An X-Ray and Electron Diffraction Study of the Channel-Type Composite Crystal $Sn_{1-p}Cr_2S_{4-p}$

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The structure of the tin and chromium sulfide $Sn_{1-p}Cr_2S_{4-p}$ was studied by powder X-ray and electron diffraction methods. A Rietveld analysis using only $h\ k\ 0$ reflections has been performed to determine the two-dimensional crystal structure projected on a hexagonal a–b plane. The results of this refinement show that this compound has the same type of structure as the channel-type composite crystals such as $Eu_{1-p}Cr_2Se_{4-p}$. In the electron diffraction patterns, diffuse streaks suggesting the existence of diffuse scattering planes normal to c^* were observed between the main strong diffraction spots. These diffuse scattering planes are attributed to the column structure around the sixfold axis. These electron diffraction patterns reveal that this compound has an incommensurate character in the c-direction. The isotypic compound $Ba_{1-p}Cr_2S_{4-p}$ was also studied by electron diffractometry. Besides main spots and diffuse scattering, weak spots corresponding to another period along c^* were observed on the patterns along the [1 0 0] or [−1 1 0] zone. © 1995 Academic Press, Inc.

INTRODUCTION

Omloo *et al.* reported the synthesis and some physical properties of the series of ternary chalcogenides MCr_2X_4 (M = Eu, Ba, Sr, and Pb; X = S, Se) in 1968 and 1971 (1, 2). Due to the large ionic radii of the divalent cations, these compounds do not crystallize in the well-known spinel type structure, but rather in the hexagonal system. Chemical analysis indicated that they do not actually have the integer composition MCr_2X_4 (e.g., $Eu_{0.69}Cr_2S_{3.80}$ for $EuCr_2S_4$ (3)).

In 1973 Sleight and Frederick synthesized "$SnCr_2S_4$," and pointed out that this tin–chromium sulfide showed a structure isotypic with Omloo's compounds, judging from its powder X-ray diffraction pattern (4).

Except for these chromium chalcogenides, only "MV_2X_4" (M = Eu, Sr; X = S, Se) and $EuTi_2S_4$ have been reported to be isotypic compounds (2). The structure of this type of compound was reported for the first time in 1977 by Brouwer and Jellinek (5). They synthesized

single crystals of $M_{1-p}Cr_2Se_{4-p}$ ($p \approx 0.3$) (M = Eu (5), Ba, and Sr (6)) by heating mixtures of elements sealed in evacuated silica ampoules. Single crystal X-ray analysis showed that these hexagonal compounds consist of three structural units. They constitute the main framework and two kinds of columns which are situated in tunnels running along the c axis. In the main framework $CrSe_6$ octahedra sharing their edges or faces form a three-dimensional network. Around the three- and sixfold axes, there are large tunnels containing the columns, which are built up with the structural units M_3Se or $M_6Cr_2Se_6$, respectively.

They also reported that the rotation diagrams about the c axis showed the next three types of layer lines: (a) strong layer lines, of which c^* corresponds to the c dimension of the unit cell, (b) weak diffuse layer lines, and (c) weak layer lines consisting of sharp spots. These layer lines are due to the main framework (a) and two kinds of columns about six- (b), and threefold (c) axes, respectively. Repeat distances along the c^* of (b) and (c) are different from those of (a). And it was concluded that these three structural units may be mutually incommensurate in the c-direction (except for $Ba_{1-p}Cr_2Se_{4-p}$), but have a common hexagonal a–b plane.

Recently powder specimens of $Pb_{1-p}Cr_2S_{4-p}$, $Sr_{1-p}Cr_2S_{4-p}$, and $Ba_{1-p}Cr_2Se_{4-p}$ were synthesized and examined by electron diffractometry (7).

