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Synthesis of Barium Ferrates in Oxygen

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Phase relations in the system BaO—Fe_2O_3—"FeO_2" at 1 atm (1 atm$=1.013\times10^5$ N/m^2) oxygen and between 800 to 1050 °C are shown in the vicinity (high Ba portion) of the 1:1 cation-cation ratio composition. A hexagonal $BaTiO_3$-like phase, $BaFeO_{3-X}$ ($a=5.676$ Å, $c=13.934$ Å), exists below 960 °C. A perovskite-like phase $BaFeO_{3-X'}$ occurs between 960 and 1050 °C. Single-phase tetragonal perovskite can be obtained at room temperature by quenching compositions with Ba-Fe ratios of 67:66 ($a=3.985$ Å, $c=4.005$ Å, 1000 °C) and 27:26 ($a=3.988$ Å, $c=4.003$ Å, 1000 °C) from above 960 °C. At the 17:16 ratio, single phase cubic perovskite ($a=3.994$ Å, 1000 °C), can be synthesized. Influence of temperature, additions of barium, and use of Pt-containers on phase relations are discussed.

Key words: Ferrates; hexagonal barium ferrate; perovskite; phase equilibria; tetravalent iron.

1. Introduction

Mixed alkaline earth-transition metal oxides are of particular importance because of their interesting electrical and magnetic properties. Characterization of such materials through phase equilibrium and x-ray diffraction studies is complicated by the tendency of the transition metal to exist in disproportioned oxidation states within a single phase. Variable oxygen stoichiometries, controlled by temperature and oxygen pressure result. The 1:1 cation-cation barium ferrates are excellent examples of this phenomenon. Tetravalent iron has been confirmed in phases within the $BaFeO_{2.5-3.0}$ compositional range by MacChesney et al. [1][1], and Gallagher et al. [2], using magnetic studies and the Mössbauer technique. Some inconsistencies, however, exist concerning the nature of the phases within this compositional range. Erchak et al. [3], reported the compound $BaFeO_{2.62}$ ($Ba_8Fe_2^{4+}Fe_6^{3+}O_{21}$) which was thought to be a cubic perovskite ($a=8.05$ Å). Subsequently, Malinofsky and Kedesdy [4] showed that this phase is not cubic, but is actually analogous to the hexagonal polymorph of $BaTiO_3$ [5] with $a=5.68$ Å and $c=13.86$ Å. They also reported a tetragonal perovskite polymorph, admixed with the hexagonal form, with $a=3.98$ Å and $c=4.01$ Å. This mixture was prepared by heating the hexagonal form at 1275 °C in oxygen and slow-cooling. MacChesney, et al. [1], and Gallagher, et al. [2], prepared hexagonal forms in the $BaFeO_{2.74-2.95}$ range using oxygen pressures from 0.2 to 2400 atm and generally below 850 °C. Gushee et al. [6], reported a $BaFeO_{2.72}$ hexagonal form with $a=5.76$ Å and $c=13.9$ Å while Goto and Takada [7] synthesized a $2BaO\cdot Fe_2O_3$ phase with a melting point at 1370 °C in 1 atm O_2. The latter phase was reported as cubic ($a=8.07$ Å) but is most likely a hexagonal barium ferrate similar to that reported by Erchak et al. [3], and originally thought to be a cubic perovskite with $a'=2a_{\text{cub}}$.

Mori [8, 9] reported a number of $BaFeO_{3-X}$ phases with X values ranging from 0.50 to 0.10. These were prepared in air and 1 atm oxygen using quenching and slow-cooling techniques within the 25 to 1080 °C range. A hexagonal $BaTiO_3$-like phase was found by quenching from below 950 °C in oxygen. Above this temperature a transitory cubic form was obtained after a ½-hr heating time. With longer heating times this form converted to a triclinic form through a rhombohedral form. Heating a $2BaCO_3$:Fe_2O_3 mixture at 1080 °C in oxygen for ½-hr and quenching also produced a cubic form, $BaFeO_{2.75}$, which upon further heating converted to a tetragonal phase, $BaFeO_{2.81}$, through a series of tetragonal phases with lower oxygen contents. The $BaFeO_{2.81}$ phase was not of the simple tetragonal perovskite type as its powder pattern gave evidence of superstructure lines. Final equilibration products were not indicated and difficulty was encountered in reproducing each phase, in terms of symmetry and oxygen content, by the quenching method.

