Exploring the Structure and Bonding of the Zintl Compounds: $A_{14}GaAs_{11}(A = Ca, Sr)$

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$Sr_{14}GaAs_{11}$ has been synthesized by reacting the stoichiometric combination of the elements in a sealed niobium tube, sealed in a quartz ampule under purified argon at 1200 °C for 24 hours. Single crystal X-ray diffraction data (130 K, a = 16.498(8) Å, c = 22.132(12) Å) were refined. The compound is isostructural to $Ca_{14}AlSb_{11}$ (tetragonal, $I4_1/acd$ (#142, origin choice 2), Z = 8, R_w = 4.4% for 770 independent reflections). The structure consists of discrete $GaAs_4$ tetrahedra, As_3 linear units and isolated As anions and Sr cations. Optical absorption data is consistent with this new compound being a semiconductor with an optical band gap of approximately 1.44 eV, very similar to that of GaAs (1.42 eV). The structure and properties are discussed and compared with $Ca_{14}GaAs_{11}$ and GaAs.

INTRODUCTION

Elucidating the structure and understanding the bonding of a compound have long been important to the field of chemistry.[1] There are a large number of solid state compounds whose structures can be understood by a simple electron counting scheme referred to as the Zintl concept.[2-6] The initial constituents of Zintl phases were binary compounds composed of an alkali or alkaline earth metal, A, and a heavier main group element, X. This group of materials was studied by E. Zintl who proposed that the structures and properties could be understood by considering the compound to be composed of an electropositive metal which transfers its electrons to the electronegative element that, in turn, forms the correct number of homoatomic bonds so that each element has a complete octet.[7] This simple formulism has been expanded to include ternary compounds so that now one can consider complex anions with both homo- and heteroatomic bonds.[2-6] Generally, these Zintl phases can be separated from either the insulators or the typical intermetallic phases because they are described by simple valence rules and are normally considered to be semiconductors.[8]

We have been studying the structure-property relationship of the ternary II-III-V[9] Zintl compounds such as Ca_3GaAs_3[10] and $Ca_5Ga_2As_6$.[11] Although the structures of these compounds have been reported, the electrical properties have not been reported.

This group of semiconductors is related to GaAs in that each compound consists of a polymeric framework of interconnected $GaAs_4$ tetrahedra. The ratio of cations to anions determines the connectivity of the $GaAs_4$ framework according to the Zintl concept.[2-5,12] In the course of investigating the synthesis and properties of these compounds, we have discovered two new ternary GaAs compounds in which the $GaAs_4$ tetrahedra are discrete, $A_{14}GaAs_{11}(A = Ca, Sr)$. In addition, this structure-type contains a unique As_3 linear polyatomic anionic unit.[12] This paper reports the new compound, $Sr_{14}GaAs_{11}$, and compares the structure and properties to $Ca_{14}GaAs_{11}$.[13]

EXPERIMENTAL

Synthesis

$Sr_{14}GaAs_{11}$ was synthesized by reacting the elements, Sr (Anderson Physics Lab, 99.95%), Ga (J. Matthey, 99,99%), and As (J. Matthey, 99,99 %) in a 14:1:11 molar ratio. The reactants and products were handled in nitrogen filled dry boxes with typical water levels less than 1 ppm. The elements were sealed in a welded niobium tube which was subsequently sealed under 1/5 atm of purified argon in a fused silica ampoule. The reaction was heated (1°/min) to 1200 °C and remained at that temperature for 24 hours before being rapidly cooled to room temperature. The air sensitive product from the reaction consisted primarily of some well-formed highly reflective black needles together with microcrystalline material that could be identified as $Sr_{14}GaAs_{11}$.

X-ray Powder Diffraction

Characterization was carried out by X-ray powder techniques (Guinier) at room temperature. The sample was mounted between pieces of tape with NBS silicon included as an internal standard. X-ray powder diffraction data were obtained with a focusing Guinier camera (Enraf-Nonius) equipped with a silican monochromator to give $CuK\alpha_1$ radiation. The powder patterns were indexed according to information obtained from the single crystal structural refinement. The corresponding room temperature lattice constants ($a = 16.513(4)$, $c = 22.14(1)$) were determined by standard least-squares refinement.