In this paper we report the structural model of $Sn_{1-p}Cr_2S_{4-p}$ refined by the Rietveld analysis (8) of powder X-ray diffraction data. To avoid the difficulties caused by the expected incommensurate structure, we performed the refinement of the two-dimensional structure projected on a hexagonal a–b plane. Using only $h\ k\ 0$ reflections in the refinement, we can neglect the influences of the incommensurability in the c-direction, and get the structure projected along the c axis. The electron diffraction patterns along the [1 0 0] and [−1 1 0] zone were used to obtain information on the crystal structure along the c axis. Furthermore, for the comparison with $Sn_{1-p}Cr_2S_{4-p}$, we have investigated the electron diffraction patterns of the isotypic composite crystal $Ba_{1-p}Cr_2S_{4-p}$.

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EXPERIMENTAL

Powder samples of $Sn_{1-p}Cr_2S_{4-p}$ were prepared from a mixture of the elements under the experimental conditions reported by Sleight (4). The purities of the elements used were as follows: Sn 99.9% 200 mesh (Rare Metallic Co., Ltd.), Cr 99.9% 200 mesh (Rare Metallic Co., Ltd.), and S 99.9999% (Rare Metallic Co., Ltd.). These elements were mixed in an agate mortar in a mole ratio of Sn : Cr : S = 1 : 2 : 4, and pressed into pellets in a glove box. After being sealed in evacuated silica ampoules, the samples were heated at 800–900°C for several days in an electric furnace, and quenched in cold water.

In all the products, two parts could be distinguished. The main product was black, and needle-like crystals (several mm in size) were sometimes found to grow on its surface. A second part, a small weight fraction, was transported to the low temperature part of the silica ampoules. It was found to be a mixture of the tin sulfides (SnS, SnS_2, Sn_2S_3).

From X-ray analysis, the main product was found to be a mixture of $Sn_{1-p}Cr_2S_{4-p}$ and small amounts of chromium sulfide (Cr_2S_3: rhombohedral type). This chromium sulfide could not be completely separated from $Sn_{1-p}Cr_2S_{4-p}$.

The best sample containing the smallest amount of Cr_2S_3 was obtained from starting mixture having a composition with a slight excess of sulfur. When the mixture was heated slowly, the amount of tin sulfides increased, and the amount of Cr_2S_3 impurity also increased. So rapid heating was necessary for the synthesis of pure $Sn_{1-p}Cr_2S_{4-p}$.

Polycrystalline samples of $Ba_{1-p}Cr_2S_{4-p}$ were synthesized according to Omloo et al. (2). Starting materials of BaS (purity 99% High Purity Chemicals), Cr (99.9% Rare Metallic Co., Ltd.), and S (99.9999% Rare Metallic Co., Ltd.) were mixed in the ratio Ba : Cr : S = 0.75 : 2 : 3.75 in a glove box, and pressed into pellets. Then the pellets were sealed in evacuated silica ampoules, heated at 1000–1100°C for 10 days, and quenched in cold water. The product was found to be a single phase of $Ba_{1-p}Cr_2S_{4-p}$.

Powder X-ray diffraction data were collected in the step scan mode on a Philips PW 1800 diffractometer with an automatic divergence slit and counterside monochromatized $CuK\alpha$ radiation system. The Rietveld analysis program used here is the total pattern fit program RIETAN (9, 10). The program RIETAN does not support the data collected by the diffractometer using an automatic divergence slit. Therefore the raw data were converted into the intensities which would be obtained if a fixed slit were used. The equation of this conversion is:

converted intensity = (intensities of raw data) / (2 sin θ).

This purely geometric relation can be derived from the relationship between both slits.

The electron diffraction study was performed using finely crushed particles on a Hitachi 500-type 100 kV electron microscope.

RESULTS AND DISCUSSION

The powder X-ray diffraction pattern of $Sn_{1-p}Cr_2S_{4-p}$ was indexed with a hexagonal cell (a = 21.322 Å, c = 3.466 Å). Sleight and Frederick reported the presence of a small amount of tin sulfide (SnS) which could not be separated from their samples (4). In our case, however, tin sulfides were formed, and transported to the low temperature area of the silica ampoules. So we were able to remove the tin sulfides from our samples. However, a small amount of Cr_2S_3 (rhombohedral type) was mixed in the products. Table 1 shows the indices, calculated and observed values of d-spacings, and observed intensities for $Sn_{1-p}Cr_2S_{4-p}$.

