Non-Stoichiometric Monoclinic Cr_5Se_8 Prepared at High-Pressure and High-Temperature and the Crystal Structure Refined from Rietveld Data

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Dedicated to Dr. Hj. Mattausch on the occasion of his 60th birthday

The non-stoichiometric chromium selenide $Cr_{5.095(5)}Se_8$ was prepared under high-pressure high-temperature conditions. The structure was refined from X-ray powder data with the Rietveld method in the non-conventional monoclinic space group $F2/m$, a = 12.2992(2), b = 7.12753(12), c = 11.4486(2) Å, β = 90.927(1)° and V = 1003.49(3) Å^3. Three of the four unique Cr sites are fully occupied, and one site is only partially occupied. The structure may be viewed as being composed of alternating full and metal deficient layers which are oriented perpendicular to the crystallographic c axis of the pseudo-hexagonal unit cell. All Cr atoms are in an octahedral environment of six Se atoms. The $CrSe_6$ octahedra of neighbouring layers share common faces whereas the octahedra with layers are joined by common edges. As a result short Cr-Cr distances of 2.867(3) and 2.951(6) Å are found across common faces while Cr-Cr separations between $CrSe_6$ octahedra sharing edges are significantly longer. From a formal point of view charge balance requires a formulation as $Cr^{4+}_{0.715}Cr^{3+}_{4.38}Se_8$. On the basis of the distortion of the $CrSe_6$ octahedra the Cr^{4+} ions are mostly located on two different sites.

Key words: Chromium Chalcogenides, High Pressure Synthesis, Rietveld Refinement

Introduction

The chromium-selenium system was investigated in the past with respect to the crystal structures and physical properties. There were several compounds reported with different stoichiometries. In the following the most important crystallographical and physical properties of the different phases are briefly summarised. The Cr deficient $Cr_{1-x}Se$ phase crystallises with hexagonal symmetry [1, 2], Cr_7Se_8 is dimorphic with a hexagonal [3] and a monoclinic modification [2, 4, 5]. The sesquiselenide is also dimorphic and a rhombohedral as well as a trigonal modification were reported [2, 4, 6 – 8]. Stoichiometric Cr_2Se_3 crystallises in a rhombohedral system whereas deviations from stoichiometry lead to trigonal symmetry [6, 15]. For Cr_3Se_4 a monoclinic symmetry was observed [2, 4, 5, 9 – 14]. The homogeneity range of $Cr_{3\pm x}Se_4$ was reported to be at about $x \leq 0.20$ [12, 13]. For monoclinic Cr_3Se_4 a reversible phase transition into a defect-type CdI_2 structure was observed at temperatures above 900 °C [13]. Under high-pressure and high-temperature conditions (89 kbar, 1200 °C) monoclinic Cr_5Se_8 was obtained [16]. The diselenide cannot be prepared by reacting the elements but via a metathesis reaction using iodine and K_xCrSe_2 [17]. The diselenide crystallises in a $Cd(OH)_2$ type structure. At about 164 K and 186 K two phase transition were reported which are accompanied by a periodic charge density wave (CDW) transition [17]. The Cr deficient phases $Cr_{1-x}Se$ and Cr_7Se_8 are conductors whereas Cr_3Se_4 and Cr_2Se_3 are semiconductors with small electronic band gaps E_g [3]. The conductivity for $Cr_{3+x}Se_4$ is typical for a poor metal [12]. For the semiconductor Cr_2Se_3 the energy gap is about 0.84 meV in the temperature range from 80 to 150 K and amounts to 2.64 meV between 150 and 250 K [18].

The magnetic properties of monoclinic $Cr_{3+x}Se_4$ strongly depend on x. For $x > 0$ antiferromagnetic ordering is observed whereas for $x < 0$ meta- or ferromagnetism occur [12]. Above about 90 K the Curie Weiss law with $\Theta < 0$ K ($x > 0$) is fulfilled and for samples with $x < 0$ the value for Θ is positive [12]. In

the Cr rich region of the phase the introduction of additional $Cr^{2+}(d^4)$ ions lead to a static Jahn-Teller distortion and the magnetic moment exhibits an appreciable contribution of the orbital momentum of the Cr^{2+} ions [12].