Single Crystal X-ray Study

The reaction container was opened in a dry box equipped with a microscope. Several suitable crystals of $Sr_{14}GaAs_{11}$ were coated with oil. These crystals were transferred from the dry box and one (dimensions: 0.5 x 0.1 x 0.16 mm^3) was mounted on a glass fiber and transferred to the diffractometer where it was placed in a cold stream of nitrogen.[14] Diffraction data in the positive octant were collected at 130 K on a Nicolet R3m diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å) equipped with a modified LT-1 low temperature apparatus. Unit cell parameters were obtained from a least-squares refinement of 15 reflections with $15° < 2\theta < 30°$. The crystal lattice was determined to be tetragonal I by the automatic indexing routine of the diffractometer software. This was verified from axial photographs and systematic extinctions. No decomposition of the crystal was observed (inferred from the intensity of two check reflections). The data were corrected for Lorentz and polarization effects. Of the 1735 unique data, a total of 770 reflections with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. The space group determination ($I4_1/acd$) was unambiguous. The initial atom positional parameters were taken from $Ca_{14}GaAs_{11}$ and the data were refined using SHELXTL PLUS (Release 3.43). As the refinement proceeded, it was noted that the U's (U_{11}, U_{22}) for As(4) was an order of magnitude larger than any of the other atoms. The reasons for this are not well understood, but the large thermal parameter may be attributed to some positional disorder. A disorder model appeared to be more appropriate and was used in the final stages of refinement. Although this model positions two As ions unreasonably close together (0.703(11) Å), it adequately accounts for the disorder of the As(4) position. The data were corrected for absorption,[15] and refined with anisotropic U's to a final R of 4.4% ($R_w = 4.4\%$). Neutral-atom scattering factors were those of Cromer and Waber.[16]

TABLE I

Crystallographic data for $Sr_{14}GaAs_{11}$

fw	2120.5
space group	$I4_1/acd$ (No. 142, origin choice 2)
crystal size	0.5 x 0.1 x 0.16 mm
a/Å	16.498(8)
c/Å	22.132(12)
V/Å^3	6024(5)
T/deg	130 K
Z	8
$\rho_{calcd.}$ /g cm^{-3}	4.676
radiation / (Å)	Mo Kα, ($\lambda = 0.71069$)
μ(Mo Kα)/ cm^{-1}	36.68
Monochromator	Highly oriented graphite crystal
Scan Type	ω
Scan Speed	Constant, 15°/min in ω
Scan Range (ω)	1.20°
$2\theta_{max}$	55°
Independent Reflections	1735
Observed Reflections	770 ($F > 6.0\sigma(F)$)
Number of Parameters refined	60
transmission factors	57–74%
R^a	0.044
$R_w{}^a$	0.044 [$w = 1/\sigma^2(F_0)$]

^{a} $R = \Sigma||F_o|-|F_c||/|Fc|$ and $R_w = \Sigma||F_o|-|F_c|| w^{1/2}/\Sigma|F_0 w^{1/2}|$

TABLE II

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)
for $Sr_{14}GaAs_{11}$

atom	x	y	z	U*
As(1)	1332(1)	−6168(1)	1250	11(1)
As(2)	39(1)	1167(1)	8113(1)	12(1)
As(3)	8699(1)	9739(1)	9535(1)	9(1)
As(4)**	9849(2)	2349(2)	1250	13(2)
Ga	5000	2500	1250	8(1)
Sr(1)	1771(1)	2933(1)	5790(1)	11(1)
Sr(2)	9768(1)	1221(1)	43(1)	12(1)
Sr(3)	3516(2)	0	2500	9(1)
Sr(4)	8209(1)	941(1)	8436(1)	11(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.
** Occupancy = 0.2500 (50%).

The compound is isostructural to the Zintl compounds, $Ca_{14}AlSb_{11}$,[17] and $Ca_{14}GaAs_{11}$.[12,13] The final difference Fourier map was flat to ±1.8 e/Å^3. Table I summarizes the crystal data and some of the data collection and refinement parameters. Table II provides the final atomic positional and thermal parameters. Anisotropic thermal parameters are provided in Table III. The observed and calculated structure factor amplitudes are available from the author (S. M. K.) on request.

