Structure Transformation in $Ca_{1-x-\delta}Sr_\delta La_x Ag_{1-y}Sb$ (0≤δ≤0.7) and Related Thermoelectric Properties

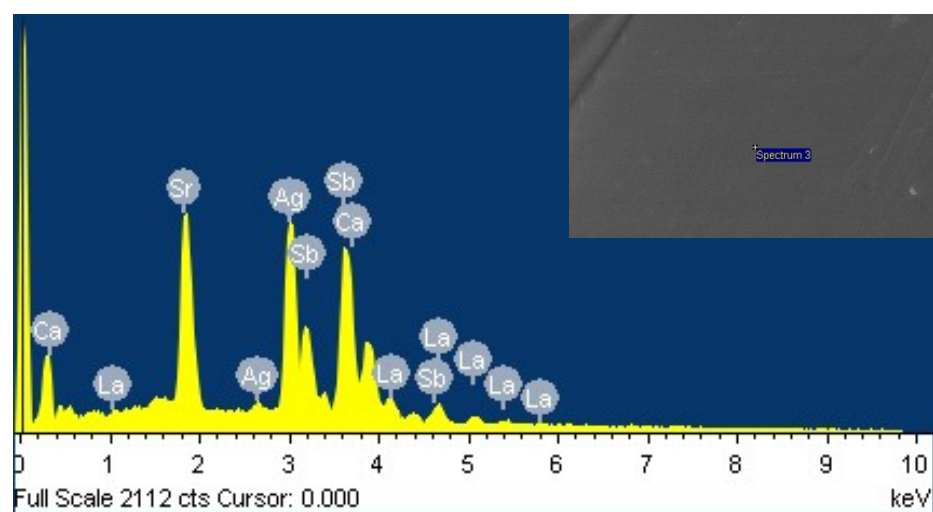*Jia Guo, Min Zhu, Xin Li, Xu-Tang Tao, and Sheng-Qing Xia**

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Supporting Information

Contents

EDS analyses on the compositions of single crystal of $Ca_{0.16(1)}Sr_{0.76(1)}La_{0.07}Ag_{0.931(3)}Sb$.

Element	Weight%	Atomic%	Composition
Ca	2.62	6.86	0.20
Sr	19.45	23.25	0.67
Ag	31.39	30.48	0.13
Sb	40.58	34.92	0.87
La	5.95	4.49	1

Table S1. Selected crystal data and structure refinement parameters for $Ca_{0.16(2)}Sr_{0.77(3)}La_{0.07(1)}Ag_{0.931(3)}Sb$.

Formula	$Ca_{0.16(2)}Sr_{0.77(3)}La_{0.07(1)}Ag_{0.931(3)}Sb$
fw/ g·mol^{-1}	305.67
T / K	273(2)
Radiation, wavelength	Mo-Kα, 0.71073 Å
Space group, No.	P6(3)mc (No.186)
Z	2
Cell dimensions	
a / Å	4.7512(4)
c / Å	8.3913(15)
V / Å^3	164.05(4)
ρ_{calc} / g·cm^{-3}	6.188
$\mu_{Mo\,K\alpha}$ / cm^{-1}	2.693
Final R indices [a] [$I>2\sigma_{(I)}$]	$R1 = 0.0132$ $wR2 = 0.0291$
Final R indices [a] [all data]	$R1 = 0.0143$ $wR2 = 0.0297$

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, and $w = 1/[\sigma^2 F_o^2 + (A·P)^2 + B·P]$, $P = (F_o^2 + 2F_c^2)/3$; A and B are weight coefficients.

Table S2. Refined atomic coordinates and isotropic displacement parameters for $Ca_{0.16(2)}Sr_{0.77(3)}La_{0.07(1)}Ag_{0.931(3)}Sb$.

Atoms	*Wyckoff*	*occ.*	*x*	*y*	*z*	U_{eq}^a (Å^2)
Ag	2b	0.931(3)	1/3	2/3	0.2465(5)	0.0230(5)
Sb	2b	1	1/3	2/3	0.7519(4)	0.0134(3)
La	2a	0.068(13)	0	0	0	0.0145(3)
Sr	2a	0.77(3)	0	0	0	0.0145(3)
Ca	2a	0.162(19)	0	0	0	0.0145(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S3. Important interatomic distances (Å) in $Ca_{0.16(2)}Sr_{0.77(3)}La_{0.07(1)}Ag_{0.931(3)}Sb$.

