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New ternary iron sulphides $A_3Fe_2S_4$ (A = K, Rb, Cs): syntheses and crystal structures

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Abstract

The compounds $K_3Fe_2S_4$, $Rb_3Fe_2S_4$ and $Cs_3Fe_2S_4$ were synthesized by reaction of the respective alkali metal carbonate with iron and sulphur in a hydrogen stream charged with sulphur at 930 K. The crystal structures of these mixed-valent compounds were determined by single-crystal X-ray diffraction (space group: *Pnma*, $Z=4$). The characteristic structural unit of these sulphides is a $^1_\infty[FeS_{4/2}]$ zig-zag chain of edge-sharing, iron-centred sulphur tetrahedra. $K_3Fe_2S_4$ and $Rb_3Fe_2S_4$ are isotypic with $Na_3Fe_2S_4$, whereas the structure of $Cs_3Fe_2S_4$ shows significant differences. $Cs_3Fe_2S_4$ is directly converted by water into $CsFeS_2$ via oxidation of the iron ions and the evolution of hydrogen.

Keywords: Ternary iron sulphides; Synthesis; Crystal structure

1. Introduction

The crystal structures of ternary alkali metal iron sulphides $AFeS_2$, where A = Na, K, Rb, or Cs [1–3], contain linear $^1_\infty[FeS_{4/2}]$ chains of tetrahedra as the characteristic structural unit. Different structure types of these compounds have been found, depending on the size of the alkali metal ions. Similarly, the mixed-valent compounds $Na_3Fe_2S_4$ [4] and $Tl_3Fe_2S_4$ [5] contain chains of tetrahedra, but, in contrast to the $AFeS_2$ compounds, $^1_\infty[FeS_{4/2}]$ zig-zag chains are formed. The syntheses of the analogous, hitherto unknown compounds $K_3Fe_2S_4$, $Rb_3Fe_2S_4$ and $Cs_3Fe_2S_4$ and the determination of their crystal structures are reported in the following.

2. Syntheses

$K_3Fe_2S_4$ and $Rb_3Fe_2S_4$ were obtained by heating a mixture of the respective alkali metal carbonate (K_2CO_3 from Ventron, stated purity 99.999%; Rb_2CO_3 from Ventron, stated purity 99.9%; both carbonates were additionally heated for 24 h in a stream of argon prior to the reaction), iron (Ventron, Puratronic grade) and sulphur (Ventron, stated purity 99.999%) in a stream of hydrogen (Linde, stated purity 99.999%) charged with sulphur. The alkali metal carbonate and sulphur were used in a two- to threefold excess. The reaction was carried out in a flow system with a quartz tube situated in a horizontal, tubular furnace. A corundum boat containing the reaction mixture and a second corundum boat containing additional sulphur were heated in a hydrogen stream such that the hydrogen was charged with sulphur before reaching the reaction mixture. After a reaction time of approximately 20 h at 930 K, the furnace was switched off and the products were allowed to cool in a stream of argon.

The resulting red crystals appeared not to adopt a particular crystalline shape. Powdered samples appeared light brown. $K_3Fe_2S_4$ was obtained in a pure form, whereas $Rb_3Fe_2S_4$ contained small amounts of $Rb_9Fe_2S_7$ [6].

$Cs_3Fe_2S_4$ could be obtained under analogous conditions, but samples of higher purity were synthesized by using a hydrogen stream without adding sulphur. Caesium carbonate was obtained from Ventron (ultrapure XTL grade).

As reported previously, we were able to synthesize the ternary sulphides Cs_3FeS_3 [7] and $Cs_9Fe_2S_7$ [6] under similar conditions. This suggests that the three caesium iron sulphides possess similar thermodynamic stabilities. The formation of the particular ternary iron sulphide appears to be influenced by kinetic factors of

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Table 1
$K_3Fe_2S_4$: summary of X-ray crystal structure analysis

Space group	*Pnma* (No. 62)
Final R, R_w (unit weights)	0.038, 0.047
Crystal size	0.15×0.09×0.08 mm
$2\theta_{max}$	60°
Number of reflections measured	4954
Number of reflections with $I_{obs} > 3\sigma(I_{obs})$	593
Min., max. peak heights in final difference Fourier map	-0.80, 0.85 e Å^{-3}
Min., max. transmission factors	0.741, 1.000

Atomic coordinates:

		x	y	z
K(1)	8d	0.0611(4)	0.4241(2)	0.1390(2)
K(2)	4c	0.0844(5)	1/4	0.7706(3)
Fe	8d	0.0515(2)	0.3767(1)	0.4690(1)
S(1)	8d	0.1542(4)	0.5548(2)	0.3871(2)
S(2)	4c	0.2880(5)	1/4	0.5334(3)
S(3)	4c	0.4041(5)	1/4	0.1580(3)