Spectroscopy

Room temperature near-I.R. and optical transmission spectroscopy was performed on a Hitachi U-2000 spectrophotometer. GaAs (99.9999%) was obtained from J. Matthey. The samples were ground into mulls in a drybox and placed between optical plates.

TABLE III

Anisotropic displacement coefficients ($\mathring{A}^2 \times 10^3$) for $Sr_{14}GaAs_{11}$

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As(1)	12(1)	12(1)	10(2)	2(1)	1(1)	−1(1)
As(2)	11(1)	12(1)	13(1)	0(1)	2(1)	1(1)
As(3)	13(1)	9(1)	6(1)	1(1)	−1(1)	0(1)
Ga	9(1)	9(1)	5(2)	0	0	0
Sr(1)	16(1)	10(1)	9(1)	0(1)	−1(1)	−1(1)
Sr(2)	10(1)	10(1)	15(1)	2(1)	−1(1)	3(1)
Sr(3)	8(1)	7(1)	11(1)	0	0	1(1)
Sr(4)	8(1)	16(1)	9(1)	1(1)	2(1)	3(1)

The anisotropic displacement exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$.

TABLE IV

Important distances ($\mathring{A}$) and angles (°) for $Sr_{14}GaAs_{11}$ and $Ca_{14}GaAs_{11}$

			$Sr_{14}GaAs_{11}$		$Ca_{14}GaAs_{11}$
As(1)–A(1)	(x2)		3.169(3)	(x2)	3.019(2)
–A(2)	(x2)		3.231(3)	(x2)	3.040(2)
–A(3)	(x2)		3.381(2)	(x2)	3.209(1)
–A(4)	(x2)		3.195(3)	(x2)	2.998(2)
–As(4)			2.756(6)		2.956(2)
–As(4')			3.459(7)		
As(2)–A(1)			3.246(3)		3.071(2)
–A(1')			3.201(3)		3.051(2)
–A(2)			3.219(3)		2.953(2)
–A(2')			3.674(3)		3.512(2)
–A(3)			3.351(3)		3.124(2)
–A(4)			3.216(3)		2.979(2)
–A(4')			3.358(3)		3.230(2)
As(3)–A(1)			3.201(3)		3.035(2)
–A(1')			3.160(3)		3.003(2)
–A(2)			3.219(3)		2.958(2)
–A(2')			3.127(3)		3.052(2)
–A(3)			3.068(3)		2.913(2)
–A(4)			3.216(3)		3.085(2)
–A(4')			3.195(3)		3.068(2)
–A(4'')			3.655(3)		3.565(3)
As(4)–A(1)	(x2)		3.363(4)		
–A(1')	(x2)		3.019(3)	(x4)	3.005(2)
–A(2)	(x2)		3.619(4)	(x4)	3.220(2)
–A(2')	(x2)		3.259(4)		
–As(4')			0.703(10)		
Ga –As(2)	(x4)		2.613(3)		2.546(1)
–A(2)			3.575(3)		3.446(2)
As(2)–Ga–As(2)			114.7(1)		113.0(1)
As(2)–Ga–As(2')			106.9(1)		107.8(1)

RESULTS AND DISCUSSION

Synthesis

Syntheses of the strontium and barium analogues of the $A_{14}GaAs_{11}$ (A = alkaline earth metal) compound were attempted. The $Sr_{14}GaAs_{11}$ compound can be obtained in high yield from the stoichiometric reaction of the elements. $Ba_{14}GaAs_{11}$, could not be prepared from the elements, and so far, the product from that reaction has not been identified as a known binary or ternary phase. We have noted[13] that high yields of the $Ca_{14}GaAs_{11}$ can also be obtained from the combination of the binary compounds in the appropriate stoichiometries, but reactions of the binaries to produce $A_{14}GaAs_{11}$ have not been explored for the strontium or the barium analogues. In the case of the strontium compound, large black needle shaped crystals appeared to be formed from vapor transport.

