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Phase Diagram and Metal Distribution of the $(Cr_xTi_{1-x})_3Se_4$ System $(0 \leq x \leq 1)$ with the Cr_3S_4-Type Structure

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The phase diagram and metal distribution of the $(Cr_xTi_{1-x})_3Se_4$ system were studied by X-ray, neutron diffraction, and DTA measurements. The metal distribution of $M'M_2X_4$ with the Cr_3S_4-type structure, which was estimated from the composition dependence of lattice parameters in the solid solution $(M'_xM_{1-x})_3X_4$ system, was in good agreement with results from other measurements such as neutron diffraction and Mössbauer effect. © 1985 Academic Press, Inc.

Introduction

In the binary M–X system (M = 3d transition metal, X = S, Se, Te), there appear many compounds such as MX, M_3X_4, M_2X_3, M_5X_8, MX_2, etc. Among them, the M_3X_4 compounds with the Cr_3S_4-type structure interest us in their chemical and physical properties. The Cr_3S_4-type structure can be derived from the CdI_2 type as follows. Anion packing is hcp, and in the CdI_2-type structure octahedral holes in the alternative layers are fully occupied by metal ions, i.e., the layer stacking along c-axis is $M^fXXM^fXX \cdots$ (M^f denotes metal ions in fully occupied metal layers). In the Cr_3S_4-type structure, half of octahedral holes between X and X (van der Waals gap) are also occupied, i.e., $M^fXM^v_{1/2}XM^f \cdots$[1] (M^v denotes metal ions in half-filled metal layers), and moreover M^v is regularly arranged (vacancy-ordered structure). Therefore, there are two sites (M^f and M^v) for metal ions in the Cr_3S_4-type structure. Hereafter we use the notation $(M)[M_2]X_4$ in order to indicate the metal distribution.

In the mixed-metal compounds $M'M_2X_4$ with the Cr_3S_4-type structure, the site preference of each metal ion is interesting. Chevreton *et al.* (*1–3*) synthesized $M'M_2X_4$ compounds with the Cr_3S_4-type structure

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[1] The ratio of the site number $N_{M^v}/N_{M^f} = \frac{1}{2}$ is important to discuss the metal distribution.

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and Andron *et al.* (*4–6*) determined the following metal distributions by neutron diffraction: (Fe)[Cr_2]Se_4 (normal) (*4*), (Ni)[Cr_2]S_4 (normal) (*5*), (Cr)[CrTi]Te_4 (inverse) (*6*).[2] Recently, Kawada and Wada (*7*) determined the distribution in (Fe)[V_2]S_4 (normal) by TOF neutron diffraction. Nozaki *et al.* (*8*) tried to determine the metal distribution of VFe_2S_4 by ^{57}Fe Mössbauer effect measurements; (Fe)[FeV]S_4 (inverse).

Oka *et al.* (*9*) discussed the general phase diagram of the M–X system from the view point of the statistical thermodynamics. According to these results, an M_3X_4 phase with the Cr_3S_4-type structure should show the successive phase transitions: Cr_3S_4 → CdI_2 → (NiAs) type structures on heating, as has been confirmed in many systems such as V–S (*10*), V–Se (*10*), Cr–Se (*11*), Fe_xVS_2 (*12*), and Cr_xTiSe_2 (*13*).

In this paper, we report a phase diagram of the $(Cr_xTi_{1-x})_3Se_4$ system and the site preference of the metal ions, as part of a series of investigations of phase diagrams and physical properties of $(M'_xM_{1-x})_3X_4$ systems (M', M = $3d$ transition metal).

Experimental

Samples were synthesized by the direct reaction from high-purity elements Ti (3N), Cr (3N), and Se (5N). The weighed mixtures were ground, pressed and sealed in an evacuated silica tube, and heated at 800°C for 1 week. The samples were reground and reheated at 800°C for 1 week, and then annealed at 300°C for 2 weeks and quenched in ice water. The phase characterization was made by powder X-ray diffraction methods. The phase transition at higher temperature was detected by high-temperature X-ray diffraction *in situ* and also by

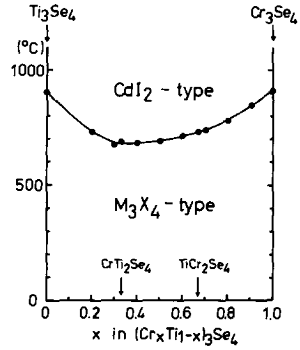

FIG. 1. Phase diagram of the $(Cr_xTi_{1-x})_3Se_4$ system. M_3X_4 type refers to the Cr_3S_4-type structure. The temperature of the phase transition was measured by DTA on heating.

