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Redetermination the basic cell trigonal Cr_5Te_8 single crystal structure and its temperature dependence Raman spectra



Boyang Fu^a, Xinjian Bao^{b,*}, Hongshan Deng^c, Min Zhang^{a,*}

^a School of Physics and Electronic Technology, Liaoning Normal University, Dalian, 116029, PR China

^b Key Laboratory of Orogenic Belts and Crustal Evolution, MOE, School of Earth and Space Sciences, Peking University, Beijing, 100871, PR China

^c Center for High Pressure Science and Technology Advanced Research, Beijing, 100094, PR China

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ABSTRACT

Single crystal Cr_5Te_8 with basic trigonal cell was grown by the chemical vapor transport (CVT) method and the crystal structure was determined by single crystal X-ray diffraction. The as grown Cr_5Te8 was crystallized in space group *P*-3*m*1 with *a* = 3.8972(11) Å and *c* = 5.9965(18) Å. Typical energy-dispersive x-ray spectra (EDS) suggesting the ratio of Cr and Te is around 38.5% and 61.5%. The electrical resistivity was measured by four-probe method at range from 2 to 350 K, and the result suggested an abnormal trend around 25 K. There is no evidence of structural transition through the Raman spectra collected at range from 8 to 325 K, which reveals the magnetic and electrical properties are independent of structural changes under low temperature. The Cr₅Te₈ crystal was expected as a potential magnetoelectric coupling material, considering the magnetic transition around 20 K.

1. Introduction

The transition metal dichalcogenides (TMDCs) have been widely studied since 1923 [1] for their remarkable electrical and optical properties, such as charge density wave (CDW), superconducting property, or anomalous Hall effect[2-8] TMDCs have the general chemical formula MX_2 , where M stands for a transition metal (M = Mo, W, Cr, Ta, Ti) and X for Se, S, or Te. Bulk TMDCs crystals are formed by vertical stacking of 2D layers that are around 0.6 nm, between which are metal vacancies[4,9]. They can also be regarded as the arrangement of metal atoms intercalated in the van der Waals gap of layered TMDCs for convenience [9,10]. Based on the different proportion of intercalation elements, a series of MX₂ derivatives could be obtained. The self-intercalation compounds Cr₅Te₈ (monoclinic/trigonal), Cr₂Te₃ (trigonal) and Cr₃Te₄ (monoclinic) are commonly observed, while additional Cr-atoms between TMDCs-layers with 1/4, 1/3, or 1/2 content of Cr in the 1T-CrTe2 family, which were extensively studied theoretical and experimental due to their ferromagnetic properties [11–15]. The intercalated atoms are arranged in a superstructure, relative to a 1 \times 1 unit cell of the TMDCs. The Cr vacancies occur in every second metal layer, and thus the metal-deficient and metal-full layers stack alternatively along the c-axis. The distribution patterns of Cr vacancies depend not only on the Cr concentration but also on manners of the heat treatment used to prepare the samples. Cr–Te Phase diagrams have been studied extensively, and three structural modifications of Cr_5Te_8 are obtained namely, trigonal basic cells [15], super-cells (space group *P-3m1*) and monoclinic super-cells(space group *F2/m*) [16]. For the lower Te content (from 59.5% to 61.5%), Cr_5Te_8 shows monoclinic symmetry and Te rich Cr_5Te_8 exhibits trigonal symmetry[17]. Trigonal Cr_5Te_8 with superlattices was firstly reported in space group *P-3m1* from single crystal by Bensch *etc.* in 1997. But the structure details about trigonal Cr_5Te_8 with basic lattices haven't been reported from single crystal till now[17,18].

In this work, single crystal Cr_5Te_8 with basic cell was grown by the chemical vapor transport (CVT) method. The crystal structure was redetermined by single crystal X-ray diffraction. The chemical composition was measured by EDS. The electrical resistivity measurements performed on the crystal using the four-probe method. And, the Raman spectroscopy at various temperatures was used to study the stability of the sample.

E-mail addresses: xinjian.bao@pku.edu.cn (X. Bao), m.zhang@live.com (M. Zhang).

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^{*} Corresponding author. No.5 Yiheyuan Road, Haidian District, Beijing, 100871, PR China.

^{**} Corresponding author. No.850 Huanghe Road, Shahekou District, Dalian, 116029, PR China.