Coefficients of anisotropic thermal parameters U_{ij} (pm^2):

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	212(11)	294(12)	262(11)	74(11)	−13(11)	10(10)
K(2)	175(16)	191(14)	183(15)	0	1(13)	0
Fe	114(5)	99(6)	144(6)	3(6)	−9(6)	−2(6)
S(1)	176(11)	151(11)	201(11)	−12(11)	68(10)	32(11)
S(2)	104(14)	200(16)	174(16)	0	−27(16)	0
S(3)	156(17)	151(15)	144(15)	0	36(13)	0

Table 2
$Rb_3Fe_2S_4$: summary of X-ray crystal structure analysis

Space group	*Pnma* (No. 62)
Final R, R_w (unit weights)	0.037, 0.047
Crystal size	0.25×0.13×0.10 mm
$2\theta_{max}$	60°
Number of reflections measured	3001
Number of reflections with $I_{obs} > 3\sigma(I_{obs})$	981
Min., max. peak heights in final difference Fourier map	-1.39, 1.18 e Å^{-3}
Min., max. transmission factors	0.626, 1.000

Atomic coordinates:

		x	y	z
Rb(1)	8d	0.0644(1)	0.42716(9)	0.13859(7)
Rb(2)	4c	0.0855(2)	1/4	0.7729(1)
Fe	8d	0.0516(2)	0.3764(1)	0.46989(9)
S(1)	8d	0.1474(3)	0.5535(2)	0.3917(2)
S(2)	4c	0.2807(4)	1/4	0.5326(3)
S(3)	4c	0.4123(4)	1/4	0.1534(3)

Coefficients of anisotropic thermal parameters U_{ij} (pm^2):

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb(1)	208(4)	271(5)	195(4)	71(4)	−2(3)	5(4)
Rb(2)	170(5)	231(6)	186(6)	0	19(5)	0
Fe	79(5)	84(5)	75(5)	−1(5)	−2(4)	1(4)
S(1)	141(9)	129(10)	116(9)	−4(8)	56(8)	17(8)
S(2)	78(12)	163(14)	127(13)	0	−23(11)	0
S(3)	112(13)	150(13)	103(12)	0	53(11)	0

Table 3
$Cs_3Fe_2S_4$: summary of X-ray crystal structure analysis

Space group	*Pnma* (No. 62)
Final R, R_w (unit weights)	0.040, 0.051
Crystal size	0.11×0.08×0.68 mm
$2\theta_{max}$	70°
Number of reflections measured	4870
Number of reflections with $I_{obs} > 3\sigma(I_{obs})$	1736
Min., max. peak heights in final difference Fourier map	-2.29, 4.57 e Å^{-3}
Min., max. transmission factors	0.613, 1.000

Atomic coordinates:

		x	y	z
Cs(1)	8d	0.10742(8)	0.47088(6)	0.21137(4)
Cs(2)	4c	0.0109(1)	1/4	0.94636(9)
Fe	8d	−0.0094(2)	0.3740(1)	0.50701(9)
S(1)	8d	0.2326(3)	0.4885(2)	0.4621(2)
S(2)	4c	0.0469(5)	1/4	0.6459(3)
S(3)	4c	0.4039(4)	1/4	0.1265(2)

Coefficients of anisotropic thermal parameters U_{ij} (pm^2):

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(1)	233(3)	391(3)	203(2)	71(3)	4	19(3)
Cs(2)	229(4)	138(3)	623(6)	0	−85(4)	0
Fe	108(4)	80(4)	151(4)	−8(4)	−2(4)	−7(4)
S(1)	107(7)	113(7)	208(8)	−2(6)	13(6)	−8(6)
S(2)	271(14)	136(12)	163(12)	0	−23(11)	0
S(3)	228(13)	100(10)	171(11)	0	40(11)	0

Table 4
$K_3Fe_2S_4$: selected interatomic distances (pm) and bond angles (degrees)

