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Composition, Structure, and Thermal Expansion of $Ca_3Fe_4S_3O_6$ and CaFeSO

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Abstract—The iron calcium oxysulfides $Ca_3Fe_4S_3O_6$ and CaFeSO are synthesized by reacting mixtures of CaO and FeS in an inert atmosphere. Their elemental compositions and lattice parameters are determined by x-ray microanalysis and x-ray diffraction. From the temperature-dependent lattice parameters of the oxysulfides (measured up to 1020 K), their thermal expansion coefficients are evaluated.

INTRODUCTION

The formation of iron calcium oxysulfides, belonging to a poorly explored class of inorganic compounds, was observed earlier in the production of ferrous and nonferrous metals [1–6]. The available data on the composition and structure of these compounds are contradictory. Based on x-ray diffraction (XRD) data, the compositions of two iron calcium oxysulfides were determined as $Ca_3Fe_4S_3O_4$ or $Ca_3Fe_4S_3O_6$ (OS-1) and CaFeSO or $Ca_2Fe_2S_2O_3$ (OS-2) [7]. According to Yarygin *et al.* [4, 8], the composition of OS-1 is $Ca_3Fe_4S_3O_6$, whereas Schuermann and Fischer [9] believe that the composition of this compound is close to $Ca_3Fe_4S_3O_4$. The results reported in [10, 11] indicate that, at temperatures from 1070 to 1270 K and an oxygen partial pressure $p_{O_2} = 10^{-25}$ Pa, the composition of OS-1 is $Ca_3Fe_4S_3O_4$, and that of OS-2 is CaFeSO. At the same time, Schuermann and Fischer [9] hold that OS-2 has the $Ca_2Fe_2S_2O_3$ stoichiometry. According to the x-ray microanalysis data reported by Koch *et al.* [12], the composition of OS-1 is Fe 40.5, Ca 23.0, S 16.0, and O 20.5 wt %, and that of OS-2 is Fe 39.0, Ca 26.5, S 25.0, and O 9.5 wt %.

The XRD pattern of CaFeSO was indexed, by analogy with CaZnSO, in hexagonal symmetry with lattice parameters $a = 0.632$ nm and $c = 0.368$ nm, as inferred from the smallest possible cation–cation distances [10, 11]. These distances are determined by the O–S–O and S–S bond lengths along the a and c axes, respectively. Detailed structural data for other iron calcium oxysulfides are missing, and their thermal properties have not been studied.

The purpose of this work was to refine the composition and structure of the iron calcium oxysulfides in question, to determine their lattice parameters, and to investigate their thermal properties in an inert atmosphere.

EXPERIMENTAL

XRD measurements were made at temperatures of up to 1020 K on a DRON-2.0 powder diffractometer (CoK_α radiation, pyrolytic graphite diffracted-beam monochromator, silicon internal standard) equipped with a UVD-2000 high-temperature attachment, which enabled studies in a helium atmosphere. Lattice parameters were determined by standard techniques [13, 14]. The temperature was measured by a Pt/Pt–10% Rh thermocouple with an accuracy of ±0.7%. The elemental composition of the synthesized phases was determined on a CAMEBAX x-ray microanalyzer.

Iron calcium oxysulfides were synthesized by heating appropriate starting mixtures in evacuated tubes or under flowing helium in a silica reactor mounted in a tube furnace (Table 1). The starting iron monosulfide

Table 1. Synthesis conditions for iron calcium oxysulfides

Sample no.	Mixture composition, wt %			T, K	τ, min	Atmosphere
	CaO	FeS	Fe			
1	38.95	61.05	–	1220	20	Vacuum (10^{-2} Pa) in a tube
2	32.62	51.14	16.24	1190	240	Flowing helium (0.1 MPa)