Fig. 1. a) SEM image of single crystal of Cr_5Te_8 . b) Typical energy-dispersive x-ray spectra suggesting the ratio of Cr and Te is around 38.5% and 61.5%. c) and d) Energy-dispersive X-ray spectra (EDS) color-maps of Cr (green) and Te (red). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 2. Schematic diagram of Cr_5Te_8 crystal structure. The stacking of TMDCs layers results in a bulk Cr_5Te_8 crystal, while randomly vacant additional Cr-atoms between TMDCs layers (indicated as red and yellow two-color ball) results in this 'self-intercalation' compounds. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

2. Experimentals

2.1. Synthesis

The new structure dichalcogenide with the composition Cr_5Te_8 was synthesized from the reaction between the powders of the individual metal and tellurium in evacuated sealed quartz-glass tube. The mixture of the powders of elemental Cr (Alfa Aesa, 99.99%) and Te (Alfa Aesa, 99.999%) powders were well-grounded as reactant with a molar ratio of Cr:Te = 1:1. The reactant mixture was loaded in the quartz-glass tube closed at one end through a long-stemmed funnel. The charged tube was evacuated and sealed, then placed in a two-temperature zone horizontal tubular furnace (Kejing, OTF 1200X). The synthesis was achieved by establishing a temperature gradient with the $T_{hot} = 1073$ K and the $T_{cold} = 773$ K for 7 days. The crystal samples were obtained on the inner surface of the tube at the cool end. Then switched off the power, and took out the tube until it cooled to room temperature under ambient condition.

2.2. Characterization

The microstructure was examined by scanning electron microscopy (SEM, JEOL JSM-7500F). The composition of the sample was determined by energy dispersive x-ray spectroscopy (EDS) attached to the SEM system. The electrical resistivity was measured using a four-probe technique on the physical property measurement system (Quantum Design, PPMS) at temperature range from 2 to 350 K. The Raman spectra were obtain with a Renishaw InVia laser Ramn microprobe. Eleven spectra were collected from 75–375 cm⁻¹ at temperature range from 8 to 325 K.

2.3. Single-crystal X-ray diffraction

Suitable single crystal of Cr₅Te₈ was selected for single-crystal X-ray diffraction analysis. Intensity data was collected on a Bruker D8 Venture diffractometer using Mo K α radiation ($\lambda = 0.071073$ nm). The raw data was processed and corrected for the absorption effects using SAINT+ and SADAB. An initial structure solution was obtained via direct methods and

Table 1

Crystal data and structure refinement for C	r ₅ Te ₈	(Cr _{1.25} Te	2).
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Empirical formula	Cr _{1.25} Te2	
Formula weight	317.20	
Temperature	296 K	
Wavelength	0.71073 Å	
Crystal system, space group	Trigonal, P-3 m 1	
Unit cell dimensions	a = 3.8972(11) Å	
	c = 5.9965(18) Å	
Volume	78.87(5) Å ³	
Ζ	1	
Crystal size	$0.1 \times 0.08 \times 0.08 \mbox{ mm}$	
Theta range for data collection	3.397–28.03°	
Limiting indices	$-5 \leq h \leq$ 4, $-5 \leq k \leq$ 4, $-7 \leq l \leq$ 7	
Reflections collected/unique	1054/94 [R(int) = 0.023]	
Completeness to theta $= 25.10$	100%	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	94/0/10	
Goodness-of-fit on F ²	1.237	
Final R indices [I > 2sigma(I)]	$R_1 = 0.0086, wR_2 = 0.0164$	
R indices (all data)	$R_1 = 0.0096, wR_2 = 0.0165$	
Largest diff. peak and hole	0.478 and $-0.468 \text{ e} \text{ Å}^{-3}$	
$lpha R_1 = \Sigma Fo - Fc / \Sigma Fo \ \omega R2 = [\Sigma \omega (Fo2 - Fc2)2 / \Sigma \omega (Fo2)2]1/2$		

Table 2

Atomic coordinates (x, y, z), site occupancies and equivalent isotropic displacement parameters (U(eq)) for Cr_5Te_8 compound.

	х	у	Z	Occupancy	U(eq)
Te1 Cr1	0.33333	0.66667	0.75327(6)	1.000	124(2) 75(18)
Cr2	0.00000	1.00000	0.50000	1.000	147(3)

Note: equivalent isotropic U defined as one-third of the trace of the orthogonalized.

