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Oxidation of potassium di-thioferrate and consequent formation of the mineral yavapaiita

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Polycrystalline potassium dithioferrate ($KFeS_2$) was studied by X-ray diffraction to detect structural changes occurring in the compound when submitted to an oxygen flux at temperatures ranging from 350 to 650° C for 24 h periods. The formation of the mineral yavapaiita ($KFe(SO_4)_2$) was observed at 400° C. Other by-products of the oxygenation were the mineral arcanite K_2SO_4, $K_2S_2O_3$ and $K_3Fe(SO_4)_3$. The reflections corresponding to yavapaiita disappear at 450° C indicating its non-stability over a wide temperature range.

1. Introduction

The alkali-dithioferrate $KFeS_2$ has been the subject of considerable experimental and theoretical study due to the tetrahedral bonding of sulphur to metal ions forming quasi one-dimensional systems, which are of interest in areas such as geology, mineralogy, geochemistry, metallurgy, molecular physics and magnetism [1–31].

The optical, electronic structure and magnetic properties of these systems have been studied using theoretical schemes such as point charge and multiple scattering $X\alpha$ molecular orbital models as well as different experimental techniques such as Mössbauer spectroscopy, electron spin resonance, absorption spectroscopy and magnetic susceptibility [1–31].

We have recently published [20, 23, 30] various papers regarding Mössbauer and electron spin resonance as well as X-ray diffraction of potassium dithioferrate subjected to a hydrogen atmosphere at 500° C which resulted in a substantial modification of spectroscopic and structural properties. It was thus considered of interest to extend this work to investigate oxidation effects on $KFeS_2$ under heat treatment taking into account the potential importance of sulphide systems as geological thermometers and in particular the occurrence of iron sulphates such as yavapaiita and goldichite in uranium deposits and other scientific and economically important ore deposits.

Establishment of widely applicable, reliable methods for precise geological thermometry would have profound importance on the earth sciences with the feasibility of developing thermometers based on physical–chemical relations demonstrated in synthetic systems. Systematic studies of synthetic sulphide systems may yield information about the stability of minerals and mineral assemblages as well as of solid solution between sulphide minerals which may be of great interest both to theoretical and economic geologists. It may thus be possible to estimate temperatures, as well as partial vapour pressures during ore formation, relative abundance of available metal, and sulphur deposition and temperature gradients which may indicate the direction of flow of the solutions of gases from which ores were deposited making it possible for field geologists to use such gradients to solve problems in prospecting as well as in the study of geological structures related to ore deposition.

In the present work we monitored, by X-ray diffraction, structural changes in potassium dithioferrate as a function of heat treatment in an oxygen flux. Of particular interest is the formation of the mineral yavapaiita ($KFe^{3+}(SO_4)_2$) at about 400° C. Previous attempts to prepare this mineral by careful dehydration of krausite, goldichite and potassium iron alums failed in every case [31].

2. Experimental procedure

2.1. Sample preparation

Polycrystalline samples of $KFeS_2$ were prepared as [19] described in our previous work and identified by X-ray diffraction.

2.2. Oxidation procedure

The samples were submitted to an oxygen flux at temperatures (held for 24 h) ranging from 350 to 650° C.

2.3. X-ray diffraction analyses

X-ray diffraction diagrams were taken at each temperature using a HZG-4 generator with a copper monochromator with $Cu(K\alpha)$ radiation.

3. Results and discussion

X-ray diagrams (Fig. 1) of the untreated samples as well as the oxygenated samples at temperatures between 350 and 650° C were obtained and compared

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TABLE I X-ray diffraction data for oxidation of $KFeS_2$ at different temperatures

