Preparation of 1T-phase of $Ta_{1\text{-}X}Ir_XS_2$ System

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(Received December 9, 1996)

The 1T-phase in the TaS_2-IrS_2 system is prepared in the temperature range from 800 °C to 1000 °C. The 1T-phase is stable in the composition range between 0% and 50% IrS_2 at 1000 °C. This 1T-phase is the compound of a new concept of the "electron-excess-1T", judging from the number of valence electrons of the metal atoms.

The layered transition metal dichalcogenides are of great interest in terms of exotic electronic properties such as the charge density wave.[1] The structures of those compounds are related to the number of valence electrons of constituent transition metal atoms.[2] IV_a-, V_a-, and VI_a-transition metal dichalcogenides form the layered structure. The IV_a-transition metal dichalcogenides crystallize into the CdI_2 structure, the VI_a-transition metal dichalcogenides crystallize into the $2H_b$-MoS_2 structure and 3R-MoS_2 structure. The V_a-transition metal dichalcogenides crystallize into the $2H_a$-NbS_2 structure or CdI_2 structure, depending on temperatures. The CdI_2 structure called "1T-structure" is observed on the solid solutions of IV_a- and V_a-transition metal dichalcogenides. This means that the 1T-structure is stable for the metal atom with the 4-5 valence electrons. For TaS_2, five polytypes, 1T, $2H_a$, 3R, $4H_b$, and 6R, have been reported by R.Brouwer and F.Jellinek,[3] L.E.Conroy and K.R.Pisharody,[4] F.Jellinek,[5] and DiSalvo *et al.*[6] IrS_2 crystallizes into the pyrite-like IrS_2 structure.[7] However, in the TaS_2-IrS_2 system, the 1T-structure is observed on the composition range between 0% and 50% IrS_2, notwithstanding the number of valence electron is 5-7. The 1T-$Ta_{1\text{-}X}Ir_XS_2$ compound is the compound of a new concept of the "electron-excess-1T", judging from the number of valence electrons of the constituent transition-metal atoms.

The starting materials, Ta-powder (99.9% pure, Mitsuwa), Ir-powder (99.9% pure, Mitsuwa), and S-blocks (99.9999% pure, Waco) were sealed in an evacuated quartz glass ampoule. The ampoule was heated at 1000 °C for 3 days to complete the reaction and quenched into water. The sample powder was processed with an acetate glue to avoid the preferred orientation on the observed powder X-ray diffraction pattern. After drying and grinding, the sample was mounted on a sample holder and the X-ray diffraction of the processed powder was measured. Data were collected by the fixed-time-step scan method with the 2θ step of 0.05° in the 2θ angular from 10° to 80°. The crystal structure parameters were refined by using Rietveld method with the computer program, RIETAN.[8] The X-ray photoelectron spectra of the core levels were measured on the pressed samples by using a Shimazu ESCA 850 spectrometer. MgKα radiation was used for the X-ray source and the FWHM was 1.0 eV. The measurements were repeated 100 times for each sample. The energy values of spectra were calibrated in each measurement with the carbon $1s_{1/2}$ peak (285 eV).

Table 1. d-Spacings of 1T-$Ta_{1\text{-}X}Ir_XS_2$

	X=0.1		X=0.3		X=0.5	
hkl	$d_{obs.}$/Å	$d_{cal.}$/Å	$d_{obs.}$/Å	$d_{cal.}$/Å	$d_{obs.}$/Å	$d_{cal.}$/Å
001	6.009	5.935	5.980	5.942	5.972	5.933
002	2.975	2.964	2.975	2.965	2.976	2.958
100	2.937	2.928	2.918	2.911	2.922	2.914
101	2.630	2.625	2.620	2.614	2.621	2.614
102	2.085	2.083	2.081	2.077	2.079	2.076
003	1.977	1.974	1.980	1.977	1.974	1.972
110	1.690	1.686	1.682	1.681	1.684	1.682
103	1.637	1.636	1.636	1.635	1.633	1.633
111	1.624	1.622	1.617	1.617	1.618	1.618
004	1.481	1.481	1.484	1.483	1.481	1.479
200					1.454	1.457
112			1.462	1.462		
201	1.418	1.418	1.414	1.414	1.415	1.415
104	1.320	1.320	1.319	1.321	1.317	1.319
202	1.307	1.309	1.306	1.306	1.310	1.310
113	1.282	1.282	1.281	1.281	1.278	1.280
	a=3.373(1)/Å c=5.923(0)/Å		a=3.362(1)/Å c=5.930(0)/Å		a=3.364(1)/Å c=5.916(0)/Å	

The crystal structure of the 1T-phase, $Ta_{1\text{-}X}Ir_XS_2$ is confirmed. For instance, the lattice parameters of the hexagonal lattice of the $Ta_{0.9}Ir_{0.1}S_2$ are a=3.373 Å and c=5.923 Å. The miller indices and the d-spacings are listed in Table 1. We consider that the Ta-atoms and the Ir-atoms of $Ta_{1\text{-}X}Ir_XS_2$ randomly occupy the same sites. The observed, the calculated, and the difference profiles of the X-ray diffraction of $Ta_{0.7}Ir_{0.3}S_2$ are shown in Figure 1. The final R_I-value is 1.22%. This result suggests that the structure of this phase is the CdI_2 structure. The 1T single phase can be obtained for the $Ta_{1\text{-}X}Ir_XS_2$ of the X-value less than 0.5.

