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Preparation and Structural Properties of Some Ternary Chalcogenides of Titanium[1]

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Six ternary chalcogenides MTi_2X_4 (M = Fe, Co, Ni; X = S, Se) were prepared having the monoclinic Cr_3S_4-type structure. This structure is characterized by ordered vacancies in alternate metal layers. An investigation was carried out to determine any evidence of a transition to a disordered trigonal structure. For the six compounds studied, no appreciable disorder was obtained without decomposition and loss of stoichiometry. In addition, the ternary cation-deficient chalcogenide $Ni_{0.8}Ti_{2.13}Se_4$ was found to have the trigonal structure. Hence any deviation from the stoichiometry MTi_2X_4 may result in the formation of the disordered trigonal phase.

Introduction

In the course of continuing the investigation of structural and electrical properties of ternary transition metal chalcogenides,[2-5] six compounds having the formula MTi_2X_4 (M = Fe, Co, Ni; X = S, Se) were prepared. The sulfides were first reported by Hahn, *et al.*,[6] and the selenides were initially prepared by Bérodias and Chevreton.[7] Hahn, *et al.*, indicated that the sulfides were trigonal and belonged to the space group P$\bar{3}$m1, whereas Bérodias and Chevreton demonstrated that the corresponding selenides had the Cr_3S_4 monoclinic defect NiAs structure (space group I2/m). In the present study, it was found that when the sulfides and selenides were prepared from high-purity elements in evacuated silica tubes, they had the Cr_3S_4-type structure. This structure, intermediate between the NiAs ($B8_1$) and CdI_2 (C6) types, Figure 1, has cation vacancies confined to alternate metal layers and ordered within these layers. For these ordered structures, in which the anion arrangement remains essentially unchanged, trigonal symmetry can be maintained only for the compositions[8] MX_2, M_2X_3, M_5X_6, and MX. When the cation-to-anion ratio is 3:4, the symmetry must be lowered in order to accommodate the vacancies.

The trigonal structure reported by Hahn, *et al.*, for compounds of the type MTi_2S_4 is indicative of a random distribution of vacancies in alternate metal layers. However, the corresponding selenides reported by Bérodias and Chevreton have the ordered monoclinic structure shown in Figure 2. Therefore it may be possible that such compounds can adopt either symmetry, depending upon whether the vacancies are ordered or randomly arranged. The present study was undertaken to determine whether the two structural forms reported are related by a reversible temperature-dependent order–disorder transformation.

Experimental Section

Preparation.—The six compounds MTi_2X_4 (M = Fe, Co, Ni; X = S, Se) were prepared by reaction of stoichiometric amounts of the high-purity elements in evacuated silica tubes. Crystal bar titanium (99.99%, Metal Hydrides, Inc.), freshly reduced iron, cobalt, and nickel (99.99+%, Gallard-Schlesinger Corp.), and powdered sulfur and selenium (99.999+%, Gallard-Schlesinger Corp.) were used. Successive 1-week firings at 600 and 800° with intermediate grinding under dry nitrogen were sufficient to prepare pure phases of all compounds except $FeTi_2S_4$. For this compound, a further firing at 1000° was necessary.

Analytical Work.—Analysis of all compounds for sulfur or selenium was performed by a weight-loss procedure. Oxidation of the cobalt and nickel compounds was carried out at 700° under dry oxygen until constant weight was attained. For the iron compounds, the oxidation was carried out at 600°. The weight loss upon oxidation to stable oxides was related to the amount of sulfur or selenium initially present. A precision of better than 0.1% was obtained by this procedure. The oxidation products were verified by X-ray analysis. Densities were determined using standard pycnometric technique. The results of the chemical analyses and density determinations are summarized in Table I.

X-Ray Measurements.—Crystallographic parameters were determined on powder samples using a Norelco diffractometer with monochromatic radiation (AMR-202 focusing monochromator) and a high-intensity copper source. Cell parameters were calculated and refined using an IBM 360 computer program of a modified Cohen least-squares method,[9] Table I. The radiation used was $\lambda(\text{Cu K}\alpha_1)$ 1.5405 A.