ASTM data file			Observed data									
$KFe(SO_4)_2$			$T = 350°C$			$T = 400°C$				$T = 450°C$		
hkl	d_f (nm)	I/I_0	2θ (deg)	d_0 (nm)	I/I_0	2θ (deg)	d_0 (nm)	I/I_0	I/I_0*	2θ (deg)	d_0 (nm)	I/I_0
			8.4	1.0525	15							
0 0 1	0.787	70				11.24	0.7871	30	(75)			
										11.7	0.7563	15
										11.92	0.7424	20
						12.15	0.7284	40				
			12.5	0.7081	13					12.22	0.7242	50
			12.9	0.6862	15							
			15.71	0.5640	15							
										17.65	0.5024	5
										18.3	0.6847	5
										19.3	0.4598	5
			19.9	0.1461	15							
1 1 0	0.4354	11				20.39	0.4354	4	(10)			
						20.9	0.4250	10		20.92	0.4246	20
						21.0	0.4230	10		21.05	0.4220	20
						21.15	0.4200	10				
			21.4	0.4152	10							
										21.7	0.4095	10
2 0 0	0.4066	50	21.82	0.4073	10	21.8	0.4076	12	(30)			
						21.95	0.4049	10		21.95	0.4049	5
						22.01	0.4038	15				
$\bar{1}$ 1 1	0.3885	70				22.89	0.3885	30	(75)			
$\bar{2}$ 0 1, 1 1 1	0.3739	65				23.76	0.3744	25	(62)			
						23.89	0.3724	10				
										24.25	0.3670	25
			24.50		15							
						25.3	0.3520	10				
2 0 1	0.3494	55	25.50	0.3493	8	25.49	0.3494	15	(40)			
						25.61	0.3478	10				
						25.75	0.3459					
			26.0	0.3426	15							
										26.35	0.3382	8
			26.82	0.3324	13							
						27.08	0.3292	95		27.10	0.3290	100
			27.15	0.3284	30	27.15	0.3284	100				
			27.35	0.3260	25	27.31	0.3265	75		27.28	0.3260	85
						28.18	0.3166	20				
			28.27	0.3156	100							
						29.6	0.3017	15				
			29.75	0.3002	30	29.8	0.2998	20				
			29.87	0.2991	30					29.85	0.2993	20
$\bar{1}$ 1 2	0.2985	100				29.93	0.2985	40	(100)			
			30.77	0.2903	32							
			30.9	0.2893	25					30.85	0.2898	20
										31.0	0.2884	15
						31.18	0.2868	15				
1 1 2	0.2854	50				31.4	0.2848	20	(50)			
			32.0	0.2796	10	31.95	0.2801	25		31.9	0.2805	11
						32.15	0.2784	25		32.1	0.2788	20
			32.25	0.2775	20	32.25	0.2775	30		32.28	0.2773	35
						32.4	0.2763	25		32.45	0.2759	20
						32.63	0.2744	20		32.6	0.2746	17
2 0 2	0.2711	6				33.1	0.2706	10	(25)			
										33.25	0.2694	60
			33.6	0.2667	60							
			34.0	0.2636	25							
0 0 3	0.2617	6										
0 2 0	0.2578	30				34.9	0.2571	10	(25)			
			35.6	0.2521	10					35.72	0.2513	50
			35.92	0.2500	15							
0 2 1	0.2449	1				36.6	0.2455	5				
			37.15	0.2420	14							
3 1 0	0.2399	55				37.48	0.2399	15	(40)			
						37.57	0.2393	15				
										37.95	0.2370	30
			38.12	0.2360	25	38.15	0.2358	30				
$\bar{3}$ 1 1	0.2345	2										
			38.9	0.2315	8							

