Novel ternary alkaline-earth and rare-earth metal antimonides from gallium or indium flux. Synthesis, structural characterization and $^{121}$Sb and $^{151}$Eu Mössbauer spectroscopy of the series $A_7Ga_8Sb_8$ ($A = Sr$, Ba, Eu) and Ba$_7$In$_8$Sb$_8$ †

Svilen Bobev,* Jonathan Hullmann,a Thomas Harmening,b and Rainer Pöttgen,*b

a Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, U.S.A. Fax: Int. Code 3028316335; Tel: Int. Code 3028318720; E-mail: bobev@udel.edu; b Institut für Anorganische und Analytische Chemie and NRW Graduate School of Chemistry, Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany

SUPPORTING INFORMATION

Crystal chemistry of Sr$_7$Ga$_2$Sb$_6$

Detailed structure description of Sr$_7$Ga$_2$Sb$_6$ can be found elsewhere [S.-Q. Xia, J. Hullmann and S. Bobev, J. Solid State Chem., 2008, 181, 1909]; herein, we succinctly recap the most important features of this structure, which at least formally, is a substitution derivative of the body-centered cubic Th$_3$P$_4$ type [“Pearson’s Handbook of Crystallographic Data for Intermetallic Phases”, ed. P. Villars and L. D. Calvert, ASM International, Materials Park, OH, 2nd edn., 1991]. Notice that in the “parent” structure, all cations are located at the centers of distorted octahedra of antimony anions (Figure S1), and there is no Sb–Sb bonding. Therefore, one can expect the formula Sr$_4$Sb$_3$ to represent an electron-deficient compound, and indeed, such binary phase is not known.

The Sr$_7$Ga$_2$Sb$_6$ structure (or rather Sr$_{7-x}$Ga$_2$xSb$_6$, $x = 1/8$) is the closest to Sr$_4$Sb$_3$, whereupon every eighth Sr$^{2+}$ cation is missing and the vacant space is filled with a pair of Ga atoms (Figure S1). This disorder is akin to the disorder detailed for $A_7Ga_8Sb_8$ ($A = Sr$, Ba, Eu), and is apparently also completely random, as there is no evidence for a crystallographic long-range order. Here, unlike the previous case, the Ga$_2$-dimers are formed by two crystallographically independent Ga atoms, which are both about 12% occupied. The actual Ga–Ga separation is ca. 2.5 Å. As a consequence, the inclusion of the two Ga atoms in this octahedral atomic arrangement results in the formation of isolated [Ga$_2$Sb$_6$]$_{14–}$ fragments, isoelectronic and isostructural with the [Sn$_2$P$_6$]$_{12–}$ anions in the Ba$_6$[Sn$_2$P$_6$] structure [B. Eisenmann, H. Jordan and H. Schäfer, Z. Naturforsch., 1983, 38b, 404]. Similar ethane-like units, parts of extended networks or arranged into double [In$_2$Pn$_5$]$_{12–}$ layers, zipped via Ga–Ga or In–In bonds are known in the structures of Ba$_3$In$_3$Pn$_5$ ($Pn = P$ or As) [J. Mathieu, R. Achey, J.-H. Park, K. M. Purcell, S. W. Tozer and S. E. Lattawner, Chem. Mater., 2008, 20, 5675], EuIn$_2$Pn$_2$ ($Pn = P$ or As) [A. M. Goforth, P. Klavins, J. C. Fettinger and S. M. Kauzlarich, Inorg. Chem., 2008, 47, 11048; J. Jiang and S. M. Kauzlarich, Chem. Mater., 2006, 18, 435], and BaGa$_2$Sb$_2$ [G. Cordier, H. Schäfer and M. Stelter, Z. Naturforsch., 1985, 40b, 1100]. Analogous, albeit disordered motifs are present in the above-discussed $A_7Ga_8Sb_8$ ($A = Sr$, Ba, Eu) and Ba$_7$In$_8$Sb$_8$ as well.

$^{121}$Sb Mössbauer spectroscopy

$^{121}$Sb Mössbauer spectroscopic study of Sr$_7$Ga$_2$Sb$_6$ was done at 78 K. The collected spectrum is presented in Figure S2, alongside the spectra for Eu$_7$Ga$_8$Sb$_8$ (both at 4.2 K and 78 K) and Ba$_7$In$_8$Sb$_8$. Sr$_7$Ga$_2$Sb$_6$ contains a single crystallographic antimony site and a Zintl conform electron precise description leads to (7Sr$^{2+}$)[Ga$_2$Sb$_6$]$_{14–}$ with isolated Sb$^{3–}$ species. Consequently, the $^{121}$Sb Mössbauer spectrum shows a single signal. Although the antimony atoms have site symmetry 4, there was no need to introduce a quadrupole splitting parameter within the fitting procedure. The $^{121}$Sb spectrum shows a single signal. The isomer shifts (Δ) is –8.06 mm/sec; experimental line width is 4.4(1) mm/sec.

Fig. S1 Crystal structure of Sr$_7$Ga$_2$Sb$_6$. The polyhedral representation emphasizes the acentric way of packing of the antimony octahedra, each centered by the Sr$^{2+}$ cations (not shown for clarity). 1/8 of the octahedra are empty, and the vacant space is filled with Ga dumbbells. The inclusion of two Ga atoms in such coordination environment results in the formation of ethane-like [Ga$_2$Sb$_6$] fragments (shown in ball-and-stick representation): Sb – black circles, Ga – crossed circles.

Electronic Supplementary Information for Dalton Transactions
This journal is © The Royal Society of Chemistry 2010
Fig.S2  Experimental and simulated $^{121}$Sb Mössbauer spectra of Eu$_7$Ga$_8$Sb$_8$, Ba$_7$In$_8$Sb$_8$, and Sr$_7$Ga$_2$Sb$_6$. 