Rhombohedral Cr_2Se_3 shows a Néel temperature between 47 K [7] and 43 K [8, 15, 17] and the unit cell volume expands near T_N [7]. According to the results of neutron scattering experiments an antiferromagnetic low-temperature structure (LT-AF) and an antiferromagnetic high temperature structure (HT-AF) exist. The order-order transition between these two structures occurs at about 45 K. In the LT-AF structure the magnetic moments show a non-collinear arrangement and the resulting monoclinic structure can be described as a 24 layer structure. In the HT-AF phase the moments exhibit a collinear arrangement and all axes of the magnetic cell are doubled compared to the nuclear cell [15]. Monoclinic Cr_3Se_4 is a metal [18] and finally, metallic behaviour was reported for Cr_5Se_8 [16].

In a previous publication [16] it was proposed that Cr_5Se_8 is isostructural to V_5Se_8. The conclusion was drawn comparing the powder diffraction pattern of Cr_5Se_8 with that of V_5Se_8. In the latter compound the three unique V sites are fully occupied. Recently, we reported the single crystal structures of monoclinic and trigonal Cr_5Te_8 [19] and of non-stoichiometric Cr_5S_8 [20]. In contrast to monoclinic V_5Se_8, in monoclinic Cr_5Te_8 two Cr positions are fully occupied and two further sites are only partially occupied. The occupancy of the latter two sites depends on the actual composition. For Cr_5S_8 only non-stoichiometric samples could be obtained until now. In the structure four different Cr sites were found of which three are fully and one is partially occupied. We started to investigate the influence of non-stoichiometry and of anion substitution in the series $Cr_{5\pm x}S_{8-y}Se_y$ onto the crystal structures and the physical properties. For an understanding of structure-property relationships the exact crystal structures must be known. Hence, we decided to synthesise the two end members of the solid solution $Cr_{5\pm x}S_{8-y}Se_y$. Here we present the results of the synthesis and the crystal structure determination of non-stoichiometric $Cr_{5.095(5)}Se_8$.

Experimental Section

Synthesis

The synthesis was undertaken in a Walker-style split-cylinder multianvil apparatus which is described in detail in [21]. The sample was prepared by mixing five parts of Cr_3Se_4 with four parts of elemental Se. Using a conventional 14/8 assembly with a boron nitride capsule (h-BN) the sample was compressed within 3 h to 7.7 GPa. Then, the temperature was raised to 1273 K within 10 min., held at this temperature for 10 min. and cooled to room temperature within another 10 min. Afterwards the sample was decompressed in additional 9 h. The total amount of the product was about 35 mg.

The Cr content of the sample was determined with AAS ($Cr_{5.12(1)}Se_8$) and agrees well with the composition determined by the full-pattern Rietveld refinement.

Table 1. Technical details of data acquisition and results of the Rietveld refinement of $Cr_{5.095(5)}Se_8$. Estimated standard deviations are given in parentheses.

a [Å]	12.2992(2)
b [Å]	7.12753(12)
c [Å]	11.4486(2)
β [°]	90.927(1)
V [Å^3]	1003.49(3)
R_{exp} [%][a]	2.64
R_{wp} [%][a]	3.96
R_B [%][a]	9.93
DW[1]	0.6977
χ^2	2.25
GOF[a]	1.6
No. reflections	317
2θ Range	10 – 100
Step width [°]	0.01
No. parameters	23
λ [Å]	1.54056

[a] The reliability factors values have the standard definitions. DW is the Durbin-Watson statistics and GOF the goodness-of-fit.

Structure refinement details

The structure was refined in space group $F2/m$ which is a non-conventional setting of $C2/m$. The transformation matrix is (0 0 −1) (0 1 0) (1/2 0 1/2). This setting is chosen to visualise the relation to the hexagonal NiAs structure. Selected technical details of the data acquisition and refinement results are summarised in Table 1. The background was modelled with a cubic-spline function and the reflection profiles with a Pseudo-Voigt function using 3 parameters. A slight preferred orientation was taken into account with the March-Dollase approach. The refinement was done with the FULLPROF suite [22].