Sulphur coordination of the potassium ions:			
K(1)–S(3)	312.0(4)	K(2)–S(2)	310.4(5)
–S(3)	323.0(4)	–S(2)	310.5(5)
–S(1)	326.1(4)	–S(1)	314.9(4) 2×
–S(1)	327.6(3)	–S(1)	329.3(4) 2×
–S(2)	338.4(4)		
–S(1)	356.2(4)		
–S(2)	393.5(3)		
Interatomic distances and bond angles in the [FeS_4] tetrahedra:			
Fe–S(3)	228.2(3)	S(1)–Fe–S(3)	113.8(1)
–S(1)	229.5(3)	S(1)–Fe–S(2)	114.3(1)
–S(2)	231.5(3)	S(1)–Fe–S(1)	102.70(9)
–S(1)	234.6(3)	S(3)–Fe–S(2)	100.3(1)
		S(3)–Fe–S(1)	111.2(1)
		S(2)–Fe–S(1)	115.1(1)
Intra- and interchain distances of the iron ions:			
Fe–Fe	278.5(2)	Fe–Fe	559.0(2) 2×
–Fe	289.8(3)		

Table 5
$Rb_3Fe_2S_4$: selected interatomic distances (pm) and bond angles (degrees)

Sulphur coordination of the rubidium ions:			
Rb(1)–S(3)	325.1(3)	Rb(2)–S(2)	322.5(4)
–S(3)	337.5(3)	–S(2)	324.7(4)
–S(1)	340.3(2)	–S(1)	327.7(3) 2×
–S(1)	341.4(3)	–S(1)	341.6(3) 2×
–S(2)	354.0(3)		
–S(1)	365.7(3)		
–S(2)	398.4(2)		
Interatomic distances and bond angles in the [FeS_4] tetrahedra:			
Fe–S(3)	228.8(3)	S(1)–Fe–S(3)	113.82(9)
–S(1)	229.7(3)	S(1)–Fe–S(2)	115.20(9)
–S(2)	233.0(3)	S(1)–Fe–S(1)	101.30(8)
–S(1)	235.4(3)	S(3)–Fe–S(2)	99.53(9)
		S(3)–Fe–S(1)	112.2(1)
		S(2)–Fe–S(1)	115.4(1)
Intra- and interchain distances of the iron ions:			
Fe–Fe	281.5(3)	Fe–Fe	566.9(1) 2×
–Fe	294.9(3)		

crystallization from the melt. Although we were able to find specific reaction conditions for each of the three caesium iron sulphides, subsequent experiments are necessary to understand the limiting reaction conditions for each sulphide. It is notable that, under the given conditions, the formation of $CsFeS_2$ [3] has not been observed.

$Cs_3Fe_2S_4$ was obtained as dark-red, needle-shaped crystals with a metallic lustre. It reacts with water producing an odourless gas which was identified as

Table 6
$Cs_3Fe_2S_4$ selected interatomic distances (pm) and bond angles (degrees)

Sulphur coordination of the caesium ions:			
Cs(1)–S(1)	338.1(3)	Cs(2)–S(1)	350.9(3) 2×
–S(1)	347.0(3)	–S(1)	359.1(3) 2×
–S(3)	350.5(3)	–S(2)	369.6(4)
–S(3)	358.2(3)	–S(3)	376.8(4)
–S(1)	361.3(3)	–S(2)	389.2(4)
–S(2)	380.4(3)	–S(2)	421.4(4)
–S(2)	415.1(3)		
Interatomic distances and bond angles in the [FeS4] tetrahedra:			
Fe–S(1)	230.3(3)	S(1)–Fe–S(3)	111.7(1)
–S(2)	230.6(4)	S(1)–Fe–S(2)	112.6(1)
–S(3)	230.7(3)	S(1)–Fe–S(1)	104.56(9)
–S(1)	231.3(3)	S(3)–Fe–S(2)	105.9(1)
		S(3)–Fe–S(1)	108.8(1)
		S(2)–Fe–S(1)	113.5(1)
Intra- and interchain distances of the iron ions:			
Fe–Fe	277.0(3)	Fe–Fe	558.9(3) 2×
–Fe	282.4(3)		

hydrogen by mass spectrometry. The needle-like shape of the crystals did not change during this reaction but their colour darkened to violet. X-ray powder diffraction experiments indicated that $Cs_3Fe_2S_4$ was converted into $CsFeS_2$ during this reaction. An alkaline solution resulted in which Cs^+ and traces of S^{2-} could be detected. Evidence for Fe^{2+} and Fe^{3+} ions could not be found. Assuming that the S^{2-} species derive from traces of binary caesium sulphides, the following reaction scheme seems to be likely:

$$Cs_3Fe_2S_4 + H_2O \longrightarrow 2CsFeS_2 + Cs^+ + OH^- + 1/2H_2.$$

For $Na_3Fe_2S_4$ a similar observation has been reported. However, in contrast, on exposure of this compound to moisture, a hydrate with the composition $NaFeS_2 \cdot xH_2O$ [1] was formed.

