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Hydrogenation and structural changes in potassium dithioferrate under heat treatment

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Polycrystalline potassium dithioferrate ($KFeS_2$) was studied using X-ray diffraction, to detect structural changes occurring in the compound when submitted to heat treatment at a temperature of 500° C under vacuum and in a hydrogen atmosphere. The changes observed in samples treated under vacuum and in a hydrogen atmosphere were similar, suggesting the presence of a new unstable phase coexisting with that of the untreated sample, and that the structural transformation observed is supposed to be primarily induced by the high-temperature treatment. The structural changes and absorbed hydrogen are correlated with previous Mössbauer and EPR experiments on hydrogenated $KFeS_2$ at 500° C.

1. Introduction

Potassium dithioferrate is a member of the alkali-dithioferrate series of compounds $AFeS_2$ (A = potassium, rubidium, caesium, sodium, lithium) which has been the object of considerable theoretical and experimental study, because the tetrahedral bonding of sulphur to metal ions forming linear chains (quasi one-dimensional systems) is of interest in widely separated areas such as molecular physics, biochemistry, magnetism and electrochemistry [1–24].

The magnetic, optical and electronic structure properties of these systems have been extensively studied using different experimental techniques, such as Mössbauer spectroscopy, electron spin resonance, absorption spectroscopy, magnetic susceptibility and thoretical schemes such as point charge and multiple scattering $X\alpha$ molecular orbital models [1–24]. The correct structure determination of $KFeS_2$ was first reported [25] in 1942 and later refined [26] by means of neutron diffraction in 1980. The monoclinic unit cell contains four molecules and has the constants $a = 0.75\,\text{nm}$, $b = 1.128\,\text{nm}$, $c = 0.540\,\text{nm}$, and $\beta = 112.5°$. The space group has unambiguously been determined as C2/c (C^6_{2h}). Structural changes [27] were suggested to occur in $KFeS_2$ in a hydrogen stream at red glow. We have also recently published various papers [20–22] regarding Mössbauer and electron spin resonance of potassium dithioferrate subjected to a hydrogen atmosphere at 500° C which resulted in a substantial modification of the measured spectroscopic properties suggesting possible structural change effects.

It was thus considered of interest to extend and support this work in the present paper by monitoring with X-ray diffraction, possible structural changes in potassium dithioferrate as a function of heat treatment both in a hydrogen atmosphere and in vacuum.

2. Experimental procedure

2.1. Sample preparation

The crystalline powder was prepared as described previously [19]. The sample was thoroughly washed in ethanol and repeatedly analysed by X-ray diffraction in order to detect the presence of any by-products of the reaction.

2.2. Heat-treatment procedure

The samples were heat treated in two different ways: (a) under a vacuum of 10^{-3} torr, and (b) under a flux of hydrogen. In both cases the temperature was increased up to 500° C and held for 30 min.

3.3. X-ray diffraction analysis

X-ray diffraction diagrams were taken using a Philips PW-1140 generator and a horizontal goniometer equipped with a bent LiF crystal monochromator. The radiation used was $CuK\alpha$.

3. Results and discussion

X-ray diagrams of the untreated samples (Figs 1a and 2a) were analysed and the spacings obtained were compared with the data existing in the ASTM file [28]. A few discrepancies were noted, in particular, one reflection located at $2\theta = 31.8°$, corresponding to a spacing of 0.281 nm, which was not listed in the file and continued to appear after careful washing of the sample. Theoretical calculation of the powder lines was performed using the single crystal data given for $KFeS_2$ by Boon and MacGillavry [25] and a computer program produced by Yvon *et al.* [29]. All reflections were then properly indexed and the peak at $2\theta = 31.8°$ identified as the 2 2 0 reflection. The results of our analysis are summarized in Table I.