Results and Discussion

The refinement of the crystal structure was started using the coordinates of Cr(1) to Cr(3) and S(1) to S(3) of the Cr_5S_8 structure. In the difference Fourier map the highest residual electron density was located on po-

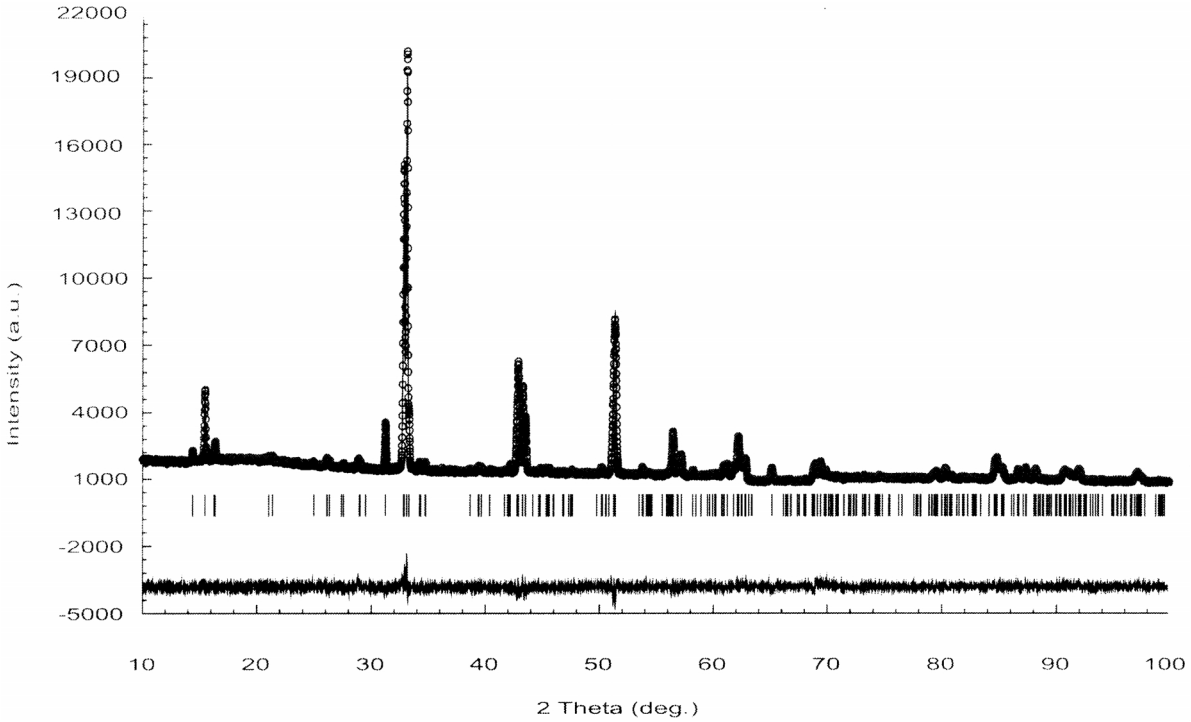

Fig. 1. The result of the Rietveld refinement of the powder pattern of $Cr_{5.095(5)}Se_8$. Open circles: experimental data; line: refined powder pattern; vertical bars: positions of the Bragg reflections; bottom line: difference between experimental and calculated data.

Table 2. Atomic coordinates for $Cr_{5.095(5)}Se_8$. Estimated standard deviations are given in parentheses.

Atom	*x*	*y*	*z*
Cr(1)	1/2	1/2	0
Cr(2)	1/4	0.2721(7)	1/4
Cr(3)	0.0079(4)	1/2	0.2425(5)
Cr(4)[2]	1/4	1/4	0
Se(1)	0.1663(3)	1/2	0.1130(4)
Se(2)	0.4141(2)	0.2515(4)	0.1230(3)
Se(3)	0.1628(3)	0	0.1379(5)

Note: Cr(1) to Cr(4) were refined with a common B_{iso} = 3.64(5) and Se(1) to Se(3) with a common B_{iso} = 2.63(2). Metal atom sites Cr(1) to Cr(3) are fully occupied, the sof for site Cr(4) is 0.024(2).

sition $\frac{1}{4}$ $\frac{1}{4}$ 0. In the next run Cr(4) was placed on this position with a site occupation factor (sof) accounting for the chemical composition. The refinement of the sof yields 0.024(2) giving as composition $Cr_{5.095(5)}Se_8$ which is in satisfactory agreement with the chemical analysis ($Cr_{5.12(1)}Se_8$). We note that the different reliability factors are significantly better with 4 Cr sites than with only Cr(1) to Cr(3). The result of the Rietveld refinement is displayed in Fig. 1.

