Synthesis and Crystal Structure of the New Hollandite-like Channel Phase Rb$_{0.73}$Cr$_5$Te$_8$

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The material Rb$_{0.73}$Cr$_5$Te$_8$ is a new channel-type structure prepared from the elements at 850°C. It crystallizes in the monoclinic space group $C2/m$ with cell dimensions $a = 20.315(4)$, $b = 3.931(1)$, $c = 14.304(3)$Å, and $\beta = 139.77(1)°$. The structure determination was performed on 1329 independant reflections ($I > 3\sigma(I)$) and refinement of 47 variables led to reliability factors of $R = 2.81\%$ and $R_w = 3.29\%$. The structure is based upon the hollandite structure, and consists of CrTe$_2$ layers connected by CrTe$_6$ octahedra, resulting in the formation of channels along the b direction. These channels are subsequently filled by rubidium. The structure described differs from those structures already determined for the other materials in the family AM_5X_8 in the mode of connection between the layers. © 1996 Academic Press, Inc.

INTRODUCTION

The family of materials AM_5X_8 (A = Li, Na, K, Rb, Cs, Cd, Sn, Pb, Tl; M = V, Cr, Ti; X = S, Se, Te) have been reported to crystallize in the space group $C2/m$ with the "hollandite-type" structure (1–12). These materials contain M_5X_8 frameworks, consisting of layers of CrTe$_6$ octahedra, connected by double chains of edge sharing CrTe$_6$ octahedra, the coupling between the layers and the double chain being of the face sharing type. The secondary metal (e.g., the alkali metal) resides in the resulting one-dimensional channels.

Much work has been carried out on the phase TlV$_5$S$_8$ (7–11) in which it has been seen that the thallium is both mobile within the tunnels and able to undergo oxidation in the presence of iodine and other oxidizing agents (7–9). Hence, these materials are currently of interest due to their inherent anisotropic ionic conductivity properties along

the direction of the channels and the possibility of intercalation/deintercalation of the secondary metals. It is probable that the ternary telluride analogs of this family will prove to be of interest, in terms of the intercalation/deintercalation and electronic properties, due to the diffuse nature of the atomic orbitals of tellurium, allowing oxidation away from the regular 2- oxidation state (13).

Previous preparations of the analogous alkali metal chromium tellurides have involved alkali metal ion exchange with the parent compound TlCr$_5$Te$_8$ (5, 6). Due to the nature of ion exchange, the framework of the TlCr$_5$Te$_8$ material is retained, thus restraining the structural form of the final product.

In this paper we report the structural characterization of the material Rb$_x$Cr$_5$Te$_8$ ($x = 0.732(7)$) from single crystal data and discuss the possibility of this compound existing in a state deficient in rubidium.

EXPERIMENTAL

Synthesis. Rb$_{0.73}$Cr$_5$Te$_8$ was prepared from Rb (0.43g, 5.0 mmol), Cr (0.33g, 6.3 mmol), and Te (1.28g, 10.0 mmol), sealed under vacuum in a quartz tube. The tube was heated to 850°C over a period of 6 h and subsequently, after 1 week, cooled to 400°C over a 12 h period. Room temperature was reached after cooling for a further 4 h. A dark metallic-grey crystalline product was obtained from which single crystals of the reported ternary telluride were isolated.

Single crystal studies. Single crystals of Rb$_{0.73}$Cr$_5$Te$_8$ were isolated from the bulk material under an atmosphere of nitrogen and sealed in silica capillaries. Weissenberg photographs were taken to select a good-quality crystal for subsequent data collections on a graphite-monochromated Siemens P4 diffractometer (AgK-L$_{2,3}$ radiation). Two data sets were obtained, both for the crystal in the sealed capil-

lary and for the crystal remounted on a glass fiber in air. No appreciable change in standard reflection intensities were observed over the period of data collection and thus the preferred data collection in air, without the silica capillary, was used for structure determination. The unit cell parameters, as determined from setting angles of 28 reflections with $10° < 2\theta < 20°$ and in agreement with the Weissenberg photographs, along with other crystallographic data, are given in Table 1 (a setting with $\beta > 130°$ was adopted for comparison with other reported structures). The data were treated for Lorentz and polarization effects, and a Gaussian absorption correction was applied with the XTAL program (14). Equivalent reflections were averaged according to the $2/m$ Laue symmetry ($R_{int} = 3.3\%$ on inten-

sity), yielding 1329 independent hkl with $I > 3\sigma(I)$ for subsequent refinement.

