



# Synthesis and structural characterization of the ternary Zintl phases $AE_3Al_2Pn_4$ and $AE_3Ga_2Pn_4$ ( $AE=Ca, Sr, Ba, Eu; Pn=P, As$ )

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## ABSTRACT

Ten new ternary phosphides and arsenides with empirical formulae  $AE_3Al_2Pn_4$  and  $AE_3Ga_2Pn_4$  ( $AE=Ca, Sr, Ba, Eu; Pn=P, As$ ) have been synthesized using molten Ga, Al, and Pb fluxes. They have been structurally characterized by single-crystal and powder X-ray diffraction to form with two different structures— $Ca_3Al_2P_4$ ,  $Sr_3Al_2As_4$ ,  $Eu_3Al_2P_4$ ,  $Eu_3Al_2As_4$ ,  $Ca_3Ga_2P_4$ ,  $Sr_3Ga_2P_4$ ,  $Sr_3Ga_2As_4$ , and  $Eu_3Ga_2As_4$  crystallize with the  $Ca_3Al_2As_4$  structure type (space group  $C2/c$ ,  $Z=4$ );  $Ba_3Al_2P_4$  and  $Ba_3Al_2As_4$  adopt the  $Na_3Fe_2S_4$  structure type (space group  $Pnma$ ,  $Z=4$ ). The polyanions in both structures are made up of  $TrPn_4$  tetrahedra, which share common corners and edges to form  ${}^2_\infty[TrPn_2]^{3-}$  layers in the phases with the  $Ca_3Al_2As_4$  structure, and  ${}^1_\infty[TrPn_2]^{3-}$  chains in  $Ba_3Al_2P_4$  and  $Ba_3Al_2As_4$  with the  $Na_3Fe_2S_4$  structure type. The valence electron count for all of these compounds follows the Zintl–Klemm rules. Electronic band structure calculations confirm them to be semiconductors.

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## 1. Introduction

In recent years, there have been numerous reports on the crystal chemistry and physical properties of ternary pnictides in the systems  $AE-Tr-Pn$  ( $AE=Ca, Sr, Ba, Eu, Yb; Tr=Al, Ga, In$ ; and  $Pn=P, As, Sb$ ). Examples include  $BaGa_2Sb_2$  [1],  $Yb_5Al_2Sb_6$  [2],  $Ba_2In_5As_5$  [3],  $Eu_3InP_3$  [4],  $Eu_3In_2P_4$  [5],  $EuIn_2P_2$  [6],  $EuGa_2As_2$  [7],  $Ca_3AlSb_3$  [8] and  $Ca_5Al_2Sb_6$  [9], to name just a few. Almost exclusively, such compounds can be classified as Zintl phases [10], where the alkaline-earth metals are the “cations” and they donate their valence electrons to the post-transition elements, which, in turn, form covalent bonds within (poly)anionic substructure. The electron transfer is typically considered to be “complete”, and all constituent atoms achieve closed-shell configurations [10,11]. These are desirable characteristics in thermoelectrics development, and many research groups are turning their attention to Zintl phases as candidate materials for solid-state energy conversion. Recent papers have already demonstrated the favorable balance of charge and heat-transport properties for the compounds  $Yb_5Al_2Sb_6$  [2], and  $Ca_3AlSb_3$  [8];  $EuIn_2As_2$  [12] can be cited as an example showing colossal magnetoresistance.

Our research group has previously explored considerable sections of the ternary  $AE-Ga-Sb$  and  $AE-In-Sb$  phase diagrams ( $AE=Ca, Sr, Ba, Eu$  and  $Yb$ ). Since these early studies had proven

