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Structure and Electrical Transport Property of a Silicopnictide ZrCuSiP

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A silicopnictide ZrCuSiP was prepared through the reaction between ZrCuSi alloy and red phosphor in evacuated quartz ampoules. Rietveld analysis of the powder X-ray diffraction pattern revealed that ZrCuSiP has the ZrCuSiAs-type structure (*P*4/*nmm*) with the lattice constants of $a = 0.35671(1)$ nm and $c = 0.94460(4)$ nm. Electrical resistivity measurements at temperatures from 5 to 300 K indicated that ZrCuSiP is a metallic compound. © 2002 Elsevier Science (USA)

INTRODUCTION

Silicochalcogenides and silicopnictides with a composition of TMX (for chalcogenides: T = Zr or Hf; M = Si or Ge; X = O, S, Se or Te, and for pnictides: T = Nb; M = Si or Ge; X = As or Sb) have been investigated from the viewpoint of structural chemistry (1–3). They have the PbFCl-type structure (*P*4/*nmm*, No. 129), where the atomic layers are stacked alternatively in a sequence of $[M_2–T–X–X–T–M_2]$ along the *c*-axis (Fig. 1). The layered nature of the PbFCl-type structure suggested the existence of a stacking variant formed by the insertion of atomic layers into the inter-layer gaps. This kind of structure has been actually found in ZrCuSiAs (4). The structure of ZrCuSiAs is derived from the PbFCl-type structure by the insertion of Cu atomic layers into the intervals between the $X–X$ layers (Fig. 1). A number of quaternary compounds with ZrCuSiAs have been reported up to now (5). This paper reports the preparation and the structural determination of a novel silicopnictide ZrCuSiP. A typical TMX-type silicochalcogenide ZrSiS was prepared as a reference to ZrCuSiP, and the electric transport properties of both the compounds are presented.

EXPERIMENTAL

Stoichiometric amounts of the pure elements Zr (99.9%), Cu (99.9%), and Si (99.999%) were melted together using an arc furnace under pure Ar atmosphere. The obtained matte silver buttons were ground into fine powder and sealed in an evacuated quartz ampoule with a stoichiometric amount of red phosphor chunk (99.99%). The bottom of the quartz ampoule was cooled by dipping in a water bath in order to prevent the evaporation of phosphor during the sealing procedure. The quartz ampoule was placed in a muffle oven and heated in the following sequence: up to 600°C for 24 h, kept at 600°C for 24 h, 24 h up to 850°C, kept at 850°C for 24 h and quenched in a water bath. After checking that there remains no residual P, the resulting grayish slug was taken out of the ampoule and ground to fine powder. The powder was pressed into small pellets using a stainless-steel piston cylinder, sealed in an evacuated quartz ampoule and sintered at 850°C for 12 h. The sintered specimens were so stable against both the humidity and the oxygen, that no apparent change was observed in XRD (X-ray diffractometry) patterns after keeping the specimens in the open air for about half a year.

ZrSiS was prepared by a similar procedure for ZrCuSiP. Stoichiometric amounts of the pure elements Zr and Si were melted by an arc furnace, and the ZrSi buttons were ground to fine powder. The ZrSi powder was sealed in an evacuated quartz ampoule with a stoichiometric amount of S chunk, and was heated in the same sequence as that for ZrCuSiP. Sintering of the ZrSiS powder was carried out at 850°C for 12 h in an evacuated quartz ampoule. XRD measurements were performed on the powdered specimens using a RINT 2100 diffractometer (Rigaku Co. Ltd, Cu*K*α radiation). Measurements of the electric resistivity of ZrCuSiP and ZrSiS were performed using a conventional four-probe method at temperatures from 5 to 300 K.

RESULTS AND DISCUSSIONS

Figure 2 shows the observed XRD pattern of ZrCuSiP and the calculated one, together with the difference curve.

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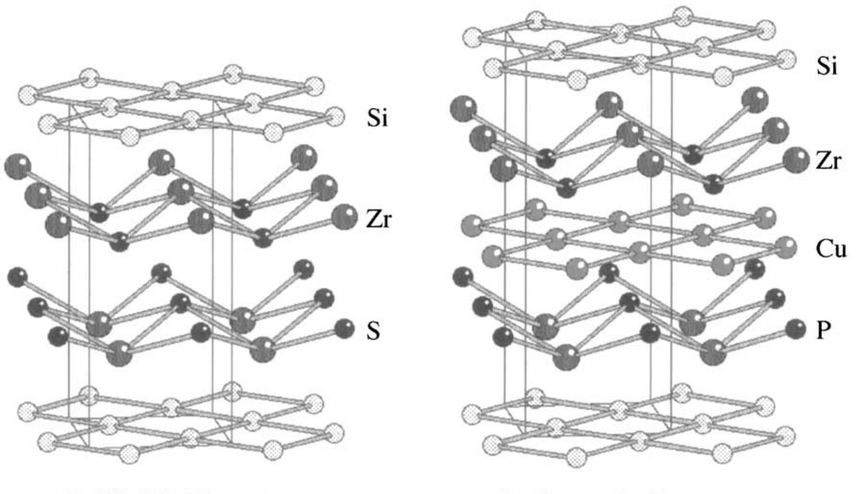

ZrSiS (PbFCl type) ZrCuSiP (ZrCuSiAs type)

FIG. 1. Crystal structures of ZrSiS (PbFCl-type structure) and ZrCuSiP (ZrCuSiAs-type structure).

