

## Summary on materials – ECT08

### B. Lenoir

*Laboratoire de Physique des Matériaux, Nancy Université, CNRS, Ecole Nationale Supérieure des Mines de Nancy, Parc de Saurupt, 54042 Nancy cedex, France*

During this 6<sup>th</sup> European Conference on Thermoelectrics that was held in Paris, about 110 papers have been presented and among them, 70 were closely related to materials. These contributions concerned many types of materials, covering topics about state of the art materials ( $\text{Bi}_2\text{Te}_3$ ,  $\text{BiSb}$ , and  $\text{PbTe}$  alloys), new intermetallic and oxide materials, Kondo systems and nanostructured materials. Most of the participants were coming from the European community but there were also attendees coming from other continents (29 countries were represented !)

The quality of the talks and posters on materials was excellent and they were all of interest. Of course, due to the great number of papers and the broad range of topics covered, it was not an easy task to summarize the material part. So, do not be offended if you or your favorite subject are not mentioned in this summary. Moreover, I would also like to apologize in advance for any omission, error or fact attributed to others.

As usual,  $\text{Bi}_2\text{Te}_3$ -based materials received a particular attention. These materials are well known to play a major role in today's commercial thermoelectric coolers and generators. Several contributions were devoted to extruded materials. Among them, Dimitri Vasilevskiy reviewed the past ten years of research on hot-extruded  $\text{BiSbTeSe}$  alloys performed at the École Polytechnique de Montréal. A reliable hot extrusion technology has been developed leading in highly orientated n and p-type materials with enhanced mechanical properties and with ZT values close to unity. Thanks to this technology, advanced bismuth telluride based thermoelectric micro-modules with extremely narrow or short legs have been manufactured.

Concerning the other contributions dealing with tellurides, it is worth mentioning the work of Dr. Powell et al. from Heriot-Watt University on complex main group tellurides. Some of these samples have shown promising ZT values near 370 K (0.65) but the difficulty to reproduce the results was also clearly mentioned. This situation is quite similar to that met in the so-called LAST materials.

Several papers on cage compounds such as skutterudites and clathrates were also presented. These materials have in common a rich chemistry allowing tuning both the electrical and thermal properties. In these compounds, the low thermal conductivity is believed to be due to the scattering of the heat-carrying phonons by the localized modes due to the rattling motion of the inserted guest atoms in the cages. The lattice dynamics of these compounds is thus important for a better understanding of the thermal properties. In this context, several interesting contributions based on nuclear inelastic neutron scattering (Grandjean et al.), Raman spectroscopy (Kume et al. and Shimizu et al.) and neutron scattering (Da Ros et al.) gave some useful information in skutterudites and clathrates.

Beside these important aspects, other attractive contributions on cage materials were presented such as the formation, the crystal chemistry and the physical properties of class I clathrates based on barium, zinc (or copper and palladium) and germanium presented by Peter Rogl from the University of Vienna and Eric Alleno from Thiais.

It is also important to underline the work of Michael Baitinger et al. from the Max Plank Institute of Dresden on a new synthesis route they developed since this technique opens new prospects to design intermetallic clathrates optimized for thermoelectric applications.

Also representative are the works of Juliusz Leszczynski et al. from Ecole des Mines (Nancy) on n-type indium partially filled skutterudites where interesting ZT values were reported between 600 and 800 K.

Many interesting contributions focused on oxides were presented. Since the discovery of a high power factor at room temperature in  $\text{Na}_x\text{CoO}_2$  compounds, there has been a resurgence of activity around oxides and especially around cobaltite materials. The origin of the high thermopower in these cobaltites is the subject is still matter of discussion A nice work of Julien Bobroff et al. from Orsay using NMR and  $\mu\text{SR}$  suggested that the large TEP in Na and Bi-misfit cobaltites are linked to strong correlations rather than to charge or spin orders.

Efforts to decrease the lattice thermal conductivity in cobaltites (Berthelot et al.) or to produce highly orientated and mechanically strong ceramics based on  $\text{Ca}_3\text{Co}_4\text{O}_9$  (Kenfaui et al.) were also discussed.

Among the most significant results on oxides presented during this conference, we can cite the investigations of David Berardan et al. from CRISMAT (Caen) and Dr. Koumoto and Dr. Ohta from Nagoya University. In the first case, it was found that the substitution of indium by a small amount of germanium in indium oxide improves markedly the dimensionless figure of merit. An additional increase is seen when the germanium content exceeds the solubility limit leading to a ZT value of about 0.45 near 1300 K. This is one of the best ZT value reported up to now for a n-type oxide.

In the second case, a ZT value of about 2.4 at room temperature was reported in quantum wells based on strontium titanate. If such a high TE performance has already been reported in 2D systems based on state of the art materials, this is the first experimental evidence in oxide materials. This is then an existing and an encouraging result but that should be moderated if additional effects, like for example the influence of barriers, are taken into account as it was already discussed in the literature for state of the art materials.

Among the possible strategies to be followed to enhance the dimensionless figure of merit, the possibility to decrease the thermal conductivity without deteriorating the thermopower and the electrical resistivity, the making of nanocomposites or nanobulks has been proposed. One fundamental question is to know if these bulk nanostructured materials could produce the same effect than those observed in low dimensional systems which are claimed to exhibit larger ZT values. Several talks or posters turned around this point in both intermetallic and oxide materials. Some of them were more concentrated on the synthesis and the characterization of nanoparticules mainly based on bismuth telluride materials while others concentrated their efforts on the fabrication and the characterization of bulk nanostructured materials. In this context, the presentation of Jean-Pierre Fleurial from JPL was particularly relevant. An impressive experimental work has been performed to produce large quantities of nanoparticules with trying to control their size and their distribution in several classes of thermoelectric materials. Promising results were obtained in Si-Ge alloys demonstrating this approach but as Jean-Pierre said, a lot of work remains to be done to optimize the processing parameters and to relate them to the thermoelectric properties.

Silicide materials were also discussed. A detailed review of the transport properties of these materials has been developed by Dr. Fedorov from the Ioffe Institute underlying their

potential for thermoelectric applications. Despite  $\text{MgSi}_2$  materials were not included in the presentation of Dr. Fedorov, three papers were devoted to this material. The work of Christophe Mars et al. from Ecole des Mines (Nancy) confirms that these materials present a real interest for cooling or for power generation at moderated temperature. A nice correlation between the electronic band structure and the transport properties was presented in Bi-doped magnesium disilicides.

Finally, new research directions were also proposed during this conference with the investigations of new compounds including Zintl phases such as  $\text{Yb}_4\text{Sb}_3$  and related compounds (Chamoire et al.) and conducting glasses (Gonçalves et al.).