Preparation, Structure, and Electronic Properties of $Ca_{11}MSb_9$ (M = Al, Ga, In)

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Two new Zintl compounds $Ca_{11}MSb_9$ (M = Al, Ga) and the Zintl compound $Ca_{11}InSb_9$ have been synthesized in quantitative yields by reacting the elements in an 11:1:9 ratio at high temperatures (850 and 1000 °C). Low-temperature (130 K) single-crystal X-ray diffraction data show that the $Ca_{11}GaSb_9$ compound is orthorhombic, space group = *Iba*2, $Z = 4$, a = 11.805(3) Å, b = 12.463(3), c = 16.651(2) Å, $R1$ = 2.50%, $wR2$ = 5.22%, and is of the $Ca_{11}InSb_9$ structure type. Powder X-ray diffraction show that $Ca_{11}AlSb_9$ is also the $Ca_{11}InSb_9$ structure type. Room-temperature lattice parameters from powder diffraction data are as follows: $Ca_{11}AlSb_9$, a = 11.832(3) Å, b = 12.505(2) Å, c = 16.674(4) Å; $Ca_{11}GaSb_9$, a = 11.839(2) Å, b = 12.536(3) Å, c = 16.716(1) Å; $Ca_{11}InSb_9$ a = 11.899(2) Å, b = 12.596(2) Å, c = 16.722(3) Å. Temperature-dependent resistivity measurements show that these materials are semiconducting.

Introduction

There are a large number of compounds with unusual structures which have been characterized only by single-crystal X-ray diffraction. In many cases, there is also only one example of a particular structure type that is obtained in low yield quite by accident. Our interest in Zintl compounds has led to the synthesis and characterization of a large number of new compounds crystallizing in the $Ca_{14}AlSb_{11}$ structure type.[1-5] These compounds display a wide variety of properties depending on the identity of the alkaline-earth metal, the metal, and the pnictogen. For example, $Ca_{14}AlSb_{11}$ is a semiconductor, whereas $Ca_{14}MnBi_{11}$ is a ferromagnetic metal.[4,6] In addition, we have found that some of these compounds can display significant nonstoichiometry.[7,8] The $Ca_{14}AlSb_{11}$ structure[1] can be described as consisting of 14 Ca^{2+} cations, a $AlSb_4^{9-}$ tetrahedron, a Sb_3^{7-} linear unit, and 4 isolated Sb^{3-} anions.

To explore the synthesis and properties of related Zintl compounds, we have synthesized the compounds $Ca_{11}MSb_9$ (M = Al, Ga, In). The structure of $Ca_{11}InSb_9$ has been reported.[9] The $Ca_{11}InSb_9$ structure can be described as consisting of 11 Ca^{2+} cations, an $InSb_4^{9-}$ tetrahedron, 2 Sb_2^{4-} dimers, and an isolated Sb^{3-} anion. Similar to the $Ca_{14}AlSb_{11}$ structure, it contains isolated tetrahedra and anions. Instead of containing Sb_3^{7-} linear anions, the $Ca_{11}InSb_9$ structure[9] contains Sb_2^{4-} dumbbells. This paper presents the synthesis, structure, and properties of these compounds.

Experimental Section

The reactions were set up in a nitrogen-filled drybox. Ca, Ga, and In metals were cut into small pieces. $Ca_{11}MSb_9$ were prepared by adding stoichiometric amounts of the elements (Ca, 99.99% Anderson Physics; Ga, 99.9999%, Alfa; In, 99.99% Johnson Matthey; Sb, 99.9999%, Johnson Matthey) in a niobium tube that was sealed on one end. The niobium tube was first cleaned with an acid solution (20% HF, 25% HNO_3, and 55% H_2SO_4) and welded shut with an argon-filled arcwelder. After crimping the filled niobium tube shut, it was quickly transferred from the drybox to the argon arcwelder to seal the other end. The niobium tube was then sealed in a quartz ampule under vacuum.

Single crystals of $Ca_{11}GaSb_9$ suitable for single-crystal X-ray diffraction were obtained in one reaction at 1000 °C. Although single crystals can be obtained at 1000 °C for $Ca_{11}GaSb_9$, the compound cannot be produced in high yield at that temperature. The predominant products produced at 1000 °C were determined by powder X-ray diffraction to be $Ca_{14}GaSb_{11}$ and $Ca_{11}Sb_{10}$. Heating the reactants 60 °C/h to 850 °C for 2 weeks and subsequently cooling at 60 °C/h to room temperature provided the highest yield of $Ca_{11}GaSb_9$. At 850 °C, no single crystals were obtained; however, the samples consisted of air-sensitive, highly reflective silver polycrystalline chunks, and this material was identified as being of the $Ca_{11}InSb_9$ structure type by Guinier powder X-ray diffraction. The yield was quantitative, based on powder X-ray diffraction.

