

Journal of Alloys and Compounds 238 (1996) 1-5

Mixed valent ternary iron chalcogenides: AFe_2X_3 (A = Rb, Cs; X = Se, Te)

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Abstract

The isostructural compounds $RbFe_2Se_3$, $RbFe_2Te_3$, $CsFe_2Se_3$ and $CsFe_2Te_3$, were obtained as coarse lustrous crystals by reacting Fe, Se or Te and the corresponding alkali monochalcogenide. They are orthorhombic, oC24, space group Cmcm, Z = 4, with a = 9.507(3) Å, b = 11.583(4) Å, c = 5.638(2) Å ($RbFe_2Se_3$); a = 10.126(9) Å, b = 12.486(7) Å, c = 5.921(1) Å ($RbFe_2Te_3$); a = 9.834(5) Å, b = 11.828(6) Å, c = 5.673(2) Å ($CsFe_2Se_3$); a = 10.438(4) Å, b = 12.501(6) Å, c = 5.958(2) Å ($CsFe_2Te_3$).

The crystal structures of $RbFe_2Se_3$, $RbFe_2Te_3$ and $CsFe_2Se_3$ were determined by single crystal diffractometer data and refined to conventional *R*-values of 0.043, 0.042 and 0.082 respectively. Isotypy of $CsFe_2Te_3$ was established from its powder diagram.

The title compounds are isostructural with rasvumite, KFe_2S_3 . Their crystal structures are characterized by infinite double chains of edge-sharing iron-centred chalcogen tetrahedra running parallel to [001]. The mean Fe–Se bond lengths are close to 2.39 Å, the mean Fe–Te bond length in $RbFe_2Te_3$ is 2.57 Å. The shortest Fe–Fe distances range from 2.765(5) Å in the selenides to 2.821(4) Å in $RbFe_2Te_3$.

Keywords: Selenoferrates; Telluroferrates; Mixed valent compounds

1. Introduction

Mixed valent linear thioferrate chains are of considerable theoretical interest because of the intermediate oxidation state of the transition metal [1]. Linear chains $\frac{1}{\infty}[\text{FeS}_2]^{x^-}$ are found in the infinitely adaptive series $\text{Ba}_p(\text{FeS}_2)_q$ [2]. They show metallic conductivity in the chain direction. In contrast, Na₃Fe₂S₄ [3], which is characterized by twisted $\frac{1}{\infty}[\text{FeS}_2]$ chains, is a semiconductor.

Another kind of mixed valent thioferrate is represented by the mineral rasvumite, KFe_2S_3 [4]; its structure is characterized by edge-sharing thioferrate double chains. It would be interesting to compare the physical properties accompanying this chain type with those of the single chains. However, detailed investigations are hampered by the fact that it is impossible to grow synthetic crystals of KFe_2S_3 of sufficient size because of its low decomposition temperature. Un-

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expectedly, rasvumite-type compounds are easily formed with rubidium and caesium and the heavier chalcogens. With the exception of $CsFe_2Te_3$ these phases can be obtained as single crystals by slow cooling of the stoichiometric melts. Their preparation and structure determination will be presented here.

2. Experimental

Starting materials: iron (Aldrich, powder 325 mesh, 99.9%), selenium (Alfa, powder 200 mesh, 99.9%), tellurium (Alfa, ingots, 99.99%), rubidium (Alfa, ampouled under argon, 99%) and caesium (Alfa, ampouled under argon, 99.9%).

The preparation of the title compounds was achieved by a two-step reaction. Firstly, the binary compounds A_2X were synthesized by reaction of the corresponding alkali metal (slight excess) and the chalcogen in carefully dried liquid ammonia, using an apparatus analogous to that described by Klemm et al.