Single Crystal X-ray Structure

The structure of the $Sr_{14}GaAs_{11}$ compound was refined by single-crystal X-ray diffraction to give the atomic coordinates and standard deviations compiled in Table II. Table IV contains the important bond lengths together with those for the analogous $Ca_{14}GaAs_{11}$ for comparison. $A_{14}GaAs_{11}$ forms tetragonal, ($I4_1/acd$) crystals, with eight
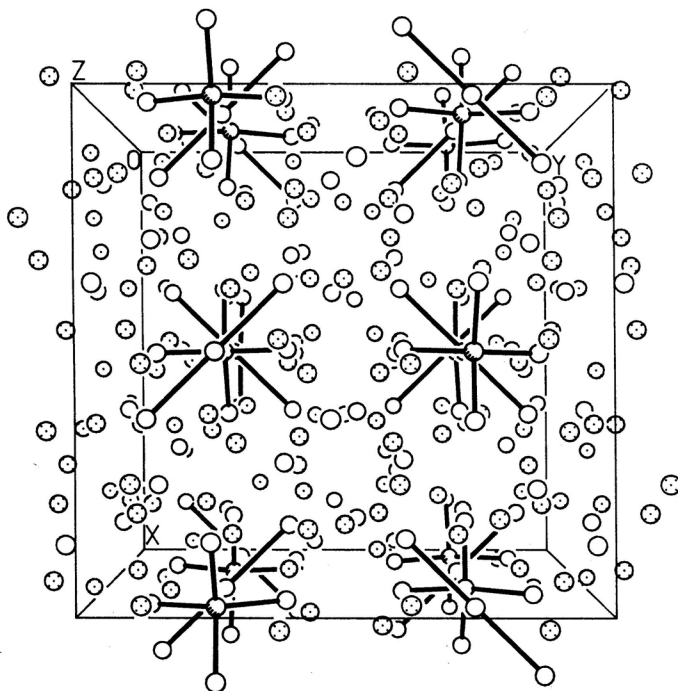

Figure 1. A perspective view of the unit cell down the c axis of $Sr_{14}GaAs_{11}$. The average position for the central As in the As_3 unit is shown (As(4) is placed at the positional coordinates. x, y, z: 0, 0.25, 0.125). The shaded, open, and dotted circles represent Ga, As, and Sr atoms, respectively.
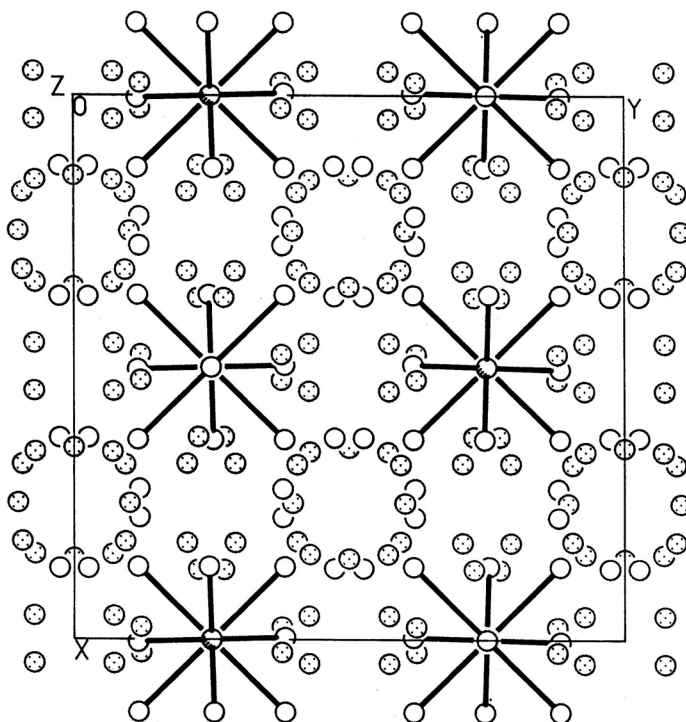
Figure 2. A [0 0 1] projection of the unit cell of $Sr_{14}GaAs_{11}$. The average position for the central As in the As_3 unit is shown (As(4) is placed at the positional coordinates, x, y, z: 0, 0.25, 0.125). The shaded, open, and dotted circles represent Ga, As and Sr atoms, respectively.