Structure refinement. Many atoms were located with the SHELXTL direct-methods program and the remaining atom positions were determined from Fourier difference maps and structure visualization. All structure refinements and Fourier syntheses were carried out using the SDS95 program package (15). Atomic scattering factors for neutral atoms with corrections for anomalous dispersion were taken from the literature (16). Full matrix refinements in the $C2/m$ space group with full occupancy for all atoms yielded a reliability factor $R = 3.6\%$ ($R_w = 4.5\%$). A Fourier difference map analysis revealed a large positive peak at the rubidium site (3.7 eÅ^{-3}), surrounded by negative residues (*ca.* 4 eÅ^{-3}). A high equivalent atomic displacement parameter (ADP) for rubidium and a corresponding low ADP for chromium and tellurium, in conjunction with the Fourier difference, clearly hinted toward a partial occupancy of rubidium atoms. However, an anharmonic refinement for rubidium was first attempted. Since little gain was achieved, a new refinement series (harmonic) includ-

TABLE 1
Crystallographic Data for $Rb_{0.73}Cr_5Te_8$

Physical, crystallographic, and analytical data	
Formula	$Rb_xCr_5Te_8$, $x = 0.732(7)$
Molecular weight (g · mol^{-1})	1343.2
Crystal system	Monoclinic
Space group	$C2/m$ (No. 12)
a (Å) 20.315(4)	
b (Å) 3.931(1)	β 139.77(1)
c (Å) 14.304(3)	
V (Å^3) 737.8(3)	$Z = 2$
Density (calc., g · cm^{-3})	6.044
Data collection	
Temperature (K)	293
Diffractometer	SIEMENS P4
Radiation	AgK-L$_{2,3}$ (0.56090 Å)
Crystal color	Black (metallic luster)
Crystal description	Platelet
Crystal size (mm^3)	$\approx 0.09 \times 0.19 \times 0.01$
Linear absorption coeff. (cm^{-1})	111.53
Monochromator	Oriented graphite (002)
Scan mode	ω
Recording range 2θ (°)	2–53
hkl range	$-32 \le h \le 32$, $-6 \le k \le 6$, $-22 \le l \le 22$
No. of measured reflections	6234
Data reduction	
No. of independent reflections	1748
$R_{int} = \Sigma |I - I_{avr}|/\Sigma I$	3.3%
Absorption correction	Gaussian integration method
Transmission coeff.	0.44–0.90
Independant reflections with $I > 3.0\ \sigma(I)$	1329
Refinement	
Refinement	F
F_{000}	1126
Weighting scheme	$w = 1/\sigma^2(F_{obs})$
R (%)	2.81 %
R_w (%)	3.29 %
No. of refined parameters (M)	47
Difference Fourier residues	$[-1.81, +1.44]$ e$^-$/Å^3
Secondary extinction	0.013(1)

TABLE 2
Refined Coordinates, Atomic Displacement Parameter (ADP), and Their Estimated Standard Deviations for $Rb_{0.73}Cr_5Te_8$

Atom	x	y	z	$B_{eq}{}^a$	τ (%)
Rb	1/2	0	1/2	4.1(2)	0.732(7)
Cr1	0	0	0	1.11(8)	
Cr2	0.3343(1)	0	0.0077(1)	0.92(7)	
Cr3	0.8155(1)	0	0.6681(1)	0.97(7)	
Te1	0.80249(4)	0	0.84446(6)	1.02(3)	
Te2	0.53520(4)	0	0.17035(6)	0.96(3)	
Te3	0.13275(4)	0	0.83018(6)	1.02(3)	
Te4	0.17290(4)	0	0.50742(6)	1.03(3)	
	$U_{11}{}^b$	U_{22}	U_{33}	U_{13}	
Rb1	0.038(1)	0.088(2)	0.025(1)	0.023(1)	
Cr1	0.0141(8)	0.0155(8)	0.0146(8)	0.0115(7)	
Cr2	0.0130(5)	0.0109(5)	0.0140(6)	0.0111(5)	
Cr3	0.0126(5)	0.0130(5)	0.0137(5)	0.0107(5)	
Te1	0.0164(2)	0.0120(2)	0.0160(3)	0.0140(2)	
Te2	0.0105(2)	0.0107(2)	0.0150(2)	0.0096(2)	
Te3	0.0127(2)	0.0139(2)	0.0143(2)	0.0109(2)	
Te4	0.0129(2)	0.0134(2)	0.0138(2)	0.0105(2)	