3. Crystal structure analysis

X-ray powder investigations on $K_3Fe_2S_4$ and $Cs_3Fe_2S_4$ using the Guinier method (Cu $K\alpha_1$ radiation) could be interpreted in terms of orthorhombic unit cells. For $Rb_3Fe_2S_4$ the lattice parameters were determined by least-squares refinement of 25 centred CAD4 reflections (Mo $K\alpha$ radiation, $20° < \theta < 30°$). The following lattice parameters were obtained:

$K_3Fe_2S_4$:
$a = 715.7(3)$ pm, $b = 1098.9(4)$ pm, $c = 1156.0(4)$ pm;
$Rb_3Fe_2S_4$:
$a = 740.69(7)$ pm, $b = 1114.1(1)$ pm, $c = 1199.7(1)$ pm;
$Cs_3Fe_2S_4$:
$a = 754.0(2)$ pm, $b = 1116.8(5)$ pm, $c = 1292.3(4)$ pm.

Single crystals of these three ternary iron sulphides could be isolated and were sealed in capillary tubes made from Lindemann glass in a glove box under an inert atmosphere. The isolation of a $Cs_3Fe_2S_4$ crystal caused problems since the needle-shaped crystals split into tiny fibres on application of small mechanical stresses.

The single-crystal analysis was performed on a four-circle diffractometer (CAD4, Enraf-Nonius, $\omega - 2\theta$ scan, Mo $K\alpha$ radiation, graphite monochromator). ψ-scans were used to correct for crystal absorption. The structure determination was carried out with the NRCVAX program system [8] on a PC. Scattering factors were taken from Ref. [9]. The results are summarized in Tables 1–3. Lists of observed and calculated structure factors can be obtained from the authors.

Selected interatomic distances and angles are given in Tables 4–6.

4. Discussion

The most significant structural feature of the sulphides $A_3Fe_2S_4$, where A = K, Rb, Cs, is the $^1_\infty[FeS_{4/2}]$ unit.

Table 7
Selected structural parameters of ternary iron sulphides with $^1_\infty[FeS_{4/2}]$ chains

Parameter	$Na_3Fe_2S_4$	$K_3Fe_2S_4$	$Rb_3Fe_2S_4$	$Cs_3Fe_2S_4$	$CsFeS_2$[a]
Fe–Fe (pm)	274.5	278.5	281.5	277.0	269.6
	274.9	289.8	294.9	282.4	272.5
Fe–S (pm)	230.2	231.0	231.7	230.7	223.1
Fe–Fe–Fe (°)	160.6	159.2	159.1	175.3	180.0
a/b	0.621	0.651	0.665	0.675	0.657
a/c	0.621	0.619	0.617	0.583	0.597
b/c	1.000	0.951	0.929	0.864	0.907

[a] To permit a better comparison of the ratios of the lattice parameters, the standard setting has been transformed using

