

LOW TEMPERATURE SYNTHESIS OF Ba-Fe MIXED OXIDES
HAVING PEROVSKITE TYPE STRUCTURES

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(Received September 12, 1985; Refereed)

ABSTRACT

The reactions between BaO_2 and FeO reported here provide new ways of dry synthesis in mild conditions of iron(IV) containing materials. The oxidant power of the peroxide ion is used to attack FeO and the presence of Ba^{2+} stabilizes the Fe(IV) state. The nature of the resulting phases depends on the ratio between the initial amounts of the reagents.

MATERIALS INDEX: mixed oxides, barium, iron.

Introduction

It is well known that the lack of economical synthetic methods has hindered, in practice, some potential applications of technological interest of iron compounds in high oxidation states (commonly named ferrates). In recent publications (1), we have shown how the usual extreme P_{O_2} and T conditions required by the dry methods of preparation can be avoided, using alkaline or alkaline-earth peroxides as alternative oxidizing agents. In these processes, the nature of the s-metal cation plays a key role, as made evident by the different oxidation states reached as well as the reaction mechanisms involved (2). The main reaction products for the system $\text{BaO}_2\text{-FeSO}_4$ are Fe(IV) derivatives having perovskite or related structures (1a). The advantages of this system rely on the raw materials character of the reactants as well as on the thermodynamic assistance provided by the simultaneous BaSO_4 formation. However, this last effect implies in turn the greatest limitation of the procedure because the BaSO_4 formed cannot be removed from the mixture of the reaction.

Taking into account our previous results and trying to improve them, we have approached the study of the reactions between BaO_2 and FeO in order to utilize the oxidant ability of the peroxide ion in the design of new, simple, clean ways of synthesizing Fe(IV) containing materials. The results reported in this paper refer to this synthesis and the subsequent characterization of the phases obtained. A detailed kinetic study of the reactions is in progress.

As far as we know, the literature does not contain any information on this system.

Experimental

FeO starting product was prepared by thermal decomposition of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (at 700°C and under a dynamic N_2 atmosphere) followed by quenching into an ice water bath. The material was characterized by means of its X-ray powder diffraction pattern (3). The BaO_2 was Merck analytical grade.

To make the samples, precise amounts of both reagents were thoroughly mixed and ground in an agate mortar. This process was carried out in a glove-box in presence of P_4O_{10} and KOH. The samples were stored in sealed flasks in a dessicator over P_4O_{10} and KOH.

Thermal analyses were made using a Setaram 870 simultaneous TG-DTA thermo-balance. Crucibles containing 100 mg of the sample were heated at $2.5^\circ\text{C} \cdot \text{min}^{-1}$ under a dynamic N_2 atmosphere. Calcined Al_2O_3 was used as a reference.

X-ray powder diffraction patterns were obtained by means of a Kristalloflex 810 Siemens diffractometer using Cu K α radiation. JCPDF cards were utilized as comparative standards.

Results and Discussion

Initial experiments which showed that the obtained phases depend on the initial BaO_2/FeO relationship, and previous results on the $\text{BaO}_2\text{-FeSO}_4$ system (1a,2), focused our study mainly on the thermal behaviour of mixtures containing BaO_2/FeO molar ratios equal to 1.00 and 2.00. The data set provided by the thermal analysis of these samples has been summarized in Table 1.

TABLE 1
Thermal Analysis Data

Sample	BaO_2/FeO molar ratio	Thermal effects	
		TG % weight loss	DTA T, $^\circ\text{C}$
I	1.00	-	354, Exo
		Slow weight loss	375, Exo
		between 365 and 575°C	450, Exo
		$\Delta = 1.7\%$	
		Continuous weight loss	
II	2.00	between 575 and 850°C	645, Endo
		$\Delta = 1.6\%$	
		$\Delta_{\text{TOTAL}} = 3.3\%$	
		-	353, Exo
		3.6	353-425, Exo

Sample I ($\text{BaO}_2/\text{FeO} = 1.00$)

The weight loss begins at ca. 365°C , that is to say, after the occurrence of the first exothermic process (DTA peak at 354°C). The O_2 evolution continues until ca. 850°C . During its course, an inflection in the TG curve slope can be clearly noted. Weak thermal effects are associated to the mass decrease.

To identify the resulting phases: 1) fresh samples are heated in the thermobalance until the suitable temperature, 2) the crucibles are immediately extracted from the oven and quickly air cooled, and 3) X-ray powder diffraction patterns of the reaction products are recorded.

As stated above, the reaction at 354°C occurs without weight loss. In concordance, the recorded pattern (Table 2) shows that the main obtained phase is BaFeO_3 (4). Nevertheless, the slightly asymmetrical widening of the peaks centered at $d=1.635 \text{ \AA}$ and $d=2.005 \text{ \AA}$ indicates the presence of some $\text{BaFeO}_{2.75}$ in the solid (5). Given the known instability of the cubic perovskite BaFeO_3 (metaferrate IV) under the working conditions (6), this partial evolution during the cooling to the oxygen deficient phase is not surprising.