Uij tensor.

Table 3

Selected interatomic distances (Å) and bond angle for basic cell Cr₅Te₈.

		*	
Te01–Cr1	2.6929 (6)	Te01–Cr2	2.7146 (6)
Cr1–Te01–Cr1 Cr1–Te01–Cr2	92.706 (17) 67.35 (2)	Te01–Cr1–Te01	87.295 (17) 92.705 (17)
Cr1–Te01–Cr2	130.818 (7)	Te01–Cr2–Te01	91.749 (17) 88.251 (17)

refined by a full-matrix least-squares method using the SHELXT software included in the SHELXTL package. All atoms were refined with anisotropic displacement parameters. The final cycles of the least-squares refinement including atomic coordinates and anisotropic thermal parameters for the atoms [I > 2sigma(I)] converged at $R_1 = 0.0086$, $wR_2 = 0.0164$, and S = 1.237 for this new structure Cr_5Te_8 compound.

3. Results and discussion

3.1. Characteizatin

Scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS) is an extensively applied elemental microanalysis method capable of identifying and quantifying all elements in the periodic table. The as-grown single crystal was analyzed using SEM/EDS to confirm the composition. The secondary electron image of test sample was shown in Fig. 1a. The average compositions of the as shown sample determined by EDS spectra of Cr and Te were 38.5% and 61.5% in Fig. 1b, respectively, which are consistent with the stoichiometric ratio of Cr_5Te_8 phase. The EDS maps of Cr and Te shown in Fig. 1(c and d) evidenced a relative uniform distribution of the elements in the sample.



Fig. 3. Temperature dependence of electrical resistance curve Cr_5Te_8 crystal. The insert is the schematic of four-probe measurement on the single-crystal sample. The solid lines are fits to Bloch–Grüneisen formula as described in the text.

3.2. Description of the structure

The single crystal X-ray diffraction was taken to confirm the crystal structure of the as-grown product. The new Cr_5Te_8 compound reveals that it crystallizes in the space group *P-3m1*. Each asymmetric unit contains one distinct Te site and two distinct Cr sites. Schematic diagram of Cr_5Te_8 crystal structure in different view directions were shown in Fig. 2. The structure of *tr*- Cr_5Te_8 is built up by distorted CrTe6 octahedrons., in which Cr atoms locate in the center of these octahedrons. These octahedrons are connected by common faces parallel to the direction of the C axis linked to a linear chain, while in the horizontal direction [CrTe6] octahedral Coplanar Edge.

The crystal data and collection information were listed in Table 1. The atomic displacement parameters were shown in Table 2. The structure parameters remain similar to those of previously reported Cr-Te compounds. As the homogeneity range of Te content was reported to be about 61.8-62.5 at% for trigonal Cr-Te and 59.6 to 61.5 at% for monoclinic Cr-Te respectively, while a disordered trigonal structure forms at 61.5% as mentioned in this work[18]. The mechanism of this phenomenon is not clear by now, but it seems that the partial disorder of Cr atoms stabilizes the product in the trigonal structure just like how the further Cr atom vacancy works. Comparing with the analytical results of single crystal in this paper, the lattice parameter is a = 3.8972(11) Å and c =5.9965(18) Å, while a powder XRD refinement data with a = 3.914 Å and c = 5.998 Å were reported previously [18]. The lattice parameter a is also smaller than that of half value of the tr- Cr₅Te₈ with super lattice. The stacking of TMDCs layers results in a bulk Cr5Te8 crystal, while additional Cr-atoms partially occupied the vacancies between TMDCs layers (indicated as red and yellow two-color ball) results in this 'self-intercalation' compounds. The Cr atoms are coordinated to six edge-sharing Te atoms to form two distinct [CrTe6] octahedra. The Cr1-Te1 bond lengths are 2.6929(6) Å and the angles of Te1–Cr1–Te1 are vary from $87.294(17)^{\circ}$ to 180.0° , while the Cr2-Te1 are 2.7146(6) and the angles of Te1-Cr2-Te1 are vary from 87.295(17) ° to 180.0° respectively. More details about the interatomic distance and bond angles are listed in Table 3. Comparing with the interatomic distances reported previously, the Cr1-Te1 bond lengths significantly shorter in this redetermination work [18].