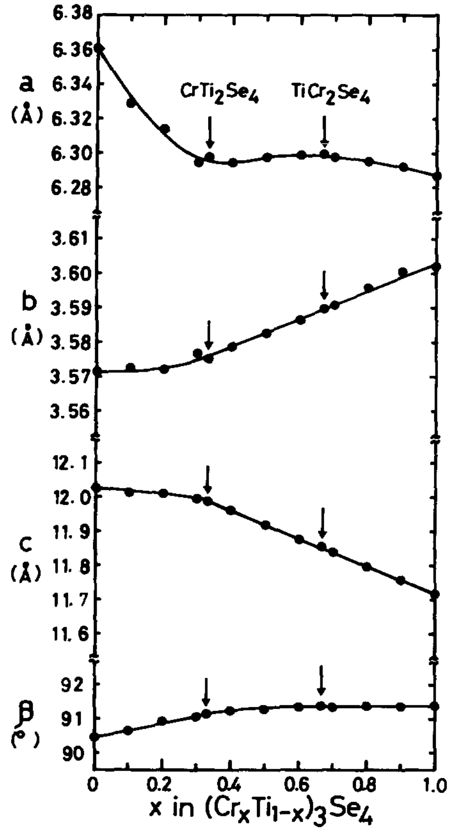

FIG. 2. Composition dependence of lattice parameters of the $(Cr_xTi_{1-x})_3Se_4$ system at room temperature.

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[2] For $M'M_2X_4$ compounds with the Cr_3S_4-type structure, Chevreton and Andron (*4*) defined the "normal" and "inverse" as (M')[M_2]X_4 and (M)[MM']X_4, respectively.

DTA measurements. Powder neutron diffraction study was done at room temperature with the double-axis neutron diffractometer installed at Kyoto University (KUR).

Results and Discussion

Figure 1 shows a phase diagram obtained for $(Cr_xTi_{1-x})_3Se_4$ up to 1000°C. The phase transition from the Cr_3S_4- to CdI_2-type structure corresponds to the disordering of M^v ions or metal vacancies in the layers. The hysteresis of the phase-transition temperature T_t measured by DTA is about 10°C. The order of phase transition seems to be first order, very close to second order.

Figure 2 shows the dependence of the lattice parameters (a, b, c, β) on composition in $(Cr_xTi_{1-x})_3Se_4$ at room temperature. The figure clearly shows the deviation from Vegard's law, and a gradient change in the composition vs lattice parameter curves at the composition $x = \frac{1}{3}$ ($CrTi_2Se_4$). These results reflect the nature of the metal distribution. Previously, it was shown (*14, 15*) that the $(Mn_xFe_{1-x})_3O_4$ system with the spinel structure shows a similar change in the lattice spacings d_{440} at $MnFe_2O_4$ ($x = \frac{1}{3}$).

The pseudobinary solid solution M'_3X_4–M_3X_4 or $(M'_xM_{1-x})_3X_4$ involves substitution

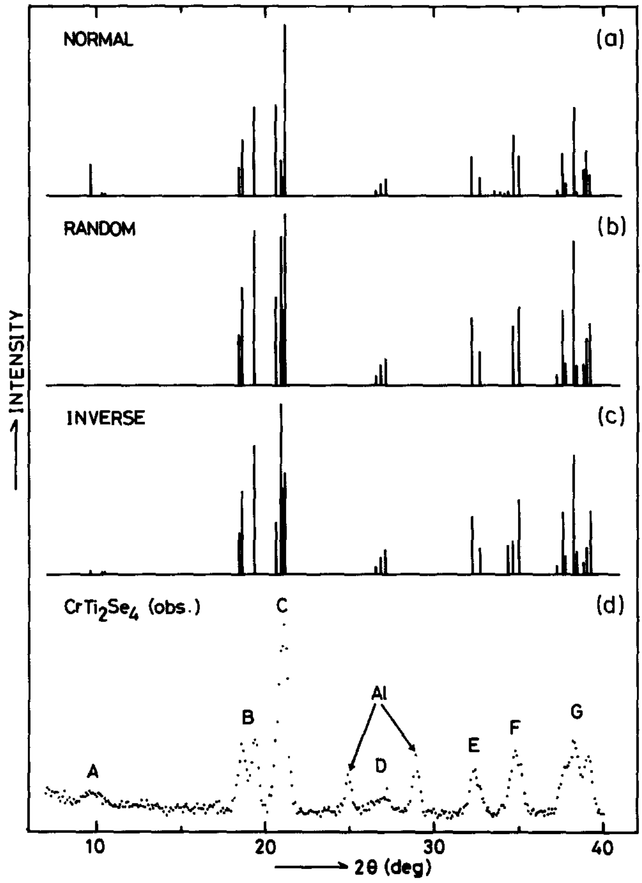

FIG. 3. Calculated (a–c) and observed (d) powder neutron diffraction patterns of $CrTi_2Se_4$ ($\lambda = 1.006$ Å).