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[5] and Föppl et al. [6]. The reaction products were annealed under vacuum at 620 K to remove traces of ammonia and alkali metal and were established to be single phase through their powder diagrams. The monochalcogenides, iron and the corresponding chalcogen, were weighed in molar ratios according to the nominal composition AFe_2X_3 , intimately mixed and sealed into silica ampoules at a pressure of 10^{-2} Pa. Thermal treatment of the samples consisted of heating to 1220 K (30 K h⁻¹), annealing for 24 h, followed by a controlled cooling (3 K h⁻¹) to ambient temperature.

The reaction products were obtained as lustrous ingots which were sensitive to moisture and air and had therefore to be handled under inert conditions. The crushed samples consisted of lamellar crystals up to 10 mm in length which were extremely sensitive to mechanical deformation. Numerous specimens had to be scrutinized by Weissenberg photographs in order to obtain roentogenographically suitable single crystals. In the case of $CsFe_2Te_3$, however, no crystals of sufficient quality were found.

Large single crystals of $RbFe_2Se_3$ (up to 10 mm in length) could be obtained with modified Bridgman apparatus. The melt was kept at 850 °C, the applied temperature gradient was determined as 50 °C cm⁻¹. The crystals were embedded in resin and cut along and perpendicular to the chain axis. Resistivity measurements were performed by the four-point technique from ambient temperature to 5 K.

3. Structure determination

Preliminary X-ray investigations by the Weissenberg technique (Co K_{α} -radiation) indicated that all four compounds were isostructural, crystallizing with orthorhombic symmetry. The systematic extinction for $hkl:h + k \neq 2n$ and $h0l: l \neq 2n$ led to Cmcm (No. 63), C2cm (No. 40) and Cmc2₁ (No. 36) as possible space groups.

For the structure determination small single crystals, sealed in glass capillaries, were mounted on a fourcircle diffractometer (Enraf Nonius CAD4) operated with graphite monochromated Mo K_{α}-radiation. Intensity data were collected at room temperature over one quadrant of the reflection sphere up to $2\theta = 54^{\circ}$ by applying $\omega - 2\theta$ scans.

The crystal structure for $RbFe_2Te_3$ was solved by direct methods (MULTAN II/82 [7]) leading to an atomic arrangement corresponding to that of rasvumite KFe_2S_3 (space group *Cmcm*, Z = 4). With the obtained positional parameters, the least-squares refinements of $RbFe_2Se_3$ and $CsFe_2Se_3$ converged rapidly. Anisotropic refinements led to the final *R*-values of about 0.043 and 0.042 for the rubidium compounds. The significantly higher *R*-value of 0.082 for $CsFe_2Se_3$ probably reflects the inferior crystal quality. Crystallographic data and details on the structure refinements are given in Table 1.

The crystallographic calculations were performed with the MOIEN crystallographic software package [8].

Table 1	
Crystallographic	data

	RbFe ₂ Se ₃	RbFe ₂ Te ₃	CsFe ₂ Se ₃	CsFe ₂ Te ₃
a (Å)	9.507(3)	10.126(9)	9.834(5)	10.438(4)
$b(\mathbf{A})$	11.583(4)	12.486(7)	11.828(6)	12.501(6)
$c(\dot{A})$	5.638(2)	5.921(1)	5.673(2)	5.958(2)
Z	4	4	4	4
$V(\text{\AA}^3)$	620.8	748.6	659.9	777.4
d_{z} (g cm ⁻³)	4.64	5.15	4.85	5.36
M.	434.04	579.96	481.48	627.40
F(000)	764	980	836	1052
$\mu(Mo K_{\alpha})(cm^{-1})$	295.39	215.53	260.61	192.85
Structure refinement				
hkl-range	$-1 \le h \le 12, 0 \le h$	$k \leq 15, -7 \leq l \leq 7$		
Unique reflections	435	468	417	
Observed reflections	281	364	222	_
Cut-off	$3.0\sigma(F_{o})^{2}$	$3.0\sigma(F_{o})^{2}$	$3.0\sigma(F_{o})^{2}$	—
Variables	21	21	21	—
$R = \sum F_{\alpha} - F_{\alpha} / \sum F_{\alpha} $	0.043	0.042	0.082	
$Rw = [\sum_{n=1}^{\infty} w \ F_n - F_n ^2 / \sum_{n=1}^{\infty} w F_n ^2]^{1/2}$	0.037	0.038	0.064	—
$\{w = [\sigma(F_{0}^{2})^{2} + (0.005F_{0}^{2})^{2}]^{1/2}\}$				
Residual electron density $(e\dot{A}^{-3})$	1.62	1.36	3.55	

Pearson symbol. oC24, space group Cmcm (No. 63).