^{a} Isotropic equivalent ADP defined as

$$B_{eq}(Å^2) = \frac{4}{3}\text{trace}(\beta\mathbf{g}) \text{ or } B_{eq} = \frac{8\pi^2}{3}\sum_i\sum_j U_{ij}|\mathbf{a}_i^*||\mathbf{a}_j^*|\mathbf{a}_i \cdot \mathbf{a}_j.$$

^{b} The expression of the harmonic displacement factor is

$$\exp\left(-2\pi^2\sum_i\sum_j U_{ij}|\mathbf{a}_i^*||\mathbf{a}_j^*|h_ih_j\right), \text{ with } U_{ij} \text{ in Å}^2 \ (U_{12} = U_{23} = 0).$$

TABLE 3
Main Interatomic Distances (Å) in $Rb_{0.73}Cr_5Te_8$

CrTe$_2$ layer (*ab* plane)	Cr1–Te1 2.7237(11) × 2	Cr2–Te1 2.726(2) × 2
	Cr1–Te2 2.7662(8) × 4	Cr2–Te2 2.752(2)
		Cr2–Te3 2.709(2) × 3
Bridging Cr–Te octahedra	Cr3–Te1 2.730(3)	Cr3–Te4 2.695(3)
	Cr3–Te2 2.7748(11) × 2	Cr3–Te4 2.7154(11) × 2
Rb–Te	Rb–Te1 3.9760(13) × 2	Rb–Te3 3.7409(11) × 4
	Rb–Te4 3.9552(12) × 4	
Principal short Te–Te	Te1–Te3 3.747(2)	Te1–Te2 3.7808(10)

ing the Rb occupation ratio was carried out. A significant effect was then observed. The Rb occupation decreased from 1.0 to 0.732(7), the R (R_w) value lowered to 2.81% (3.29%), and the electron density residues became featureless. Table 2 reports the refined coordinates, ADPs, and standard deviations, while in Table 3 are gathered important interatomic distances. Lists of structure factors have been deposited.[2]

DISCUSSION

The $Rb_{0.73}Cr_5Te_8$ structure is based upon a three-dimensional lattice of chromium in an octahedral coordination with tellurium. This lattice is made up of two approximately orthogonal layers, the first layer consisting of edge sharing $CrTe_6$ octahedra only and the second layer of both face sharing and edge sharing $CrTe_6$ octahedra. The intersection points of these layers occur every third $CrTe_6$ unit, thus forming a one-dimensional channel in the direction of the b axis, as shown in Fig. 1, with the angle between the two layer planes being *ca.* 85°. This slight distortion away from complete orthogonality is due to the succession of face and edge sharing octahedra.

All previous preparations of the materials in the family AM_5X_8 have been reported as being of a hollandite-*type* structure. This description represents the fact that this structural family consists of layers of MX_6 edge sharing octahedra, connected by double chains of edge sharing MX_6 octahedra. Although this arrangement results in a channel-like structure, it is however somewhat different from the true hollandite family. Hollandite ($BaMn_8O_{16}$) (17) consists of layers with intersections at the same point along an edge sharing $CrTe_2$ layer, thus forming layers of infinite length, as shown in Fig. 2a. The arrangement in

the AM_5X_8 family, in which opposite double chains connect at different points (see Fig. 2c), will hence be referred to as a pseudo-hollandite phase for the remainder of this report. The schematic view of $Rb_{0.73}Cr_5Te_8$ (Fig. 2b) shows that this material actually has a true hollandite anionic framework. However, it differs from the hollandite phase by the fact that the octahedral site at the point of intersection is occupied (see Fig. 3). It should be noted that although the material $Rb_{0.73}Cr_5Te_8$ has a very similar structure to that of hollandite, the skeletal stoichiometry is the same as for the pseudo-hollandite phases due to the filling of this octahedral site of intersection.