of M' for M. The possible types of substitution, which reflect the site preference (M^{f} or M^{v}) of each ion, are

$$\begin{array}{lll}
\text{(A)} & (M'_{3x}M_{1-3x})[M_2]X_4 & 0 \le x \le \frac{1}{3} \\
 & (M')[M'_{3x-1}M_{3-3x}]X_4 & \frac{1}{3} \le x \le 1 \\
\text{(B)} & (M)[M'_{3x}M_{2-3x}]X_4 & 0 \le x \le \frac{2}{3} \\
 & (M'_{3x-2}M_{3-3x})[M'_2]X_4 & \frac{2}{3} \le x \le 1 \\
\text{(C)} & (M'_xM_{1-x})[M'_{2x}M_{2-2x}]X_4 & 0 \le x \le 1
\end{array}$$

In case (A), M' prefers to occupy M^{v} sites up to $x = \frac{1}{3}$, but over $x = \frac{1}{3}$, M' is obliged to occupy M^{f} sites because the M^{v} sites are fully occupied by M'. Conversely M prefers to occupy M^{f} sites. In case (B), M' and M prefer to occupy M^{f} and M^{v} sites, respectively. In case (C), M' and M have no preference for either of the crystallographic sites.

"Normal" or "inverse" as defined by Chevreton and Andron (*4*) has meaning only at $x = \frac{1}{3}$ or $\frac{2}{3}$ in both cases (A) and (B). The composition $x = \frac{1}{3}$ for case (A), $(M')[M_2]X_4$, and $x = \frac{2}{3}$ for case (B), $(M)[M'_2]X_4$, are *turning points*, because over these composition M' starts to substitute for M in new sites, M^{f} and M^{v}, respectively.

The site preference type "normal" or "inverse" or "random" can be estimated by measuring the composition dependence of lattice parameters. In case (A), an anomalous change in the composition vs lattice parameter curves around $x = \frac{1}{3}$ indicates the compound $M'M_2X_4$ belongs to the normal $(M')[M_2]X_4$ type and M'_2MX_4 to the inverse one. In case (B), an anomalous change around $x = \frac{2}{3}$ indicates the compound $M'M_2X_4$ belongs to inverse $(M)[MM']X_4$ type and the compound M'_2MX_4 to the normal one. In case (C), there would be no anomalous change in the curves.

As shown in Fig. 2 $(Cr_xTi_{1-x})_3Se_4$ has a turning point around $x = \frac{1}{3}$. This suggests that Cr ions prefer to occupy the M^{v} site and that $CrTi_2Se_4$ belongs to normal $(Cr)[Ti_2]Se_4$ type. In order to confirm this, a powder neutron diffraction study on $CrTi_2Se_4$ was done. In Fig. 3 the bottom (d) shows the powder neutron diffraction data, and for comparison the top (a) to the third (c) show the calculated intensity for normal, random, and inverse type, respectively. The peak resolution in the observed diffraction pattern is not enough to compare the calculated intensity with the observed one for each line. So the observed diffraction lines were grouped (A, B, · · · G as shown in Fig. 3d) and compared with the calculated intensity. The results in Table I confirm the normal type, $(Cr)[Ti_2]Se_4$, in accord with the estimation from the composition vs lattice parameter curves.

TABLE I

INTENSITY OF NEUTRON DIFFRACTION FOR PATTERNS CALCULATED (NORMAL, RANDOM, AND INVERSE MODEL) AND OBSERVED

Line groups[a]	Calculated			Observed
	Normal	Random	Inverse	
A	12	0	3	13
B	55	63	62	58
C	100	100	100	100
D	11	12	12	14
E	19	21	21	25
F	37	34	35	38
G	77	84	83	78

[a] See Fig. 3d.

Here we show a couple of other examples. The composition dependence of lattice parameters for $(Fe_xV_{1-x})_3S_4$ (*16*), clearly shows a gradient change around $x = \frac{1}{3}$ (FeV_2S_4). This suggests that the substitution mode belongs to type (A), i.e., $(Fe)[V_2]S_4$ (normal) and $(Fe)[FeV]S_4$ (inverse). These were confirmed by neutron diffraction (*7*) and Mössbauer effect measurements (*8*), respectively. Figure 4 shows the lattice parameter change in the $(Cr_xTi_{1-x})_3Te_4$ system.[3] This suggests that the substitution mode also belongs to type (A), i.e., $(Cr)[Ti_2]Te_4$ (normal) and (Cr)[Cr

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[3] The study of this system, including some physical properties, is now in progress.