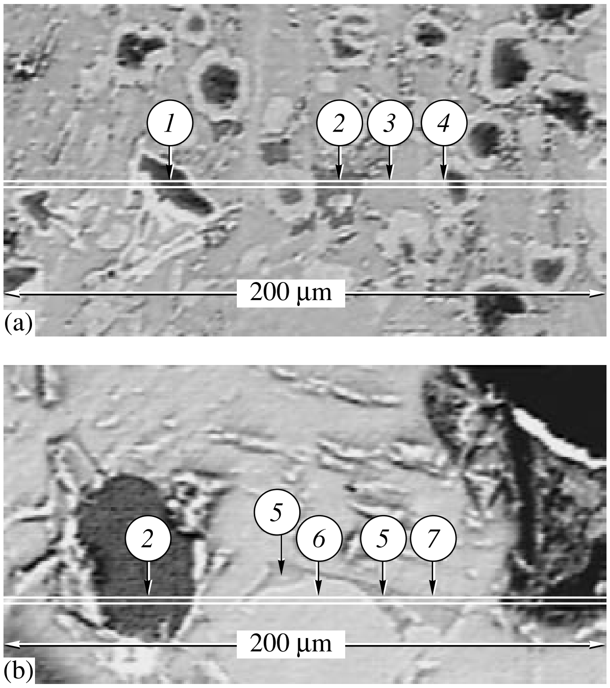

Fig. 1. X-ray scan images of samples (a) 1 and (b) 2; (*1–7*) see Table 2.

was prepared by slowly heating a mixture of carbonyl iron and extrapure-grade sulfur to 1270 K in evacuated (10^{-2} Pa) silica tubes, followed by holding for 50 h. The purity of the reaction product was checked by XRD and chemical analysis. Calcium oxide (pure grade) was precalcined at 1270 K.

To prepare compound OS-1, a mixture of calcium oxide and iron monosulfide powders (less than 0.1 mm in particle size) in the molar ratio 1.0 : 1.0 was pressed into pellets, which were then placed in corundum crucibles and fired in evacuated tubes at 1220 K for 20 min (sample 1). Oxysulfide OS-2 was prepared from a mixture of calcium oxide, iron sulfide, and metallic iron powders in the molar ratio 1.0 : 1.0 : 0.5, which were pressed into pellets and fired at 1190 K for 4 h in flowing helium (100 ml/min) (sample 2). Fe metal was introduced into the reaction system in order to drive the reaction

$$3FeO \rightleftharpoons Fe + Fe_2O_3 \quad (1)$$

to the left and to bind excess CaS.

RESULTS AND DISCUSSION

The x-ray microanalysis data for samples 1 and 2 (Table 2, Fig. 1) indicate that phase-pure iron calcium oxysulfides are rather difficult to obtain. Sample 1 contained, along with OS-1, a significant amount (about 20%) of calcium sulfide and a small amount of calcium oxide. In addition, the sample contained Fe metal particles (2–5 wt %), which probably resulted from FeO decomposition into Fe_2O_3 and Fe during cooling. According to x-ray microanalysis results, the composition of OS-1 was $\approx Ca_3Fe_4S_3O_6$. At the same time, the present and earlier results [4, 8, 9] do not rule out the possibility that this compound has a variable oxygen stoichiometry.

The major phase in sample 2 was OS-2, as determined by x-ray microanalysis. Its composition was Ca 27.52, Fe 38.57, S 21.98, and O 12.12 wt %, which corresponds to the stoichiometry CaFeSO. Sample 2 also

Table 2. X-ray microanalysis data for iron calcium oxysulfides

No.		Weight percent				Atomic percent				Phase
sample	phase*	Ca	Fe	S	O**	Ca	Fe	S	O**	
1	*1*	71.5	1.4	1.0	28.5	49.9	0.1	0.1	49.9	CaO
	2	0.6	98.7	0.9	–	0.77	97.7	1.53	–	Fe
	3	23.5	42.6	19.0	14.9	20.4	26.6	20.6	32.4	$Ca_3Fe_4S_3O_6$
	4	55.2	0.8	43.7	0.2	49.8	0.5	49.4	0.3	CaS
2	*2*	0.1	97.8	0.01	–	0.01	99.8	0.01	–	Fe
	5	3.7	68.9	2.6	24.7	3.2	41.8	2.7	52.3	FeO
	6	27.5	38.6	22.0	12.1	24.4	24.4	24.3	26.9	CaFeSO
	5	3.2	68.8	2.1	25.9	2.6	41.2	2.2	54.0	FeO
	7	3.6	64.4	32.0	–	4.0	44.4	51.5	–	FeS

* See Fig. 1.

