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ARTICLE

Systematic study of the $UNiX_2$ ternary compounds (X=C, Si, Ge)

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We attempted to grow $UNiX_2$ ternary compounds by the arc melting method. $UNiC_2$ and $UNiGe_2$ may not melt congruently because both compounds contain impurity phases. $UNiC_2$ crystallizes into the tetragonal $UCoC_2$-type structure with space group *P4/nmm*, the annealed sample consists of $UNiC_2$ and U_2NiC_3 as the main and secondary phases, respectively. The lattice constants were obtained to be a = 3.512 Å, c = 7.339 Å. $UNiGe_2$ also contains two phases. We assumed that primary phase is isostructural to $UNiSi_2$ that crystallizes into the orthorhombic $CeNiSi_2$-type structure with the space group of *Cmcm*. On the other hand, it is reasonable to assume that UNi_2Ge_2 exists in the compound as secondary phase. The unit cell volume tends to increase as increasing the anomic number of X (C, Si, Ge). It comes from the fact that the atomic radius of X becomes larger as the atomic number becomes larger.

Keywords: uranium; nickel; ternary compounds; arc-melting method; X-ray powder diffraction

1. Introduction

Intermetallic compounds including Ce or U atoms have been investigated extensively because these compounds give important information for studying the role of strong electron correlations in metallic systems [1-4]. In these compounds, the ferromagnetic/ antiferromagnetic interaction and Kondo effect compete with each other.

The ternary compounds $CeTX_2$ (T = transition metal and X = Si, Ge, Sn) form a large family having the orthorhombic $CeNiSi_2$-type layered structure with space group *Cmcm*, and are constructed from deformed fragments of the $CeGa_2Al_2$ and α-$ThSi_2$ structures [5]. The lattice parameter along *b*-axis is extremely large compared to those along *a*- and *c*- axes, and the highly anisotropic magnetic property is expected. Indeed, these compounds have drawn considerable interest of a great variety of magnetic behaviors [6-8].

$UNiSi_2$ also crystallizes in orthorhombic $CeNiSi_2$-type layered structure, and is a ferromagnet at T_C= 95 K [9, 10]. Single crystals can be grown by Czochralski pulling method because $UNiSi_2$ melts congruently. The large anisotropic behavior is observed in the measurement of the magnetization of $UNiSi_2$ single crystal in the low-temperature ferromagnetic phase. The easy magnetization direction is in the *ac* plane. From the result of the magnetic susceptibility along the *ac* plane, the effective magnetic moment is obtained to be $\mu_{eff} \sim 2.47\mu_B$ which is smaller than the value expected for the free U^{4+} or U^{3+} ions. It may come from highly anisotropic magnetic property of $UNiSi_2$ [11].

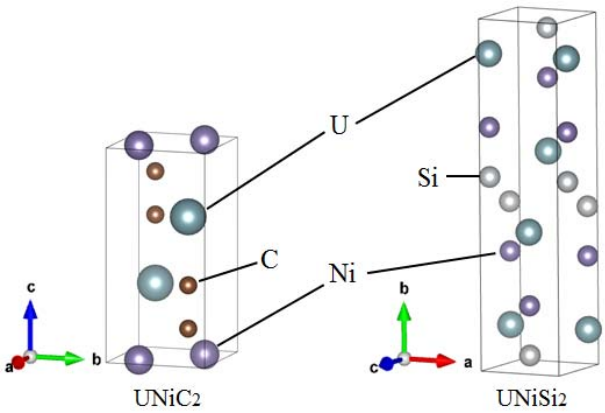

Figure 1. Crystal structure of $UNiC_2$ and $UNiSi_2$.

On the other hand, there are few reports about $UNiX_2$ compounds except for $UNiSi_2$. Gerss *et al.*, determined that $UNiC_2$ crystallizes into the tetragonal $UCoC_2$-type structure with space group *P4/nmm* [12]. So, there may be much interest in the magnetic and electronic properties of $UNiC_2$ which is one of uranium compounds without a center of inversion. However, the physical properties of $UNiC_2$ such as magnetic susceptibility and heat capacity have not been reported yet. Recently Molčanová *et al*. synthesized $UNiGe_2$ by splat cooling, but the crystal structure has been unknown yet [13]. As for $UNiSn_2$, there have not been reported at all. In the present work, we report on the synthesis of a ternary uranium compound $UNiX_2$.

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2. Experimental details

Polycrystalline samples of $UNiX_2$ (X=C, Ge) were synthesized by arc melting with a stoichiometric composition in an Ar gas atmosphere. To improve homogeneity, the samples were turned over and re-melted several times. The samples were subsequently sealed in an evacuated quartz tube and annealed. The samples of $UNiC_2$ and $UNiGe_2$ were annealed at 1100 °C for 7 days and 840 °C for 7 days, respectively. The samples were characterized by X-ray powder diffraction experiments using a Rigaku MiniFlex II diffractometer with Cu-Kα radiation. The simulation of the powder diffraction pattern and the visualization of the crystal structure were carried out by the VESTA 3 program [14].

3. Results and discussion

3.1. $UNiC_2$

Figure 2 shows the X-ray diffraction pattern of $UNiC_2$ for as-grown sample and annealed one. Almost all Bragg peaks became sharp after annealing. We indexed the Bragg peaks as the tetragonal type structure. The lattice constants were obtained to be a = 3.512 Å, c = 7.339 Å. These results are consistent with those of the previous report [12]. The result of the simulation also support that the main phase is the tetragonal $UCoC_2$-type structure with space group *P4/nmm*. On the other hand, small unknown peaks appear in the annealed sample and can be indexed as the X-ray diffraction pattern of U_2NiC_3 [15]. In preliminary measurement of dc magnetic susceptibility of annealed sample, two magnetic phase transitions are observed at 57 K and 140 K for annealed sample.