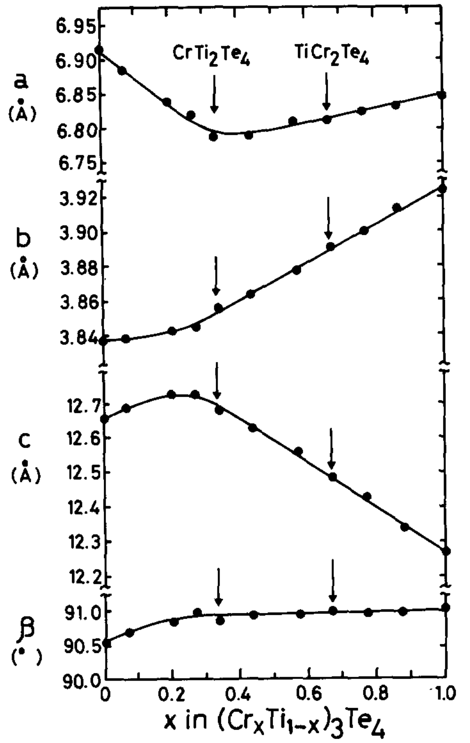

FIG. 4. Composition dependence of lattice parameters of the $(Cr_xTi_{1-x})_3Te_4$ system at room temperature.

Ti]Te_4 (inverse). Andron *et al.* (*6*) have determined the metal distribution to be inverse, (Cr)[CrTi]Te_4, by neutron diffraction. Note that the Cr ion prefers to occupy the M^v sites in both $(Cr_xTi_{1-x})_3X_4$ systems (X = Se or Te). It is likely that the site preference of metal ions M' depends only on partner metal ions M, regardless of anion.

The composition dependence of lattice parameters in $(M'_xM_{1-x})_3X_4$ systems with Cr_3S_4-type structures gives us the information about the substitution modes (A), (B), (C), from which we can guess "normal" or "inverse" or "random" distribution of metal ions for compounds $M'M_2X_4$ or M'_2MX_4.

Phase diagram and metal distribution study on all possible $(M'_xM_{1-x})_3X_4$ systems with the Cr_3S_4-type structure are now in progress, together with complementary studies using neutron diffraction, Mössbauer effect, nuclear magnetic resonance, magnetic susceptibility measurements, etc.

References

1. G. BÉRODIAS AND M. CHEVRETON, *C. R. Acad. Sci. Paris* **261,** 2202 (1965).
2. M. CHEVRETON AND A. SAPET, *C. R. Acad. Sci. Paris* **261,** 928 (1965).
3. M. CHEVRETON AND G. BÉRODIAS, *C. R. Acad. Sci. Paris* **261,** 1251 (1965).
4. M. CHEVRETON AND B. ANDRON, *C. R. Acad. Sci. Paris* **264,** 316 (1967).
5. B. ANDRON AND E. F. BERTAUT, *J. Phys.* (*Paris*) **27,** 619 (1966).
6. B. ANDRON, G. BÉRODIAS, M. CHEVRETON, AND P. MOLLARD, *C. R. Acad. Sci. Paris* **263,** 621 (1966).
7. I. KAWADA AND H. WADA, *Physica B + C* (*Amsterdam*) **105,** 223 (1981).
8. H. NOZAKI, H. WADA, AND H. YAMAMURA, *Solid State Commun.* **44,** 63 (1982).
9. Y. OKA, K. KOSUGE, AND S. KACHI, *J. Solid State Chem.* **24,** 41 (1978).
10. Y. OKA, K. KOSUGE, AND S. KACHI, *J. Solid State Chem.* **23,** 11 (1978).
11. T. OHTANI, R. FUJIMOTO, H. YOSHINAGA, M. NAKAHIRA, AND Y. UEDA, *J. Solid State Chem.* **48,** 161 (1983).
12. Y. OKA, K. KOSUGE, AND S. KACHI, *Mater. Res. Bull.* **15,** 521 (1980).
13. N. OHTSUKA, K. KOSUGE, N. NAKAYAMA, Y. UEDA, AND S. KACHI, *J. Solid State Chem.* **45,** 411 (1982).
14. A. MUAN AND S. SŌMIYA, *Amer. J. Sci.* **260,** 230 (1962).
15. H. J. VAN HOOK AND M. L. KEITH, *Amer. Mineral.* **43,** 69 (1958).
16. H. WADA, *Bull. Chem. Soc. Jpn.* **52,** 2130 (1979).