



# Uncovered

## Thermoelectrics

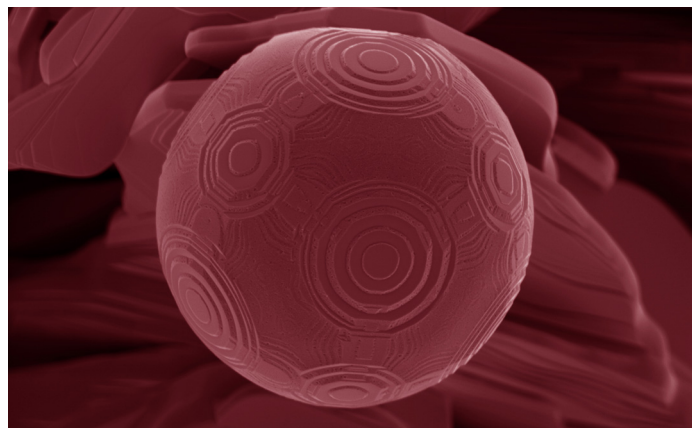
### Metallic Ag microsphere in a ceramic matrix

**M.A. Madre<sup>\*</sup>, Sh. Rasekh, M.A. Torres, J.C. Diez and A. Sotelo**

Dpto Ciencia de Materiales, ICMA (CSIC-Universidad de Zaragoza), Zaragoza, Spain

<sup>\*</sup>Corresponding author: Madre, M.A. ([amadre@unizar.es](mailto:amadre@unizar.es))

Thermoelectricity is the direct solid-state conversion between thermal and electrical energy, without any moving parts, due to the well-known Seebeck effect. Currently, more than half of the energy produced ends up in the form of wasted heat: thermoelectric harvesting and energy conversion constitutes an solution to improve the energy efficiency of classical industrial and domestic energy transforming processes, through thermoelectric modules.



These modules are composed of two different types of thermoelectric materials, *n*- and *p*-type, mainly governed by electronic and hole conduction respectively. A typical thermoelectric module is composed of a number of each type of material (called legs) which are connected electrically in series and thermally in parallel. The performances of the individual legs are determined using the

dimensionless Figure-of-Merit ( $ZT = S^2\sigma T/\kappa$ , where *S*, *T*,  $\sigma$ , and  $\kappa$  are the Seebeck coefficient, absolute temperature, electrical conductivity, and thermal conductivity, respectively). From the *ZT* expression, it is clear that a good thermoelectric material should possess high *S*,  $\sigma$ , and working *T*, together with a low  $\kappa$ . On the other hand, good prospects for practical applications require *ZT* values higher than 1, otherwise, they will be limited to a very narrow market niche.

These *ZT* values are obtained at room temperature in bismuth antimony chalcogenides which are, at present, the best option for thermoelectric applications at room temperature. For mid-temperature applications lead chalcogenide alloys are currently the most common materials, with *ZT* values up to 2.2. However, these materials are very limited in their working temperatures due to their intrinsic nature which leads to degradation, oxidation, and possible release of toxic and heavy elements when they work at high temperatures under air. As a consequence, many processes where the wasted heat is produced at high temperatures cannot be harvested with these types of materials, leading to waste a number of very important potential energy sources (power plants, refineries, etc.).

In this scenario, two kinds of materials emerge as adequate for these extreme operational environments: silicides and transition metal oxides. Among them, silicides possess, at present, higher thermoelectric performances but much higher costs, as they are prepared from high purity silicon. On the other hand, transition metal oxides are very promising materials due to their low cost, abundance in the earth crust, and lower environmental risks. They have been in the spotlight since 1997, when larger thermoelectric properties than expected were found in the Na-Co-O compound [1]. Since then, many efforts have been made to find suitable materials in the CoO-based family, leading to the discovery of  $\text{Ca}_3\text{Co}_4\text{O}_9$ , and  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$  compounds [2,3], among others. All these materials are characterized by a high Seebeck coefficient and relatively low electrical resistivity, together with high thermal stability, allowing their high temperature applications. Moreover, the complex misfit crystal structure of these materials leads to a relatively low lattice thermal conductivity.

In spite of these advantages, the *ZT* values of these oxide compounds are still too low to be considered for most practical

applications. As a consequence, the most important task to be performed on these materials should be the drastic increase of their ZT values at high temperatures ( $T > 1000$  K). The main strategies performed so far for the improvement of ZT values involved the use of different synthesis methods [4], cation doping [5], and/or texturing techniques [6], which have shown their potential to enhance ZT values.

On the other hand, there is a large number of publications showing that metallic Ag additions in many different systems produce very important benefits when it is immiscible with the ceramic matrix [7]. The benefits are reflected in lower electrical resistivity and higher mechanical properties in the bulk material.

The cover of *Materials Today* shows in this issue a metallic Ag microsphere inside a  $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_x$  ceramic matrix produced by directional growth from the melt, using the laser floating zone technique. The image has been recorded in a fractured transversal section of  $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_x + 3$  wt.% Ag after the growth process. The initial material has been prepared using a sol-gel method via nitrates in order to obtain a very homogeneous Ag distribution all along the bulk material, additionally producing very small particle sizes. This compound was then textured through a directional solidification process performed at 30 mm/h growth rate. The shape of Ag particles is clearly due to the immiscibility of Ag and ceramic melts. As a consequence, Ag displays a spherical shape into the molten ceramic, which is conserved after solidification due to the higher melting point of Ag, compared with the one of the ceramic matrix. Moreover, in the image the preferred growth

planes of Ag can be clearly observed all around the sphere, as it has been observed and discussed in other works [8].

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### Further reading

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