THERMOELECTRIC TRANSITION METAL OXIDES BASED ON 2D TRIANGULAR NETWORKS/ THE CASE OF MISFITS AND DELAFOSSITE STRUCTURES.

W. Kobayashi, E. Guilmeau, S. Hébert, D. Pelloquin, C. Martin and A. Maignan

Laboratoire CRISMAT, CNRS/ENSICAEN, 6 boulevard du Maréchal Juin, 14050 Caen cedex 4 - France

In the frustrated magnetic systems, the magnetic order tends to be suppressed and replaced by strong spin fluctuations. Furthermore, in the case of the CdI_2 type planes, such as MO_2 layers (M = Co or Rh), the edge-shared MO_6 octahedra favour a low spin-state for the M^{4+}/M^{3+} cations which allows charge delocalization and large Seebeck values by avoiding a charge localization associated to long range magnetic ordering. Among these compounds, the structure of the misfit cobaltites $[(AO_{1-\delta})_n]^{RS}[CoO_2]_{b1/b2}$ appears to be complex. They can be described as a 1:1 intergrowth of n rocksalt (RS)-type $AO_{1-\delta}$ layers and one CoO_2 slab, both being monoclinic but incommensurate in the $\vec{b}$ direction so that the b_1/b_2 ratio corresponds to the incommensurability ratio. The study of crystals and ceramic samples of the n = 4 Bi-based misfit cobaltites has allowed to draw the following conclusions:

- the 300 K Seebeck coefficient (S) values can be varied between $90\mu V.K^{-1}$ and $150\mu V.K^{-1}$ by the control of the b_1/b_2 ratio showing that the $(AO_{1-\delta})$ layers plays the role of charge reservoir for the CoO_2 conducting slab.
- accordingly, for a constant b_1/b_2 ratio, it is found that the oxygen content can also be varied in a reversible way at the level of the RS block to enhance S up to 210 $\mu V.K^{-1}$, demonstrating that oxygen nonstoichiometry in the RS sublattice plays a crucial role on S.
- the commensurate character is not a necessary criterion to observe a metal like ($d\rho/dT>0$) behaviour as shown for Bi(Pb)-based metallic crystals characterized by b_1/b_2= 1.86. This metal-like behaviour is similar to the one reported for Na_xCoO_2 crystals with x = 0.7.
- in all this series, the power factor ($PF = \frac{S^2}{\rho}$) is found to be constant. This puts severe constraints on the models used to describe the physics of these materials since the S^2 and ρ values vary in such a way that their ratio is constant and equal to $PF_{300K} = 2.10^{-4}Wm^{-1}K^{-2}$.
- high temperature measurements confirm the structural thermodiffraction study showing a decomposition beyond ~ 600°C and the maximum Z values are around ZT = 0.05-0.1 at 500°C for the BiCaCoO cobaltite.

More recently, several $CuMO_2$ delafossites, containing isostructural MO_2 planes to those of the misfit cobaltites, have been studied for M = Cr, Fe, Rh. A comparison between the thermoelectric performances of the compounds crystallizing in these two different structural types will be also made.

E-mail presenting author: antoine.maignan@ensicaen.fr