From the similarity of the powder X-ray diffraction pattern, $Sn_{1-p}Cr_2S_{4-p}$ was expected to have the same type of structure as $Eu_{1-p}Cr_2Se_{4-p}$, etc. (4). $Eu_{1-p}Cr_2Se_{4-p}$ has a crystal structure described as an intergrowth of three structural units (5). They are two types of columns situated in channels, and a framework leaving wide channels. These three structural units have the common hexagonal a–b plane, but three different c axes. The columns in the triangular channels have a threefold axis, so we call these triangular columns, and their repeat distance in the c direction is called c_3. The other types of columns are in the hexagonal channels, so c_6 represents the repeat distance of these columns. The fundamental repeat distance of the framework is represented as c_0. These three structural units are mutually incommensurate, so $Eu_{1-p}Cr_2Se_{4-p}$ is called the channel-type composite crystal. The same types of compounds having such a composite crystal structure are listed in Table 2, in which the lattice constants and the ratios of c axes can be seen. Only $Ba_{1-p}Cr_2Se_{4-p}$ was reported to have a commensurate structure. But our sample of $Ba_{1-p}Cr_2Se_{4-p}$, which was synthesized and examined in our previous work (7), had an incommensurate structure, judging from its electron diffraction pattern. The other compounds were reported to have incommensurate c axes (5).

We tried to confirm the crystal structure of $Sn_{1-p}Cr_2S_{4-p}$ by applying the Rietveld method to the powder X-ray diffraction data. However, $Sn_{1-p}Cr_2S_{4-p}$ has a complicated structure in the c direction, like $Eu_{1-p}Cr_2Se_{4-p}$ and $Ba_{1-p}Cr_2Se_{4-p}$, and it was expected that we would have considerable difficulties in the refinement of the three-dimensional structure of such complicated crystals from powder X-ray diffraction data. So we performed the refinement of the two-dimensional crystal structure projected along the c-direction. It is possible to refine such a projected structure by using only $h\,k\,0$ reflections in the

TABLE 1

Indices and Calculated and Observed Values of d Spacings, and Observed Intensities for Sn$_{1-p}$Cr$_2$S$_{4-p}$ ($a = 21.322$ Å, $c = 3.466$ Å)

h	k	l	d_{calc}	d_{obs}	I_{obs}	h	k	l	d_{calc}	d_{obs}	I_{obs}
2	1	0	6.98	6.96	9	6	4	0	2.118	2.117	3
1	2	0				4	6	0			
3	0	0	6.16	6.15	3	4	4	1	2.113	2.112	2
4	0	0	4.62	4.61	2	5	3	1	2.099	2.098	20
2	3	0	4.24	4.23	43	3	5	1			
3	2	0				6	2	1	2.060	2.059	2
4	1	0	4.03	4.02	17	2	6	1			
1	4	0				9	0	0	2.052	2.054	6
3	3	0	3.55	3.55	2	8	2	0	2.015	2.015	4
2	4	0	3.49	3.49	56	2	8	0			
4	2	0				7	1	1	1.998	1.997	2
0	0	1	3.47			1	7	1			
1	0	1	3.41	3.40	1	5	6	0	1.936	1.934	5
5	1	0	3.32	3.31	3	6	5	0			
1	5	0				9	1	0			
1	1	1	3.30	3.29	11	1	9	0			
2	0	1	3.25	3.24	2	6	3	1	1.932	1.930	8
2	1	1	3.104	3.102	5	3	6	1			
1	2	1				8	0	1	1.921	1.920	1
6	0	0	3.078	3.076	8	7	4	0	1.915	1.914	5
4	3	0	3.036	3.031	8	4	7	0			
3	4	0				7	2	1	1.891	1.890	3
3	0	1	3.020	3.017	12	2	7	1			
5	2	0	2.957	2.953	3	8	3	0	1.875	1.874	5
2	5	0				3	8	0			
2	2	1	2.906	2.904	3	10	0	0	1.847	1.845	1
3	1	1	2.870	2.866	3	5	5	1	1.816	1.816	3
1	3	1				3	7	1	1.782	1.781	6
4	0	1	2.772	2.769	4	7	3	1			
3	2	1	2.683	2.679	11	6	6	0	1.777		
2	3	1				9	0	1	1.766	1.765	12
4	4	0	2.665	2.662	5	4	8	0	1.745	1.742	11
3	5	0	2.638	2.636		8	4	0			
5	3	0				8	2	1	1.742		
7	0	0			100	2	8	1			
4	1	1	2.628	2.629		0	0	2	1.733	1.733	14
1	4	1				1	1	2	1.711	1.713	2
6	2	0	2.561	2.559	22	3	9	0	1.707	1.707	5
2	6	0				9	3	0			
5	0	1	2.527	2.525	45	2	0	2	1.703		
3	3	1	2.481	2.479	11	6	5	1	1.690	1.690	17
4	2	1	2.459	2.456	9	5	6	1			
2	4	1				7	4	1			
7	1	0	2.446	2.444	4	4	7	1	1.676	1.676	4
1	7	0				8	3	1			
5	1	1	2.396	2.395	5	3	8	1	1.649	1.648	4
1	5	1				2	2	2	1.648		
5	4	0	2.364	2.362	8	3	1	2	1.642		
4	5	0				1	3	2			
8	0	0	2.308	2.306	3	7	6	0	1.639	1.638	2
6	0	1	2.301	2.300	4	6	7	0			
4	3	1	2.284	2.283	4	10	0	1	1.630	1.629	2
3	4	1				8	5	0			
2	7	0	2.256	2.254	14	5	8	0	1.626		
7	2	0				9	2	1	1.611	1.611	1
5	2	1	2.249			2	9	1			
6	1	1	2.186	2.184	44	3	2	2	1.604	1.600	4
1	6	1				9	4	0	1.601		
8	1	0	2.161	2.161	4	4	9	0			
1	8	0									