TABLE I Continued

ASTM data file			Observed data									
$KFe(SO_4)_2$			T = 350° C			T = 400° C				T = 450° C		
h k l	d_f (nm)	I/I_0	2θ (deg)	d_0 (nm)	I/I_0	2θ (deg)	d_0 (nm)	I/I_0	I/I_0*	2θ (deg)	d_0 (nm)	I/I_0
$\bar{2}03$, 113	0.2228	10										
						40.1	0.2248	10				
			40.7	0.2216	10							
113	0.2197	3	41.09	0.2196	10	41.0	0.2201	10		41.0	0.2201	40
220	0.2176											
022	0.2154											
$\bar{2}21$, 203	0.2120	18	42.60	0.2122	10	42.65	0.2119	10	(25)			
						42.85	0.2110	10		42.8	0.2112	8
										43.52	0.2079	11
221	0.2073	2	43.67	0.2072	10					43.6	0.2075	8
										44.22	0.2048	70
400	0.2031	7	44.48	0.2036	65	44.45	0.2038	60				
										44.85	0.2020	17
$\bar{4}01$	0.2007	1	45.2	0.2006	8	45.17	0.2007	5				
			45.46	0.1995	10							
312	0.1980	2										
004	0.1963	3	46.24	0.1963	13	46.24	0.1963	2				
			46.4	0.1956	13							
$\bar{2}22$	0.1941	13										
401	0.1927	3	47.1	0.1929	5							
										48.18	0.1888	8
$\bar{4}02$, 222	0.1869	12	48.9	0.1862	5	48.71	0.1869	7				
			49.18	0.1852	8							
313, 023	0.1837	10								49.57	0.1838	20
										49.7	0.1834	11
$\bar{2}04$	0.1829	14	49.95	0.1825	5	49.9	0.1827	8	(20)			
$\bar{1}14$	0.1821	5										
114	0.1759	6				52.0	0.1758	4	(10)			
402	0.1745	11	52.55	0.1741	11	52.48	0.1743	5	(12)			
$\bar{2}23$, 204	0.1711	4				53.55	0.1711	4	(10)			
313	0.1705	3										
			54.25	0.1690	10	54.03	0.1697	10		54.15	0.1693	30
										54.3	0.1689	25
130	0.1680	2				54.45	0.1685	15		54.6	0.1680	8
										54.9	0.1672	15
						55.1	0.1666	10				
$\bar{1}31$	0.1649	5										
			56.35	0.1632	5							
			56.8	0.1620	12							
										57.35	0.1606	11
										57.85	0.1593	5
$\bar{4}21$	0.1583	2	58.35	0.1581	8							
005	0.1569	4	58.75	0.1571	5							
024	0.1560	4								59.1	0.1563	8
221	0.1555	8				59.35	0.1557	5	(12)			
510	0.1550	8								59.44	0.1554	8
132	0.1535	4				60.37	0.1533	5	(12)			
										60.95	0.1520	5
$\bar{4}22$	0.1513	12										
511	0.1497	5										
$\bar{2}24$	0.1491	9	62.37	0.1488	6	62.22	0.1492	10	(25)			
512	0.1482	2								62.55	0.1484	18
314	0.1465	6										
330	0.1451	9				64.13	0.1452	5	(12)	64.05	0.1453	12
422	0.1445	10				64.37	0.1447	5	(12)	64.33	0.1448	8
			64.55	0.1443	5	64.52	0.1444	5	(12)	64.75	0.1439	5
			65.2	0.1430	8							
224, $\bar{1}13$	0.1425	2								65.6	0.1423	5
$\bar{4}23$, 512	0.1403	5				66.6	1.404	3	(7)			
600, $\bar{6}01$	0.1353	2										

*I/I_0 = relative data for yavapaiite for reflection $\geqslant 5$ at 400° C.

with existing ASTM files for possible oxidation products. The $KFeS_2$ monoclinic [25, 26] unit cell (Fig. 1a) contains four molecules and has the constants a = 0.75 nm, b = 1.128 nm, c = 0.540 nm and β = 112.5° with space group C2/c (C_{2H}^6). We observe at 400° C (Fig. 1c) the appearance of reflections corresponding to the yavapaiita [31] a mineral from Jerome, Arizona with composition $KFe^{3+}(SO_4)_2$ having two formula units per unit cell supposedly crystallized as the result of extensive fires that first started in the mines in the

