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**Synthesis and Crystal Structure of $\text{Ca}_2\text{Ag}_{1.83}\text{Al}_{0.67}\text{Ge}_{1.50}$
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Synthesis and Crystal Structure of $\text{Ca}_2\text{Ag}_{1.83}\text{Al}_{0.67}\text{Ge}_{1.50}$ – A Solid Solution with the NbCoB-type structure

Siméon Ponou^{*[a]} and Sven Lidin^[a]

Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

Abstract: The crystal structure of the new phase, $\text{Ca}_2\text{Ag}_{1.83}\text{Al}_{0.67}\text{Ge}_{1.50(1)}$ (**1**) was determined by single crystal X-ray diffraction, after the compound was obtained by high temperature synthesis technique. **1** crystallizes with the NbCoB type structure in the orthorhombic space group *Pmmn* (no. 59) with unit cell parameters: $a = 20.505(1) \text{ \AA}$, $b = 4.3807(2) \text{ \AA}$, $c = 7.2211(3) \text{ \AA}$, $V = 648.65 \text{ \AA}^3$ ($Z = 5$). The structure of the title compound represent a rare intergrowth of the well known KHg_2 (or CeCu_2) and Fe_2P type structures.

Keywords: Intermetallics, Solid Solution, Intergrowth Structure, Crystal Structure

Introduction

The structure of intermetallic compounds as well as their bonding characteristic remain the least understood among inorganic solids [1-3]. This is because the main factors that govern the formation, stability, and properties of intermetallic phases like relative sizes and electronegativity, and number of valence electrons (ve) vary strongly and almost continuously with composition and the nature of the elements involved [4-7]. A typical illustration of the difficulty to predict the structure and bonding of intermetallic compounds may be found in the systems CaAgPn ($\text{Pn} = \text{As}, \text{Sb}$), [8] with the phase CaAgSb [9] crystallizing in the TiNiSi type (an ordered ternary variant of the KHg_2 or CeCu_2 type); in contrast, the arsenic homologous CaAgAs [10] adopts the ZrNiAl type structure (an ordered ternary variant of the Fe_2P type) [11]. Here, the structure selection seems to be determined by the increase of electronegativity from Sb to As, which in turn determines the degree of polarity of the Ag–Pn bond. Thus, since the Ag–As bond is highly polar, the ZrNiAl type is preferred whereas the TiNiSi type is realized in the Sb phase due to the stronger covalent character of the Ag–Sb bond. On the other hand, ZrPdSb [12] still crystallizes in the TiNiSi type, but ZrPdAs [12]

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adopts the NbCoB type which may be described as an intergrowth of the TiNiSi type and the ZrNiAl type structures, indicating a more complex bonding picture [13].

In the course of the systematic investigation of the pseudo-quaternary system $\text{CaAg}_{1-x}\text{Al}_x\text{Ge}$ ($x < 1$), we discovered a solid solution with the composition $\text{Ca}_2\text{Ag}_{1.83}\text{Al}_{0.67}\text{Ge}_{1.50(1)}$ with the NbCoB type structure. We report herein on the synthesis and crystal structure determination by single crystal diffraction. The structural relationship to the TiNiSi type and the ZrNiAl type structures and the observed ‘differential fractional site occupancy’ [14] are discussed.

Experimental Section

The title compounds was prepared from the elements, (all from ABCR GmbH, Karlsruhe, Germany) in a two steps synthesis. At first, the precursor was made from a mixture of Ca (granule, 99.5%), Ag (60 μ powder, 99.9%) and Ge (50 μ powder, 99.999%), with the atomic ratio Ca:Ag:Ge = 3:2:2, were loaded in a niobium ampoule, weld-sealed at both ends under Argon atmosphere and reacted at 950°C for 3 hrs in a tubular furnace. The resulting air- and moisture sensitive product consisted mainly of $\text{Ca}_3\text{Ag}_3\text{Ge}_3$, [15] and $\text{Ca}_3\text{Ag}_{1+x}\text{Ge}_{3-x}$ ($x \sim 0.33$) [15] with the Sc_3NiSi_3 type structure [16]. Afterwards 500 mg of the precursor was mixed with 100 mg of Al (ingot, 99.999%) and heated at 750°C for two days and slowly cooled down to room temperature at the rate of 2K/min. The reaction was originally designed to produce an Al poor phase of $\text{CaAg}_{1-x}\text{Al}_x\text{Ge}$ with $x < 0.5$ (presumably with the KHg_2 or TiNiSi type), after unsuccessful synthesis attempts by direct combination of the elements.