The crystal structure of $Cr_{5.095(5)}Se_8$ is displayed in Fig. 2. The four crystallographically independent Cr atoms are in an octahedral environment of 6 Se atoms. Perpendicular to the *c* axis fully occupied and partially occupied metal atom positions alternate. Within the *ab* plane the $CrSe_6$ octahedra are connected via common edges and octahedra of neighbouring layers share common faces. The Cr-Se bond lengths range from 2.440(3) to 2.622(3) Å with no significant differences for the average ⟨Cr-Se⟩ bonds for Cr(1) to Cr(4) (Table 3).

The distortion of the octahedra expressed as the difference δ (Å) between the shortest and the longest Cr-Se distances scatters from 0.023 Å for Cr(1)Se_6 to 0.182 Å for Cr(4)Se_6 (Table 3). The Cr-Se bond lengths are comparable with those reported for other binary and ternary chromium selenides [23, 24]. We note that for Cr_5S_8 a similar distortion pattern of the CrS_6 octahedra occurs [20]. According to the occupancy in the full and metal deficient layers the formula of the selenide may be written as $Cr_4[Cr_{1.095}\square_{2.905}]Se_8$ ($\square$ denotes the vacancies).

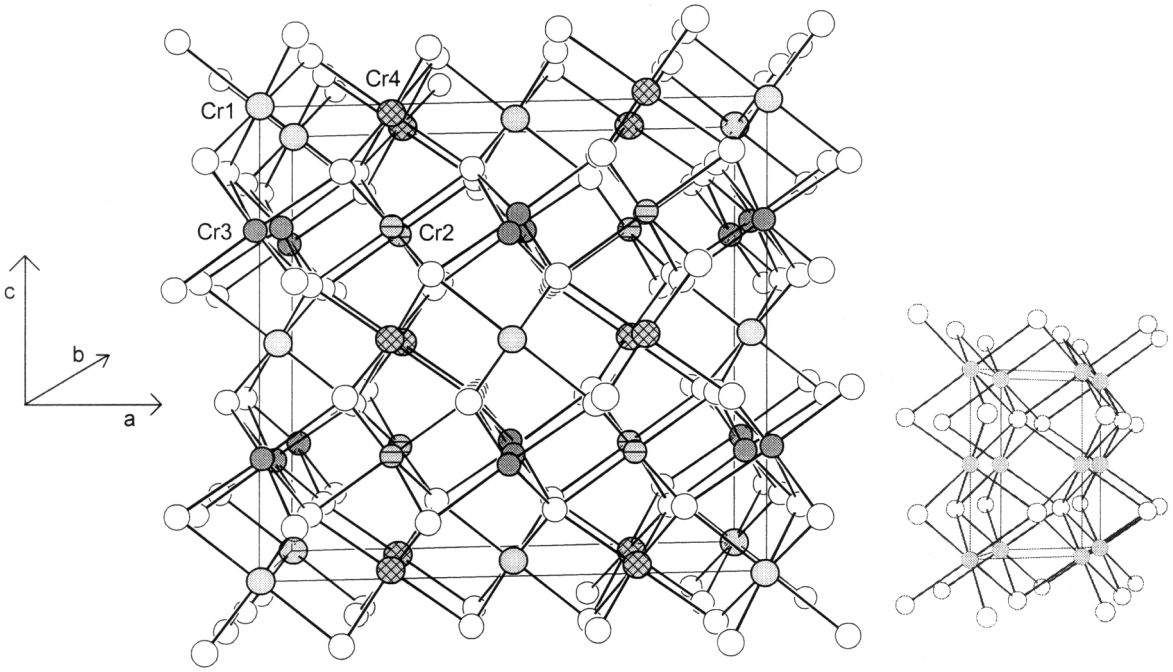

Fig. 2. The Crystal structure of $Cr_{5.095(5)}Se_8$. Note that Cr(4) is only partially occupied. The inset (right) shows the arrangement of Cr (gray circles) and Se (open circles) atoms in the NiAs type structure.