The reactions to produce $Ca_{11}AlSb_9$ were set up identically to that of $Ca_{11}GaSb_9$ (described above), and only air-sensitive, reflective silver polycrystalline chunks were obtained as products at 850 °C. The product was identified as being of the $Ca_{11}InSb_9$ structure type by powder X-ray diffraction. The yield of $Ca_{11}AlSb_9$ was determined to be quantitative by Guinier powder diffraction. Reactions heated at 1000 °C for 2 weeks produced $Ca_{14}AlSb_{11}$ and $Ca_{11}Sb_{10}$.

Stoichiometric amounts of the elements to produce $Ca_{11}InSb_9$ were heated 60 °C/h to 1000 °C, maintained at that temperature for 76 h, and subsequently cooled at 20 °C/h to room temperature. The resulting air sensitive product was typically made up of highly reflective silver chunks of material. Guinier powder X-ray diffraction indicated that the product was $Ca_{11}InSb_9$. The yield was >95% based on Guinier powder X-ray diffraction.

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Table 1. Room-Temperature Lattice Parameters for $Ca_{11}MSb_9$ (M = Al, Ga, In)

compound	a (Å)	b (Å)	c (Å)	vol (Å^3)
$Ca_{11}AlSb_9$	11.839(2)	12.536(3)	16.716(1)	2480.8(1)
$Ca_{11}GaSb_9$	11.832(3)	12.505(2)	16.674(4)	2467.1(1)
$Ca_{11}InSb_9$	11.899(2)	12.596(2)	16.722(3)	2506.3(1)

Powder X-ray Diffraction. Diffraction patterns were obtained with an Enraf Nonius Guinier powder camera (monochromatic Cu $K\alpha_1$ radiation, wavelength 1.540 562 Å) at room temperature. Powder samples were prepared in a nitrogen-filled drybox in which powder sample and NIST silicon standard were placed between two pieces of tape. Powder diffraction patterns were calculated with the program POWDER,[10] which uses atom positions obtained from single-crystal X-ray diffraction, and compared to the experimental powder diffraction patterns. Diffraction lines were measured with an Enraf Nonius Guinier viewer and lines were converted to 2θ by standard nonlinear least-squares refinement using the program GUIN.[11] 2θ values were indexed using the program LATT[12] and room-temperature lattice parameters obtained. Lattice parameters calculated from several different reactions were found to be the same within standard deviations. Room-temperature lattice parameters are given in Table 1. Tables of calculated versus experimental d spacings and intensities are provided as supplemental material.

Single-Crystal X-ray Diffraction. Suitable crystals of $Ca_{11}GaSb_9$ were selected from the reaction in a nitrogen-filled drybox equipped with a microscope. The crystals were placed in Paratone oil to minimize air exposure. The crystal selected for data collection was mounted on a glass fiber and quickly positioned on the diffractometer in which a cold stream of nitrogen protected it from air exposure. Data were collected on a Siemens R3m diffractometer (Mo Kα, wavelength 0.710 69 Å, graphite monochromator) at 130 K. The unit-cell dimensions and crystal system were determined by least-squares refinement of 17 reflections ($14° > 2\theta > 21°$) using the automatic indexing routine of the diffractometer. Axial photos were taken at long exposure (30 min) to confirm Laue symmetry, cell dimensions and to check for possible superstructure. Small data sets were taken ($2\theta = 25–35°$) to confirm I centering. No decomposition of the crystal was observed during the data collection based on the intensity of two check reflections monitored every 198 reflections. The data were corrected for Lorentz and polarization effects. The crystallographic parameters are summarized in Table 2.