X-ray powder diffraction patterns were collected on an X’Pert-Pro diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range of 5–90°. The generator voltage was 45 kV and the tube current was 40 mA. The Title compound could be indexed in the measured X-ray powder patterns of the resultant products using crystal parameters obtained from single crystal diffraction experiments. It also revealed the presence of several impurity phases in large amounts, such as CaAl_2Ge_2 (CaAl_2Si_2 type) [17], $\text{CaAg}_{1-x}\text{Al}_x\text{Ge}$ (TiNiSi type with $x \sim 0.5$) [15] as well as other unidentified compounds.

Irregularly shaped crystals could easily be isolated from the resulting sample. The chemical composition of selected crystals was determined using a field emission scanning electron microscope (JSM-7000F, JEOL, Japan) operating at 15 kV and equipped with an energy dispersive X-ray spectrometer (INCAx-sight, Oxford Instruments, UK). Elemental cobalt was used as standard, Corrections for atomic number, absorption, and fluorescence were applied. Microprobe elemental analyses on several single crystals confirmed the presence of the four

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3 elements Ca/Ag/Al/Ge, but quantitative analysis were difficult perhaps due to the rough
4 surface of the crystals.

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6 Single crystal X-ray diffraction data were collected at ambient temperature using an Oxford
7 Diffraction Xcalibur CCD diffractometer with graphite-monochromatized Mo-K α radiation
8 ($\lambda = 0.71073 \text{ \AA}$) operating at 50 kV and 40 mA, and a detector-to-crystal distance of 50 mm.
9
10 The integration of the reflection intensities and the absorption corrections were made using
11 the software supplied by the manufacturers of the diffractometer [18-19]. The structures were
12 solved by direct methods using the SHELXS [20] program and Full matrix least-squares
13 refinement on F^2 was carried out using the SHELXL [21]. It is not possible to assign the all
14 atomic sites based only on the electron density. Hence, the atomic distribution in the
15 prototype NbCoB (or ZrPdAs) was also considered in the model. The refined composition
16 was $\text{Ca}_2\text{Ag}_{1.83}\text{Al}_{0.67}\text{Ge}_{1.50(1)}$ with satisfactory residuals (all data) $R_1 = 0.0585$, $wR_2 = 0.0991$.
17 Relevant crystallographic and refinement details are listed in Table 1 and, Table 2 contains
18 the atomic positions and equivalent displacement parameters. Further details of the crystal-
19 structure investigation can be obtained from the Fachinformationszentrum Karlsruhe,
20 Eggenstein-Leopoldshafen, Germany (fax: +49-7247 808 666; e-mail: CrysDATA@FIZ-
21 Karlsruhe.de) on quoting the depository number CSD-380297. The images were rendered
22 using the program Diamond, version 2.1c [22].
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36 Results and Discussion