Fig. 4. Raman spectra of Cr_5Te_8 crystal under different temperatures. Spectra acquired at different temperatures are shifted vertically for clarity. The peaks were marked as peak 1 to peak 4.



Fig. 5. Temperature dependence of (a,d) the linewidth, (b,e) the frequency, (c,f) the Fano asymmetry 1/|q|. a,b,c are corresponding to peak 2, and d,e,f are corresponding to peak 3.

3.3. Electrical resistivity properties

Electrical resistivity measurements were performed using a Quantum Design Physical Property Measurement System (PPMS). The four-probe method was used to measure the electrical resistivity. Schematic of a four-probe measurement of Cr₅Te₈ crystal along the ab plane was shown in Fig. 3 (insert). Connections I^+ and I^- source the current, and the electric potential difference is measured through V⁺ and V⁻. The temperature dependence of the in-plane electrical resistivity $\rho(T)$ of Cr₅Te₈ single crystal were shown in Fig. 3. It is found that the ρ decreases monotonically with decreasing T, indicating a metallic behavior at high temperature region. Under cooling, a clear metal-insulator transition appears at low temperature. The transition temperature T_{M-L} , defined as the extreme point of $d\rho/dT$ at low temperature region, was 25 K. Since, there is no extra electrical resistivity peak observed when the sample was heated continuously from 20 to 350 K. Furthermore, $\rho(T)$ at relatively high temperature (137–300 K) can be well fitted by one expression of the Bloch–Grüneisen formula: $\rho(T) = \rho(0) + AT^n$, in which the parameter A is a constant related to the electron velocity of the Fermi surface, the Debve radius and the number density of electrons, n is an integer that is depending on different interactions. For example, n = 2 means that the resistance is caused by electron-electron interaction, n = 3 indicates that the resistance is caused by *s*-*d* electron scattering. And in this work, n = 5implies the intra-bands s-s electron phonon scattering is dominant near room temperature, though this phenomenon often occurs at lower temperatures in two-dimensional layered structures [19,20].

A serious of Raman spectra were collected under different temperatures as shown in Fig. 4. The peaks tend to broaden while increasing temperature, in accordance with the increasing probability of phononphonon scattering, and exhibit a slight redshift, which was tentatively attributed to long-range lattice disorder [21]. Importantly, there is no appearance of new peak while increasing temperature, which suggested that there is no structure phase transition occurs under low temperature. Although the resistance anomaly at low temperature has no relation with structural phase transition, the magnetic changes mentioned in previous reports around 20 K cannot be ignored. The peak 2 and peak 3 were fitted to Fano profile [22]:

$$y = C + \frac{\left(q + \frac{x - w_0}{G}\right)^2}{\left(1 + \frac{x - w_0}{G}\right)^2} \tag{1}$$

where G is full width at half maxima (FWHM), q is the asymmetry parameter as shown in Fig. 5. Two clear abnormal can be found around 50 K for the FWHM and 200 K for the 1/|q|. The abnormal around 50 K indicates the electrical transition which is agrees with the electrical resistivity measurements. The unusual behaver around 200 K accords with the magnetic transition reported previously[23].

4. Conclusions

In summary, Cr_5Te_8 single crystal with basic cell was synthesized by the chemical vapor transport (CVT) method. The chemical composition and crystal structure were confirmed by EDS and single crystal X-ray diffraction. The electrical resistivity measurements performed on the four-probe method suggested an interesting abnormal trend around 20 K [24,25]. There is no evidence of structural transition was identified in terms of the appearance or elimination of the Raman peaks, which suggesting excellent low temperature stability.

CRediT authorship contribution statement

Boyang Fu: synthesizing and characterizing the material, interpreting the results, and writing the paper. **Xinjian Bao:** collecting and refining the single-crystal X-ray data, interpreting and finalizing the results, writing and finalizing the paper. **Hongshan Deng:** characterizing the material and interpreting the results. **Min Zhang:** designing the project, discussing and interpreting the results, and writing the paper.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://do i.org/10.1016/j.jssc.2021.122222.

Author contributions

Boyang Fu, synthesizing and characterizing the material, interpreting the results, and writing the paper; Xinjian Bao, collecting and refining the single-crystal X-ray data, interpreting and finalizing the results, writing and finalizing the paper; Hongshan Deng, characterizing the material and interpreting the results; Min Zhang, designing the project, discussing and interpreting the results, and writing the paper.

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