Although the existence of the hexagonal form is well documented, synthesis of a stable single-phase tetragonal perovskite or a stable, truly cubic perovskite has not been demonstrated. This study was conducted

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[1] Figures in brackets indicate the literature references at the end of this paper.

to examine the latter possibility and, therefore, considers only the existence and stabilities of phases encountered. Chemical analyses establishing Fe^{4+}:Fe^{3+} ratios (oxygen concentration) and Mössbauer data will be reported in the future.

2. Experimental Procedure

Starting material was prepared from appropriately weighed (±0.1 mg) quantities of $BaCO_3$ and Fe_2O_3. These were hand mixed under acetone, packed in gold envelopes, and calcined in air at 800 °C for two weeks with periodic remixing and reheating. Gold was used as the container instead of platinum because of the tendency of uncombined $BaCO_3$ to react with the latter. Another problem with platinum will be discussed later. Calcined specimens were equilibrated at elevated temperatures in 1 atm (1 atm $= 1.013 \times 10^5$ N/m^2) oxygen using the quench method. A vertical tube, resistance type, furnace, modified for vacuum and gas flow capability with endclosures and "O"-ring seals, was used for the quenching experiments. Oxygen was passed through the furnace at 10^{-6} m^3/s flow rate. Open gold envelopes were used as containers to 1050 °C. A few experiments were conducted above 1050 °C using platinum. Temperatures were measured with Pt-Pt 10 percent Rh thermocouples calibrated against the melting points of NaCl (801 °C) and Au (1063 °C). The furnace was controlled by an a-c Wheatstone bridge controller capable of maintaining temperature to at least ±2 °C. Specimens were quenched into an ice-cooled brass cold finger which constitutes the lower portion of the furnace. X-ray patterns were made using a high-angle Geiger counter-diffractometer and nickel-filtered Cu radiation at a 1/4° 2θ/min scanning rate. Reported unit cell data are considered accurate to about ±2 in the last decimal place listed.

3. Experimental Results

A portion of the BaO-"iron oxide" pseudobinary in the vicinity (high baria portion) of the 1:1 cation-cation compound is shown in figure 1. The diagram was constructed from the data in table 1. It is emphasized that the diagram represents stability of phases present (determined by room temperature x-ray patterns) as a function of starting Ba:Fe ratio. Absolute compositions involving Ba:Fe^{4+}:Fe^{3+} ratios belonging to the BaO—Fe_2O_3—"FeO_2" ternary are not indicated.

The 1:1 hexagonal $BaTiO_3$-like phase, $BaFeO_{3-X}$ ($a = 5.676$ Å, $c = 13.934$ Å), exists at low temperatures as previously observed by others. An indexed powder pattern is provided in table 2. MacChesney et al. [1], reported the hexagonal form, $BaFeO_{2.82}$ and $BaFeO_{2.84}$, at low temperatures in 1 atm O_2 and air, respectively. The value of X for the $BaFeO_{3-X}$ in this study is, therefore, probably within the 0.20–0.15 range. Above approximately 960° C the phase transforms to a perovskite-like form, probably by further reduction of part of the available Fe^{4+} to Fe^{3+}. The powder pattern, given in table 3, bears a superficial resemblance to a tetragonal perovskite but is rather diffuse and contains a number of extra lines. This phase may be represented as $BaFeO_{3-X'}$, where $0.5 > X' > 0$ and $X' > X_{\text{hex}}$, where X_{hex} refers to the oxygen deficiency in the hexagonal form. It is not $Ba_2Fe_2O_5$, ($BaFeO_{2.5}$, $X' = 0.5$), a brownmillerite-like compound also reported by MacChesney et al. [1]. Within this temperature range, however, a $Ba_2Fe_2O_5$-like phase was found to exist in air. Although the transformation near 960 °C in this study correlates well with that observed by Mori [9] (>950 °C), a definitive correlation of phases could not be made. It seems very likely, however, that Malinofsky and Kedesdy [4] observed the $BaFeO_{3-X'}$ of this study or one of the tetragonal phases reported by Mori when they heated and slow-cooled the hexagonal form from 1275 °C in oxygen.