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38 The phase $\text{Ca}_2\text{Al}_{0.67}\text{Ag}_{1.83}\text{Ge}_{1.50(1)}$ (**1**) crystallizes with an orthorhombic unit cell in the space
39 group $Pm\bar{m}n$ (No. 59, $Z = 5$) in the prototypical NbCoB structure [23]. ZrPdAs is another
40 isotopic compound, and was recently described by Mewis et al. [12]. The main noticeable
41 feature in this structural family is the fact that the same p -block element (B or As), is found
42 simultaneously in three markedly different coordination environments, namely, tetrahedral,
43 trigonal planar and, trigonal prismatic geometry. This indicates rather different chemical
44 bonding characteristics for one element in the same crystal structure. As illustrated in Figure
45 1, the structure of **1** may be best described with the chemical twinning approach as an
46 intergrowth of slabs cut from simple parent compounds with the TiNiSi-type and the ZrNiAl
47 type structures. The unit cell contains nine independent atomic positions of which three are on
48 special positions. For the sites assignments (Table 2), Ca atoms were placed at Nb positions in
49 agreement with the observed interatomic distances since $d_{\text{Ca-E}} > 3.0 \text{ \AA}$ ($E = \text{Al, Ge, Ag}$).
50 These Ca atoms are located in two types of channels; the pentagonal channels with one row of
51 Ca atoms are typical of the ZrNiAl structure. Meanwhile, the largest channel of the structure
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3 with two rows of Ca, as well as the atomic square ladders with rectangular distortion are
4 reminiscent of the TiNiSi type structure. The three positions occupied by Co in the prototype
5 were refined as Ag/Al mixed occupied. This resulted on refinement in higher Al occupancy at
6 Al6/Ag position with tetrahedral coordination geometry, in the block related to the TiNiSi
7 structure where the Al/Ag atomic ratio is of 0.6/0.4. In contrast, Ag is the major component in
8 the block related to the ZrNiAl structure where, the Ag occupancy is highest (100%) on one
9 atomic site (Ag1) and 54% on the other (Ag5/Al, Wyck. 2a). This is clearly an indication of a
10 'differential fractional site occupancy' with Ag preferring the block with the ZrNiAl type
11 structure. Finally, all the B positions in the prototype were refined as Ge/Ag mixed occupied
12 sites because Ge has the highest electronegativity followed by Ag. But, this is also in
13 agreement with the observed electron density that is intermediate between Ge and Ag. Here
14 also a 'differential fractional site occupancy' is observed between Ge and Ag atoms, since the
15 Ag occupancy in the two atomic sites located in the block with the ZrNiAl structure is
16 roughly 24 and 35% for the site with either trigonal planar or trigonal prismatic coordination
17 geometry, respectively. Meanwhile, in the block with TiNiSi structure which features atomic
18 square ladders with tetrahedral coordination of the atoms (albeit strongly distorted for Ge/Ag
19 position), the Ag occupancy at Ge/Ag position is lowest of 21%. The Ag preference for
20 trigonal prismatic coordination geometry, may at first glance be assigned to the bigger size of
21 the silver atom, but most likely its greater tendency for multicenter bonding compared to Ge
22 is also noteworthy since Ge remains the major element at this site. Reversibly, the sites with
23 trigonal planar or tetrahedral coordination geometries which imply more localized (covalent)
24 bonds are preferred by the smaller *p*-block elements. The bond distances (Table 3) in this
25 compound lie within reasonable ranges as estimated from standard metal-metal single bond
26 distances [24] giving the atomic radius of Ca (1.97 Å), Ge (1.22 Å), Ag (1.44 Å) and Al (1.25
27 Å).

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29 Interestingly, the fact that Ag atoms are present on all atomic sites within the anionic
30 framework also emphasizes the very peculiar atomic property of this noble metal. Indeed, Ag
31 can be found in intermetallic phases as either cation or anion, because its electronegativity is
32 similar to those of the late main group elements [25]. When the completely filled d^{10} -orbitals
33 are located in the valence band, well below the Fermi energy, the *s*- and *p*-orbitals which are
34 higher in the energy landscape can be used in covalent bond formations, thereby acting as
35 pseudo *p*-block elements [26-27].

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Conclusion.

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3 The solid solution $\text{Ca}_2\text{Al}_{0.67}\text{Ag}_{1.83}\text{Ge}_{1.50(1)}$ have been obtained by reaction the precursor
4 'Ca₃Ag₂Ge₂' with the Al metal flux. Its crystal structure was refined from single crystal
5 diffraction data, and represent as a rare example of compound with the NbCoB type structure.
6
7 This structural family is best described as an intergrowth between the ZrNiAl type (ordered
8 Fe₂P) and the TiNiSi type (ordered KHg₂) structures. Interestingly, while CaAlAg [27]
9 crystallizes with the MgZn₂ hexagonal Lave's phase structure, the structure of CaAlGe is still
10 unknown. However, Ca₃Al₂Ge₃ [28] is also structurally related to both the TiNiSi type and the
11 ZrNiAl type. Therefore, the investigation of the main driving forces which determine the
12 structure selection between the two parent structures is of special interest.
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References.