The diffraction pattern of the sample heated under vacuum showed extra reflections at 2θ = 12.8, 26.2,

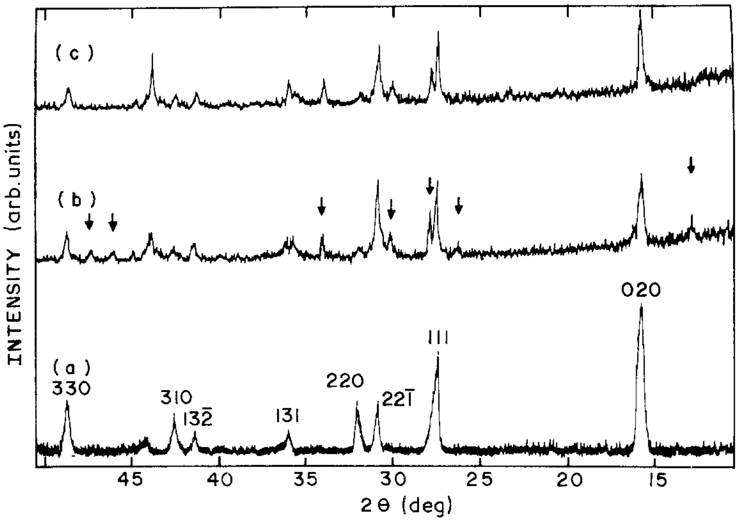

Figure 1 X-ray powder diffraction diagrams of $KFeS_2$, (a) without heat treatment (b) immediately after heat treatment at 500° C under vacuum, (c) 5 days after heat treatment. The arrows indicate the position of the extra reflections.

27.8, 30.0, 33.9, 45.8, and 47.1° (see Fig. 1b). The diffraction peaks were broadened because of the smaller crystallite size in the sample. The average crystallite dimension in the [1 1 0] direction was estimated using the Scherrer formula to be 50 nm.

In order to follow the time evolution of the changes mentioned above, diffraction diagrams were taken immediately after heat treatment and every 24 h during the next 5 days. The intensity of some of the new peaks decreased during this time. The peaks located at angles $2\theta = 12.8$, 26.2, and 30.0° practically disappeared after 5 days (see Fig. 1c). On the other hand, some of the new structures produced by the heat treatment still remained, as can be noted in Fig. 1c.

The sample heated in a hydrogen atmosphere was analysed in the same way as that treated in vacuum. Some of the new reflections that appeared in the diffraction pattern almost coincided with those detected for samples heated in vacuum. The extra peaks were now located at $2\theta = 13.2$, 25.8, 26.5, 29.8 and 31.0° (see Fig. 2b). In addition, several wide bands, centred at $2\theta = 32.6$, 36.8, 43.5 and 53° were detected. The diffraction pattern 5 days after heat treatment in a hydrogen atmosphere was very similar to that of the untreated sample, except for line broadening, which still remained. In this case, most of the new reflections had disappeared (see Fig. 2c).

Conventional hydrogenation procedures were also performed on the sample reaching a hydrogen pressure

TABLE I X-ray diffraction data for $KFeS_2$

	Calculated spacings*			Observed data†			ASTM data file		
hkl	2θ	d_c (nm)	I/I_0	2θ	d_0 (nm)	I/I_0	*hkl*	d_f (nm)	I/I_0
110, 020	15.71	0.564	32, 100	15.75	0.562	100	110, 020	0.570	100
200, 130	27.39	0.326	23, 10	–	–	–	130, 200	0.327	70
111	27.51	0.324	48	27.5	0.324	42	–	–	–
$22\bar{1}$	30.82	0.290	70	30.75	0.290	7	$22\bar{1}$	0.292	36
220, 040	31.73	0.282	11, 12	31.80	0.281	21	–	–	–
$11\bar{2}$	34.15	0.262	29	–	–	–	–	–	–
131	35.69	0.252	23	35.7	0.251	2	$002, 20\bar{2}$	0.250	20
002	36.00	0.249	9	–	–	–	–	–	–
022	39.50	0.228	8	39.4	0.228	1	$022, 12\bar{2}$	0.229	8
$13\bar{2}$	41.16	0.219	27	41.1	0.219	3	300	0.220	20
310	42.20	0.213	11	42.3	0.213	10	310	0.213	12
$112, 31\bar{2}$	44.31	0.204	9	–	–	–	051	0.204	12
330	48.41	0.188	15	48.4	0.188	16	–	–	–
151	48.49	0.187	6	48.5	0.187	12	‡	0.187	20
042	48.74	0.186	7	–	–	–	‡	0.183	8
$15\bar{2}$	52.88	0.173	19	52.9	0.173	1	‡	0.174	12
$202, 40\bar{2}$	54.21	0.169	5, 19	54.7	0.167	1	‡	0.170	4
$30\bar{3}, 26\bar{1}$	55.92	0.164	5, 9	55.8	0.165	1	–	–	–
400	56.51	0.163	7	56.5	0.163	10	‡	0.163	12
$42\bar{2}$	56.82	0.162	5	56.75	0.162	7	–	–	–
023	57.80	0.159	11	–	–	–	‡	0.158	8
350	59.05	0.156	10	59.1	0.156	4	–	–	–
062	61.79	0.150	7	61.7	0.150	1	‡	0.150	2
$44\bar{2}$	64.18	0.145	11	64.6	0.144	1	–	–	–
080	66.3	0.141	7	66.2	0.141	10	–	–	–
$20\bar{4}$	69.65	0.135	5	69.4	0.135	1	‡	0.135	4