fruitful [13–16], not long ago, we embarked on investigations of the corresponding arsenide and phosphide systems. For the synthesis of new compounds with novel structures, by and large, we have focused on the metal flux method [17,18], since the triel elements Ga and In are particularly well-suited for such endeavors. Published structures from our prior systematic work include  $BaGa_2Pn_2$  ( $Pn=P, As$ ) [19], and  $CaGa_2P_2$ ,  $CaGa_2As_2$ , and  $SrGa_2As_2$  [20], which all crystallize with different structures. Attempts to extend the “1–2–2” chemistry to the  $AE-Al-Pn$  system led to the identification of two series of new compounds  $AE_3Ga_2Pn_4$  and  $AE_3Al_2Pn_4$ , which are the subject of this paper. Herein, we present the ten newly synthesized compounds— $Ba_3Al_2P_4$  and  $Ba_3Al_2As_4$  with the  $Na_3Fe_2S_4$  structure type [21], and  $Ca_3Al_2P_4$ ,  $Sr_3Al_2As_4$ ,  $Eu_3Al_2P_4$ ,  $Eu_3Al_2As_4$ ,  $Ca_3Ga_2P_4$ ,  $Sr_3Ga_2P_4$ ,  $Sr_3Ga_2As_4$ , and  $Eu_3Ga_2As_4$ , isostructural with the previously reported  $Ca_3Al_2As_4$  [22] and  $Sr_3Al_2P_4$  [23]. Their bonding characteristics are elaborated and the topological relationships to the structures of compounds with formulae  $AE_3TrPn_3$  are discussed as well. The electronic band structures, calculated with the aid of the TB-LMTO method [24], are also discussed.

## 2. Experimental

### 2.1. Synthesis

All synthetic and post-synthetic manipulations were performed inside an argon-filled glove box or under vacuum. The elements with stated purity greater than 99.9 wt% were purchased from either Alfa Aesar or Aldrich and used as received.

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All initial reactions were done in a manner, consistent with the synthesis of  $\text{CaGa}_2\text{P}_2$ ,  $\text{CaGa}_2\text{As}_2$ , and  $\text{SrGa}_2\text{As}_2$  [20], where excess Ga was utilized as a reactive flux; details of the metal flux method can be found elsewhere [17,18]. Such reactions were aimed at the “missing” members of any of the three structures above, but by serendipity afforded crystals of the new compounds  $\text{Ca}_3\text{Ga}_2\text{P}_4$  and  $\text{Sr}_3\text{Ga}_2\text{P}_4$ . Subsequent to the structure elucidation by single-crystal X-ray diffraction, the syntheses of these three compounds were replicated using mixtures of the corresponding elements with the proper stoichiometric  $AE:Pn$  ratio of 3:4 and a 25-fold excess of Ga. The mixtures of the elements were loaded in alumina crucibles, which were then flame-sealed in fused silica tubes under vacuum. The evacuated silica tubes were heated at 960 °C for 20 h, and then cooled to 500 °C at a rate of 5 °C/h. The molten Ga was decanted at this temperature. Previous successful application of Pb flux for the crystal growth of other  $AE\text{--Ga--Pn}$  ternary compounds [20] prompted us to undertake Pb flux reactions again. They were done in a similar way, starting with the corresponding elements in the 3:2:4 ratio and a large amount of Pb (20-fold excess)—large single-crystals of  $\text{Ca}_3\text{Ga}_2\text{P}_4$ ,  $\text{Sr}_3\text{Ga}_2\text{P}_4$ ,  $\text{Sr}_3\text{Ga}_2\text{As}_4$ , and  $\text{Eu}_3\text{Ga}_2\text{As}_4$  were obtained from such experiments.

Attempts to synthesize isotypic  $\text{Ba}_3\text{Ga}_2\text{P}_4$  and  $\text{Ba}_3\text{Ga}_2\text{As}_4$  compounds were unsuccessful—the outcome, depending on the  $AE:Pn$  ratio (1:2 or 3:4), and the choice of flux (Ga or Pb) were

$\text{BaGa}_2\text{P}_2$  and  $\text{BaGa}_2\text{As}_2$  [19], or  $\text{Ba}_7\text{Ga}_4\text{P}_9$  and  $\text{Ba}_7\text{Ga}_4\text{As}_9$  [25], which are isotypic to  $\text{Ba}_7\text{Ga}_4\text{Sb}_9$  [26].  $\text{Ca}_3\text{Ga}_2\text{As}_4$  and  $\text{Eu}_3\text{Ga}_2\text{P}_4$  are also still unknown and could not be obtained under the studied experimental conditions. In these cases, crystals of  $\text{CaGa}_2\text{As}_2$  [19],  $\text{Ca}_{14}\text{GaAs}_{11}$  [27], and  $\text{EuGa}_4$  [28] were obtained. Analogous reactions with Yb afforded only the binary phases YbP, YbAs, GaAs, and GaP [28].