The occurrence of infinite layers perpendicular to the edge sharing $CrTe_2$ layer in the $Rb_{0.73}Cr_5Te_8$ structure results in the formation of a block of three face sharing octahedra and consequently of a chain of two consecutive Cr–Cr distances ($d_{Cr1–Cr3}$ = 3.068 Å to be compared with $d_{Cr1–Cr2}$ = 3.972 Å in the edge sharing mode). This motif is not found in the pseudo-hollandite structure, in which only isolated short (but longer) transition metal–transitional metal distances occur ($d_{Cr–Cr}$ = 3.153 Å in $TlCr_5Te_8$ (12), for instance). The chromium environments are shown in Fig. 3 for the hollandite, the $Rb_{0.73}Cr_5Te_8$, and the pseudo-hollandite phases. A direct comparison between the material prepared in this study and the corresponding pseudo-hollandite phase $RbCr_5Te_8$ prepared from ion exchange of $TlCr_5Te_8$ (5) is not possible as a
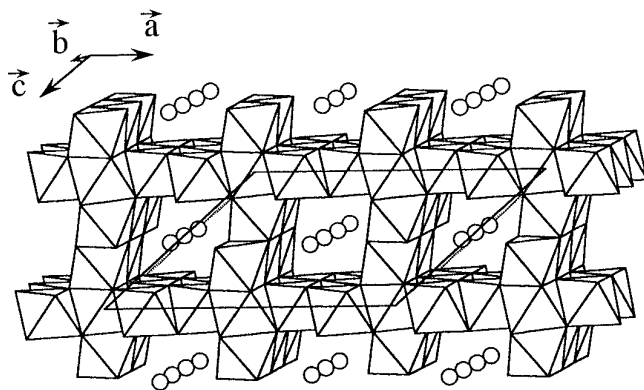
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[2] See NAPS document No. 05287 for 13 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material, $1.50 for postage of any microfiche orders.
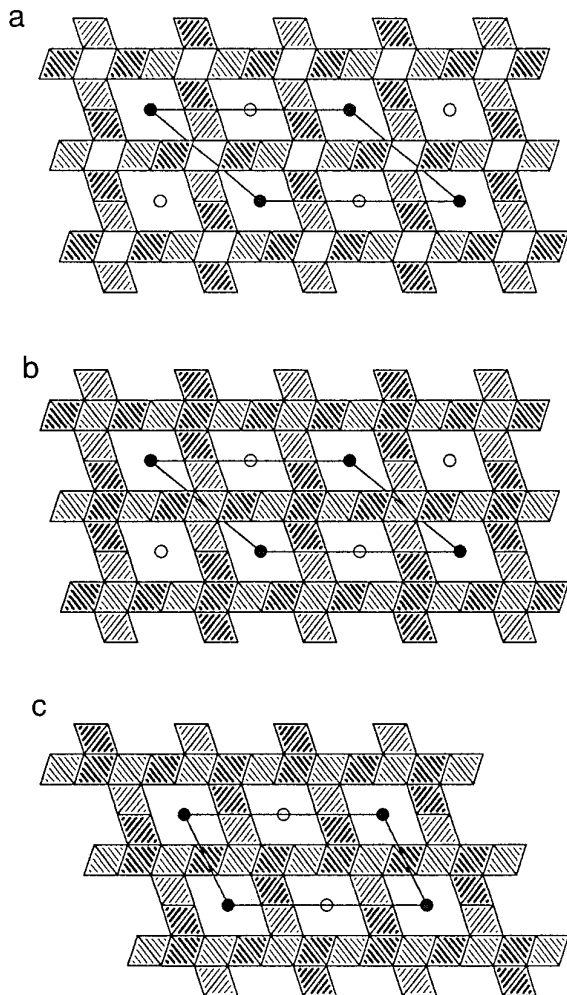

FIG. 1. Channel structure of $Rb_{0.73}Cr_5Te_8$.

a

b

c

FIG. 2. Schematic view of (a) hollandite, (b) $Rb_{0.73}Cr_5Te_8$, and (c) AM_5X_8.

a

b

c

FIG. 3. Chromium environments for (a) hollandite, (b) $Rb_{0.73}Cr_5Te_8$, and (c) AM_5X_8.

definitive structural determination for this $RbCr_5Te_8$ phase has not yet been performed. However, it is reasonable to assume an increased interaction between the chromium atoms for the phase $Rb_{0.73}Cr_5Te_8$, as compared to that presumably found in the pseudo-hollandite structure. This increased interaction is expected to yield some interesting magnetic and electronic structural properties.

The $Rb_{0.73}Cr_5Te_8$ structure can be compared with that of Cr_2Te_3 (18), in which one finds the same edge sharing $CrTe_2$ layers and identical blocks of three face sharing octahedra joining the layers. The Cr–Cr distance calculated (of 3.018 Å) for those blocks compares well with that found in the title compound (3.068 Å).