The oxidation states of the Ta-atom, Ir-atom, and S-atom of 1T-$Ta_{1\text{-}X}Ir_XS_2$ are estimated by chemical shift of the each atom. The binding energy values of 1T-$Ta_{1\text{-}X}Ir_XS_2$ are listed in Table 2. The reference values of energies for Ta metal:$5d_{5/2}$, Ir metal:$4d_{5/2}$, Ir metal:$4f_{7/2}$, and S2p are 226.4 eV,[9] 296.3 eV,[9] 60.75 eV,[9] and 164.25 eV[10] respectively. The energy value of $Ir4d_{5/2}$ is about 298 eV and is shifted toward the high energy side by about 2 eV. The energy of $Ir4f_{7/2}$ is about 62 eV. It is known that the energy values of $Ir4f_{7/2}$ in K_3IrBr_6 and K_3IrCl_6 are 61.8 eV[11] and 62.5 eV.[12] The oxidation state of Ir atom in those compounds is the 3+ state. Therefore, we consider that the Ir atom in $Ta_{1\text{-}X}Ir_XS_2$ is the 3+ state. As the oxidation state of chalcogen atoms in the 1T-structure is considered as -2, four electrons transfer from the d-band of the metal to the p-band of S. The Ir^{3+} ion favors the d^6 low spin state of the octahedral environment and three electrons always transfer to the p-band of S. The valence of the Ta-atom is varied in the range from 4 to 5. This situation is written in the next formulae, (1), (2), and (3),

$$xIr \rightarrow xIr^{3+} + 3xe^- \qquad (1)$$

$$(1-x)Ta \rightarrow (1-x)Ta^{p+} + p(1-x)e^- \qquad (2)$$

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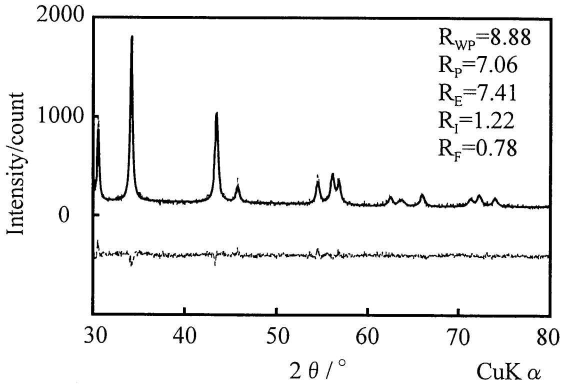

Figure 1. Powder X-ray diffraction profile of 1T-$Ta_{0.7}Ir_{0.3}S_2$
dotted line:observed
solid line:calculated
below:difference.

Table 2. X-Ray photoelectron spectra of 1T-$Ta_{1-X}Ir_XS_2$

X	Ir $4d_{5/2}$	Ir $4f_{7/2}$	Ta $5d_{5/2}$	S 2p
0.40	298.3/eV	62.8/eV	227.6/eV	162.9/eV
0.20	298.7/eV	63.1/eV	228.9/eV	163.0/eV
0.10	297.8/eV	62.1/eV	230.7/eV	162.0/eV
0.05	297.7/eV	62.1/eV	231.0/eV	161.9/eV

$$2S + 4e^- \rightarrow 2S^{2-} \quad (3)$$

where "p" is the valence of the Ta-atom. The balance of the transferring electrons leads the next equation (4).

$$3x + p(1 - x) = 4 \quad (4)$$

If the valence of the Ta-atom will be allowed between 4 and 5, the allowed range of the x-value is deduced from the equation (4),

$$0 \leq x \leq \frac{1}{2} \quad (5).$$

The observed range of the 1T-phase is well agreed with the range deduced from this consideration. The 1T-structure is observed on the solid solutions with the number of valence electron between 4 and 5. However, the 1T-structure in $Ta_{1-X}Ir_XS_2$ is observed on the solid solution with the number of valence electron between 5 and 7. Therefore, the $Ta_{1-X}Ir_XS_2$ is a special compound, judging from the apparent number of the valence electrons. The XPS reveals that the valence of the Ir-atom is 3. This valence well-explains the balance of the valence electrons of the compound, and the stability range of the 1T-phase. However, the 1T-transition metal dichalcogenides constructed with the triple valenced metal atom have never been observed. Therefore, the 1T-$Ta_{1-X}Ir_XS_2$ is still the compound of a new concept of the "electron-excess-1T", judging from the number of valence electrons.

The authors would like to thank Mr. Matthew Main for reading the manuscript and giving me the advice for English expressions

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