- [1] R. Nesper, *Prog. Solid State Chem.* **1990**, 20, 1.
- [2] G. J. Miller in *Structure and Bonding of Zintl Phases and Ions* (Ed.: S. Kauzlarich), VCH, New York, 1996.
- [3] H. Schäfer, B. Eisenmann, W. Müller, *Angew. Chem.* **1973**, 85, 742; *Angew. Chem. Int. Ed. Engl.* **1973**, 12, 694.
- [4] T. F. Fässler, S. Hoffmann, *Z. Kristallogr.* **1999**, 214, 722.
- [5] G.J. Miller, C.-S. Lee, W. Choe, in: G. Meyer, D. Naumann, L. Wesemann (Eds.), *Inorganic Chemistry Highlights*, Cea, Berlin, 2002.
- [6] S. Ponou, T. F. Fässler, L. Kienle, *Angew. Chem. Int. Ed.* **2008**, 47, 3999 - 4004.
- [7] D. C. Fredrickson, S. Lee, R. Hoffmann, *Angew. Chem.* **2007**, 119, 2004; *Angew. Chem. Int. Ed.* **2007**, 46, 1958.
- [8] F. Merlo, M. Pani, M. L. Fornasini. *J. Alloys Comp.* **1996**, 232, 289-295
- [9] F. Merlo, M. Pani, M. L. Fornasini. *J. Less-Common Met.* **1990**, 166, 319.
- [10] A. Mewis, *Z. Naturforsch.*, **1979**, 34B, 14-17.
- [11] B. Carlsson, M. Goelin, S. Rundqvist, *J. Solid State Chem.* **1973**, 8, 57-67.
- [12] A. Heerdmann, D. Johrendt, A. Mewis, *Z. Anorg. Allg. Chem.* **2000**, 626, 1393-1399.
- [13] S. Ponou, N. Müller, T. F. Fässler, U. Häussermann, *Inorg. Chem.* **2005**, 44, 7423.
- [14] (a) H.F. Franzen, M. Köckerling, *Prog. Solid State Chem.* **1995**, 23, 265. (b) X. Yao, G.J. Miller, H.F. Franzen, *J. Alloys Compd.* **1992**, 183, 7.
- [15] (a) S. Ponou, S. Lidin, *Z. Kristallogr. NCS*, **2008**, 223, 329-330. (b) S. Ponou, S. Lidin, D. C. Fredrickson, unpublished results.
- [16] B.Ya. Kotur, E.I. Gladyshevskii, *Sov. Phys. Crystallogr.* **1983**, 28, 271.
- [17] E. I. Gladyshevskii, P.I. Kipyakevich, O.I. Bodak, *Ukr. Fiz. Zh. (Russ. Ed.)* **1967**, 12, 447-453.
- [18] Oxford Diffraction, *CrysAlis CCD* **2006**, p171.31.2.
- [19] Oxford Diffraction, *CrysAlis RED* **2006**, p171.31.2.
- [20] G. M. Sheldrick, *Acta Crystallogr. Sect. A*, **1990**, 46, 467.
- [21] G. M. Sheldrick, *SHELXL-97, Program for the Solution and Refinement of Crystal structures*; University of Göttingen, Germany, 1997.
- [22] K. Brandenburg, *DIAMOND*, **1999**, Version 2.1c, Crystal Impact, Bonn, Germany.
- [23] P.I. Kripyakevich, Yu.B. Kuz'ma, Yu.V. Voroshilov, C. Brink-Shoemaker, D.P. Shoemaker, *Acta Crystallogr. Sect. B* **1971**, 27, 257-261.
- [24] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, **1960**.
- [25] A. S. Karpov, J. Nuss, U. Wedig, M. Jansen, *Angew. Chem.* **2003**, 115, 4966; *Angew. Chem., Int. Ed.* **2003**, 42, 4818.
- [26] M.-H. Whangbo, C. Lee, J. Köhler, *Angew. Chem.* **2006**, 118, 7627; *Angew. Chem. Int. Ed. Engl.* **2006**, 45, 7465.
- [27] J. Köhler, M.-H. Whangbo, *Chem. Mat.* **2008**, 20, 2751-2756.
- [28] M. Pani, F. Merlo, M. L. Fornasini. *Z. Kristallogr.* **2007**, 222, 218-225.
- [29] G. Cordier, H. Schaefer, *Z. Anorg. Allg. Chem.* **1982**, 490, 136-140.

Table 1. Selective details on X-ray single crystal data collection and refinement parameters

Chemical formula	Ca ₂ Al _{0.67} Ag _{1.83} Ge _{1.50(1)}
formula weight	404.71
crystal color and habit	silver metallic irregular block
temperature	293(2) K
crystal system/space group	Orthorhombic / <i>Pmmn</i> (no. 59)
unit cell parameters	$a = 20.505(1) \text{ \AA}$ $b = 4.3807(2) \text{ \AA}$ $c = 7.2211(3) \text{ \AA}$
unit cell Volume / Z	648.65(5) \AA^3 / 5
density calculated	5.180 g/cm ³
Abs. Coeff. (Mo K α)	17.377 mm ⁻¹ ($\lambda = 0.71073 \text{ \AA}$)
index range	$-29 \leq h \leq 25$, $-6 \leq k \leq 6$, $-10 \leq l \leq 7$
reflections collected	5604 ($R_\sigma = 0.0566$)
independent reflections	1236 ($R_{\text{int}} = 0.0643$)
F(000)	914
absorption correction	empirical
refinement method	Full-matrix least-squares on F ²
Parameters	55
Goodness-of-fit on F ²	1.073
observed reflns [$I > 2\sigma(I)$]	882
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0369$ / $*wR_2 = 0.0948$
final R indices (all data)	$R_1 = 0.0585$ / $*wR_2 = 0.0991$
extinction coefficient	0.0026(2)
residual map (e ⁻ / \AA^3)	2.262 / -1.625