TABLE 2

Unit Cell Dimensions of Channel Type Composite Crystals

	A_{1-p}Cr$_2$X$_{4-p}$				
	a (Å)	c_0 (Å)	c_3/c_0	c_6/c_0	
Ba$_{1-p}$Cr$_2$S$_{4-p}$	21.99	3.433	1.292	1.691	
	21.97	3.436	1.294	1.692	This work
Sr$_{1-p}$Cr$_2$S$_{4-p}$	21.54	3.445	1.205	1.655	
	21.55	3.449	1.24	1.67	a
Eu$_{1-p}$Cr$_2$S$_{4-p}$	21.41	3.446	1.224	1.646	
Pb$_{1-p}$Cr$_2$S$_{4-p}$	21.43	3.476	1.207	1.638	
	21.41	3.473	—b	1.63	a
Sn$_{1-p}$Cr$_2$S$_{4-p}$	21.325	3.4690	—c	—c	Ref. (4)
	21.322(1)	3.4659(6)	—b	1.636	This work
Ba$_{1-p}$Cr$_2$Se$_{4-p}$	22.93	3.620	1.250	1.667	Commensurate
			1.264	1.675	a
Sr$_{1-p}$Cr$_2$Se$_{4-p}$	22.49	3.623	1.274	1.660	
Eu$_{1-p}$Cr$_2$Se$_{4-p}$	22.43	3.622	1.272	1.649	
Pb$_{1-p}$Cr$_2$Se$_{4-p}$	22.37	3.640	1.261	1.641	

[a] Measured for the specimens synthesized in the previous work (7).
[b] Independent repeat distance of triangular columns (c_3^*) was not observed in the electron diffraction patterns.
[c] There was no mention of the incommensurate structure.

TABLE 3

Crystal Data and Refined Atomic Parameters of Sn$_{1-p}$Cr$_2$S$_{4-p}$

Space group $P6/m$ (No. 175)
$a = 21.322(1)$ Å, $c = 3.4659(6)$ Å
$R_{WP} = 7.69\%$, $R_F = 1.90\%$