$$(a'b'c') = (abc)\begin{pmatrix}100\\001\\020\end{pmatrix}.$$

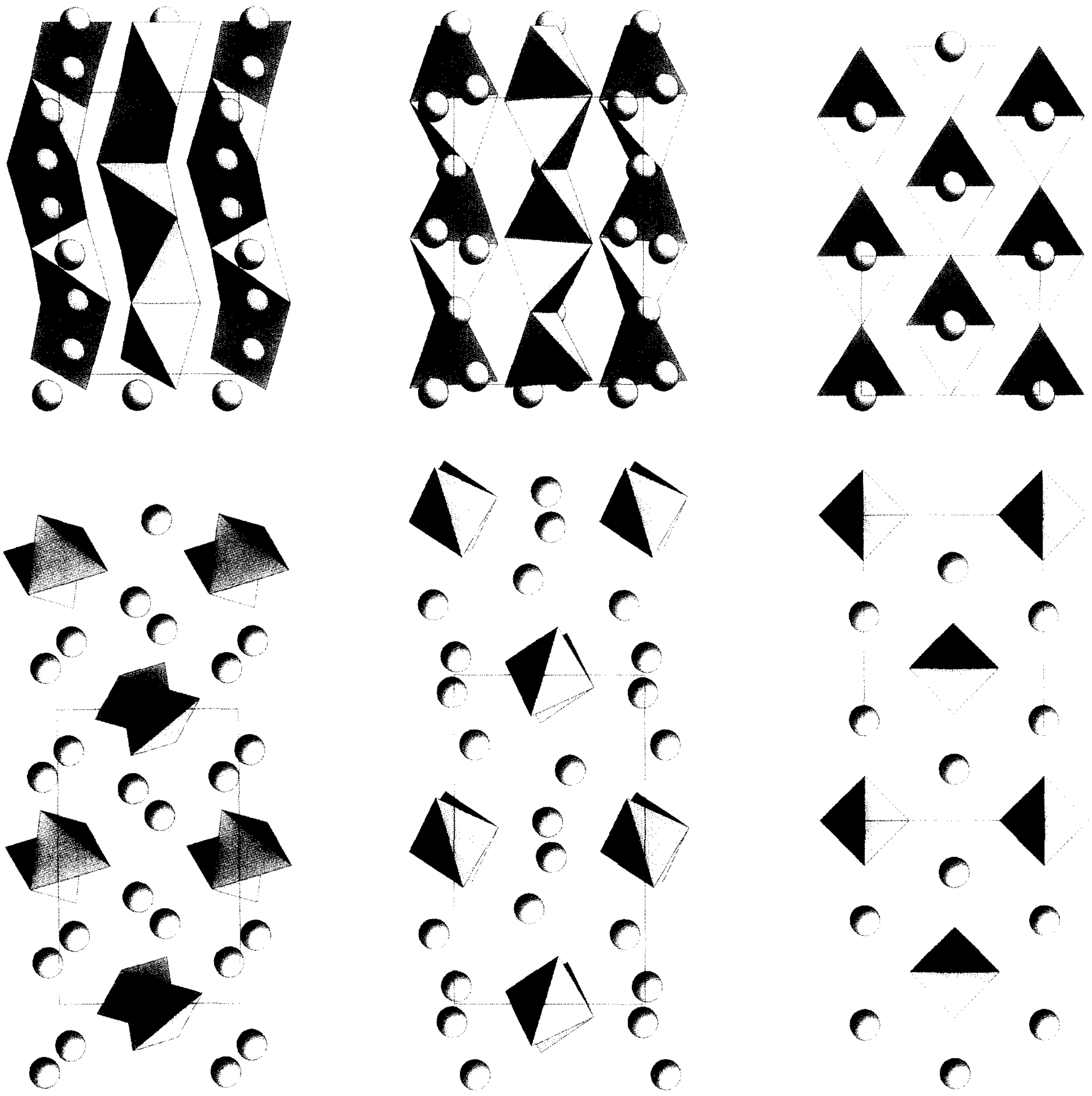

Fig. 1. The upper pictures show the [$FeS_{4/2}$] chains of, from left to right, $K_3Fe_2S_4$, $Cs_3Fe_2S_4$ and $CsFeS_2$ and are depicted with respect to the *b*-, *b*- and *c*-axes, respectively. The *a*-axes point to the right. The lower pictures show cross-sections of the unit cells perpendicular to the chains. The dotted circles signify the alkali metal atoms.

The edge-sharing, iron-centred sulphur tetrahedra form zig-zag chains, in contrast to the structurally-related $CsFeS_2$ (see Fig. 1), which contains linear chains like the other $AFeS_2$ compounds.

$K_3Fe_2S_4$ and $Rb_3Fe_2S_4$ are isotypic with $Na_3Fe_2S_4$ [4] and $Tl_3Fe_2S_4$ [5]. However, $Cs_3Fe_2S_4$ shows significant differences in its atomic arrangement, as can be seen in the configuration of the ${}^{1}_{\infty}[FeS_{4/2}]$ units (see Fig. 1). The Fe–Fe–Fe angles in the chains of $K_3Fe_2S_4$ and $Rb_3Fe_2S_4$ are 159.2° and 159.1°, respectively. $Na_3Fe_2S_4$ shows an almost identical value (160.6°, see Table 7), whereas an angle of 175.3° has been found for $Cs_3Fe_2S_4$. Furthermore, the coordination of the alkali metal ions by the sulphur ligands is different in both compounds. As expected, the ECON values [10] are consistently higher for the caesium compound than the potassium and rubidium compounds.

The structural relationship between $Cs_3Fe_2S_4$ and $CsFeS_2$ may explain the redox reaction which converts the former into the latter compound by oxidation of the iron ions. Unfortunately, there is no experimental evidence to indicate how the necessary reorientation of the atomic arrangement takes place. A stepwise oxidation and a simultaneous X-ray investigation of a $Cs_3Fe_2S_4$ single crystal could give further insight into this matter. A corresponding reaction for the compounds $K_3Fe_2S_4$ and $Rb_3Fe_2S_4$ has hitherto not been observed. This seems to indicate that the necessary transformation is only possible for the structurally related compounds $Cs_3Fe_2S_4$ and $CsFeS_2$.

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