Table 2 Positional and thermal parameters for RbFe₂Se₃

Atom	Position	x	у	z	B _{eq}
Rb	4c	0.500	0.1662(3)	0.250	1.79(7)
Fe	8e	0.3546(4)	0.500	0.000	0.84(5)
Se(1)	4c	0.000	0.1236(3)	0.250	0.78(6)
Se(2)	8g	0.2203(3)	0.3839(2)	0.250	1.25(4)

Table 3

Positional and thermal parameters for RbFe₂Te₃

Atom	Position	x	y	z	Beq
Rb	4c	0.500	0.1595(3)	0.250	3.27(6)
Fe	8e	0.3607(2)	0.500	0.000	1.63(4)
Te(1)	4c	0.000	0.1294(1)	0.250	1.65(3)
Te(2)	8g	0.2216(1)	0.37957(9)	0.250	2.42(2)

Table 4

Positional and thermal parameters for CsFe₂Se₃

Atom	Position	<i>x</i>	у		B _{eq}
Rb	4c	0.500	0.1621(5)	0.250	1.6(1)
Fe	8e	0.3593(7)	0.500	0.000	1.1(1)
Se(1)	4c	0.000	0.1212(7)	0.250	0.9(1)
Se(2)	8g	0.2279(5)	0.3860(5)	0.250	1.5(1)

Scattering factors for neutral atoms and coefficients for anomalous dispersion were taken from *International Tables for X-Ray Crystallography* [9]. A correction

Table 5 Powder diagram of CsFe₂Te₃

hkl	Int. calculated	Int. observed	2θ calculated	2θ observed
110	66	m	11.04	11.05
020	27	vw	14.17	14.15
220	33	vw	22.19	22.20
130	62	w	22.98	23.00
221	1000	vs	26.82	26.80
131	38	w	27.48	27.40
040	108	s	28.56	28.60
002	123	vs	30.00	30.00
311	35	VW	30.60	30.60
041	27	vw	32.35	32.35
022	32	m	33.32	33.30
400	63	s	34.36	34.35
312	61	s	40.51	40.50
042	208	vs	41.90	41.85
350	53	S	44.63	44.60
440	130	S	45.27	45.30
402	146	vs	46.25	46.20
261	120	s	49.53	49.50
223	163	vs	51.35	51.35
442	50	w	55.26	55.30
621	70	w	57.09	57.10
004	39	m	62.34	62.35
263	52	w	67.59	67.65

vs, very strong; s, strong; m, medium; w, weak; vw, very weak. Cu K_{α} -radiation.

for secondary isotropic extinction was included in the last stages of the refinements. Absorption effects were accounted for by an empirical correction originally performed on the redundant data set (DIFABS [10]), followed by averaging. The final positional and equivalent isotropic thermal parameters are given in Tables 2–4. Further details on the structure refinement have been deposited with the Fachinformationszentrum Karlsruhe.

Isotypy of $CsFe_2Te_3$ (Table 5) was corroborated by its Guinier powder diagram. The quoted cell dimensions are based on the Guinier data and were refined using the FINAX [11] program.

4. Discussion

The title compounds are isostructural with the complex sulphides $BaFe_2S_3$ [12] and KFe_2S_3 [4] which crystallize with the $CsCu_2Cl_3$ [13] structure type.