Crystallographic programs used were SHELXTL-PLUS Version 4.21 and SHELXL-93.[13] In the SHELXL-93 program F^2 is used in the refinement rather than F such that all the data are used and that the specified threshold for F is eliminated. The $wR2$ index is minimized during the refinement and is generally twice as large as the conventional $R1$ index. Scattering factors and absorption coefficients used in SHELXL-93 are from the *International Tables for Crystallography*.[14]

$Ca_{11}GaSb_9$ structure was solved and refined with SHELXL-93 by taking initial positional parameters from $Ca_{11}InSb_9$. $Ca_{11}GaSb_9$ refined with isotropic U's and at this stage $R1$ was at 2.92% and $wR2$ at 6.26%. The Fourier difference map was flat in which the largest residual peak was less than 2 e$^-$/Å^3. After convergence of isotropic U's, an absorption correction[15] was applied and the final $R1$ and $wR2$ were 2.50% and 5.42%, respectively. Table 3 summarizes atomic coordinates and isotropic thermal parameters. Tables of anisotropic U's, F_o's, and F_c's are provided as supplementary material.

Table 2. Crystallographic Parameters for $C_{11}GaSb_9$

formula	$Ca_{11}GaSb_9$
fw	1606.33
crystal size	0.28 mm × 0.04 mm × 0.04 mm
color and habitat	silver needle
space group	*Iba*2
Z	4
T, K	130
a, Å	11.805(3)
b, Å	12.463(3)
c, Å	16.651(2)
V, Å^3	2449.8(9)
μ (Mo Kα), mm^{-1}	13.123
ϱ_{calc}, Mg/m^3	4.355
rel transm factor, min/max	0.922–1.126
$2\theta_{max}$	60
octants collected	*hkl*
scan speed, deg/min	2.00
no. of data collected	2006
no. of unique data	1847
no. of obsd refn [$F_o > 4\sigma > (F_o)$]	1744
no. of params refined	96
R [$I > 2\sigma > (I)$][a]	2.50
$wR2$ [$I > 2\sigma > (I)$][a]	5.22

[a] $R1 = ||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = \sqrt{(w(F_o^2 - F_c^2)^2/\Sigma wF_o^4)}$, $w = 1/[\sigma^2(F_o^2) + P^2 + P]$ where $P = (\max(F_o^2,0) + 2F_c^2)/3$.

Table 3. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $Ca_{11}GaSb_9$

atom	site	x	y	z	U
Ca(1)	8c	4279(2)	2232(2)	6969(1)	8(1)
Ca(2)	8c	6841(2)	533(2)	6264(1)	11(1)
Ca(3)	8c	4095(2)	2256(2)	3393(1)	10(1)
Ca(4)	8c	6845(2)	595(2)	3682(1)	13(1)
Ca(5)	8c	8398(2)	1728(2)	9976(2)	12(1)
Ca(6)	4a	0	0	6751(2)	12(1)
Ga(1)	4a	0	0	3922(1)	9(1)
Sb(1)	8c	8694(1)	1136(1)	5000	8(1)
Sb(2)	4b	0	5000	2491(1)	7(1)
Sb(3)	8c	1773(1)	1777(1)	6808(1)	8(1)
Sb(4)	8c	4652(1)	1087(1)	4954(1)	8(1)
Sb(5)	8c	1438(1)	1363(1)	3101(1)	8(1)

Resistivity. Pure powder samples were pressed into pellets in a nitrogen-filled drybox. The pellet was placed in a four-prong sample holder in which small pieces of indium were pressed onto the tips of the stainless steel prongs to make contact with the pellet. The sample was then mounted on a closed-cycle refrigerator, and the sample chamber evacuated. The temperature dependent resistivity was measured using the four-probe technique and samples were measured from 15 to 300 K, in 5 K increments. Several samples of each compound were measured, and the results were highly reproducible. The resistivity apparatus has been described in detail previously.[16] Minimization of thermal voltages were achieved by reversal of current bias. All samples exhibited ohmic behavior.

Results and Discussion

Structure. The $Ca_{11}GaSb_9$ formula unit consists of 11 Ca^{2+} cations, a $[GaSb_4]^{9-}$ tetrahedron, a $[Sb_2]^{4-}$ dumbbell, and three isolated Sb^{3-} anions. Figures 1 and 2 show perspective views down the c and a axis, respectively. Important bond lengths and angles are

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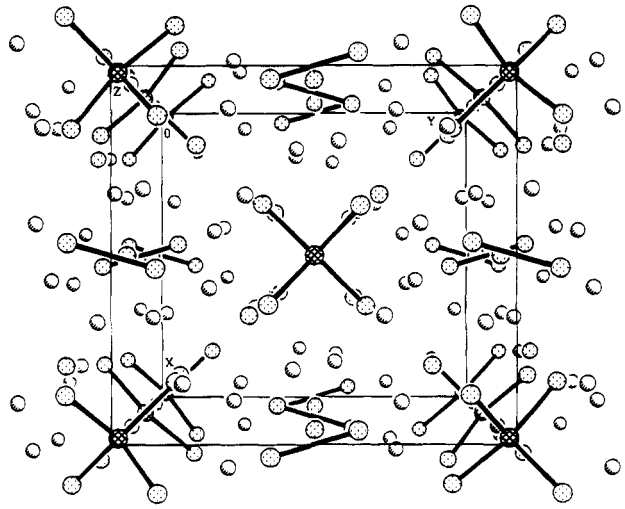

