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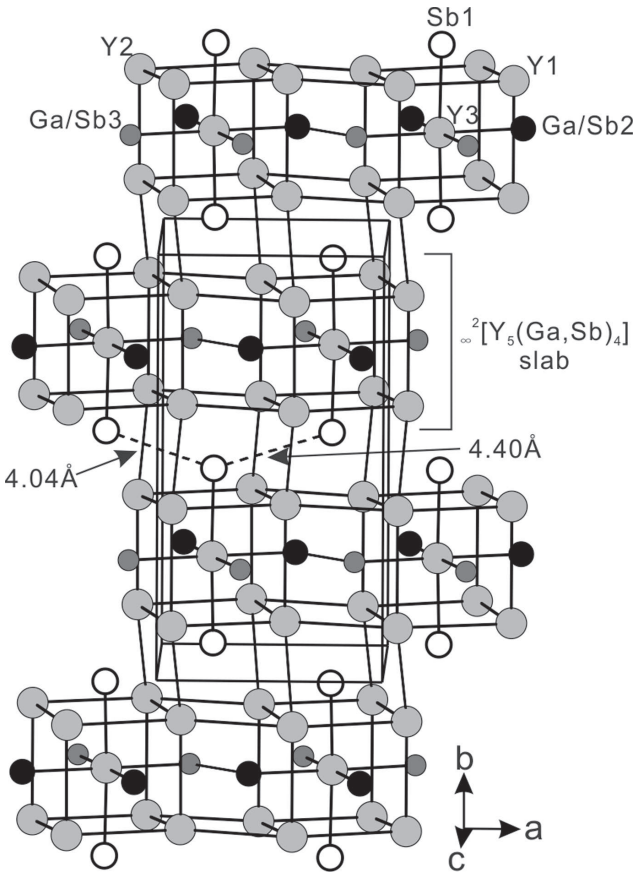
Crystal structure of yttrium gallium antimonide, $Y_5Ga_{1.24}Sb_{2.77}$



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Abstract

$Y_5Ga_{1.24}Sb_{2.77}$, orthorhombic, *Pnma* (no. 62), $a = 7.9629(1)$ Å, $b = 15.175(2)$ Å, $c = 7.9795(1)$ Å, $V = 964.2(2)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0701$, $wR_{ref}(F^2) = 0.0741$, $T = 293$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	metallic block
Size:	0.08 × 0.06 × 0.05 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	406.4 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS-II, ω-scans
$2\theta_{max}$, completeness:	58.4°, >96%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7461, 1312, 0.175
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 727
$N(param)_{refined}$:	49
Programs:	SHELX [10], DIAMOND [11]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Y1	−0.0615(2)	0.61264(12)	0.1735(3)	0.0133(4)
Y2	0.3985(2)	0.12097(12)	0.1592(3)	0.0107(4)
Y3	0.2306(4)	0.2500	0.5038(4)	0.0088(5)
Sb1	0.23791(19)	0.04534(6)	0.48282(17)	0.0104(3)
Sb2[a]	0.0983(3)	0.2500	0.1258(3)	0.0095(8)
Ga2[b]	0.0983(3)	0.2500	0.1258(3)	0.0095(8)
Sb3[c]	0.3664(4)	0.2500	0.8599(4)	0.0101(11)
Ga3[d]	0.3664(4)	0.2500	0.8599(4)	0.0101(11)

[a]Occupancy: 0.61(3); [b]Occupancy: 0.39(3); [c]Occupancy: 0.14(3); [d]Occupancy: 0.86(3).

Source of material

The starting materials were pieces of yttrium (99.99 wt.%, distilled grade, Metall Rare Earth Limited, China), gallium (99.99 wt.%, Alfa Aesar), and antimony (99.999 wt.%, CERAC

Inc). A mixture of Y, Ga and Sb with the molar ratio of 5:1:3 was loaded into a sealed tantalum ampoule under argon atmosphere. The ampoule was heated at 1573 K for 15 hours in a high frequency induction furnace, and then cooled down to room temperature by turning off the furnace. Single crystals were selected from the crushed sample.

Experimental details

The composition of single crystals was estimated by employing energy dispersive X-ray spectroscopy (Hitachi SU8010 Octane Super EDS detector). The obtained atomic ratio of Y:Ga:Sb was approximately 5:1:3, close to the composition of $Y_5Ga_{1.24}Sb_{2.77}$ revealed by the crystal structure refinement.

Discussion

The discovery of giant magnetocaloric effect in $Gd_5Si_2Ge_2$ has stimulated exploring new structures and phases of R_5X_4 (R = rare-earth atoms, X = p-block elements) [1]. Most of the studies are focused on the group-14-element-containing compounds, i.e., silicides [2, 3], germanides [4, 5] and stannides [6]. Here we reported the crystal structure of a new R_5X_4 compound without group 14 elements, $Y_5Ga_{1.24}Sb_{2.77}$. It crystallizes in the orthorhombic Sm_5Ge_4-type structure with the space group *Pnma*. The Y3 atom is coordinated by a rare-earth distorted cube on the Y1 and Y2 sites and a p-element octahedron, forming a $[Y_9(Ga,Sb)_6]$ unit. The $[Y_9(Ga,Sb)_6]$ blocks share rectangular faces to construct a two dimensional $\infty^2[Y_5(Ga,Sb)_4]$ slab in the ac-plane, which interconnects the adjacent slabs with the Y—Y bonds along the b-axis. There are three non-equivalent atomic positions for the p-elements, one eightfold site on the $\infty^2[Y_5(Ga,Sb)_4]$ slab surface (namely, the interslab Sb1 site) and two fourfold ones within the slab (namely, the intraslab Ga/Sb2 and Ga/Sb3 sites). The interslab Sb1 site is fully occupied by the antimony atom, exhibiting the preferential occupation of larger atoms as in the known R_5X_4 system, e.g., $R_5Sb_2Si_2$ [7], $R_5Sb_2Ge_2$ [7], $Gd_5Sb_xGe_{4-x}$ [8] and $Gd_5Sb_xSi_{4-x}$ [9]. Interestingly, compared to the intraslab Ga/Sb3 site, the Ga/Sb2 site preferentially accommodates Sb, in contrast to the statistical distribution of p–elements within the $\infty^2[Y_5(Ga,Sb)_4]$ slab observed in the previously reported systems [7–9]. The interatomic distance of innterslab Sb atoms is within the range of 4.04–4.40 Å, indicating practically no bonds between the Sb atoms. Accroding to the Zintl-Klemm formalism, the charge–balanced formula of $Y_5Ga_{1.24}Sb_{2.77}$ can be written as $(Y^{3+})_5(Ga^{4-})_{1.24}(Sb^{2-})_{0.77}(Sb^{3-})_2(2.5e^-)$, suggesting its metallic conductivity.

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