ layers (the second subsystem and the electrical conducting one) displaying a distorted CdI_2-type structure [1]. In order to improve the performance of these layered materials texturing techniques can be applied.

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At the Department of Materials Science, Universidad de Zaragoza (Spain) much effort has been devoted to optimizing material properties by texturing using the laser floating zone (LFZ) technique. Our group is pioneering the application of the LFZ technique on cobaltites to enhance grain orientation and, consequently, thermoelectric properties [2]. $Bi_2Sr_2Co_{1.8}O_x$ and $Bi_2Ca_2Co_{1.7}O_x$, nominal composition ceramics, have been successfully textured using the LFZ method [3,4]. The growth processes have been performed downwards using different growth rates, ranging from 5 to 100 mm/h, using a LFZ device equipped with a continuous power Nd:YAG laser ($\lambda = 1064$ nm). The process usually starts with the production of polycrystalline thermoelectric powders with the desired nominal composition. Different synthetic methods can be applied, for example a classical solid state or via solution. The resulting powders are then cold isostatically pressed at 200 MPa in order to obtain green ceramic cylinders with variable diameters between 2 and 4 mm, depending on the dye. These cylinders are subsequently used as the feed in the LFZ device. Finally, after the texturing process, long (~10–30 cm, depending on the relative speed between feed and seed) and geometrically homogeneous textured cylindrical rods are obtained. In some cases, and depending on the growth conditions, some annealing processes must be performed on the as-grown samples in order to remove secondary phases and/or adjust the oxygen content. On the other hand, new improvements on the performance of these thermoelectric ceramics have been obtained using an electrically assisted laser floating zone (EALFZ) technique [5] in collaboration with other groups.

The image on this issue's cover shows a square-like formation recorded with secondary electrons in an FE-SEM (Carl Zeiss Merlin) on a transverse fractured section of a $Bi_2Sr_2Co_{1.8}O_x$ sample grown at 30 mm/h. Polycrystalline thermoelectric ceramics, with nominal $Bi_2Sr_2Co_{1.8}O_x$ composition, have been prepared using the conventional solid state synthesis route using commercial Bi_2O_3, $SrCO_3$ and Co_2O_3 powders. They were weighed in the adequate proportions, ball milled and thermally treated twice at 750 and 800 °C for 12 h in air, with intermediate manual milling, to assure total CO_2 elimination from the strontium carbonates. This is a critical step to avoid their decomposition during the LFZ growth process, which can lead to bubble formation inside the melt and, as a consequence, disturb the solidification front. Observation shows plate-like crystals with the *ab* crystallographic planes parallel to the growth direction (perpendicular to the micrograph plane). The random orientations adopted by the *c*-axes in the different grains leads to the curious ceramic square-like formation.

Further reading

[1] H. Leligny, et al. Acta Crystallogr. Sect. B: Struct. Sci. 56 (2000) 173.
[2] A. Sotelo, et al. J. Eur. Ceram. Soc. 27 (2007) 3967.
[3] J.C. Diez, et al. Solid State Ionics 180 (2009) 827.
[4] J.C. Diez, et al. J. Electron. Mater. 39 (2010) 1601.
[5] N.M. Ferreira, et al. Mater. Lett. 83 (2012) 144.