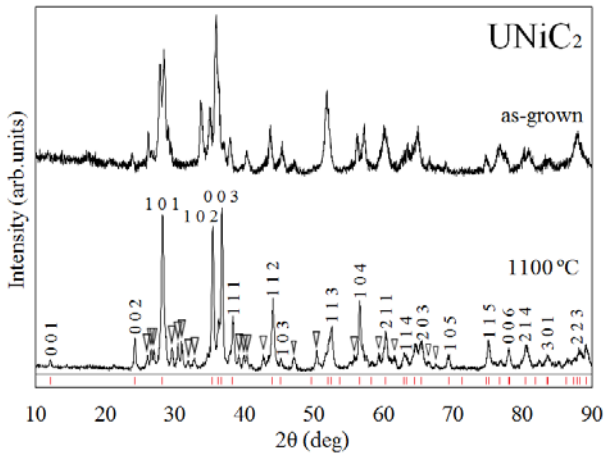

Figure 2. X-ray powder diffraction pattern of $UNiC_2$. Symbols (▽) show unknown peaks. The ticks correspond to 2θ Bragg positions.

Taking account that U_2NiC_3 is an antiferromagnet at T_N = 52 K [16], the sample may consist of $UNiC_2$ dominant phase of the tetragonal structure and U_2NiC_3 secondary phase.

3.2. $UNiGe_2$

Figure 3 shows the X-ray diffraction pattern of $UNiGe_2$ for as-grown sample, and annealed one. Bragg peaks became sharp after annealing. Here we assumed that $UNiGe_2$ has the same crystal structure as $UNiSi_2$ and indexed the Bragg peaks as the orthorhombic $CeNiSi_2$-type structure with the space group of *Cmcm*. Because of the preferred orientation of powdered samples, the relative relations of peak-intensities between several Bragg peaks in the diffraction pattern are different from those in the simulation. But, as shown in Figure 3, almost all peaks correspond to 2θ Bragg positions calculated by the simulation. The lattice constants were obtained to be a = 3.993 Å, b = 16.26 Å, c = 4.094 Å. However, some peak expected to appear from the simulation are missing in the diffraction pattern. It may come from the fact that several Bragg peaks of the experimental result are hidden in the background.

On the other hand, Molčanová *et al*. also synthesized $UNiGe_2$ by splat cooling. They found a new phase with some tetragonal structure [13]. It is unknown whether the new phase is same as the one we found because no experimental data has been described in their report.

Several unknown peaks are also observed in the X-ray diffraction pattern, and may correspond to the diffraction of UNi_2Ge_2 as a secondary phase [17]. Similar behavior is also described in the recent report of Molčanová *et al*. [13]. Recently we report on the magnetic characterization of $UNiGe_2$ and the magnetic susceptibility shows the large peak at 45 K and the small one at 65 K [18]. We associate the first transition with dominant magnetic phase of $UNiGe_2$ while the second one may correspond to T_N of UNi_2Ge_2 [17].

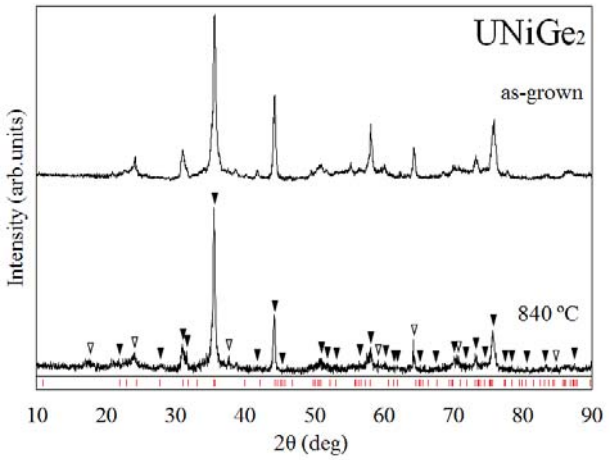

Figure 3. X-ray powder diffraction pattern of $UNiGe_2$. Symbols (▼) and (▽) show $UNiGe_2$ peaks and unknown peaks. The ticks correspond to 2θ Bragg positions.

4. Summary

Finally, we summarize the lattice parameters for the $UNiX_2$ compounds in **Table 1**. The unit cell volume tends to increase as increasing the anomic number of X (C, Si, Ge). It comes from the fact that the atomic radius

of X becomes larger as the atomic number becomes larger. Although we tried to synthesize $UNiSn_2$ by arc melting, our result of the powder X-ray diffraction indicated the presence of UNi_2Si_2 phase and $U_3Ni_3Sn_4$ one [19, 20].

$UNiC_2$ and $UNiGe_2$ may not melt congruently because both compounds contain two phases. Although we assumed that $UNiGe_2$ crystallizes into the orthorhombic structure in our preliminary study, it is needed to grow single crystal to verify our assumption. Further experiments are in progress to improve quality of samples and to investigate magnetic property.

Table 1. The lattice parameters for the $UNiX_2$ compounds.

	$UNiC_2$	$UNiSi_2$ [11]	$UNiGe_2$
a (Å)	3.512(1)	4.010	3.993(8)
b (Å)		16.10	16.26(6)
c (Å)	7.339(4)	4.009	4.094(3)
V (Å ^{3})	90.5(1)	258.8	266(1)

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