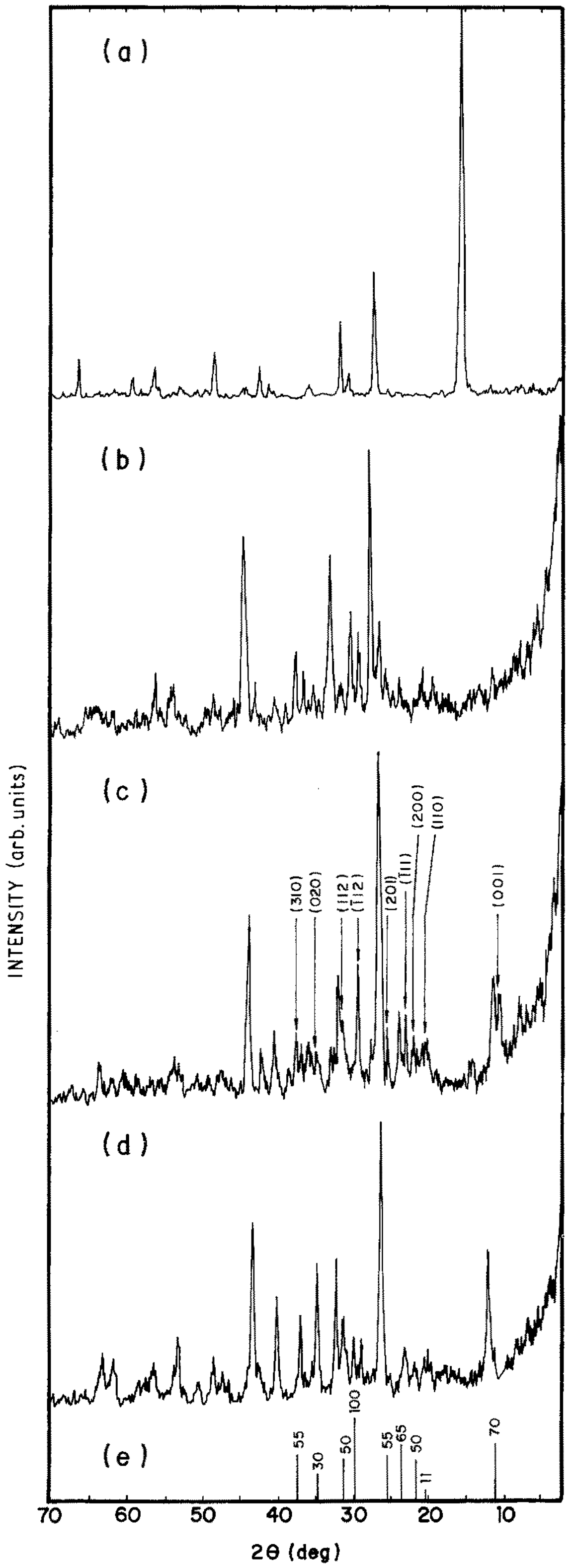

Figure 1 X-ray diffraction diagrams of $KFeS_2$, (a) without oxygen flux and heat treatment, (b) oxygen flux for 24 h at 350° C, (c) oxygen flux for 24 h at 400° C, (d) oxygen flux for 24 h at 450° C and (e) X-ray diffraction diagram of yavapaiita from ASTM Data File.

autumn of 1894. Attempts by other authors to prepare yavapaiita by careful dehydration of krausite, goldichite and potassium iron alums yielded X-ray diffraction patterns that were in any way [31] comparable to that typical of yavapaiita. Other minerals formed from the oxidation process identified from the ASTM files are K_2SO_4, $K_2S_2O_3$, $K_3Fe(SO_4)_2$ and at least one other sulphate which has not been satisfactorily diagnosed at this time. The mineral arcanite K_2SO_4 appears at 350° C, $K_2S_2O_3$ at 400° C and $K_3Fe(CO_4)_3$ at 450° C.

It has been suggested that conditions for the crystallization of the sulphates must have varied from time to time as the naturally occurring sulphates are not mutually intergrown, but occur as crystals of one composition resting on those of another. In addition, for the identification of the mineral yavapaiita [31] the presence of at least two other non-identified sulphates has been suggested.

It may also be observed from Fig. 1d, (Table I) that the reflections corresponding to yavapaiita disappear for an oxygen flux at 450° C for 24 h.

As most minerals are stable over a considerable pressure and temperature range, the occurrence of a mineral usually is not precisely diagnostic of conditions during formation. The limits of stability of silicate-mineral assemblages have long been used by geologists as a means of estimating pressure–temperature conditions which existed during the formation or metamorphism of rocks. Sulphide mineral assemblages, or assemblages of certain common sulphides with common oxides may likewise be used to estimate the conditions under which the assemblages were formed.

It has been reported that [31] when finely powdered yavapaiita is added to hot water, the mineral decomposes immediately with concommitant precipitation of ferric hydroxide, and production of a weakly acidic solution. In cold water, on the other hand, solution is extremely slow and precipitation of the hydroxide is not evident for several days. The mineral yavapaiita is thus not stable over a wide temperature range and the disappearance of the corresponding reflections as the temperature is raised to 450° C can be understood.

4. Conclusion

The X-ray diagrams suggest the formation of the mineral yavapaiita ($KFe(SO_4)_2$) on oxygenating $KFeS_2$ at 400° C for 24 h. Other by-products of this oxygenation are the minerals arcanite K_2SO_4 as well as $K_2S_2O_3$ and $K_3Fe(SO_4)_3$ which appear at 350, 400 and 450° C respectively. The mineral yavapaiita is not stable over a wide temperature range and the corresponding reflections disappear at 450° C. The sulphides and sulphates are found in uranium deposits and other important geological ore deposits. Chemical–physical investigations relating to the formation of these systems may have important geological and mineralogical applications yielding experimental information on the natural temperatures of formation.

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