Figure 1. Perspective view down the *c* axis of $Ca_{11}GaSb_9$. The Sb, Ga, and Ca atoms are indicated by dotted, cross-hatched, and half-shaded circles, respectively.

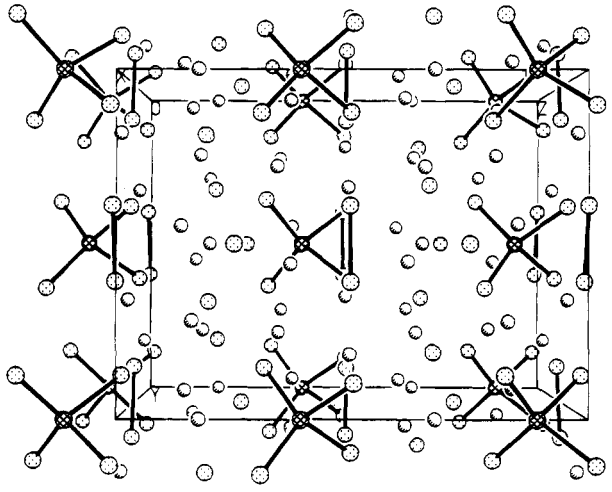

Figure 2. Perspective view down the *a* axis of $Ca_{11}GaSb_9$. The Sb, Ga, and Ca atoms are indicated by dotted, cross-hatched, and half-shaded circles, respectively.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $Ca_{11}GaSb_9$

Sb(1)–Ga(1) × 2	2.758(1)	Sb(4)–Sb(4′)	2.831(1)
Sb(1)–Ca(1)	3.382(2)	Sb(4)–Ca(1)	3.076(2)
Sb(1)–Ca(2)	3.128(2)	Sb(4)–Ca(2)	3.451(2)
Sb(1)–Ca(3)	3.372(2)	Sb(4)–Ca(2′)	3.454(2)
Sb(1)–Ca(4)	3.168(2)	Sb(4)–Ca(3)	3.053(2)
Sb(1)–Ca(5)	3.511(2)	Sb(4)–Ca(4)	3.402(2)
Sb(1)–Ca(5′)	3.586(2)	Sb(4)–Ca(4′)	3.465(2)
Sb(1)–Ca(5″)	3.632(2)	Sb(4)–Ca(5)	3.566(2)
Sb(1)–Ca(6)	3.589(3)	Sb(4)–Ca(5′)	3.689(2)
Sb(2)–Ca(1) × 2	3.290(2)	Sb(5)–Ga(1) × 2	2.763(1)
Sb(2)–Ca(2) × 2	3.056(2)	Sb(5)–Ca(1)	3.207(2)
Sb(2)–Ca(3) × 2	3.362(2)	Sb(5)–Ca(3)	3.294(2)
Sb(2)–Ca(4) × 2	3.037(2)	Sb(5)–Ca(3′)	3.364(2)
		Sb(5)–Ca(4)	3.316(2)
Sb(3)–Ca(1)	3.038(2)	Sb(5)–Ca(5)	3.163(2)
Sb(3)–Ca(1′)	3.217(2)	Sb(5)–Ca(6)	3.289(2)
Sb(3)–Ca(2)	3.433(2)		
Sb(3)–Ca(3)	3.076(2)	Sb(5)–Ga(1)–Sb(5)	120.69(6)
Sb(3)–Ca(4)	3.817(2)	Sb(5)–Ga(1)–Sb(1)	110.49(2) × 2
Sb(3)–Ca(5)	3.057(3)	Sb(5)–Ga(1)–Sb(1)	107.12(2) × 2
Sb(3)–Ca(6)	3.049(1)	Sb(1)–Ga(1)–Sb(1)	98.73(6)