formula units per unit cell. The formula unit consists of 14 A cations, 4 As anions, a $GaAs_4$ tetrahedron and a linear As_3 unit. The $GaAs_4$ tetrahedra are translated by 1/2 along the c axis while the As_3 anions are staggered by 90° with respect to each other, as shown in Figure 1. The As anions are located between the $GaAs_4$ tetrahedra and As_3 linear units and form a spiral along a screw axis coincident with the c axis. Figure 2 shows a [0 0 1] projection of the unit cell which clearly shows the As(3) anions. The closest As ion to As(3) is another As(3) anion in the spiral at 3.92 Å (A = Ca) and 4.11 Å (A = Sr), all other As(3)···As distances are ≥4.2 Å. These A atoms are considered to be isolated and not bonded to another As atom. In the framework of the Zintl-Klemm-Busmann concept,[2-5,12,13,17] the formal charges can be assigned as follows: 14 A^{2+} cations, 4 As^{3-} anions, $GaAs_4^{9-}$ tetrahedra and an As_3^{7-} polyatomic anion.

Figure 3 shows a perspective of the polyatomic anions with important distances and angles indicated. The $GaAs_4^{9-}$ tetrahedra are slightly distorted. The distortion is larger for A = Sr, with angles of 114.7° and 106.9°, than for the Ca analogue which has angles of 113.0° and 107.8°. This distortion is attributed to cation-anion interactions. There is also a lengthening of Ga-As bond distance with 2.546(1) Å for A = Ca to 2.613 Å for A = Sr. Typical Ga-As bond lengths in these ternary Zintl compounds

range from 2.476–2.698 Å, longer than that observed in the binary GaAs semiconductor (2.448 Å). This elongation in the bond length can be attributed to the electron donating ability of the cation. The strontium cation donates more charge than the calcium cation to the $GaAs_4^{9-}$ polyanion and, therefore, there is a lengthening of the Ga-As bond in $Sr_{14}GaAs_{11}$ compared to $Ca_{14}GaAs_{11}$. This affect on bond lengths as a function of electron donating ability has been observed in several alkali metal and alkaline earth metal binary compound series.[2]

The most obvious difference in the anionic units between the two compounds is seen in the As_3^{7-} unit. This X_3^{7-} unit is seen in $Ca_{14}AlSb_{11}$,[17] and the $A_{14}MnX_{11}$ (A = = Ca, Sr, Ba; X = As, Sb, Bi) compounds.[12,18-20] In $Ca_{14}GaAs_{11}$, the bond length for As(1)···As(4) is 2.956(2) Å and the central As ion is elongated along the bond. This is attributed to some positional disorder that would make the two As-As distances inequivalent.[13] In $Sr_{14}GaAs_{11}$, this disorder apparently increases and can be modeled either with an extremely large thermal parameter for As(4), or with two As(4) sites that are both half occupied. Figures 1 and 2 show views of the structure with the averaged position for the central As. Figure 3 shows a view of the polyatomic units with the disordered position indicated. This model leads to two inequivalent As(4)-As(1) distances of 3.459(8) Å and 2.756(6) Å. In $Ca_{14}GaAs_{11}$, the distances are equivalent at 2.956 Å. The distances in this As_3^{7-} unit for either the Ca or Sr analogous are larger than a normal As-As single bond which is about 2.4 Å,[11,21] but which is consistent with the longer distances observed in the analogous Sb_3^{7-} (3.196(2) Å) and Bi_3^{7-} (3.336(2) Å) units observed in $Ca_{14}AlSb_{11}$[17] and $Ca_{14}MnBi_{11}$, respectively.[18,19] All other As-As distances are considerably longer (≥3.904 Å) and are not considered to be homoatomically bonded. The bond distances in the linear unit can be considered in a similar manner to the I_3^- anion[22] which has I-I bond distances in the range 2.90–3.10 Å, compared to I_2 which has a I-I bond distance of 2.67 Å. Theoretical calculations[23] indicate that
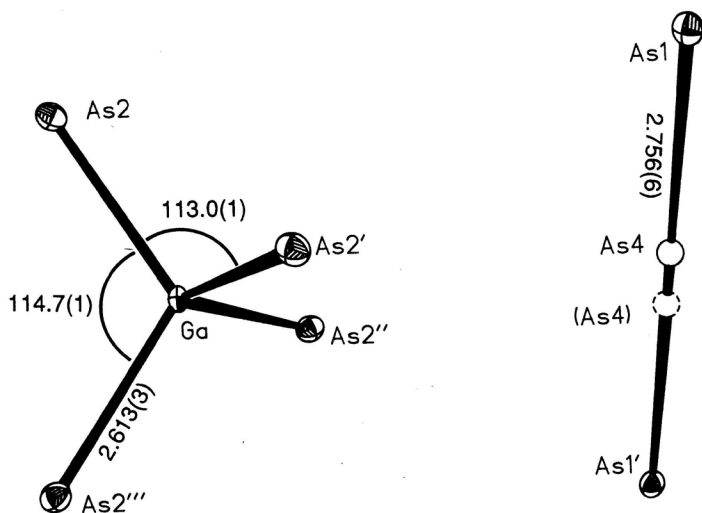