Order–Disorder Studies.—Each monoclinic compound was heated at various temperatures up to its decomposition point or 1300° (whichever was lower) in an effort to disorder the vacancies thermally. Subsequent quenching was carried out to "freeze in" any disordering that might have occurred. A hollow Globar furnace was constructed to facilitate rapid quenching of samples from elevated temperatures. This furnace maintained a 1-in. constant temperature zone (±3°) at operating temperatures up to 1300°. Rapid quenching was performed by cutting the nichrome wire which suspended an evacuated sample tube in the furnace. The sample tube dropped out through the bottom of the furnace into ice water. The six compounds were heated 1–3 hr at each particular temperature, then rapidly quenched, and X-rayed. The samples were then annealed at 800–1000° and slow-cooled at the rate of 10°/hr. The resulting products were also X-rayed.

The symmetry of the defect NiAs structure alters from monoclinic to trigonal as the vacancies are randomized within alternate metal layers. It is possible to ascertain changes in the degree of ordering from changes in the relative intensities of monoclinic reflections. The 101, 011, $\bar{1}03$, 103, 013, 211, 105, 301, $\bar{2}13$, $\bar{3}03$, 121, and $\bar{1}07$ reflections are particularly sensitive

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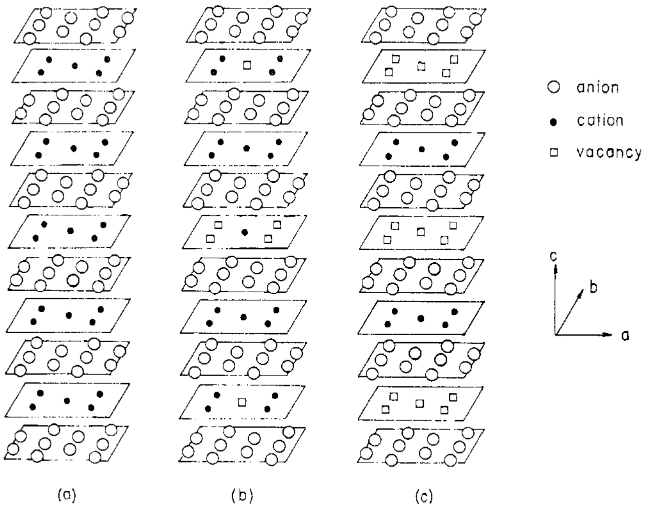

Figure 1.—Idealized representation of the close-packed layers of (a) NiAs, (b) Cr_3S_4, and (c) CdI_2.

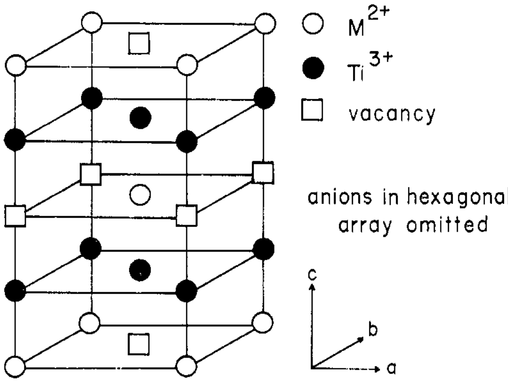

Figure 2.—The metal substructure of the monoclinic defect NiAs structure: M. Chevreton and F. Bertaut, *Compt. Rend.*, **253,** 145 (1961).

to the ordering. All are quite intense for the monoclinic structure but disappear entirely in the transformation to the trigonal structure. Changes in the relative intensities of such reflections were measured and the relative percentage change in the degree of ordering could thus be estimated. Diffraction patterns were obtained at slow scanning speed, *i.e.*, 0.25° advance in 2θ per min, in order to optimize resolution of closely spaced reflections.