The rubidium is found within the channels holding a tenfold coordination. In the refinement procedure it was found that the Rb site occupation was ca. 0.73 (*vide supra*). This apparant nonstoichiometry of rubidium is expected to be accompanied by a change in the overall charge of the Cr_5Te_8 framework. This is thought to be plausible as
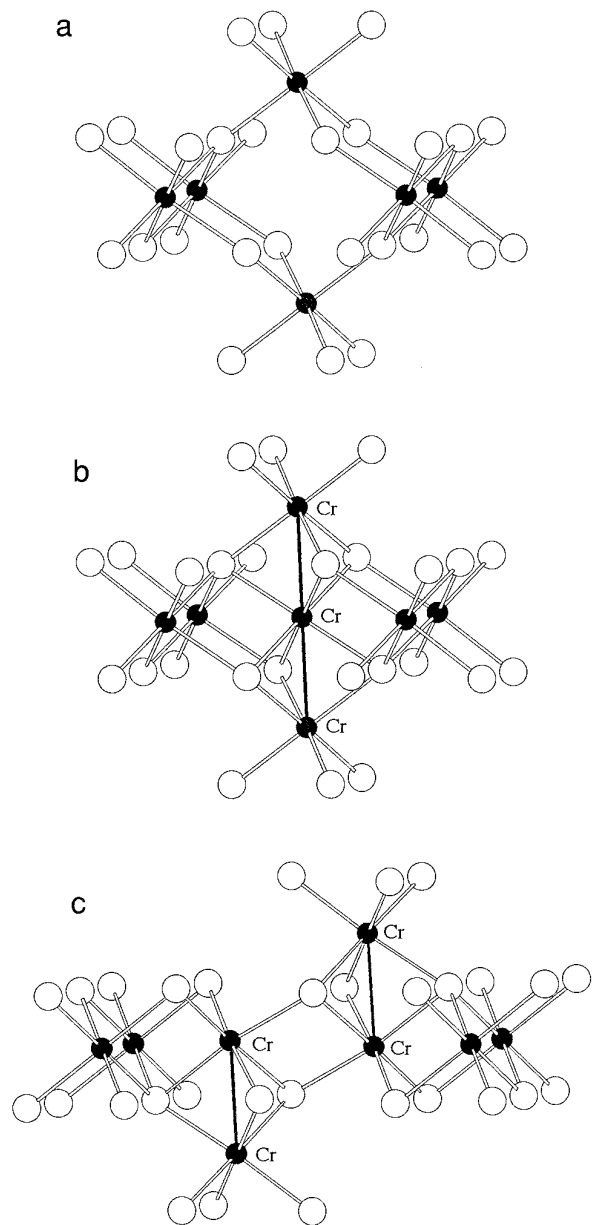
oxidation of tellurium has been observed for some binary telluride systems, such as the transition metal ditelluride family (18), and is accompanied by a shortening of the Te–Te contact distances corresponding to the affected tellurium atoms. Thus, the electronic restraint induced by nonstoichiometry in the channel structure described in this work may be simply accomodated by a change in the framework structure. A thorough analysis of the Te–Te distances in the material $Rb_{0.73}Cr_5Te_8$ did not, however, reveal such a modification; the Te–Te bond distances were found within a 3.747–3.981 Å range, to be compared with 3.67–3.98 in $TlCr_5Te_8$ and 3.64–3.98 in Cr_2Te_3. Therefore, the

change must be subtle as indicated by the expected Te oxidation change : $Te^{-2} \rightarrow Te^{-1.97}$.

CONCLUSION

It has been seen that the previous pseudo-hollandite structure reported for the family of materials AM_5X_8 is not the only structural type possible for this class of compounds. Single crystal structure determination has shown that the material $Rb_{0.73}Cr_5Te_8$ crystallizes with the same general structure as the true hollandite phase with the addition of a chromium atom at the site of intersection of the approximately orthogonal layers. The occurrence of this structural type for this material allows differences in interactions, such as the Cr–Cr short interactions, which may prove to be interesting in the study of the electronic and magnetic structures of these materials.

Finally, the preparation of this new phase from the elements indicates that this group of materials is, in fact, a complicated system and a number of structural types may well be found with slight modifications in preparative conditions.

ACKNOWLEDGMENT

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