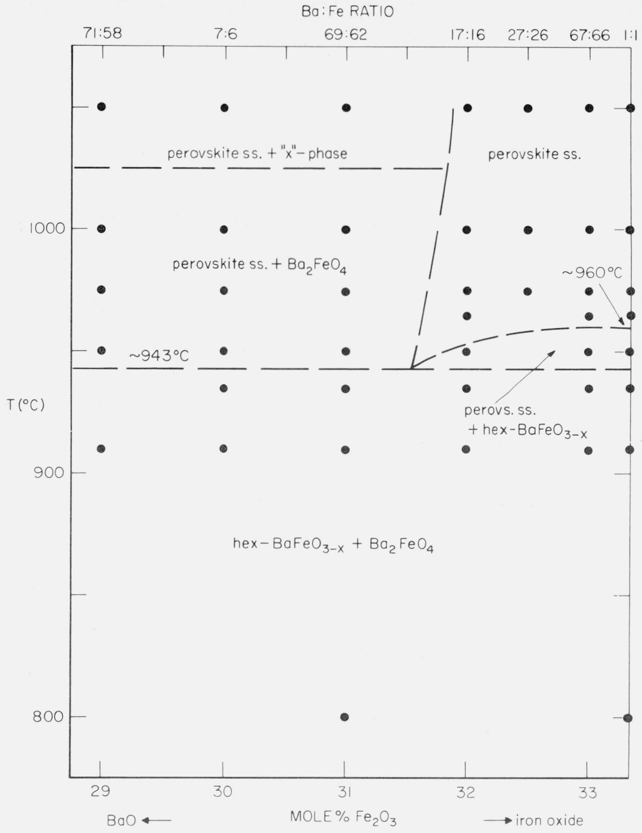

FIGURE 1. *Subsolidus relations at 1 atm O_2 for that portion of the BaO-"iron oxide" pseudobinary near the 1:1 barium-iron ratio.*

Absolute Ba-Fe-O concentrations are not indicated.

Hexagonal $BaFeO_{3-X}$ does not appear to form solid solutions in the high baria portion of the system below 960 °C. Changes in oxygen stoichiometry may occur as a function of temperature to 960 °C. Cell parameters, however, do not change from 800 to 960 °C and it is, therefore, expected that change in oxygen concentration within this temperature range is limited. Below approximately 943 °C, the phase assemblage consists

TABLE 1. *Experimental data for compositions in the system* BaO-"*iron oxide*" *at 1 atm oxygen*

Composition	Heat treatments				X-ray diffraction analyses[a]
	Initial[b]		Final[c]		
	Temp.	Time	Temp.	Time	
Ba:Fe ratio	°C	hr	°C	hr	
1:1	800	335			
			800	70	Hex-BaFeO$_{3-X}$ $a=5.676$ $c=13.934$
			910	70	Hex-BaFeO$_{3-X}$ $a=5.676$ $c=13.934$
			935	45	Hex-BaFeO$_{3-X}$ $a=5.676$ $c=13.934$
			950	70	Hex-BaFeO$_{3-X}$ $a=5.676$ $c=13.934$
			965	45	Hex-BaFeO$_{3-X}$ + BaFeO$_{3-X'}$ [d]
			975	70	BaFeO$_{3-X'}$
			1000	70	BaFeO$_{3-X'}$
			1050	70	BaFeO$_{3-X'}$
67:66	800	335			
			910	70	Hex-BaFeO$_{3-X}$ [e]
			935	45	Hex-BaFeO$_{3-X}$ [e]
			950	70	Hex-BaFeO$_{3-X}$ + perovskite
			965	45	t. p.[f]
			975	70	t. p. $a=3.984$ $c=4.005$
			1000	70	t. p. $a=3.985$ $c=4.005$
			1050	70	t. p. $a=3.987$ $c=4.004$
27:26	800	335			
			975	70	t. p. $a=3.986$ $c=4.003$
			1000	70	t. p. $a=3.988$ $c=4.003$
			1050	70	t. p. $a=3.992$ $c=4.001$
17:16	800	335			
			910	70	Hex-BaFeO$_{3-X}$ + Ba$_2$FeO$_4$
			935	45	Hex-BaFeO$_{3-X}$ + Ba$_2$FeO$_4$
			950	70	c. p.[g] + Hex-BaFeO$_{3-X}$
			965	45	c. p.
			975	70	c. p. $a=3.993$
			1000	70	c. p. $a=3.994$
			1050	70	c. p. $a=3.997$
69:62	800	335			
			800	70	Hex-BaFeO$_{3-X}$ + Ba$_2$FeO$_4$
			910	70	Hex-BaFeO$_{3-X}$ + Ba$_2$FeO$_4$
			935	45	Hex-BaFeO$_{3-X}$ + Ba$_2$FeO$_4$
			950	70	c. p. + Ba$_2$FeO$_4$ + Hex-BaFeO$_{3-X}$ [h]
			975	70	c. p. ($a=3.992$) + Ba$_2$FeO$_4$
			1000	70	c. p. ($a=3.993$) + Ba$_2$FeO$_4$
			1050	70	c. p. ($a=3.996$) + unknown phase "X"
7:6	800	335			