Atomic parameters

Atom	x	y	G^a
Cr(1)	0.5	0.0	1.0
Cr(2)	0.427(2)	0.092(4)	1.0
Cr(3)	0.373(2)	0.197(4)	1.0
Cr(4)	0.334(5)	0.304(4)	1.0
S(1)	0.397(8)	0.010(8)	1.0
S(2)	0.325(7)	0.093(4)	1.0
S(3)	0.269(4)	0.212(6)	1.0
S(4)	0.546(8)	0.083(6)	1.0
S(5)	0.483(5)	0.181(3)	1.0
S(6)	0.426(5)	0.284(5)	1.0
Sn(1)	0.569(1)	0.347(2)	0.60(5)
S(7)	0.66667	0.33333	0.60^b
Sn(2)	0.166(4)	0.051(3)	0.32(4)
Cr(5)	0.0	0.0	0.63^c
Cr(6)	0.0	0.0	0.63^c
S(8)	0.073(12)	−0.016(19)	0.32^c

Note. Overall isotropic thermal parameter = 6.0(10) Å^2
[a] Occupational factor.
[b] G(Sn(2)) = G(S(7)).
[c] G(Cr(5)) = 2*G(Sn(2)), G(Cr(6)) = 2*G(Sn(2)), G(S(8)) = G(Sn(2)).

refinement. In this way we could neglect the influences of the incommensurability in the c-direction. In the refinement, 28 peaks of $h\ k\ 0$ reflections (2θ region: from 18° to 50°) were used. The Rietveld analysis program used here is the total pattern fit program RIETAN (9, 10).

The space group $P6/m$ was adopted, and all atomic sites were given a common isotropic thermal vibrational parameter. The lattice constant a, the $x\ y$ coordinates of all atomic sites, and some site occupancies were refined. The lattice constant c was fixed for c_0, which is derived from all observed reflections by least-squares. From this refinement we finally obtained the result giving the smallest R-values, $R_{WP} = 7.69\%$ and $R_F = 1.90\%$. The refined $x\ y$ coordinates, thermal and occupational parameters, lattice constants, and some R-values are given in Table 3. In these calculations, the unit cell was defined as the fundamental structure ($a = 21.322$ Å, $c = c_0 = 3.466$ Å). So in the refinement of the projected crystal structure, the different c axes of the column parts have an influence on the site occupancies of the atom sites composing the column units. For instance, if the repeat distance c_{column} of a column unit is longer than c_0 of the fundamental structure (framework), the site occupancies of the atoms composing the column are $c_0/c_{column} < 1$. For the opposite case, these site occupancies are larger than 1. We performed the refinement of the site occupancies of the atoms composing a triangular column (Sn1, S7) and a hexagonal column (Sn2, Cr5, Cr6, S8). In the structural model, a columnar structure was assumed (5), and the ratio of atoms composing the structural unit of the column was fixed. In the refinement, therefore, we put some linear constraints on the occupational factors, that is, $G(Sn1) = G(S7)$ for the triangular column, and $G(Cr5) = 2*G(Sn2)$, $G(Cr6) = 2*G(Sn2)$, and $G(S8) = G(Sn2)$ for the hexagonal column.

Now it must be mentioned that the hexagonal column parts are assumed to have a sixfold screw axis (5). Then the space group of these parts is not $P6/m$ (as for framework and triangular columns) but $P6_3/m$. Such a structural model cannot be analyzed by the ordinary three-dimensional structural analysis method. But here, we performed a refinement of the projected two-dimensional structure. So the difference in the space group of three structural units only influences the site occupancies of Sn(2) and S(8). This is why constraints were adopted for the hexagonal column unit. In the projected structure, Cr(5) and Cr(6), of course, can be brought together (in such a case the occupational factor becomes 1.26 (twice 0.63)), but to clarify the column structure, we put two Cr atoms into the refinement. In this way, the structural unit of the column per repeat distance becomes Sn_3S for the triangular column and $Sn_6Cr_2S_6$ for the hexagonal column by these constraints. As a result, these occupational factors become less than 1. This does not suggest a defective

structure, but one where c_{column} is longer than c_0. The number of atoms in the fundamental unit cell calculated from the data shown in Table 3 is $Sn_{7.4}Cr_{22.3}S_{41.0}$. This ratio is $Sn_{0.67}Cr_2S_{3.68}$, so we describe the composition of this compound as $Sn_{1-p}Cr_2S_{4-p}$ ($p = 0.3$). Such an apparent deviation from the stoichiometric composition is a distinctive feature of composite crystals. From this composition, we calculated the valence of chromium, and obtained a value of $+3.0$.