Crystallographic parameters were obtained by a computational least-squares refinement using the computation program RIETAN-2000 (6), assuming that ZrCuSiP has the same type of structure as ZrCuSiAs: space group *P*4/*nmm*, the lattice parameters $a = 0.35671(1)$ nm and $c = 0.94460(4)$ nm, $R_{\mathrm{wp}} = 6.92\%$, $R_{\mathrm{p}} = 5.11\%$, $R_{\mathrm{F}} = 4.33\%$, goodness-of-fit $(S) = 1.40$. It is concluded that ZrCuSiP is isostructural with ZrCuSiAs, from the low amplitudes of the reliability factors. The structural data of ZrCuSiP are summarized in Table 1.

Figure 3 shows the resistivities of ZrCuSiP and ZrSiS as functions of temperature. The resistivity curves of both the compounds show a monotonous increase with increasing temperature. This indicates that there is no finite energy gap in the energy bands of either ZrCuSiP or ZrSiS, i.e., both systems are metallic. The electrical properties of compounds with PbFCl-type structure have been discussed in connection with the valence. Several PbFCl-type compounds with normal valence, ZrOS ($\mathrm{Zr}^{4+}\mathrm{O}^{2-}\mathrm{S}^{2-}$) (7), ThOS ($\mathrm{Th}^{4+}\mathrm{O}^{2-}\mathrm{S}^{2-}$) (8) and UOS ($\mathrm{U}^{4+}\mathrm{O}^{2-}\mathrm{S}^{2-}$) (9) are insulators. On the other hand, assumptive valence formula for the TMX compounds and ZrCuSiAs have been proposed by Johnson and Jeitschko: TMX-silicochalcogenides $= T^{4+}[M^{2-}]X^{2-}$ (T = Zr or Hf; M = Si or Ge: X = O, S, Se or Te), TMX-silicopnictides $= \mathrm{Nb}^{5+}[M^{2-}]X^{3-}$ (M = Si or Ge; X = As or Sb) and ZrCuSiAs $= \mathrm{Zr}^{4+}\mathrm{Cu}^{1+}[\mathrm{Si}^{2-}]\mathrm{As}^{3-}$ (3, 4).

According to the hypothetical valence formula, the metallic behavior observed in the transport properties of

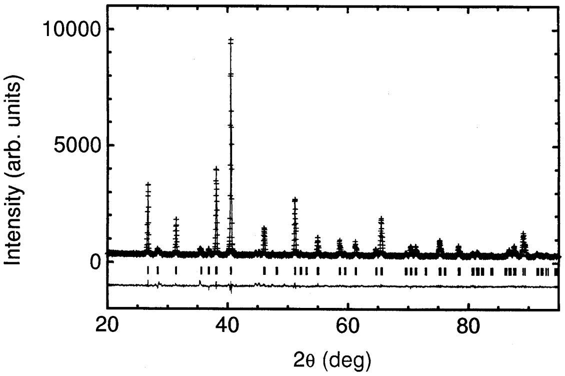

FIG. 2. Result of the Rietveld refinement for ZrCuSiP (XRD intensity vs $2-\theta$, Cu$K\alpha$). The experimental data and the calculated profile are represented by crosses and solid curves, respectively. The vertical markers represent the calculated Bragg angles. The difference curve is indicated at the bottom of the figure.

TABLE 1
Results of the Rietveld Refinement for ZrCuSiP

Space group
*P*4/*nmm* No. 129
Lattice constants
$a = 0.35671(1)$ nm, $c = 0.94460(4)$ nm; $V = 0.12019(4)$ nm^3

Atomic coordinates

Atom	Position	x	y	z
Zr	2*c*	$\frac{1}{4}$	$\frac{1}{4}$	0.2269(2)
Cu	2*b*	$\frac{1}{4}$	$\frac{3}{4}$	0.5
Si	2*a*	$\frac{1}{4}$	$\frac{3}{4}$	0
P	2*c*	$\frac{1}{4}$	$\frac{1}{4}$	0.6721(5)

Note. Isotropic thermal parameters (B) were fixed to be 0.003 nm^2. The occupancy of each atom was fixed to be 1.0.

ZrCuSiP and ZrSiS can be understood as a result of the unusual valence of M (= Si or Ge).

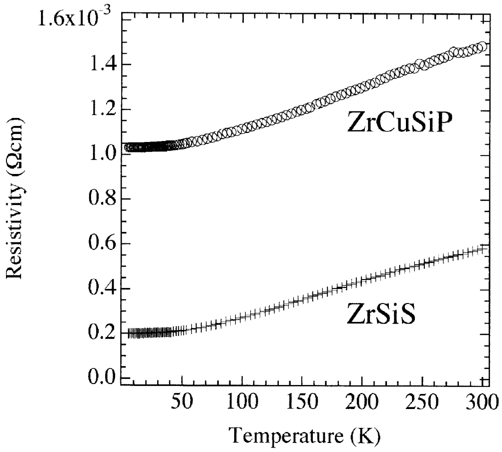

FIG. 3. Temperature dependence of the resistivities for ZrSiS and ZrCuSiP. The crosses and open circles correspond to ZrSiS and ZrCuSiP, respectively.

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