Atom pairs		Distances (Å)
Sr/La/Ca –	Sb × 6	3.434(2)
	Ag × 2	3.446(3)
	Ag × 3	3.461(3)
Ag –	Sb × 3	2.7435(3)

Table S4. Unit cell parameters refined from the powder diffraction patterns of $Ca_{1-x-\delta}Sr_\delta La_x Ag_{0.89}Sb$ with various compositions.

$Ca_{1-x-\delta}Sr_\delta La_x Ag_{0.89}Sb$	a	b	c	αβγ
x=0.15, δ=0	4.703(1)Å	4.703 Å	7.792(2) Å	
x=0.15,δ=0.1	4.706(1) Å	4.706 Å	7.853(1) Å	
x=0.15,δ=0.2	4.708(1) Å	4.708 Å	7.935(1) Å	
x=0.15,δ=0.3	4.720(1) Å	4.720 Å	7.985(3) Å	α=90°
x=0.15,δ=0.4	4.730(2) Å	4.730 Å	8.070(4) Å	β=90°
x=0.15,δ=0.5	4.729(1) Å	4.729 Å	8.136(3) Å	γ=120°
x=0.15,δ=0.6	4.742(1) Å	4.742 Å	8.217(1) Å	
x=0.15,δ=0.7	4.749(2) Å	4.749 Å	8.299(7) Å	
x=0, δ=0.85	4.762(1) Å	4.762 Å	8.532(1) Å	

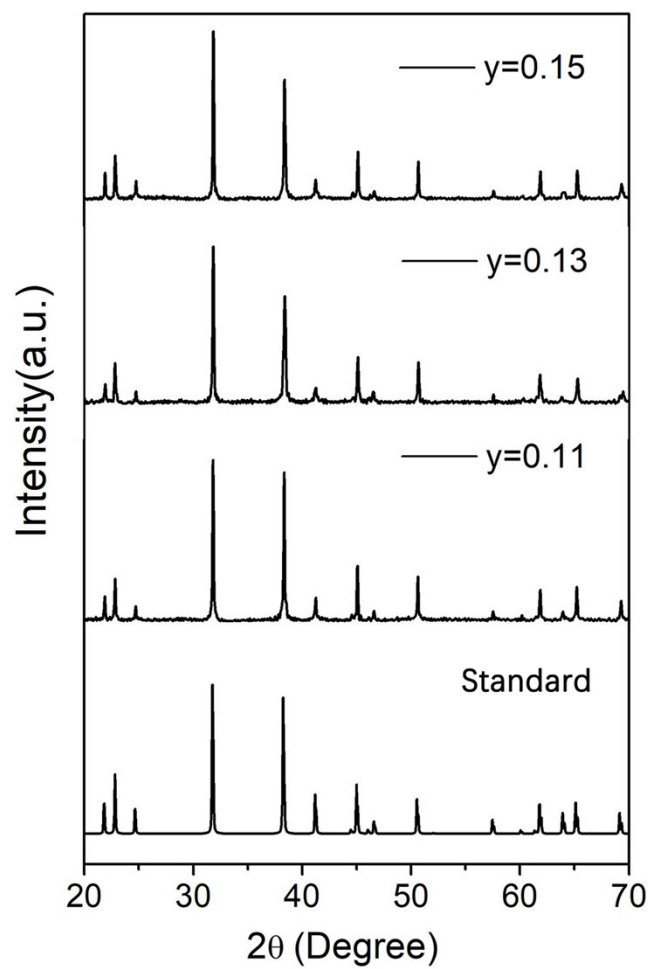**Figure S1.** Powder X-ray diffraction patterns for $Ca_{0.85}La_{0.15}Ag_{1-y}Sb$ (y = 0.11, 0.13, 0.15) materials.