Table 3. Interatomic distances (Å) for $Cr_{5.095(5)}Se_8$ derived from Rietveld refinements. Estimated standard deviations are given in parentheses.

Cr(1)-Se(2)	2.507(3) 4×	Cr(1)-Se(3)	2.530(4) 2×
⟨Cr-Se⟩	2.515	δ[a]	0.023
Cr(2)-Se(1)	2.471(5) 2×	Cr(2)-Se(2)	2.510(3) 2×
Cr(2)-Se(3)	2.552(5) 2×		
⟨Cr-Se⟩	2.511	δ	0.081
Cr(3)-Se(1)	2.467(7)	Cr(3)-Se(2)	2.523(5) 2×
Cr(3)-Se(2)	2.526(5) 2×	Cr(3)-Se(3)	2.525(7)
⟨Cr-Se⟩	2.515	δ	0.059
Cr(4)-Se(1)	2.440(3) 2×	Cr(4)-Se(2)	2.442(3) 2×
Cr(4)-Se(3)	2.622(3) 2×		
⟨Cr-Se⟩	2.501	δ	0.182
Cr(1)-Cr(3)	2.951(6)	Cr(1)-Cr(4)	3.554(3)
Cr(2)-Cr(2)	3.250(7)	Cr(2)-Cr(3)	3.392(5)
Cr(2)-Cr(4)	2.867(3)	Cr(3)-Cr(3)	3.573(6)
Cr(4)-Cr(4)	3.564(1)		

[a] δ is the difference between the longest and shortest Cr-Se bond length.

Interesting features of the structure are the short Cr-Cr bond lengths of about 2.867(3) (Cr(2)-Cr(4)) and 2.951(6) Å (Cr(1)-Cr(3)) which are shorter than in other binary or ternary chromium selenides with $CrSe_6$ octahedra sharing common faces. The two distances are about 12.6% and 15.9% longer than in elemental chromium. The short separations are indicative of Cr-Cr interactions which may be important for the stability of the compound. Due to the larger radius of Se^{2-} compared with S^{2-} the Cr-Cr interatomic distances are longer than in the isostructural sulfide [20].

Within the metal atom layers the Cr-Cr distances are significantly longer and range from 3.250(7) Å (Cr(2)-Cr(2)) to 3.573(6) Å (Cr(3)-Cr(3)) (see Table 3).

The negative charges of the eight Se^{2-} anions must be compensated by 5.095 Cr atoms. Within an ionic picture the sample must be formulated as $Cr^{4+}{}_{0.715}Cr^{3+}{}_{4.38}Se_8$. The electronic configuration of the Cr^{4+} (d^2) ion should lead to a Jahn-Teller distortion and one would expect that this ion could be located analysing the environment of the Cr atoms. The Cr(2) and Cr(4) atoms show the strongest distortions of the environment with δ = 0.081 and 0.182 Å (Table 3). Compared with the previously investigated sulfides $Cr_{5.20}S_8$ to $Cr_{5.26}S_8$ (formal charge balancing formula: $Cr^{4+}{}_{0.40}Cr^{3+}{}_{4.80}S_8$ and $Cr^{4+}{}_{0.22}Cr^{3+}{}_{5.04}S_8$) the amount of Cr^{4+} in $Cr_{5.095}Se_8$ is significantly larger. In the sulfides the distortion of the $Cr(2)S_6$ and $Cr(4)S_6$ octahedera decreases with decreasing Cr^{4+} content. In the selenide the $Cr(2)Se_6$ and $Cr(4)Se_6$ octahedra show the

strongest distortions, suggesting that Cr^{4+} is located on Cr(2)/Cr(4).

Finally, a short comparison with the lattice parameters reported for Cr_5Se_8 [16] is given. The values for a = 12.353(4), b = 7.148(4), c = 11.462(3) Å, β = 91.06(3)° and V = 1011.9(5) Å^3 are significantly different from those obtained in the present study. For the Cr sulfides we observed an increase of the axes and of the unit cell volume with increasing Cr content. Hence, it can be assumed that the sample studied in [16] was richer in Cr than the compound investigated in our laboratory.

Further syntheses are under way to determine the stability range of $Cr_{5\pm x}Se_8$ and investigations of the magnetic and electrical properties are planned.

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