Refinement of the crystal structure of monocalcium dialuminide digermanide, $\text{Ca}[\text{Al}_2\text{Ge}_2]$

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Abstract

Al_2CaGe_2 , trigonal, $P\bar{3}m1$ (No. 164), $a = 4.1759(3)$ Å, $c = 7.1767(4)$ Å, $V = 108.4$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.045$, $wR_{\text{ref}}(F^2) = 0.080$, $T = 293$ K.

Source of material

Exploring the Ca–Al–Ge system to get compounds isostructural to $\text{Eu}_3[\text{Ga}_4\text{Ge}_6]$ [1,2] or $\text{Eu}[\text{Ga}_4\text{Ge}_6]$ [2,3] we obtained single crystals of $\text{Ca}[\text{Al}_2\text{Ge}_2]$, which can be prepared by high-frequency induction melting (argon atmosphere) of the corresponding elements (Ca: 99.9 %, Al: 99.999%, Ge: 99.9999%). The compound (light-gray with metallic luster) is unstable in air.

Experimental details

The unit cell parameters were determined from the least-squares refinement using the 2θ values of 28 reflections ($24^\circ < 2\theta < 96^\circ$; powder data, $\lambda(\text{CuK}\alpha_1) = 1.540598$ Å; LaB_6 standard, $a = 4.15695(6)$ Å).

Discussion

$\text{Ca}[\text{Al}_2\text{Ge}_2]$ was only characterized from X-ray powder data so far [4]. In the present study, we report the crystal structure refinement of the title compound by using single-crystal data.

$\text{Ca}[\text{Al}_2\text{Ge}_2]$ crystallizes in the $\text{Ca}[\text{Al}_2\text{Si}_2]$ -type of structure (Pearson symbol $hP5$) [4]. The structure contains double layers of puckered $\text{Al}_{3/3}\text{Ge}_{3/3}$ hexagons parallel to the (001) plane, which are held together by Ca^{2+} cations located in between. In the double layers, the Al and Ge atoms are four-fold and three-fold bonded, respectively. The Al–Ge bond distances in the title compound (2.534(1) Å, 2.635(3) Å) are very similar to those in the analogous compounds $\text{Yb}[\text{Al}_2\text{Ge}_2]$ [5,6] (2.533 Å, 2.635 Å [5]) and $\text{Eu}[\text{Al}_2\text{Ge}_2]$ [6] (2.548 Å, 2.634 Å).

$\text{Ca}[\text{Al}_2\text{Ge}_2]$ and analogous compounds of the alkaline earth metals are considered as Zintl phases [7]. Thus, the title compound can be crystal chemically written as: $\text{Ca}^{2+}_\infty[\text{Al}_2\text{Ge}_2]^{2-}$.

Table 1. Data collection and handling.

Crystal:	light-grey metallic fragment, size $0.07 \times 0.10 \times 0.18$ mm
Wavelength:	Ag $K\alpha$ radiation (0.56087 Å)
μ :	79.57 cm^{-1}
Diffractionmeter, scan mode:	Stoe IPDS, 180 exposures, $\Delta\varphi = 1^\circ$
$2\theta_{\text{max}}$:	54.82°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	1827, 227
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 188
$N(\text{param})_{\text{refined}}$:	9
Programs:	SHELXL-97 [8], ATOMS [9]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	1a	0	0	0	0.0131(7)	U_{11}	0.011(1)	$U_{11}/2$	0	0
Al	2d	1/3	2/3	0.6293(4)	0.0114(7)	U_{11}	0.014(1)	$U_{11}/2$	0	0
Ge	2d	1/3	2/3	0.2622(2)	0.0115(3)	U_{11}	0.0103(4)	$U_{11}/2$	0	0

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