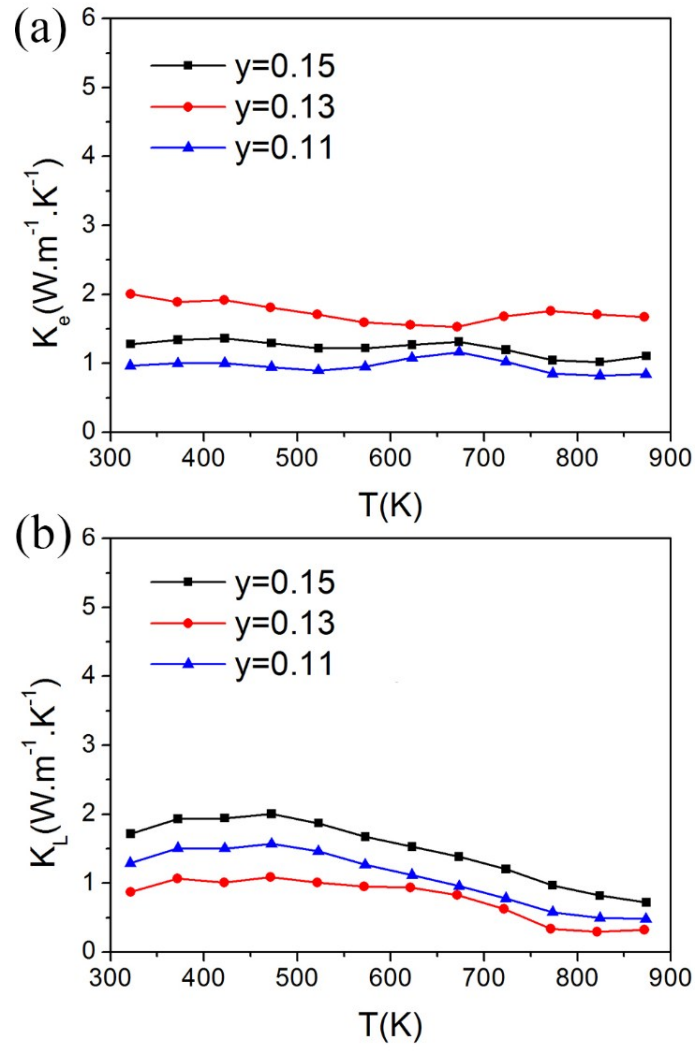**Figure S2.** Components of the electronic (a) and lattice thermal conductivity (b) for materials $Ca_{0.85}La_{0.15}Ag_{1-y}Sb$ ($y = 0.11, 0.13, 0.15$).