The refined two-dimensional structure of $Sn_{1-p}Cr_2S_{4-p}$ projected on the a–b plane is shown in Fig. 1 (ball and stick). The rhombus in Fig. 1 represents the hexagonal unit cell (projected along c axis, $a = 21.622$ Å). There are a wide hexagonal channel around the sixfold axis at $x = 0$, $y = 0$, and triangular channels around the threefold axis at $x = 1/3$, $y = 2/3$; $x = 2/3$, $y = 1/3$. These channels run along the c axis and are separated from one another by the framework formed from Cr and S. The columns composed of S and Sn are situated in the triangular channels. The columns consisting of Sn, S, and Cr are situated in the hexagonal channels. These three structural subunits, that is, two types of columns and the framework, are combined as in Fig. 1, and make up the crystal structure having a common hexagonal basal plane. Such a structure is isotypic with the structure of $Eu_{1-p}Cr_2Se_{4-p}$, and so it has been confirmed that $Sn_{1-p}Cr_2S_{4-p}$ has the same type of two-dimensional structure as the channel type composite crystals listed in Table 2.

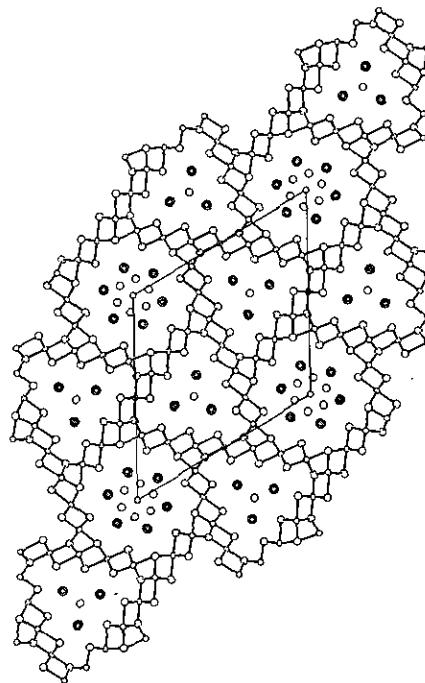FIG. 1. The structure of $Sn_{1-p}Cr_2S_{4-p}$ projected along the c-axis. Large open, small open, and hatched circles represent S, Cr, and Sn atoms, respectively. The rhombus represents a hexagonal unit cell.
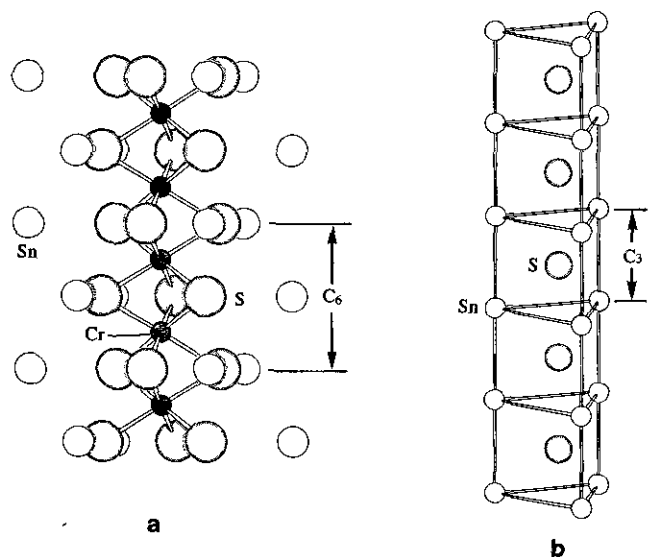
FIG. 2. (a) The structure of the hexagonal column. C_6 is the repeat distance of this column. (b) The structure of the triangular column. C_3 is the repeat distance of this column.

