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Growth and characterization of large single crystalline thermoelectric clathrates $A_8Ga_{16}M_{30}$ (A = Eu, Sr, Ba; M = Ge, Sn)

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Intermetallic clathrates with general formula $A_8(M,M')_{46}$ have been subject of intense theoretical and experimental investigation in the past few years.[1] The interest in this family of compounds arises mainly from the fact that some of the members have been found to display surprisingly low and even glass-like thermal conductivity, while still maintaining reasonably good electronic transport properties. Thus, these members fulfill the phonon-glass/electron-crystal (PGEC) concept of a high-performance thermoelectric material, with obvious potential for practical applications.

The physical origin of this unusual behavior resides in the particularities of their complex, diamond-like structures. The A atoms (usually alkali and alkaline-earth metals) are sited within oversized cages formed by the M and M' metals (usually group 12, 13 and 14 elements) and, as such, have enough room to vibrate strongly and rather independently from the host cage. This "rattling" effect can scatter acoustic phonons and consequently lower thermal conductivity, while it does not significantly interfere with the conduction bands formed mainly by the M,M' electron states.

In this work we focus on three clathrate compounds among those with the most promising thermoelectric properties - $Eu_8Ga_{16}Ge_{30}$, $Sr_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Sn_{30}$. We report on the growth of high-quality single crystals of these compounds with typical volumes of order 1 cm^3. These growths are based on direct mixture of high purity elements in carbonized quartz tubes with partial Argon atmosphere, and slow cooling within appropriate temperature intervals.

$Eu_8Ga_{16}Ge_{30}$ and $Sr_8Ga_{16}Ge_{30}$ crystals have been grown from stoichiometric A:Ga:Ge mixtures (8:16:30) and from Ga flux (ex: 8:38:30). Both compounds crystalize in the Type-I clathrate structure, and our single crystalline $Eu_8Ga_{16}Ge_{30}$ sample did not change to Type-VIII structure with annealing, contrary to a report for polycrystals.[2] $Sr_8Ga_{16}Ge_{30}$ displays anomalies in the low temperature specific heat which cannot be described by a simple combination of Debye and Einstein oscillators.

$Ba_8Ga_{16}Sn_{30}$ crystallizes in the Type-VIII structure and has been grown both from Ga flux and from Sn flux, with strong dependence of transport and thermoelectric properties on the flux element, despite the fact that the final crystal composition is very close to 8:16:30 in both cases. Samples grown from Sn flux show negative thermopower and Hall coefficient, while samples grown from Ga flux show positive values for these quantities. These results make evident a high sensitivity of the charge carriers to the growth process, and open the possibility of "tuning" the thermoelectric properties of this compound.

A comprehensive characterization of our Sn flux-grown crystals has been performed and recently published.[3] The occurrence of large atomic displacements and local vibration modes of the Ba atoms was confirmed. The Einstein temperature was estimated as 50 K and the Debye temperature as 200 K. This local vibration of Ba atoms should be responsible for the low thermal conductivity of 1.1 W/m K at 150 K.

The availability of large, oriented crystals with well defined surfaces allows exploration through powerful techniques such as ultrasound attenuation[4] and inelastic neutron scattering to study the rattling and tunneling behavior of the A guest atoms inside the host cages. These

studies, as well as Raman scattering, optical absorption and other techniques, are currently under way in collaboration with other research groups.

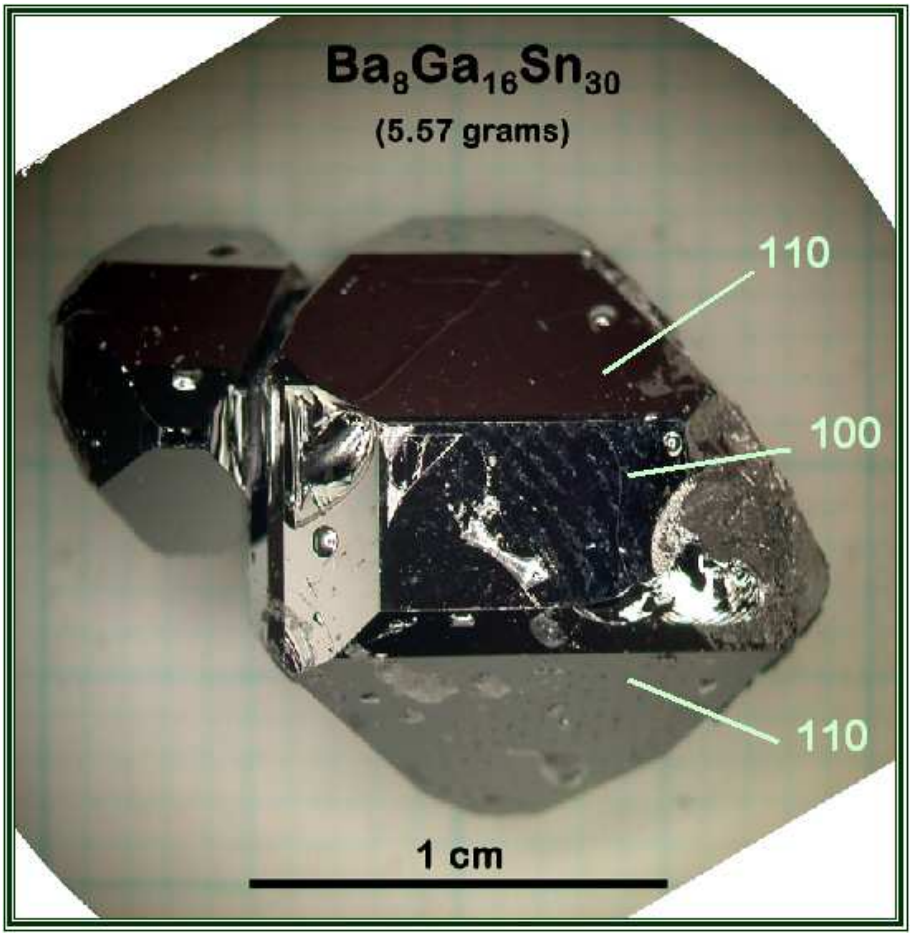

Figure 1: Large single crystal of $Ba_8Ga_{16}Sn_{30}$ grown from Sn flux.

[1] G. S. Nolas, in *Chemistry, Physics and Materials Science of Thermoelectric Materials*, edited by Kanatzidis *et al.*, Kluwer Academic/Plenum Publishers (2003) 107.

[2] S. Paschen *et al.*, *Phys. Rev. B* **64** (2001) 214404

[3] D. Huo *et al.*, cond-mat/0409531 (accepted in *Phys. Rev. B*)

[4] I. Zerec *et al.*, *Phys. Rev. Lett.* **92** (2004) 185502