Z. Kristallogr. NCS **217** (2002) 161–162

Crystal structure of cerium silver phosphide (1:1.08:1.90), $CeAg_{1.08}P_{1.90}$

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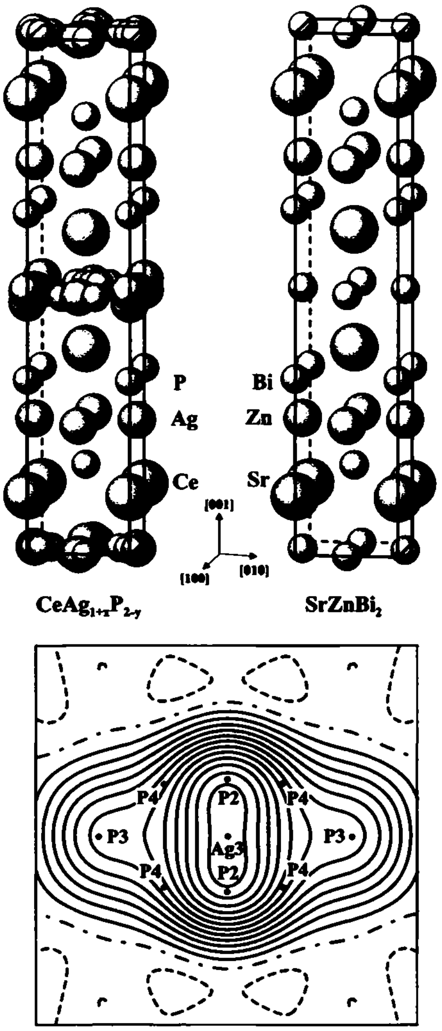
Received March 25, 2002, accepted and available on-line April 10, 2002; CSD-No. 409613



Abstract

$Ag_{2.16}Ce_2P_{3.80}$, tetragonal, *I4/mmm* (No. 139), $a = 4.0037(2)$ Å, $c = 20.435(1)$ Å, $V = 327.6$ Å^3, $Z = 2$, $R_{gt}(F) = 0.049$, $wR_{obs}(F) = 0.049$, $T = 293$ K.

Source of material

Initial components in atomic ratio 1:1:2 were mixed, pressed into pellets and sealed together with 0.15 g of iodine into evacuated silica ampoule with the length of 25 cm. Total mass of the sample was about 1 g. A two-zone heating with the temperatures of 1070 K and 870 K on the "hot" and "cold" end of the ampoule, respectively, was used for the synthesis. The sample was kept at those conditions for 100 h and slowly cooled to room temperature during 24 h. Plate-like single crystals with maximum dimensions of about 0.1 mm were obtained on the "cold" end of the ampoule. The EDX analysis of the synthesized compound revealed the composition $Ce_{1.00(1)}Ag_{1.06(1)}P_{1.85(2)}$.

Experimental details

The lattice parameters were obtained from X-ray powder data (Huber Image Plate Guinier Camera, $CuK_{\alpha1}$ radiation, λ = 1.540562 Å).

Discussion

Formation of a ternary phosphide with approximate composition $CeAgP_2$ was observed during investigation of the phase diagram of the Ce–Ag–P system. Preliminary single crystal investigation have showed tetragonal body-centered unit cell with lattice parameters $a = 4.0$ Å and $c = 20.3$ Å [1].

So far as symmetry and lattice constants of the title compound were similar to those for earlier known compound $CeCu_{1.09}P_{1.87}$ [2], the space group *I4/mmm* was chosen for crystal structure determination. The atomic coordinates of Ce, Cu1 and P1 were used as initial for the Ce, Ag1 and P1 atoms for crystal structure refinement. On this stage, the difference Fourier map revealed additional maximum at the point 0 0 1/2 (Ag2) and very complex distribution of the electronic density around the position 0 1/2 1/2 (figure, lower part) which could be described using at least four partially occupied crystallographic sites (Ag3, P2, P3). Atomic decoration of these positions was made according to the following considerations. We prefer the P2 and P4 positions to be occupied by phosphorus atoms because their shortest interatomic distances to Ce atoms, *d*(Ce—P2) = 2.87 Å and *d*(Ce—P4) = 2.89 Å, are to short for the distances Ce—Ag ($r_{Ce} = 1.83$ Å, $r_{Ag} = 1.44$ Å) and are more similar to the *d*(Ce—P1) = 3.003 Å with well defined ligand. For the same reasons, the Ag2 position should be occupied by silver: *d*(Ce—Ag2) = 3.51 Å. This leads to the obvious occupation of the P3 site by phosphorus with the reasonable distance of 2.67 Å to Ag2. The remaining position Ag3 should be occupied by silver in order to keep the Ag/P ratio in the structure and shows a relatively short distance to the cerium atom (3.054 Å). The total composition of the structure from the X-ray data $CeAg_{1.08(2)}P_{1.89(40)}$ reflects well the results of EDX analysis. The large e.s.d. for phosphorus content can not be improved because of the extreme difficulties in the refinement of the strongly correlated atomic parameters for Ag3 and P2–P4 positions. The structure of $CeAg_{1.08}P_{1.90} = CeAg(P_{0.95}Ag_{0.02})_2Ag_{0.04}$ is a distorted and partially filled variant of the $SrZnBi_2 = SrZnBi_2\square_{0.0}$ structure type [3] (figure, upper part). The environments of the Ce, Ag1 and P1 atoms (CN = 20, 12 and 9, respectively) are similar to the coordination of corresponding atoms in the $CeCu_{1.09}P_{1.87}$ structure.

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Table 1. Data collection and handling.

Crystal:	metallic lustre, platelet, size 0.04 × 0.14 × 0.15 mm
Wavelength:	Ag K_α radiation (0.56088 Å)
μ:	106.6 cm^{-1}
Diffractometer, scan mode:	STOE IPDS, 300 exposures, $\Delta\phi = 0.8°$
$2\theta_{max}$:	56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3839, 816
Criterion for F_{obs}, $N(hkl)_{gt}$:	$F_{obs} > 4\,\sigma(F_{obs})$, 240
$N(param)_{refined}$:	25
Programs:	WinCSD [4], ATOMS [5]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{iso}
Ag(2)	4*e*	0.045(9)	0	0	0.511(2)	0.008(9)
Ag(3)	4*c*	0.034(9)	1/2	0	1/2	0.003(10)
P(2)	8*i*	0.15(3)	1/2	0.074(8)	1/2	0.005(6)
P(3)	8*j*	0.14(2)	0.34(1)	0	1/2	0.006(5)
P(4)	16*l*	0.08(2)	0.43(1)	0.07(1)	1/2	0.004(7)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ce	4*e*	0	0	0.11286(8)	0.0047(5)	U_{11}	0.0091(7)	0	0	0
Ag(1)	4*d*	1/2	0	1/4	0.0096(6)	U_{11}	0.0048(8)	0	0	0
P(1)	4*e*	0	0	0.3381(3)	0.007(2)	U_{11}	0.006(3)	0	0	0

Acknowledgments. The authors are thanking to Mrs. M. Eckert for metallographical preparation. R. D. acknowledges gratefully the financial support of the Max Planck Society.

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