Figure 2 shows structural models of the hexagonal and triangular columns of $Eu_{1-p}Cr_2Se_{4-p}$ proposed by Brouwer and Jellinek (5). These columns have the structural unit M_3X (triangular), or $M_6Cr_2X_6$ (hexagonal). In most cases the repeat distances along the c direction, c_3 (triangular) or c_6 (hexagonal), are incommensurate with c_0 (framework). The ratios of the c axes of the channel-type composite crystals, c_3/c_0 and c_6/c_0, are shown in Table 2.

The hexagonal column is formed with a chain composed of face-shared CrX_6 octahedra surrounded by divalent cations. The repeat distance c_6 corresponds to twice the thickness of this octahedron. On the other hand, the framework surrounding these channels is also composed of the CrX_6 octahedra. The repeat distance c_0 corresponds to the length of the edge of CrX_6. So if these structural subunits are constructed from ideal octahedra, the ratio of c_0 and c_6 will be close to $c_6/c_0 = 1.633$ (= $\sqrt{8}/3$). As seen in Table 2, such a relationship holds in the Pb and Sn system. The repeat distance c_3 of the triangular column corresponds to the neighboring $M-M$ distance.

To obtain detailed information on such a complicated crystal structure along the c axis, the electron diffraction patterns of $Sn_{1-p}Cr_2S_{4-p}$ were observed. The diffraction photographs containing c^* axis are shown in Fig. 3. Indices (h, k, and l) are based on the fundamental hexagonal cell ($a = 21.322$ Å, $c = 3.4659$ Å). In these photographs, besides the main strong diffraction spots corresponding to the framework, diffuse streaks having another repeat distance are observed. This repeat distance corresponds to c_6^*. Therefore these diffuse streaks come from the hex-

agonal columns. The reason for the existence of such a diffuse scattering plane was examined in the case of $M_{1-p}Cr_2S_{4-p}$ (M = Pb, Sr) and $Ba_{1-p}Cr_2Se_{4-p}$ previously (7). Such diffuse scattering is explained by a model of two-directional disorder of the position of the hexagonal columns. These hexagonal columns can be situated in any position along the c-direction in the channels. So these columns are disordered in the positional relationship along the c axis with respect to one another.

In the diffraction photographs of $Sn_{1-p}Cr_2S_{4-p}$, no reflections from the triangular columns were observed. From these electron diffraction photographs, a ratio of c_6/c_0 equal to 1.636 for $Sn_{1-p}Cr_2S_{4-p}$ is obtained. This observed value is close to the ideal value of 1.633 mentioned above. On the other hand, the value of the ratio calculated from the occupational factor of atoms composing the hexagonal columns derived in the Rietveld analysis is 1.59.