TABLE 1. *Experimental data for compositions in the system* BaO-"*iron oxide*" *at 1 atm oxygen* — Continued

Composition	Heat treatments				X-ray diffraction analyses[a]
	Initial[b]		Final[c]		
	Temp.	Time	Temp.	Time	
Ba:Fe ratio	*°C*	*hr*	*°C*	*hr*	
			910	70	Hex-$BaFeO_{3-X}$ + Ba_2FeO_4
			935	45	Hex-$BaFeO_{3-X}$ + Ba_2FeO_4
			950	70	c. p. + Ba_2FeO_4 + Hex-$BaFeO_{3-X}$[h]
			975	70	c. p. + Ba_2FeO_4
			1000	70	c. p. + Ba_2FeO_4
			1050	70	c. p. + unknown phase "X"
71:58	800	335			
			910	70	Hex-$BaFeO_{3-X}$ + Ba_2FeO_4
			950	70	c. p. + Ba_2FeO_4
			975	70	c. p. + Ba_2FeO_4
			1000	70	c. p. + Ba_2FeO_4
			1050	70	c. p. + unknown phase "X"

[a] Phases identified are given in the order of amount present at room temperature. The phases are not necessarily those present at the temperature to which the specimen was heated.

[b] Heated in air in Au.

[c] Heated in 1 atm oxygen in Au.

[d] Perovskite-like phase.

[e] Ba_2FeO_4 in insufficient amount to detect.

[f] t. p. = tetragonal perovskite.

[g] c. p. = cubic perovskite.

[h] Incomplete reaction.

TABLE 2. *X-ray diffraction powder data for the hexagonal* $BaTiO_3$-*like phase*, $BaFeO_{3-X}$[a]

d_{obs}[b]	I/I_0[c]	$\frac{1}{d^2_{calc}}$	$\frac{1}{d^2_{obs}}$	hkl[d]
4.017	9	0.0620	0.0620	102
3.376	23	.0877	.0878	103
2.838	100	.1238 .1242	.1242	104 110
2.421	13	.1705 .1707	.1706	113 201
2.322	15	.1854	.1855	006
2.318	17	.1861	.1861	202
2.173	21	.2119	.2119	203
2.009	28	.2479	.2479	204
1.8433	12	.2943 .2948	.2943	205 211
1.7954	8	.3103	.3102	212
1.7251	7	.3361	.3361	213
1.6388	28	.3721 .3725	.3724	214 300
1.5457	8	.4185 .4188	.4186	215 303
1.4837	[e] 2	.4538 .4549	.4543	118 304
1.4765	5	.4586	.4587	109
1.4209	7	.4952	.4953	208
1.4190	12	.4966	.4966	220
1.3573	5	.5429	.5428	223
1.3389	[e] 3	.5564 .5579 .5586	.5578	1,0,10 306 312
1.3084	6	.5844	.5842	313
1.2696	8	.6204	.6204	314
1.2242	3	.6673	.6673	401
1.2106	6	.6820 .6828	.6824	226 402
1.1881	4	.7085	.7085	403
1.1589	4	.7446	.7446	404
1.1245	3	.7909	.7909	405
1.0727	8	.8691	.8691	410

[a] Prepared at 910 °C, 1 atm O_2.

[b] Interplanar spacing, A.

[c] Observed intensity.

[d] Indexed on the basis of a hexagonal cell with $a = 5.676$ Å and $c = 13.934$ Å.

[e] Broad.

