

**Clathrate Type I Thermoelectrics:**  $\{\text{Ba, Sr}\}_8\text{M}_x\{\text{Ge, Si}\}_{46-x-y}\square_y$

P. Rogl<sup>1</sup>, M. Falmbigl<sup>1</sup>, I. Zeiringer<sup>1</sup>, N. Nasir<sup>1</sup>, M.X. Chen<sup>1</sup>, R. Podloucky<sup>1</sup>, N. Melnychenko<sup>1</sup>, A. Grytsiv<sup>1</sup>, E. Royanian<sup>2</sup>, E. Bauer<sup>2</sup>

<sup>1</sup> *Institute of Physical Chemistry, University of Vienna, Waehringerstr. 42, A-1090 Wien, Austria*

<sup>2</sup> *Institute of Solid State Physics, University of Technology, Wiedner Hauptstr. 8-10, A-1040 Wien, Austria*

Submitted : 09-09-2011

Keywords : Clathrates, Thermoelectrics, Phase stability

Thermoelectric properties among the manifold of "intermetallic" clathrates have hitherto shown most interesting features in two series of clathrate type I compounds:  $\text{EA}_8\text{M}_{16}\text{X}_{30}$  and  $\text{EA}_8\text{M}_x\text{X}_{46-x-y}\square_y$  (EA=earth alkaline metal; X is Si or Ge;  $\square$  is a structural vacancy in a lattice site). The present talk will focus on a systematic study of clathrate formation, phase relations, clathrate structures, bonding and structure-property relation in novel multi-component clathrate type I materials  $\text{EA}_8\{\text{M, M}'\}_x\{\text{Si, Ge}\}_{46-x-y}\square_y$  where M, M' are predominantly 3d, 4d, 5d elements from the end of the d-series. Significant differences in formation and consequently in thermodynamic stability exist between barium-based and strontium-based clathrate type I compounds defining the existence of a clathrate phase. These differences are partially due to the different thermodynamic stabilities of the phases surrounding the clathrate phase, but in part are due to the intrinsic lower thermodynamic stability of the strontium based clathrate compounds and/or solid solutions. Density functional theory calculations of the ground state energies of the corresponding Ba- and Sr-containing clathrate I solid solutions confirm the differences in stability. The implications of these stabilities on physical properties will be outlined particularly with respect to thermoelectric applications.