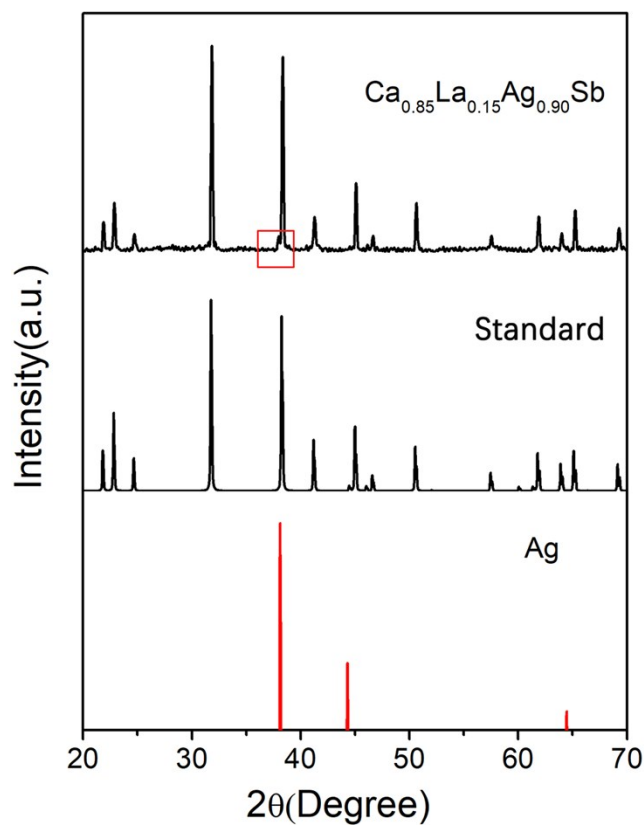**Figure S3.** Powder X-ray diffraction patterns of material $Ca_{0.85}La_{0.15}Ag_{0.90}Sb$. The theoretical predictions of $Ca_{0.85}La_{0.15}Ag_{0.85}Sb$ and Ag were provided for comparison as well.
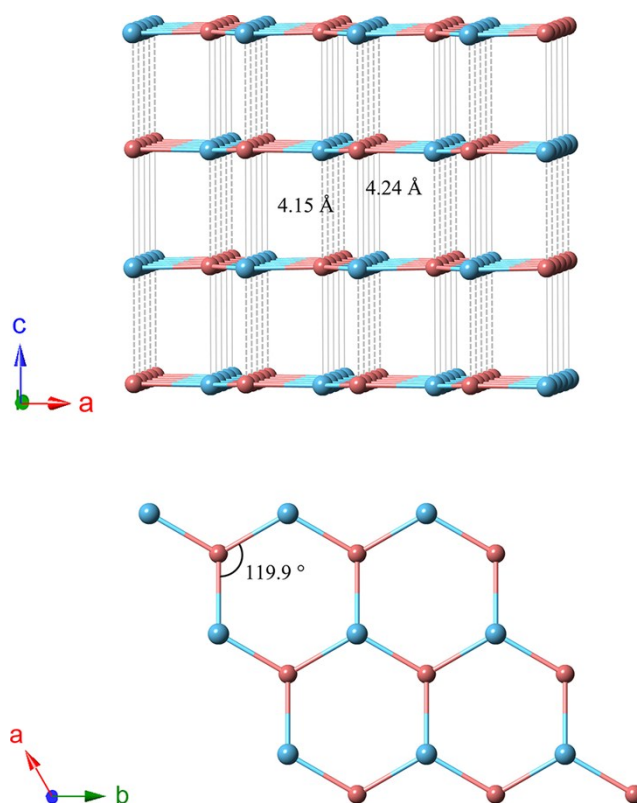
Figure S4. [AgSb] anionic framework structure of $Ca_{0.16(2)}Sr_{0.77(3)}La_{0.07(1)}Ag_{0.931(3)}Sb$ viewed along the *b*-axis. The long interlayered Ag-Sb distances (4.15 and 4.24 Å) as well as the almost planar [AgSb] net (in-plane Ag−Sb−Ag angle: 119.9°) both suggest high similarity to the SrAgSb structure, which evidently suggest the structure transformation of $Ca_{1-x-\delta}Sr_{\delta}La_xAg_{1-y}Sb$ from the LiGaGe type towards the ZrBeSi type.