For the purpose of comparison with $Sn_{1-p}Cr_2S_{4-p}$, we investigated the electron diffraction of $Ba_{1-p}Cr_2S_{4-p}$, hav-
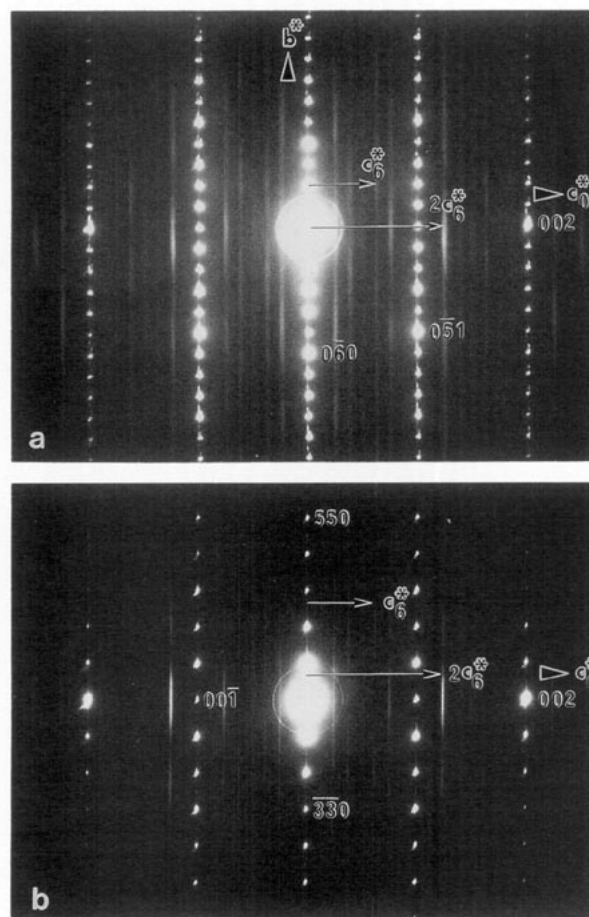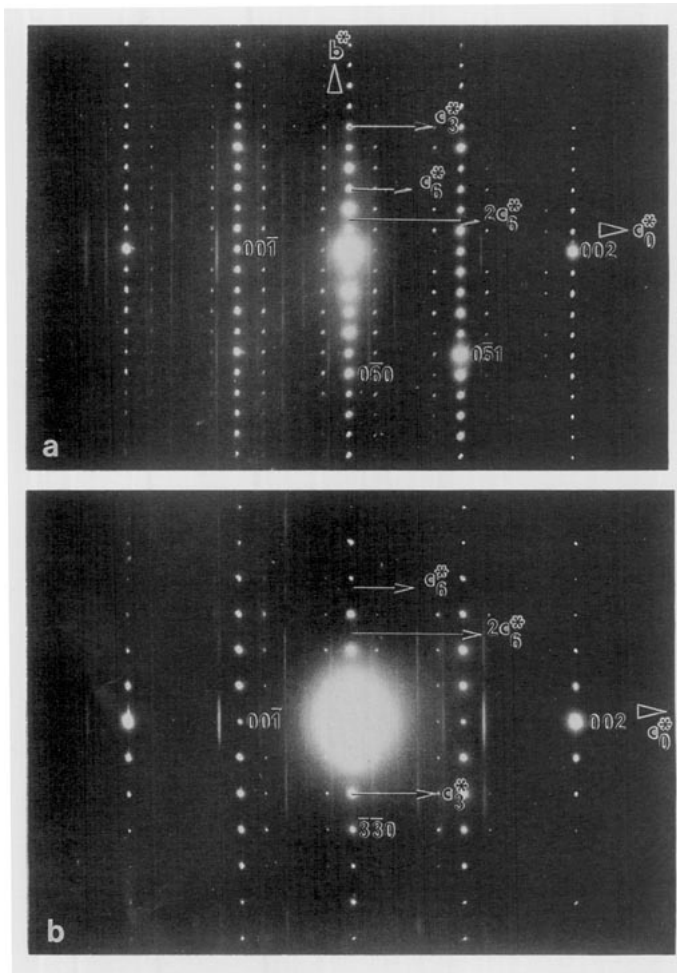

FIG. 3. Electron diffraction patterns of $Sn_{1-p}Cr_2S_{4-p}$. Indices (h, k, and l) are based on the fundamental hexagonal cell ($a = 21.322$ Å, $c = 3.4659$ Å). (a) The incident beam is parallel to [1 0 0]. (b) The incident beam is parallel to [−1 1 0].

FIG. 4. Electron diffraction patterns of $Ba_{1-p}Cr_2S_{4-p}$. Indices (h, k, and l) are based on the fundamental hexagonal cell ($a = 21.97$ Å, $c = 3.436$ Å). (a) The incident beam is parallel to [1 0 0]. (b) The incident beam is parallel to [−1 1 0].

ing the same type of composite crystal as $Eu_{1-p}Cr_2Se_{4-p}$ (6). The electron diffraction patterns of $Ba_{1-p}Cr_2S_{4-p}$ are shown in Fig. 4. In the case of $Ba_{1-p}Cr_2S_{4-p}$, besides the main strong diffraction spots, diffuse scattering is also observed as in the case of $Sn_{1-p}Cr_2S_{4-p}$. In this case, however, some sharp satellite spots around the main spots are observed. These spots are considered to be the reflections from the triangular columns. These results of the electron diffraction indicate that $Sn_{1-p}Cr_2S_{4-p}$ is a channel-type composite crystal having at least two mutually incommensurate c axes, in contrast with three mutually incommensurate c axes for $Ba_{1-p}Cr_2S_{4-p}$.

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