Switching to aluminum as a reactive flux proved to be somewhat more challenging, although we identified six new compounds— $\text{Ba}_3\text{Al}_2\text{P}_4$ ,  $\text{Ba}_3\text{Al}_2\text{As}_4$ ,  $\text{Ca}_3\text{Al}_2\text{P}_4$ ,  $\text{Sr}_3\text{Al}_2\text{As}_4$ ,  $\text{Eu}_3\text{Al}_2\text{P}_4$ , and  $\text{Eu}_3\text{Al}_2\text{As}_4$ . First, the higher melting point of Al metal (660 °C) [29] required the corresponding reactions to be equilibrated at 960 °C for 20 h, and then cooled to 750 °C. Second, since Al is a strong reducing agent and Al vapors are known to react quickly with  $\text{SiO}_2$ , extreme care had to be exercised when the ampoules were removed from the furnace and the molten Al was decanted. Third, yields of the title compounds were lower, and AlP or AlAs [28] were common side products; the crystals were also smaller compared to the crystals obtained from analogous Ga flux reactions.

The crystals exhibit characteristic colors, indicative of them being intrinsic semiconductors:  $\text{Ca}_3\text{Al}_2\text{P}_4$  is orange;  $\text{Sr}_3\text{Al}_2\text{As}_4$ ,  $\text{Ca}_3\text{Ga}_2\text{P}_4$ ,  $\text{Sr}_3\text{Ga}_2\text{P}_4$ , and  $\text{Ba}_3\text{Al}_2\text{P}_4$  are red;  $\text{Eu}_3\text{Al}_2\text{P}_4$  is dark brown; and  $\text{Eu}_3\text{Al}_2\text{As}_4$ ,  $\text{Eu}_3\text{Ga}_2\text{As}_4$ ,  $\text{Sr}_3\text{Ga}_2\text{As}_4$ , and  $\text{Ba}_3\text{Al}_2\text{As}_4$  are black.

## 2.2. Powder X-ray diffraction

X-ray powder diffraction patterns were collected at room temperature on a Rigaku MiniFlex powder diffractometer using filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The diffractometer was enclosed and operated inside a glove-box. The observed peak-positions and the peaks' relative intensities, analyzed using the JADE 6.5 software package, matched well with those calculated from the single-crystal work. According to powder patterns collected for specimens kept under inert atmosphere and to those collected after being exposed to air, all of the title compounds are unstable at ambient conditions. The air-sensitivity was found to vary considerably, with the Ba-containing samples being the most reactive and the Eu-containing samples being the least sensitive, respectively.

## 2.3. Single-crystal X-ray diffraction

Single-crystal X-ray diffraction data were collected on a Bruker SMART CCD-based diffractometer, employing monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Crystals from freshly prepared samples

**Table 1**

Selected single-crystal data collection and structure refinement parameters for  $\text{Ba}_3\text{Al}_2\text{Pn}_4$  ( $Pn = \text{P, As}$ ).