** Determined as the balance.

Table 3. Indexing scheme for $Ca_3Fe_4S_3O_6$

h	k	l	$2\theta_{obs}$, deg	$2\theta_{calc}$, deg	$\Delta(2\theta)$, deg	d_{obs}, nm	I_{obs}, %
0	0	2	23.59	23.58	−0.01	0.4381	37
2	0	2	35.63	35.57	+0.06	0.2926	10
2	2	0	37.36	37.45	−0.09	0.2795	13
2	2	1	39.39	39.37	+0.02	0.2656	11
2	0	3	44.88	44.85	+0.03	0.2345	100
0	0	4	48.09	48.25	−0.17	0.2197	78
4	0	0	53.99	54.00	−0.01	0.1972	19
2	0	4	55.77	55.75	+0.02	0.1914	6
4	1	3	68.08	68.03	+0.05	0.1599	7
4	2	3	72.65	72.73	−0.08	0.1511	16
2	2	5	74.31	74.23	+0.08	0.1482	5
4	0	4	75.32	75.30	+0.02	0.1465	8
5	1	2	75.69	75.72	−0.03	0.1459	17
4	4	0	79.90	79.88	+0.02	0.1394	5
6	2	0	91.65	91.74	−0.08	0.1248	1
4	2	5	92.13	92.14	−0.01	0.1243	1
6	0	3	96.58	96.62	−0.04	0.1199	3
2	0	7	97.31	97.26	+0.08	0.1192	6
4	0	6	99.36	99.44	−0.08	0.1174	5
4	0	6	99.50	99.44	+0.06	0.11728	5
2	2	7	103.31	103.26	+0.05	0.11413	3
6	4	3	121.78	121.83	−0.05	0.10245	2
2	2	8	122.80	122.87	−0.07	0.10195	7

Table 4. Indexing scheme for CaFeSO

h	k	l	$2\theta_{obs}$, deg	$2\theta_{calc}$, deg	$\Delta(2\theta)$, deg	d_{obs}, nm	I_{obs}, %
0	0	2	18.11	18.12	−0.01	0.5687	25
1	0	0	31.90	31.94	−0.03	0.3257	19
1	0	1	33.27	33.25	+0.02	0.3127	38
0	0	4	36.69	36.71	−0.02	0.2844	69
1	0	2	36.97	36.96	+0.01	0.2823	100
1	0	3	42.53	42.52	+0.01	0.2468	74
1	0	4	49.40	49.44	+0.04	0.2142	16
0	0	6	56.47	56.38	+0.09	0.1892	9
1	1	0	56.90	56.91	−0.01	0.1879	40
1	0	8	66.20	66.28	−0.07	0.1639	39
1	1	4	69.77	69.82	−0.05	0.1565	23
2	0	3	73.50	73.56	−0.06	0.1496	9
2	0	6	92.80	92.87	−0.16	0.1236	9
2	1	3	99.82	99.85	−0.03	0.1170	8
2	1	6	120.50	120.39	+0.11	0.1031	8

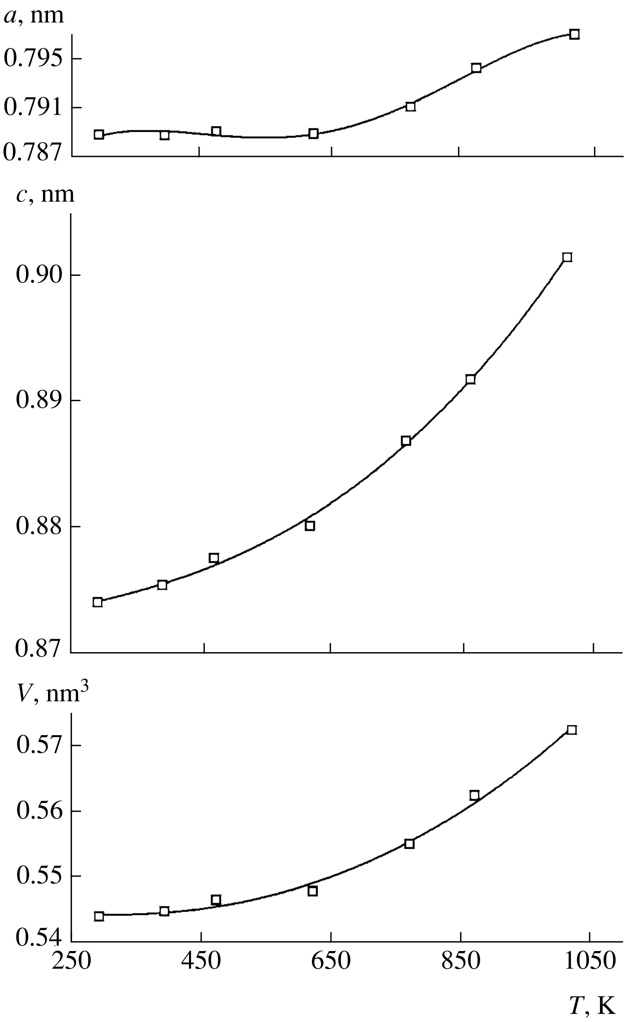

Fig. 2. Temperature dependences of lattice parameters for $Ca_3Fe_4S_3O_6$.