Results and Discussion

The X-ray and analytical data for the six MTi_2X_4 compounds are summarized in Table I. In all cases, every peak in the X-ray patterns for the ternary chalcogenides could be indexed on a monoclinic cell. All observed reflections satisfy the condition $h + k + l = 2n$ (n = integer), which is required by the space group[8] I2/m. Cell parameters for the selenides agree closely with those reported by Bérodias and Chevreton.[7] However, the trigonal phases reported by Hahn, *et al.*,[6] for the sulfides were not reproduced.

The results of the high-temperature experiments indicate that it is not possible to disorder any of the monoclinic sulfides or selenides appreciably without decomposition and loss of stoichiometry. For example, $NiTi_2Se_4$ decomposes at 1000° to yield a trigonal phase and a small amount of NiSe. After quenching the sample, the NiSe is not readily detected by X-ray examination. However, after the product was annealed, X-ray examination revealed both the trigonal and NiSe phases. The peak positions and intensities of the lines present for the major trigonal phase are consistent with space groups $P\bar{3}m1$ and $P6_3/mmc$. The space group $P\bar{3}m1$ was found to be the unique space group for the structure since the presence of all of the $00l$ reflections excluded space group $P6_3/mmc$. This trigonal phase is similar to the one reported by Hahn for the compositions MTi_2S_4 and shows a random distribution of cation vacancies in alternate metal layers. Thus monoclinic $NiTi_2Se_4$ transforms to the trigonal structure because of a change in stoichiometry rather than as the result of an order–disorder transition. Similar results were obtained for the other five compounds studied. In some cases elemental sulfur or selenium was also observed in the tubes after the high-temperature treatment.

These findings imply that for the titanium compounds studied, there exists a limited homogeneity range for the ordered structure. Appreciable deviation from the stoichiometry represented by the formula MTi_2X_4 results in the formation of a disordered structure which has fairly broad limits of homogeneity and shows the symmetry ($\bar{3}$m) of the trigonal system. It thus seems that for these compounds the ordered structure cannot tolerate appreciable loss of cations or anions. This was confirmed by the preparation of a composition $M_{1-y}Ti_2Se_{4-y}$ for a small value of y.

Table I

X-Ray Data and Analyses

Compound	a (±0.005), A	b (±0.005), A	c (±0.01), A	β (±0.05), deg	Vol, A^3	% S (Se) Calcd	% S (Se) Found	Density, g cm^{-3} Calcd	Density, g cm^{-3} Measd (±0.05)[a]
$FeTi_2S_4$	5.929	3.426	11.46	90.10	232.8	45.82	45.89	3.99	3.95
$CoTi_2S_4$	5.891	3.399	11.22	90.35	224.7	45.32	45.33	4.18	4.16
NiT_2S_4	5.891	3.400	11.33	90.25	226.9	45.36	45.42	4.14	4.10
$FeTi_2Se_4$	6.221	3.582	11.93	90.25	265.8	67.56	67.67	5.84	5.70
$CoTi_2Se_4$	6.193	3.576	11.72	90.38	259.6	67.12	67.07	6.02	5.92
$NiTi_2Se_4$	6.179	3.568	11.80	90.53	260.2	67.15	67.20	6.00	5.87

[a] Water at 25° was used as the liquid. Under these conditions there is no apparent hydrolysis of the compounds.

The composition $Ni_{0.8}Ti_{2.13}Se_4$ ($Ni_{0.75}Ti_2Se_{3.75}$) was prepared at 800° followed by slow cooling to maximize ordering. X-Ray analysis of the product indicated the formation of a disordered trigonal structure, with lattice parameters (based on a hexagonal cell) of a = 3.559 ± 0.005 A and c = 5.926 ± 0.005 A (selenium analysis: calcd, 67.92%; found, 67.99%). The re-

