

A thermoelectric by any other name...

Thermoelectric ceramic materials, and the quest to improve their performance

Andrés Sotelo, Maria A. Madre, Shahed Rasekh, Gabriel Constantinescu, Miguel A. Torres, and Juan C. Diez

Thermoelectric materials are those capable of directly converting a temperature difference into an electric voltage due to the so called Seebeck effect. This characteristic has allowed, since its discovery in 1823, the use of metallic junctions in order to effectively monitor temperatures. These so called thermocouples are characterized by a low electrical resistivity and Seebeck coefficient while possessing high thermal conductivity. The thermoelectric performance is evaluated through the dimensionless Figure-of-Merit ($ZT = S^2 T / \rho \kappa$, where S is the Seebeck coefficient, T the absolute temperature, ρ the electrical conductivity, and κ the thermal conductivity); values obtained from measurements on metallic materials indicate they possess poor thermoelectric properties. This situation started to change with the introduction of intermetallic semiconductor materials which demonstrate better thermoelectric performances compared to metallic materials. These superior properties have allowed their use in thermoelectric modules, called Peltier, for refrigeration purposes, or Seebeck ones when used for electrical energy generation in relatively low temperature applications. Current applications of this kind of material include the environmentally friendly recovery of wasted heat from industry and transport, and the production of electrical energy in radioisotope thermoelectric generators installed on spacecrafts, lighthouses, and navigation beacons placed in isolated regions. Nevertheless, the application of semiconductor materials for energy generation has been limited due to the relative low thermal stability under air, which can produce heavy and/or toxic elements and degrade and/or oxidize at high temperature.

In 1997, with the discovery of larger thermoelectric properties than expected in NaxCoO_2 , a broad research field opened up: thermoelectric ceramic materials. These materials are characterized not only by their high Seebeck coefficient and relatively low electrical resistivity and thermal conductivity, but also by their high thermal stability which allow them to be used at high temperatures. Moreover, they are mostly composed of more abundant, cheaper and more environmentally friendly elements, compared to the intermetallic compounds. The main drawback of these compounds can be found in their relatively low (compared with the intermetallic materials) ZT values; meaning that increasing this value is the most important challenge that must be overcome before these materials can be used in practical, power generating thermoelectric devices. The main routes to obtain these improved materials have been the use of texturing techniques, and/or doping with different elements, and/or the use of synthetic methods.

Research at the Department of Materials Science, Universidad de Zaragoza (Spain) has been pioneering the use of new synthetic methods for obtaining thermoelectric materials with enhanced properties, for example in $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ or $\text{Bi}_2\text{Ca}_2\text{Co}_{1.7}\text{O}_x$ ceramics.

The most promising method involves the preparation of a solution of metallic acetates in a mixture of acetic acid and distilled water and the addition of a water soluble polymer, polyethyleneimine. This polymer coordinates the metallic cations through the nitrogen

groups. After solvent evaporation, a coordination complex is produced, in the form of a thermoplastic pink polymer with a very good cation distribution inside the matrix. In order to obtain an homogeneous mixture of the oxides and carbonates, the complex is heated at about 350 °C until self-combustion is achieved, reaching temperatures of approximately 750 °C inside the crucible. After this step, the mean particle size is about 0.4 µm, as previously measured in other layered systems. These powders are thermally treated twice at 750 and 800 °C for 6 hours before uniaxially pressing at 400 MPa in form of parallelepipeds (~3 × 3 × 14 mm³) which are sintered at 810 °C for 24 hours with furnace cooling. In the sintered materials the grain sizes easily exceed 10 – 15 µm in the a or b directions. The Bi₂Sr₂Co_{1.8}O_x prepared materials have shown power factor values higher than the obtained for single crystals and very close to those measured in textured materials.

This month's cover image shows a desert rose-like formation which was recorded using a JEOL 6000 electronic microscope with secondary electrons. The sample was prepared from powders obtained after the first thermal treatment (750 °C for 6 hours). They were suspended in an acetone medium using ultrasonic stirring for around 5 minutes. Part of this suspension was extracted using a dropper and then several drops were smoothly placed onto a conductive sample holder. The acetone was evaporated under an IR lamp and the remaining powders were gold covered by sputtering (SCD 004 Sputter Coater Device, Balzers) in order to improve their conductivity. Observation shows flattened crystals in their ab crystallographic planes, fanning out along their characteristic cleavage plane, and corresponding to the thermoelectric Bi₂Sr₂Co_{1.8}O_x phase, covered by many small crystals of unreacted material.

This work represents part of the ongoing effort to improve the performance of thermoelectric ceramic materials for their application in more efficient power generation systems.

Departamento Ciencia de Materiales, ICMA (CSIC-Universidad de Zaragoza), Zaragoza. Spain
E-mail: asotelo@unizar.es