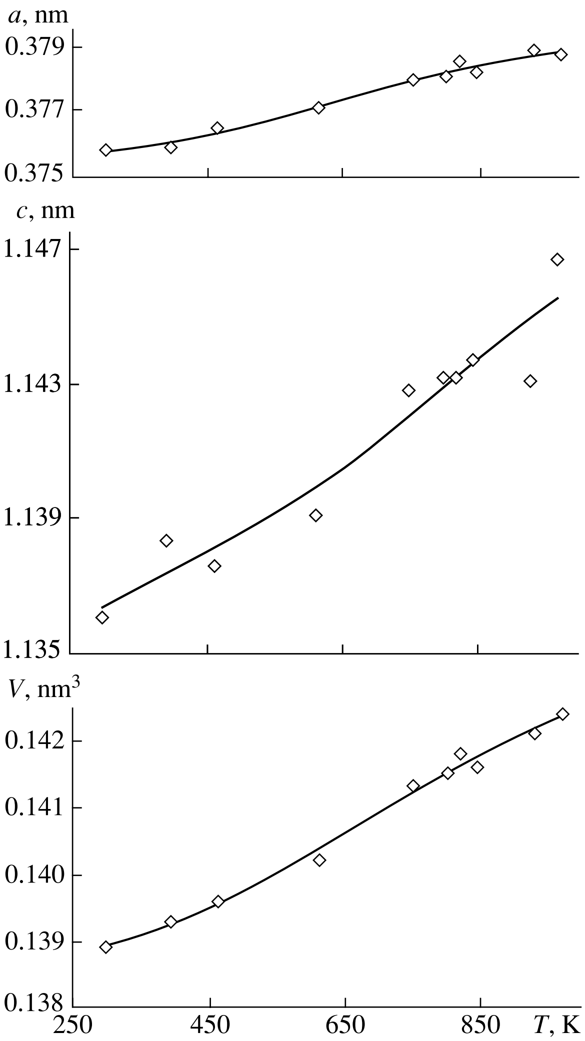

Fig. 3. Temperature dependences of lattice parameters for CaFeSO.

contained Fe metal and trace levels of FeO, FeS, and CaS (Table 2).

The XRD data for $Ca_3Fe_4S_3O_6$ could be indexed in the tetragonal system (Table 3), with lattice parameters $a = 0.7889(1)$ nm and $c = 0.8741(1)$ nm ($V = 0.5440(1)$ nm^3). The main diffraction peaks agreed well with earlier results [8, 9]. The x-ray density of this oxysulfide, $\rho_x = 3.32$ g/cm^3, is consistent with the density of sample 1 determined by the Archimedes method, $\rho_{meas} = 3.51$ g/cm^3, given that the sample contained impurity phases.

The XRD pattern of CaFeSO (Table 4) is close to that given in the ICDD Powder Diffraction File for $Ca_2Fe_4S_3O_4$ (card 43-0600) [7]. In contrast to earlier studies [10, 11], we observed a splitting of the reflection with $d = 0.283$ nm into two components with d spacings of 0.2844 and 0.2823 nm and revealed a line with $d = 0.2142$ nm. Detailed analysis of XRD data suggests that CaFeSO is isostructural with CaZnSO [15] and has a hexagonal cell with $a = 0.37571(8)$ nm, $c = 1.13691(43)$ nm, and $V = 0.1390(1)$ nm^3. These values differ somewhat from the data reported by Jha *et al.* [10] and Igiehon *et al.* [11]. The x-ray density of OS-2, $\rho_x = 3.45$ g/cm^3, is substantially lower than the measured density of sample 2, $\rho_{meas} = 3.85$ g/cm^3, which is associated with the presence of impurity phases, in particular, Fe metal.

Measurements of lattice parameters as functions of temperature for $Ca_3Fe_4S_3O_6$ in helium (Fig. 2) demonstrate that a remains almost constant up to 600 K and slightly increases above this temperature. At the same time, the c parameter and unit-cell volume of OS-2 increase rapidly over the entire temperature range studied. The anisotropic thermal expansion of the crystal lattice influences the c/a ratio, which can be accounted for in terms of chemical deformation related to compositional changes during heating.