*) $w = 1/[\sigma^2(F_o^2) + (0.0504 \cdot P)^2 + 0.4298 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2 \times F_c^2)/3$

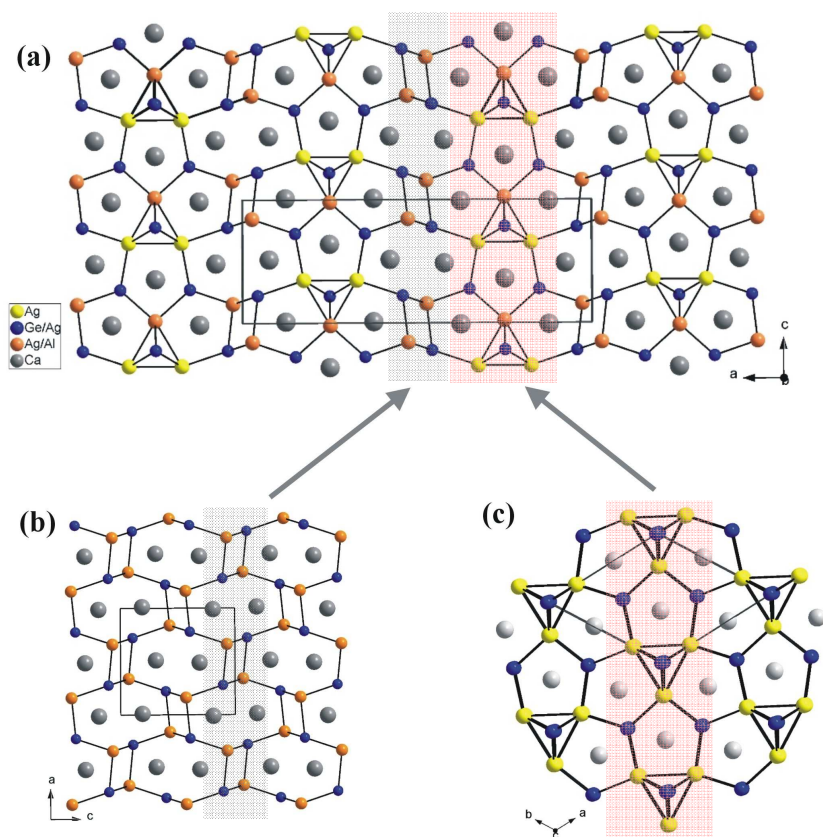
Table 2. Wyckoff Sites, Atomic Coordinates, and Equivalent Isotropic Displacement parameters. Standard deviations are indicated in brackets.

Atom	Wyck.	occupancy	x	y	z	U_{eq} (\AA^2)
Ag1	4f	1	0.32574(4)	¼	0.6534(1)	0.0206(2)
Ge2/Ag	4f	0.76(1)/0.24(1)	0.34983(4)	¼	0.2745(1)	0.0151(3)
Ge3/Ag	4f	0.79(1)/0.21(1)	0.45756(4)	¼	0.7776(1)	0.0174(3)
Ge4/Ag	2b	0.66(1)/0.34(1)	¾	¼	0.2172(2)	0.0223(4)
Ag5/Al	2a	0.54(1)/0.46(1)	¼	¼	0.0214(2)	0.0159(5)
Al6/Ag	4f	0.60(1)/0.40(1)	0.4730(1)	¼	0.1557(2)	0.0157(4)
Ca1	4f	1	0.5770(1)	¼	0.5143(2)	0.0109(3)
Ca2	4f	1	0.8759(1)	¼	0.0103(2)	0.0115(4)
Ca3	2b	1	¾	¼	0.6354(3)	0.0116(5)