At 575°C , the only observed phase is the tetragonal perovskite $\text{BaFeO}_{2.75}$ (Table 3). This phase can now be unambiguously identified based on the position of the 111 plane peak ($d=2.308 \text{ \AA}$). In addition, according to the symmetry lowering, the peaks assignable to the planes 200 and 002 are clearly differentiated ($d=2.006$ and $d=2.001 \text{ \AA}$, respectively), as occurs with the corresponding 112 and 211 planes ($d=1.634$ and $d=1.630 \text{ \AA}$, respectively) (5). The X-ray powder diffraction pattern shows a pronounced increase in the crystallinity of this material with regard to that obtained at a lower temperature.

TABLE 2

Outstanding Peaks in the X-Ray Powder Diffraction Pattern

Sample I heated at 360°C

$d, \text{ \AA}$	hkl assigned
2.841	110
2.328	111
2.020	200
1.635	211
1.420	220

TABLE 3

Outstanding Peaks in the X-Ray Powder Diffraction Pattern

Sample I heated at 575°C

$d, \text{ \AA}$	hkl assigned
4.00	001, 100
2.828	101, 110
2.308	111
2.006	200
2.001	002
1.634	112
1.630	211
1.416	202
1.412	220

TABLE 4

Outstanding Peaks in the X-Ray Powder Diffraction Pattern

Sample I heated at 850°C

$d, \text{ \AA}$	hkl assigned
4.08	100
2.956	110
2.890	110
2.370	111
2.414	111
2.038	200
1.708	211
1.665	211
1.657	211

TABLE 5

Outstanding Peaks in the X-Ray Powder Diffraction Pattern

Sample II heated at 500°C

$d, \text{ \AA}$	$d, \text{ \AA}$	$*I/I_0 = 1.00$
3.48	3.07*	
3.21	2.99	
3.16	2.97	
hkl assignation was not possible (see ref. 9).		

Lastly, although the measured weight loss (TG curve) at 850°C would agree with the formation of the triclinic iron(III) $\text{BaFeO}_{2.5}$ phase, what is actually identified after cooling is the rhombohedral $\text{BaFeO}_{2.64}$ (Table 4) (7), which is reasonable given its higher stability in air (6).

Notwithstanding, to guarantee the reproducibility of the above results, special care must be paid to the true nature of the "ferrous oxide" used as reactant. Besides its known trend to non-stoichiometry (8), there is often a segregation of α -Fe crystals during the oxide preparation. As we have verified, the use of such "impurified" material as a starting reagent leads systematically to the apparition of Ba-Fe(III) mixed oxides ($\text{Ba}_3\text{Fe}_2\text{O}_6$ and BaFe_2O_4) as secondary contaminant phases. This effect can be greatly lessened by the presence of an adequate BaO_2 excess in the initial mixture.

Sample II ($\text{BaO}_2/\text{FeO}=2.00$)

In the same way as that of the above case, an exothermic process occurring at 353°C without mass variation just precedes the O_2 evolution.

The total weight loss in the course of the reaction is consistent with the orthoferrate Ba_2FeO_4 formation. In fact, this phase (whose structure could be formally related with that of the perovskite type (1a) is the only one identified (9) when the X-ray powder diffraction patterns of samples heated above 450° (Table 5) are run off.

The coincidence in the temperature and character of the first thermal effect with the Sample I case suggests that the initial attack by BaO_2 results in the formation of metaferrate intermediate (1a).

Conclusion

The literature-reported methods for the preparation of Ba-Fe(IV) phases involve strong P_{O_2} and T conditions. The results described here can open a new perspective in ferrate synthesis. Its advantage with respect to our own previous results (1) lies in the "clean" character of the synthesis. As to the rest, the results are similar to those obtained for the BaO_2 - FeSO_4 system. However, it can be noted that the metaferrate formation (even though not assisted by the BaSO_4 formation) occurs now at a slightly lower temperature. This fact must have a kinetic interpretation involving a decrease in the high activation energy required by the diffusion mechanism (2) of the reaction between BaO_2 and FeSO_4 .

Acknowledgments

Grateful acknowledgment is made to the CAICYT for partial financial support of this research under Grant No. 2930/83.

References

1. E. Martínez Tamayo, A. Beltrán-Porter and D. Beltrán-Porter, *Thermochim. Acta*, a) in press; b) submitted.
2. E. Martínez Tamayo, A. Beltrán-Porter and D. Beltrán-Porter, *Thermochim. Acta*, submitted.
3. JCPDF card No. 6-615.
4. JCPDF card No. 14-180.
5. JCPDF card No. 20-128.
6. S. Mori, *J. Am. Ceram. Soc.*, **49**, 600 (1966).
7. JCPDF card No. 20-131.
8. J.B. West and H.P. Broida, *J. Chem. Phys.*, **62**, 2566 (1975).
9. JCPDF card No. 23-1022.