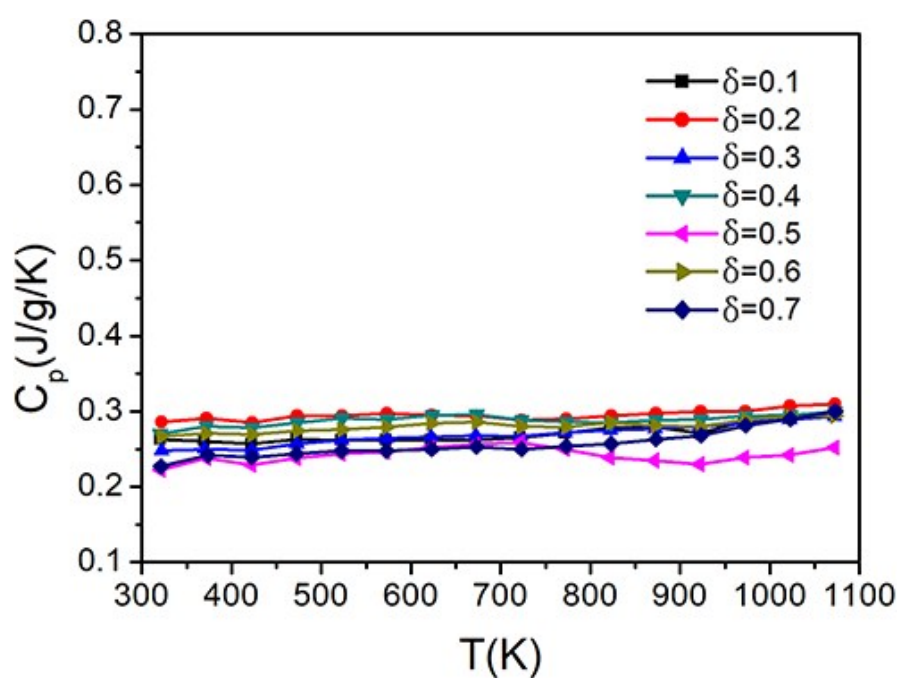**Figure S5.** Temperature dependence of the heat capacity of materials $Ca_{1-\delta}Sr_{\delta}La_{0.15}Ag_{0.89}Sb$ (δ= 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7).
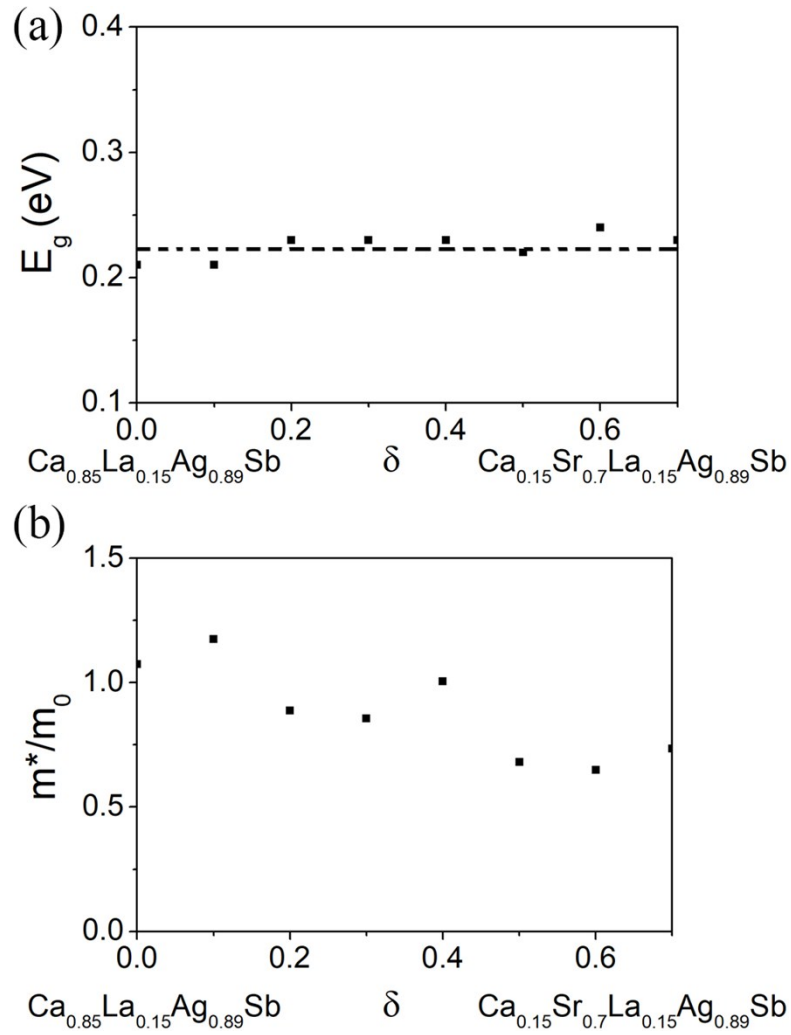
Figure S6. Band gaps (a) evaluated by the peaks of Seebeck coefficient measurements and corresponding effective mass (b) with various Sr contents in $Ca_{0.85-\delta}Sr_\delta La_{0.15}Ag_{0.89}Sb$.