Figure 3. A perspective view showing the relative orientation of the polyatomic units. As(4) and As(4') are 50% occupied and represent a disorder model for that site. Important bond lengths (Å) and angles (°) are indicated. The thermal ellipsoids are drawn at 70%.

it is more appropriate to view the As_3^{7-} unit as a 3-center 4-electron hypervalent bond[24] rather than dsp^3 hybridization around the central atom. This As_3^{7-} anion is stabilized by several short A-As(1) and A-As(4) bonding interactions. The central As(4) atom in this structure is surrounded by two Sr(1) atoms at 3.363(4) Å and two at 3.019(3) Å, compared with four Ca(1) at 3.005(2) Å in $Ca_{14}GaAs_{11}$. The terminal As(1) atoms are surrounded by a total of six cations with three distinct distances of 3.231(3), 3.169(3) and 3.195(3) Å, consistent with the $Ca_{14}GaAs_{11}$ structure which has As(1)-Ca distances of 3.040(2), 3.019(2) and 2.998(2) Å. The thermal parameters for the alkaline earth cations are spherical, indicating very little disorder of the cation sites.

The As^{3-} anions are shown in Figures 1 and 2. These atoms are located between the tetrahedra and the As_3^{7-} unit and spiral along c. This anion is coordinated by eight cations. There are seven cations that have distances of 3.07–3.22 Å, similar to those observed in binary Zintl phases,[21] and one with a longer distance of 3.655(3) Å.

Near-I.R. and Optical Spectroscopy.

This structure consists of discrete $GaAs_4$ tetrahedra and an unusual As_3 linear polyatomic unit. This compound can be described as consisting of small groups of atoms (molecules) within which the interatomic bonds are strong but between which the bonds are weak. These molecules are held in place by electrostatic or ionic bonding in a continuous network within the solid and can be considered an extended solid. At this point, a question comes to mind, will these compounds be semiconductors or insulating salts? According to the Zintl-Klemm-Busmann concept[2-6] these compounds should be semiconductors. They should show an increasing electronic resistivity with decreasing temperature in contrast to metals. The boundary between semiconductors and insulators is defined in terms of an energy, E_g, that is necessary to promote an electron from the valence band (highest occupied states) to the conduction band (lowest unoccupied states). Compounds with $E_g \leq 2$ eV are generally considered to be semiconductors while those with $E_g \geq 2$ eV are insulators. To date, we have been unable
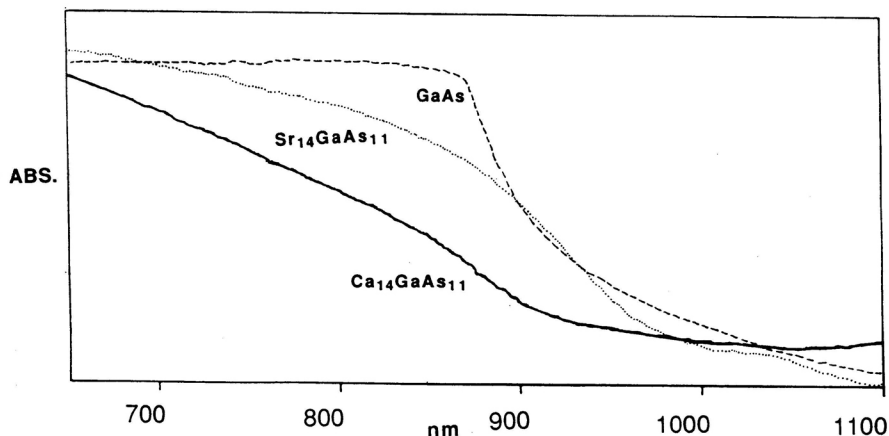