Table 5. Coefficients in the best fit equations for the temperature-dependent lattice parameters of iron calcium oxysulfides

Compound	Lattice parameters	K_0	$K_1 \times 10^5$	$K_2 \times 10^8$	R^2, %
$Ca_3Fe_4S_3O_6$	a, nm	0.79313	–2.07336	2.41108	97.5
	c, nm	0.87693	–2.11735	4.39143	99.8
	V, nm^3	0.55193	–4.32335	6.20648	99.3
CaFeSO	a, nm	0.37414	0.49358	0	97.8
	c, nm	0.37647	–0.77639	2.08908	98.3
	V, nm^3	0.13926	–0.52873	1.64538	99.2

In the case of CaFeSO, c also rises with temperature more rapidly than a (Fig. 3). In contrast to that of OS-1, the a parameter of CaFeSO increases steadily, starting at room temperature.

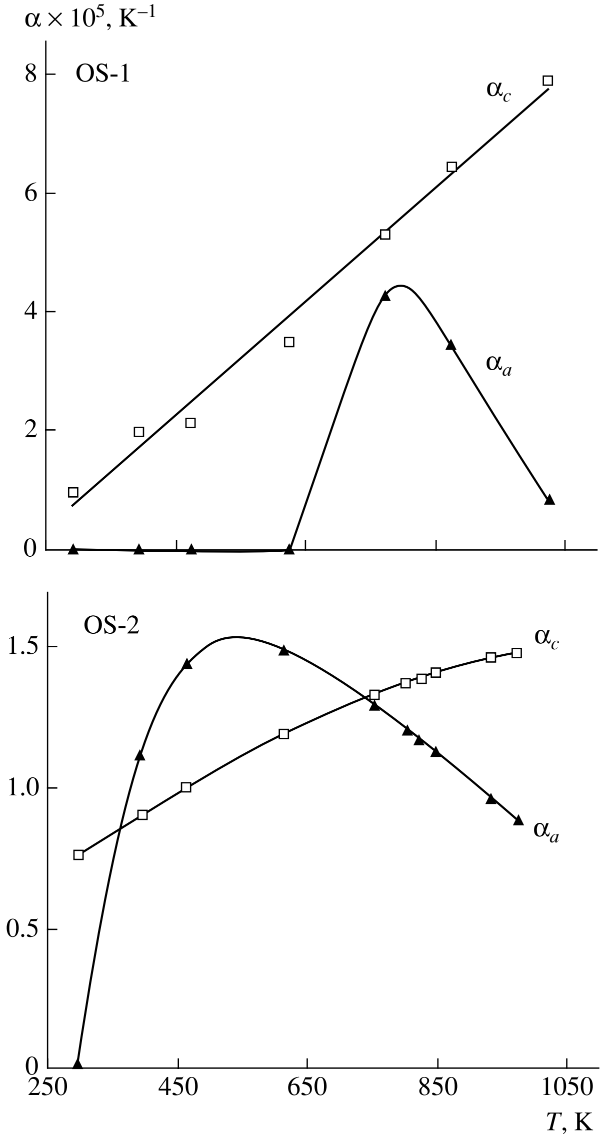

Fig. 4. Temperature dependences of thermal expansion coefficients for iron calcium oxysulfides.

The temperature-dependent lattice parameters of the two oxysulfides can be represented by polynomials of the form

$$P = K_0 + K_1T + K_2T^2, \quad (2)$$

where $P = a$ (nm), c (nm), or V (nm^3), and K_0, K_1, and K_2 are regression coefficients (Table 5).

The thermal expansion coefficients (α) of the oxysulfides were evaluated as [14]

$$\alpha = 1/P(dP/dT). \quad (3)$$

The results (Fig. 4) demonstrate that the α_a of $Ca_3Fe_4S_3O_6$ is close to zero up to ≈600 K and passes through a maximum at about 800 K. At the same time, the α_c of this oxysulfide rises almost linearly, from 1.0×10^{-5} to 8.0×10^{-5} K^{-1}, with increasing temperature. The thermal expansion coefficients of OS-2 are, on the whole, smaller than those of OS-1, but the α_c and α_a versus temperature curves for OS-2 are similar in shape for those for OS-1.

CONCLUSIONS

The compositions of the iron calcium oxysulfides obtained in this work are $Ca_3Fe_4S_3O_6$ and CaFeSO. According to XRD results, $Ca_3Fe_4S_3O_6$ has a tetragonal structure, and CaFeSO has a hexagonal structure. It seems likely that both $Ca_3Fe_4S_3O_6$ and CaFeSO have variable oxygen stoichiometries. The thermal expansion of these oxysulfides is anisotropic: c increases with temperature more rapidly than a.

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