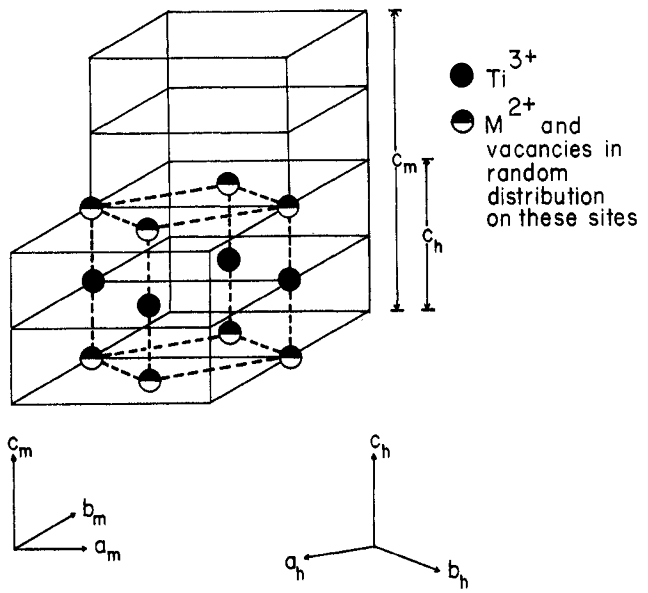

Figure 3.—Relationship between the ordered and disordered defect NiAs structures.

lationship between the dimensions of the monoclinic cell and the hexagonal cell associated with it is apparent from Figure 3, namely, $a_m \simeq a_h\sqrt{3}$, $b_m \simeq a_h$, $c_m \simeq 2c_h$, $\beta \simeq 90°$. The hexagonal cell associated with monoclinic $NiTi_2Se_4$, Table I, would have $a = 3.568$ A and $c_h = 5.90$ A. Accurate lattice parameters found for $Ni_{0.8}Ti_{2.13}Se_4$ and given above are evidence of the change in lattice parameters associated with changes in stoichiometry.

High stability of the ordered monoclinic structure for the compounds MTi_2X_4 (M = Fe, Co, Ni; X = S, Se) is shown by the absence of a temperature-dependent order–disorder transition in these compounds. Since marked disordering occurs only when the stoichiometry departs from MTi_2X_4, this ordered structure appears to have a limited homogeneity range for these sulfides and selenides. Stoichiometric ternary transition metal chalcogenides MTi_2X_4 with the trigonal structure could not be prepared under the conditions described in this paper. However, their existence cannot be totally excluded.

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Titanium(III) Chloro Complexes Containing Methanol, Methoxide Ion, or Acetonitrile

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A series of compounds has been prepared from $TiCl_3$ solutions in methanol and acetonitrile. The solutions were acidic with HCl, neutral, or basic with methoxide ion. All but one of the compounds isolated from acidic or neutral media appear to be octahedral and have near the spin-only magnetic moments. Basic compounds and species in basic solutions appear to have mostly tetrahedral Ti(III) and some contain polymeric, diamagnetic species. Electronic and infrared spectra and magnetic susceptibilities have been measured. Some properties and reactions of the compounds are described. Among the acidic compounds is a yellow, crystalline product, $(C_5H_6N)_4HTiCl_8$, isolated from acetonitrile, which had been saturated with pyridinium chloride and HCl. The compound does not appear to be a double salt and is *not* a mixture of C_5H_6NCl and $(C_5H_6N)_3TiCl_6$.

Introduction

Recent interest in this laboratory has centered on the preparation of d^1 transition element alkoxides and complexes containing alkoxide groups as ligands.[1-3] It was decided that titanium(III) alkoxides, alkoxide-containing complexes, and alcoholates might also be of interest because one could anticipate tetrahedral, octahedral, and tetragonal complexes, depending on the ligands which were used.

Schläfer and Götz have prepared a number of alcoholates of titanium trichloride and tribromide and have measured the magnetic moments of the compounds.[4] Hartmann, Schläfer, and Hansen[5] have examined solutions of Ti(III) in alcohols and measured spectra of various species formed in the solutions. Adams, *et al.*,[6] have prepared the titanium(III) methoxide.

In this study we have endeavored to prepare a variety of complex compounds of Ti(III) from acidic (with

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