An outstanding feature of the crystal structure is the formation of tetrahedral double chains $\frac{1}{\infty}[Fe_2X_3]$ formed by edge-sharing FeX_4 -tetrahedra (Fig. 1). These chains run parallel to [001] and are arranged in a simple hexagonal rod packing. The alkali cations which separate the chalcogenoferrate chains are in a bicapped trigonal-prismatic coordination through the chalcogen atoms. This coordination is expanded to 8 + 2 by pairs of chalcogen atoms capping the remaining rectangular face. The trigonal prisms share common triangular faces to form infinite rods.

Se(1) Se(2)

Fig. 1. Projection of the crystal structure of $RbFe_2Se_3$ along [001]. Open and shaded circles represent z = 0.25 and 0.75 respectively.

The formal oxidation state of the iron atoms (+2.5) is nonintegral. Since all iron atoms are crystallographically equivalent, an alternating occurrence of Fe^{II} and Fe^{III} can be ruled out.

The average Fe-Se bond distances for RbFe₂Se₃ and CsFe₂Se₃ (Table 6) have fairly comparable values of $\bar{d}_{\text{Fe-Se}} = 2.384$ Å and 2.395 Å respectively. These values lie, in fact, between those of BaFe₂Se₃ (\bar{d} = 2.42 Å) [12] and those in the selenoferrate(III) single chain of RbFeSe₂ (\bar{d} = 2.365 Å) [14] or CsFeSe₂ (\bar{d} = 2.355 Å) [15]. Since RbFe₂Te₃ and CsFe₂Te₃ represent the first compounds with infinite telluroferrate chains, comparison of the Fe-Te bond distance $(d_{\text{Fe-Te}} = 2.57 \text{ Å})$ with topologically similar compounds is not possible. Nevertheless, condensed Fe-Te tetrahedra are present in the complex cluster anions of $Cs_7Fe_4Te_8$ [16] and $K_7Fe_4Te_8$ [17]. The average Fe-Te bond lengths in these compounds are significantly larger (≈ 2.62 Å). It is, however, doubtful whether these discrepancies can be attributed to the different oxidation states (2.5 vs. 2.25) of the iron atoms.

Table 6 Selected interatomic distances (Å) and bond angles (°)

The bonding situation in the $\frac{1}{\infty}$ [Fe₂S₃] double chain of the rasvumite-type compounds appears to be rather delicate and the formal oxidation state may be misleading for the prediction of the physical properties. Thus BaFe₂S₃ [12], formally a valence compound of divalent iron, is reported to show rather high electrical conductivity [18]. In addition, its Mössbauer ⁵⁷Fe isomer shift of 0.41 [18] is atypically low for divalent iron in tetrahedral sulphur environment. Application of the semi-empirical Hoggins-Steinfink relationship: $\delta = 14-0.5$ n (n = empirical oxidation state) rather indicates a nonintegral empirical oxidation state of +2.5. Likewise, the 57Fe isomer shift of KFe₂S₃ of 0.29 [19] implies an empirical oxidation state definitely higher than the formal one. A bonding model for the thioferrate chain of BaFe₂S₃ was proposed by Goodenough and coworker [20,21]. It is assumed that the minority spin electrons of Fe¹¹ are for one part delocalized in a band along the chain direction, responsible for the high conductivity, while the remaining electrons are localized between two iron atoms in the perpendicular direction (one electron per iron