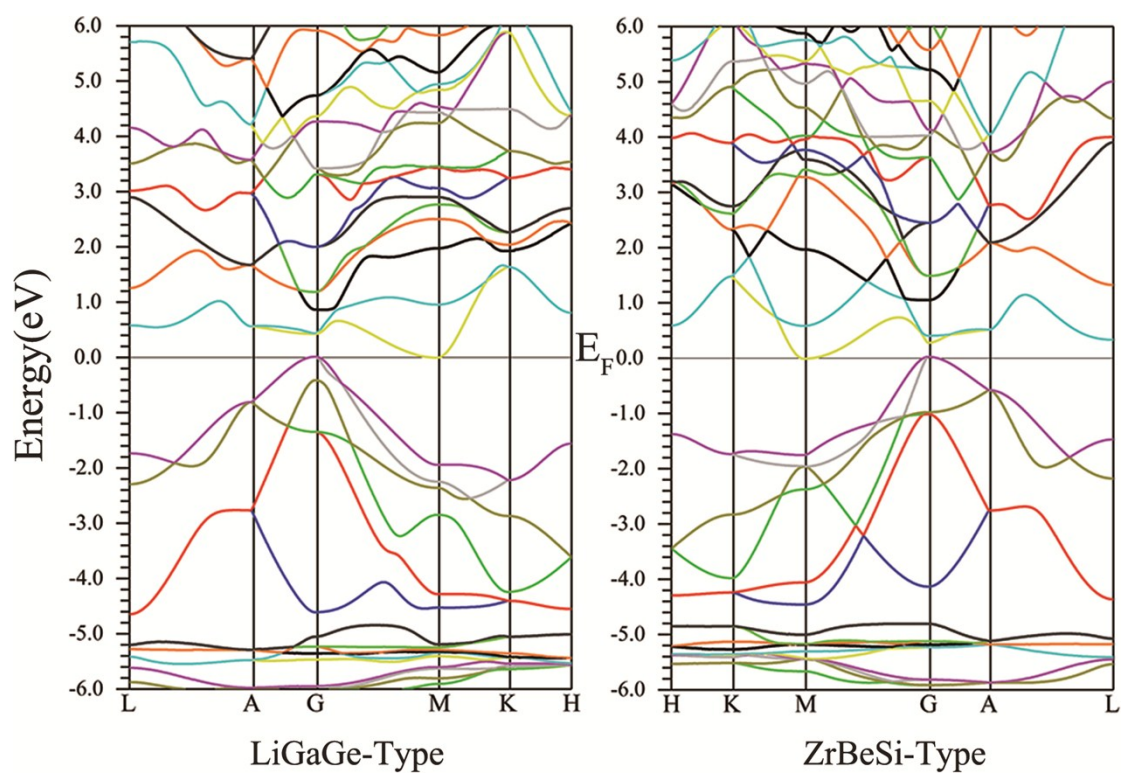**Figure S7.** Electronic band structures calculated for hypothetical LiGaGe-type Ca$_{1-x}$La$_x$Ag$_y$Sb (left) and ZrBeSi-type SrAgSb (right).
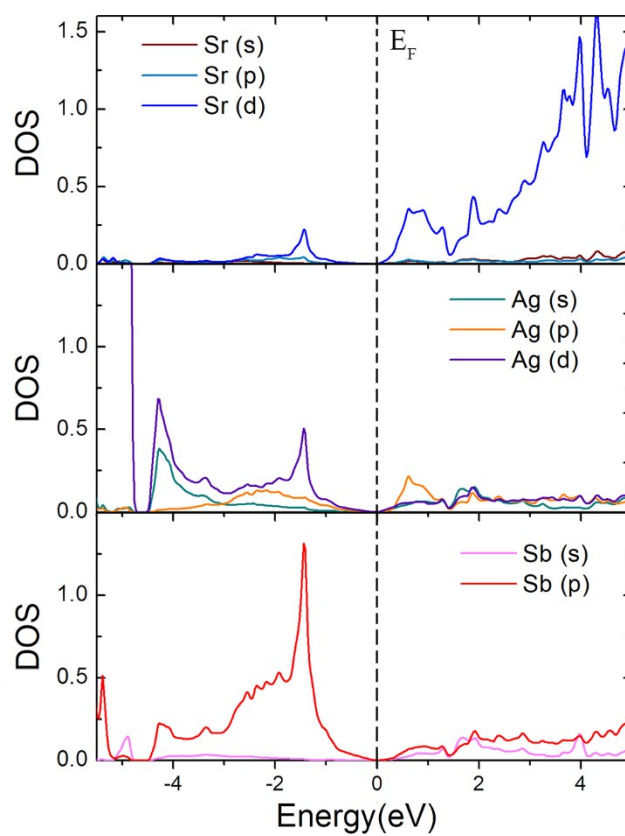
Figure S8. Partial density of states (DOS) for ZrBeSi-type SrAgSb.