*Only calculated reflections with $I/I_0 \geqslant 5$ are listed.

†Missing reflections and discrepancies in relative intensities are attributed to preferential orientation in the sample.

‡Unindexed reflections.

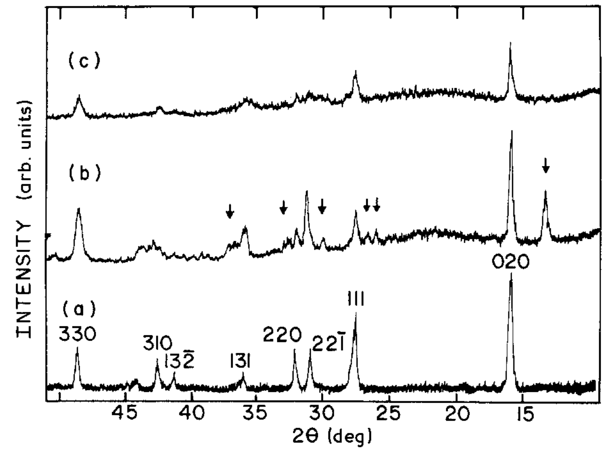

Figure 2 X-ray powder diffraction diagrams of $KFeS_2$, (a) without heat treatment, (b) immediately after heat treatment at 500° C in a hydrogen atmosphere, (c) 5 days after heat treatment. The arrows indicate the position of extra reflections.

of 5 torr and a sample temperature of 500° C. The results indicated that a very small amount of hydrogen could be absorbed by the compound under these conditions, and the amount estimated could not exceed 2H atoms per unit cell.

4. Conclusions

The X-ray patterns suggest the presence of unaltered $KFeS_2$ in the samples heated under vacuum or in a hydrogen atmosphere coexisting with unstable phases formed after heat treatment. The conversion of part of $KFeS_2$ into a structurally different phase has also been observed by Jacobson and McCandlish [24] on the formation of the complex $KLiFeS_2$.

Our primary objective in the present work, however, was not to identify the new phase, but to support the conclusions in our previous work that the significant modifications of the Mössbauer and EPR spectroscopic parameters of hydrogenated $KFeS_2$ at 500° C could be attributed to structural and chemical changes not directly measurable by those techniques. To this effect we note that Mössbauer spectroscopy indicated an apparent distribution of hyperfine parameters which was attributed to inequivalent iron sites whereas electron spin resonance indicates significantly smaller linewidths. 22.

If upon hydrogenation and heat treatment new phases with an iron content are formed, they can originate structurally and chemically inequivalent iron sites which could effectively cause a distribution of the Mössbauer hyperfine parameters and also modify the EPR spectroscopic parameters.

Although the heat treatment seems to be the main factor responsible for the structural changes, the absorbed hydrogen may also modify the Mössbauer and EPR spectroscopic parameters via reduction of the Fe–S covalency and increase of the interchain coupling.

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