RbFe ₂ Te ₃						
Rb-Te(1)	3.964(2) 2×	Fe-Fe	2.821(4)	Te(1)-Te(1)	4.383(2) 2×	
Rb-Te(2)	3.747(1) 4×	Fe-Fe	2.961(0) 2×	Te(1)-Te(2)	3.846(2) 2×	
Rb-Te(2)	3.936(3) 2×	Fe-Fe	4.090(3) 2×	Te(1)-Te(2)	4.089(1) 4×	
Rb-Te(2)	4.154(3) 2×	Fe-Te(1)	$2.606(1) 2 \times$	Te(1)-Te(2)	4.204(2) 2×	
		Fe-Te(2)	2.537(1) 2×	Te(2)-Te(2)	4.220(1) 2×	
Te(1)-Fe-Te(1)	114.5(1)		Fe-Te(1)-Fe	65.5(1)		
Te(1)-Fe-Te(2)	105.3(0)×		Fe-Te(1)-Fe	69.2(0)		
Te(1)-Fe-Te(2)	$109.7(0) \times$		Fe-Te(2)-Fe	71.4(0)		
Te(2)-Fe-Te(2)	112.6(1)		Fe-Te(1)-Fe	103.4(1)		
$RbFe_2Se_3$						
Rb-Se(1)	3.724(3) 2×	Fe-Fe	2.765(5)	Se(1)-Se(1)	4.019(3) 2×	
Rb-Se(2)	3.560(2) 4×	Fe-Fe	2.819(1) 2×	Se(1)-Se(2)	3.671(3) 2×	
Rb-Se(2)	3.664(3) 2×	Fe-Fe	3.949(3) 2×	Se(1)-Se(2)	3.845(3) 2×	
Rb-Se(2)	3.884(4) 2×	Fe-Se(1)	2.439(3) 2×	Se(1)-Se(2)	3.876(2) 4×	
		Fe-Se(2)	2.329(3) 2×	Se(2)-Se(2)	3.897(2) 2×	
Se(1)-Fe-Se(1)	110.9(1)		Fe-Se(1)-Fe	69.1(1)		
Se(1)-Fe-Se(2)	107.5(0)×		Fe-Se(1)-Fe	70.6(1)		
Se(1)-Fe-Se(2)	108.7(0)×		Fe-Se(2)-Fe	74.5(1)		
Se(2)-Fe-Se(2)	113.5(2)		Fe-Se(1)-Fe	108.1(1)		
CsFe ₂ Se ₃						
Cs-Se(1)	3.823(7) 2×	Fe-Fe	2.766(9)	Se(1)-Se(1)	4.033(8) 2×	
Cs-Se(2)	3.660(3) 4×	Fe-Fe	2.836(1) 2×	Se(1)-Se(2)	3.852(8) 2×	
Cs-Se(2)	3.765(7) 2×	Fe-Fe	3.962(7) 2×	Se(1)-Se(2)	3.859(8) 2×	
Cs-Se(2)	3.961(7) 2×	Fe-Se(1)	2.445(6) 2×	Se(1)-Se(2)	3.900(3) 4×	
		Fe-Se(2)	2.345(6) 2×	Se(2)-Se(2)	3.914(5) 2×	
Se(1)-Fe- $Se(1)$	111.1(3)		Fe-Se(1)-Fe	68.9(2)		
Se(1)-Fe-Se(2)	107.3(1)×		Fe-Se(1)-Fe	70.9(2)		
Se(1)-Fe-Se(2)	109.0(2)×		Fe-Se(2)-Fe	74.4(2)		
Se(2)-Fe-Se(2)	113.1(3)		Fe-Se(1)-Fe	108.2(3)		



Fig. 2. Electrical resistivity along and perpendicular to the chain direction of RbFe₂Se₃.

pair) accounting for the low isomer shift. The Mössbauer data of KFe₂S₃, correspond to an empirical oxidation state of ≈ 2.75 , which indicates that the population of the minority spin electrons is reduced by comparable amounts along and perpendicular to the chain direction.

The Fe-Fe distances in the present mixed valent selenides are significantly larger than those in BaFe₂Se₃ (d = 2.72 Å) [12]. It is found that the increase of the formal oxidation state predominantly affects the Fe-Fe distances along the chain direction. Comparison of the Fe-Fe distances in the sulphides BaFe₂S₃ and KFe₂S₃ reveals the same trend, though to a smaller extent. In RbFe₂Te₃, however, there is a very large difference of 0.15 Å between the Fe-Fe distances along and across the chain direction.

Resistivity measurements performed on $RbFe_2Se_3$ corroborate the metallic character of this compound. The pseudo one-dimensional structure becomes apparent from the high anisotropy of the electrical resistivity along and perpendicular to the chain direction (Fig. 2).

Further investigations on the electrical properties of these new compounds are in preparation.

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