listed in Table 4. Sb_2 dimers alternate with isolated Sb atoms (Sb(2)) down the *c* axis (Figure 1). The $GaSb_4$ tetrahedra are stacked along the *c* axis, have ..2 point symmetry, and alternate with Ca cations. The perspective view down the *a* axis shows that the tetrahedra and dumbbell units are stacked in an eclipsed fashion as they alternate (Figure 2). Isolated Sb atoms, Sb(3), are also located in between tetrahedral units, clearly shown in Figure 3. Notice that the two Sb(3) atoms and Ca cation are almost aligned in a linear fashion, the angle Sb(3)–Ca(6)–Sb(3) being 176.4(1)°. This resembles the stacking motif in the Zintl compound $Ca_{14}AlSb_{11}$ in which isolated $AlSb_4$ tetrahedra alternate with Sb_3 linear units. In $Ca_{14}AlSb_{11}$, the center Sb atom in the three-member linear chain is located directly between $AlSb_4$ units. In $Ca_{11}GaSb_9$, the Ca cation sits in this similar position.

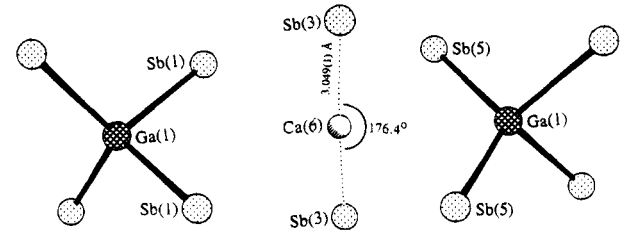

Figure 3. Perspective view down the *b* axis showing the location of the isolated Sb^{3-} anions and Ca^{2+} cation.

Despite the differences in temperatures at which the $Ca_{11}GaSb_9$ (130 K) and $Ca_{11}InSb_9$ (room temperature) single-crystal X-ray data were taken, structural features of the compounds can be compared. Although the Ga–Sb bonds are not the same by symmetry, the bond distances are nearly the same; they are Ga(1)–Sb(1), 2.758(1) Å and Ga(1)–Sb(5), 2.763(1) Å. In $Ca_{11}InSb_9$, the In–Sb bond lengths in the $InSb_4$ tetrahedron[9] are basically identical: In(1)–Sb(1), 2.886(2) Å and In(1)–Sb(5), 2.881(2) Å. As expected, the Ga–Sb distances are shorter than the In–Sb. The Ga–Sb and In–Sb bond distances are slightly longer than in the binary semiconductors (GaSb, 2.64 Å; InSb, 2.80 Å) but comparable to other Zintl compounds[17] ($Ca_5Ga_2Sb_6$, 2.72 Å; $Ca_5In_2Sb_6$, 2.82 Å). In both the In and Ga compounds, Sb(1) is coordinated to 8 Ca cations, and distances are $Ca_{11}GaSb_9$, 3.128(2)–3.817(2) Å; $Ca_{11}InSb_9$, 3.118(6)–3.629(6) Å. $Ca_{11}GaSb_9$ exhibits a coordination sphere of 6 Ca cations for Sb(5), and distances are 3.207(2)–3.364(2) Å. A coordination sphere of 7 Ca cations is observed for Sb(5) in $Ca_{11}InSb_9$, and distances are 3.195(6)–3.411(6) Å. The Sb–Ca distances observed in $Ca_{11}GaSb_9$ and $Ca_{11}InSb_9$ are typical compared to Zintl compounds $Ca_5Ga_2Sb_6$ and $Ca_5In_2Sb_6$, respectively,[17] and $Ca_{11}Sb_{10}$.[18] The $GaSb_4$ tetrahedral angles are slightly distorted; Sb–Ga–Sb angles are 110.49(2)° and 107.12(2)°. Similarly, the $InSb_4$ tetrahedral angles are also slightly distorted, with Sb–In–Sb angles of 109.6° and 106.7°.

The $Ca_{11}GaSb_9$ Sb–Sb bond distance in the Sb_2 dumbbell unit is 2.831(1) Å and the In analogue exhibits a slightly longer distance of 2.843(3) Å. Examples of Sb–Sb distances are found in Sb metal (2.9 Å), $Ca_5Ga_2Sb_6$[17] (2.84 Å), and $Ca_5In_2Sb_6$ (2.82 Å).[17] Isolated Sb(2) atoms in both the Ga and In compounds are coordinated to 8 Ca cations, and distances range from 3.056(2) to 3.362(2) and 3.055(6) to 3.378(6) Å, respectively. Isolated Sb(3) atoms in both Ga and In compounds are