Table 3. Selected interatomic distances for $\text{Ca}_2\text{Al}_{0.67}\text{Ag}_{1.83}\text{Ge}_{1.50(1)}$

Atom pair	Distances /Å	Atom pair	Distances /Å
Ag1– Ge2/Ag	2.780(1)	Ag5/Al – Ge2	2.744(1)
– Ge4/Ag	2.843(1) (×2)	– Ge4	2.787(1)
– Ge3/Ag	2.848(1)	– Ag1	3.078(1)
– Ag5/Al	3.078(1)		
– Ag1	3.106(2)	Ge2/Ag – Al6	2.667(1)
		– Ag5	2.744(1)
Ge3/Ag – Al6/Ag	2.657(1) (×2)	– Ag1	2.780(1)
– Al6/Ag	2.749(2)		
– Ag1	2.848(1)	Al6/Ag – Ge3	2.657(1) (×2)
		– Ge2	2.667(1)
Ge4/Ag – Ag5/Al	2.787(1) (×2)	– Ge3	2.749(1)
– Ag1	2.843(1) (×4)		
		Ca1 – Ge2 ⁱ	3.062(1)
Ca2 – Ge4 ⁱ	2.982(2)	– Ag ⁱⁱ	3.200(1)
– Al6 ⁱⁱ	3.194(2)	Ca3 – Ge4 ⁱ	3.050(3)
		– Ag5 ⁱⁱ	3.285(2)

ⁱ Shorter and ⁱⁱ Longer Ca – E bond (E = Ge, Ag, Al)



33 **Figure 1.** The structure of the (a) $\text{Ca}_2\text{Ag}_{1.83}\text{Al}_{0.67}\text{Ge}_{1.50(1)}$ viewed down the b -axis and showing
34 two different alternating blocks (highlighted by the rectangles) that are fragments with either
35 (b) the TiNiSi type or (c) the ZrNiAl type structures.
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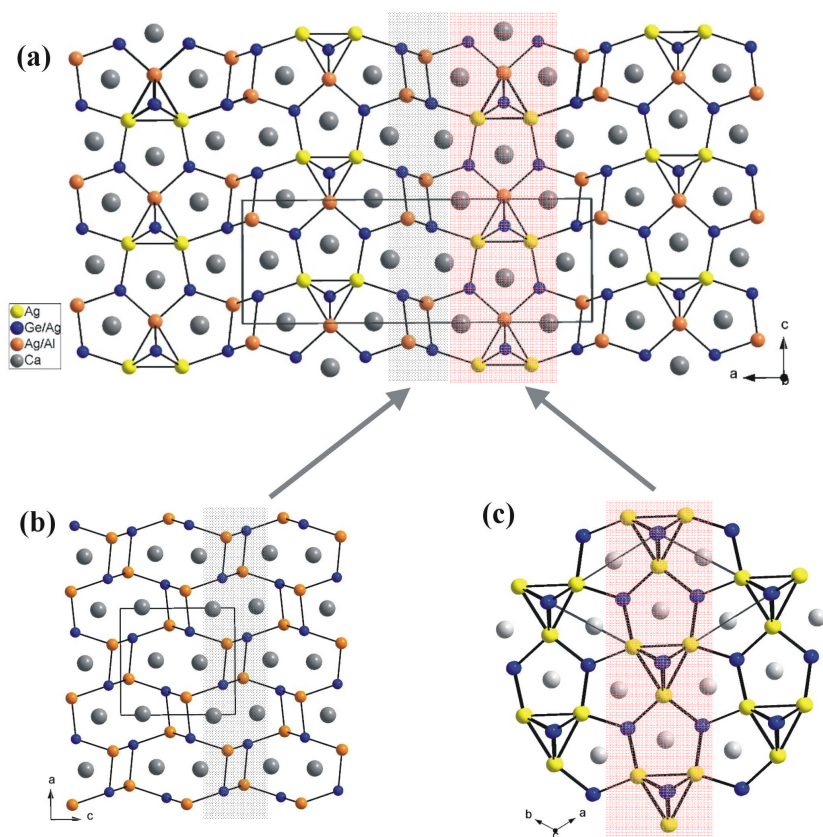


Figure 1. The structure of the (a) $\text{Ca}_2\text{Ag}_{1.83}\text{Al}_{0.67}\text{Ge}_{1.50(1)}$ viewed down the b -axis and showing two different alternating blocks (highlighted by the rectangles) that are fragments with either (b) the TiNiSi type or (c) the ZrNiAl type structures.