Figure 4. The near-I.R. and optical absorption spectra of GaAs (dashed line), $Ca_{14}GaAs_{11}$ (solid line) and $Sr_{14}GaAs_{11}$ (dotted line). Absorbance (ABS.) is in arbitrary units.

to measure temperature dependent resistivity on single crystals. We have, however, been able to obtain near-I.R. and optical spectra of these compounds and these data are shown in Figure 4. Interaction of a solid with near-I.R. and visible radiation involves excitation of valence electrons, in the simplest picture, from filled to empty bands. Therefore, the threshold for optical absorption can be used to estimate the band gap.[25] The near-IR and optical spectrum of GaAs is also shown for comparison in Figure 4. The energy of the absorption edge observed for these spectra is indicative of semiconducting behavior. The spectrum of GaAs (dashed line) shows a maximum in the absorption edge at approximately 874 nm or 1.42 eV, which is attributed to the band gap.[26] The absorption edges of $Ca_{14}GaAs_{11}$ (solid line) and $Sr_{14}GaAs_{11}$ (dotted line) are at a slightly lower wavelength (834 and 864 nm, respectively)[13,27] and the band gap is estimated to be 1.49 and 1.44 eV, respectively, slightly higher in energy than GaAs. As the size of the cation increases, from Ca to Sr, the band gap becomes smaller. The absorption edges for the $A_{14}GaAs_{11}$ compounds are broader and less well defined, as compared to GaAs. This may be due to an indirect absorption process or the presence of other absorption processes. However, further interpretation of the optical data is not possible without single crystal and temperature dependent studies.

CONCLUDING REMARKS

The $A_{14}GaAs_{11}$ structure can be understood by applying the Zintl-Klemm-Busmann concept. These compounds contain the first examples of a hypervalent As_3^{7-} unit and an isolated $GaAs_4^{9-}$ polyatomic anion. The near-I.R. and optical properties of these compounds are indicative of semiconducting and not insulating behavior. Because of the importance of GaAs and other III-V semiconductors, we are continuing our efforts to measure the electronic properties of these compounds. Further work on the properties of these unusual semiconductors and their analogues is under way.

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27. Alternatively, in a broad absorption, it may be more appropriate to estimate the value of the band gap at the inflection point of the absorption threshold. This would give values of 875 and 912 nm (1.42 and 1.36 eV) for $Ca_{14}GaAs_{11}$ and $Sr_{14}GaAs_{11}$, respectively.

SAŽETAK

Istraživanje strukture i kemijskog vezanja nekih Zintl-spojeva: $A_{14}GaAs_{11}$ (A = Ca, Sr)

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Sintetiziran je spoj $Sr_{14}GaAs_{11}$ i ispitana je njegova struktura metodom difrakcije X-zraka. Utvrđeno je da se sastoji od diskretnih linearnih fragmenata As_3, tetraedara $GaAs_4$, te od izoliranih aniona As i kationa Sr. Proizlazi da ima istu strukturu kao i $Ca_{14}AlSb_{11}$. Također je pokazano da $Sr_{14}GaAs_{11}$ ima svojstva poluvodiča s debljinom vrpce od 1.44 eV.