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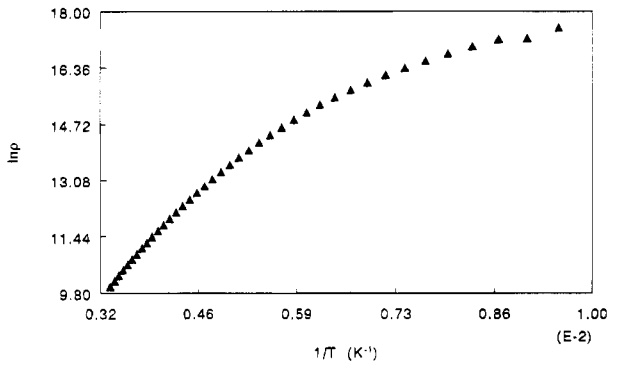

Figure 4. ln ϱ versus $1/T$ (T = 300−100 K) for $Ca_{11}InSb_9$ pressed pellet.

coordinated to 7 Ca cations, and distances range from 3.038(2) to 3.817(2) Å and 3.045(6) to 3.513(6) Å, respectively. In most examples of isolated Sb atoms in Zintl compounds,[4,5,8] the cation coordination is between 6 and 8.

Resistivity. Figure 4 shows ln ϱ vs $1/T$ data for $Ca_{11}InSb_9$. Data were collected over the range 300−100 K on a pressed pellet sample. Saturation effects are apparent at low-temperature, typical of semiconductors.[7] Data were collected for Al and Ga samples in the temperature ranges 300−220 and 300−240 K, respectively. The resistance at temperatures lower than 220 K is too large to be measured on the apparatus described above. Figure 5 shows the ln ϱ vs $1/T$ (300−220 K) data used to calculate the activation energies for all three compounds. Activation energies, obtained from fitting the data (300−240 or 300−220 K) to the equation ln $\varrho = E_a/2k_BT + \varrho_0$, and room-temperature resistivities are given in Table 5. The room-temperature resistivities for the Al, Ga, and In compounds are consistent with periodic trends. The resistivities should decrease upon progression down the group 13 column, which reflect the metal's electron-donating ability with increased size. The room-temperature resistivities for $Ca_{11}AlSb_9$ and $Ca_{11}GaSb_9$ are similar in value, 1.1(1) × 10^6 and 1.8(1) × 10^6 Ω cm respectively. The $Ca_{11}InSb_9$ compound has the smallest value (1.0(1) × 10^4 Ω cm). Al and Ga compounds have similar activation energies of 0.59(1) and 0.64(1) eV, respectively, and In has the smallest,

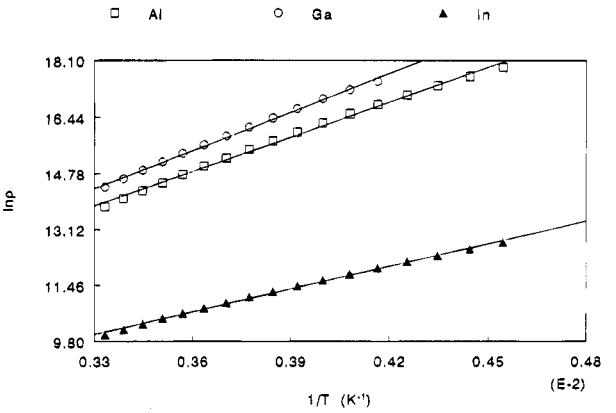

Figure 5. ln ϱ versus $1/T$ (T = 300−220 K) for $Ca_{11}MSb_9$ (M = Al, Ga, In) pressed pellets.

Table 5. Resistivity Data for $Ca_{11}MSb_9$

M	temp (K)	E_a (eV)	ϱ_{300} (Ω cm)	ϱ_0 (Ω cm)
Al	300−220	0.59(1)	1.1(1) × 10^6	11.9(1)
Ga	300−240	0.64(1)	1.8(1) × 10^6	12.9(1)
In	300−220	0.43(1)	1.0(1) × 10^4	8.3(1)

0.38(1) eV. $Ca_{11}GaSb_9$ has the largest activation energy although only by a small margin. Typically, the energy gaps decrease in the binary semiconducting compounds MPn (M = Al, Ga, In; Pn = P, As, Sb).[19] Since $Ca_{11}GaSb_9$ has an ionic component associated with the bonding, the higher activation energy may be attributed to the greater electronegativity of Ga compared with Al and In.

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Supplementary Material Available: Tables of anisotropic displacement parameters and calculated and observed d spacings (7 pages); table of calculated and observed structure factors (5 pages). Ordering information is given on any current masthead page.

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