Empirical formula	$\text{Ba}_3\text{Al}_2\text{As}_4$	$\text{Ba}_3\text{Al}_2\text{P}_4$
Formula weight	765.66	589.86
Temperature	200(2) K	
Radiation, $\lambda$	MoK $\alpha$ , 0.71073 Å	
Space group, Z	Pnma (No. 62), 4	
a (Å)	7.425(2)	7.2540(5)
b (Å)	11.784(3)	11.5416(8)
c (Å)	11.842(3)	11.5770(8)
V (Å <sup>3</sup> )	1036.0(5)	969.26(12)
$\rho_{\text{cal}}$ (g/cm <sup>3</sup> )	4.909	4.042
$\mu$ (cm <sup>-1</sup> )	240.49	128.13
Goodness-of-fit on $F^2$	1.079	1.106
$R_1$ ( $I > 2\sigma_I$ ) <sup>a</sup>	0.0348	0.0189
$wR_2$ ( $I > 2\sigma_I$ ) <sup>a</sup>	0.0664	0.0394
Largest diff. peak/hole ( $e^-/\text{Å}^{-3}$ )	2.133/−1.453	1.143/−0.777

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ , where  $w = 1 / [\sigma^2 F_o^2 + (AP)^2]$ , and  $P = (F_o^2 + 2F_c^2) / 3$ ; A—weight coefficient.

**Table 2**

Selected single-crystal data collection and structure refinement parameters for  $\text{AE}_3\text{Al}_2\text{Pn}_4$  ( $AE = \text{Ca, Sr, Eu}$ ;  $Pn = \text{P, As}$ ).

Empirical formula	$\text{Ca}_3\text{Al}_2\text{P}_4$	$\text{Sr}_3\text{Al}_2\text{As}_4$	$\text{Eu}_3\text{Al}_2\text{P}_4$	$\text{Eu}_3\text{Al}_2\text{As}_4$	$\text{Ca}_3\text{Ga}_2\text{P}_4$	$\text{Sr}_3\text{Ga}_2\text{P}_4$	$\text{Sr}_3\text{Ga}_2\text{As}_4$	$\text{Eu}_3\text{Ga}_2\text{As}_4$
Formula weight	298.08	616.5	633.72	809.52	383.56	526.18	701.98	895.00
Temperature	200(2) K							
Radiation, $\lambda$	MoK $\alpha$ , 0.71073 Å							
Space group, Z	C2/c (No. 15), 4							
a (Å)	12.6236(11)	13.5017(16)	13.0304(17)	13.404(2)	12.623(3)	13.1522(13)	13.497(3)	13.386(4)
b (Å)	9.8358(8)	10.4565(13)	10.0974(13)	10.3935(17)	9.870(2)	10.1989(10)	10.497(2)	10.426(3)
c (Å)	6.4469(6)	6.8109(8)	6.5857(8)	6.7502(11)	6.4435(15)	6.6290(7)	6.7903(16)	6.732(2)
$\beta$ (°)	90.454(1)	90.457(2)	90.607(2)	90.023(2)	91.050(3)	90.314(1)	90.275(4)	90.742(4)
V (Å <sup>3</sup> )	800.44(12)	961.5(2)	866.45(19)	940.4(3)	802.6(3)	889.19(16)	962.0(4)	939.5(5)
$\rho_{\text{cal}}$ (g/cm <sup>3</sup> )	2.474	4.259	4.858	5.718	3.174	3.931	4.847	6.327
$\mu$ (cm <sup>-1</sup> )	29.82	303.42	222.97	338.31	93.24	244.90	356.25	392.88
Goodness-of-fit on $F^2$	1.053	0.993	1.195	1.038	1.037	1.000	1.001	1.159
$R_1$ ( $I > 2\sigma_I$ ) <sup>a</sup>	0.0219	0.0325	0.0161	0.0164	0.0187	0.0248	0.0222	0.0185
$wR_2$ ( $I > 2\sigma_I$ ) <sup>a</sup>	0.0464	0.0528	0.0362	0.0352	0.0419	0.0507	0.0492	0.0430
Largest diff. peak and hole ( $e^-/\text{Å}^{-3}$ )	0.429/−0.361	1.102/−1.139	0.773/−1.075	0.878/−0.795	0.437/−0.467	0.832/−0.875	0.934/−0.900	0.969/−1.004

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ , where  $w = 1 / [\sigma^2 F_o^2 + (AP)^2 + (BP)^2]$ , and  $P = (F_o^2 + 2F_c^2) / 3$ ; A, B—weight coefficients.

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