TABLE 3. *X-ray diffraction powder data for the perovskite-like phase,* $BaFeO_{3-X'}$[a]

line	d[b]	I/I_0[c]
1	4.09	[d] 2
2	4.01	6
3	3.98	7
4	2.91	[d] 9
5	2.86	[d, e] 7
6	2.82	100
7	2.31	4
8	2.30	15
9	2.02	[d] 3
10	2.00	9
11	1.989	15
12	1.789	4
13	1.781	4
14	1.633	10
15	1.627	18
16	1.413	11
17	1.408	[d] 8

[a] Prepared at 1000 °C, 1 atm O_2.

[b] Interplanar spacing, Å.

[c] Observed intensity.

[d] Broad.

[e] Appears only after long exposure to air.

of hex-$BaFeO_{3-X}$ and Ba_2FeO_4. The latter phase is extremely sensitive to moisture and tends to deteriorate when exposed to air and during x-ray analysis. The compound was made from a $4BaCO_3$:Fe_2O_3 mixture at 900 °C in air and at 900 °C in 1 atm O_2. A portion of its powder pattern, indexed by analogy with K_2SO_4 is given in table 4. The phase is orthorhombic with $a = 5.93$ Å, $b = 10.36$ Å, and $c = 7.64$ Å.

Above 943 °C, phase assemblages are quite interesting, as true perovskite-like phases appear. At the 67:66 Ba:Fe ratio single-phase tetragonal perovskites may be quenched from 960 to 1050 °C. The indexed powder

TABLE 4. *X-ray diffraction powder data for the compound,* Ba_2FeO_4 [a]

d_{obs} [b]	I/I_0 [c]	$\frac{1}{d^2_{calc}}$	$\frac{1}{d^2_{obs}}$	hkl [d]
4.279	10	0.0544 .0549	0.0546	021 111
3.824	12	.0685	.0684	002
3.581	12	.0779	.0780	012
3.474	64	.0828	.0829	121
3.211	33	.0970	.0970	102
3.149	21	.1010	.1009	031
3.069	100	.1058 .1063	.1062	022 112
2.985	91	.1123	.1122	130
2.964	71	.1138	.1138	200

[a] Prepared at 900 °C in air.
[b] Interplanar spacing, Å.
[c] Observed intensity.
[d] Indexed on the basis of an orthorhombic cell with $a=5.93$ Å, $b=10.36$ Å, $c=7.64$ Å.

pattern of a typical tetragonal phase is given in table 5. Single-phase tetragonal perovskites can also be quenched from above 960 °C at the 27:26 Ba:Fe ratio. Tetragonal perovskites at the 67:66 ratio transform to cubic on heating near 75 °C while those at the 27:26 ratio transform near 45 °C. Single phase cubic perovskites are obtained at room temperature at the 17:16 Ba:Fe ratio. An indexed pattern of a typical cubic phase is given in table 6. Figure 2 shows the variation of room temperature-determined cell parameters with temperature and composition from 975 to 1050 °C. Compositions more BaO-rich than 17:16 yield cubic perovskite solid-solution plus Ba_2FeO_4 between 943° and about 1025 °C. Above 1025 °C an unknown phase exists with the perovskite and is characterized by the appearance of lines with $d=4.19$, 3.84, 3.66, 3.23, 3.12, and 2.97 Å in the low angle region. Variation of cell parameters as a function of cation-cation

TABLE 5. *X-ray diffraction data for the tetragonal perovskite at the 67:66* Ba-Fe *ratio* [a]

d_{obs} [b]	I/I_o [c]	$\frac{1}{d^2_{calc}}$	$\frac{1}{d^2_{obs}}$	hkl [d]
4.003	8	0.0624	0.0624	001
3.981	12	.0630	.0631	100
2.824	100	.1253	.1254	101
2.818	90	.1259	.1259	110
2.304	29	.1883	.1884	111
2.002	13	.2494	.2494	002
1.9922	26	.2519	.2520	200
1.7892	4	.3124	.3124	102
1.7836	7	.3142	.3143	201
1.7823	5	.3148	.3148	210
1.6321	18	.3754	.3754	112
1.6281	35	.3772	.3772	211
1.4124	13	.5013	.5013	202
1.4090	14	.5037	.5038	220
1.3349	4	.5612	.5612	003
1.3284	4	.5667	.5667	300
1.2657	6	.6242	.6242	103
1.2606	10	.6290 .6296	.6293	301 310
1.2064	4	.6871	.6872	113
1.2021	5	.6920	.6921	311
1.1524	7	.7531	.7531	222
1.0684	6	.8760	.8760	213
1.0666	10	.8791	.8791	312
1.0655	8	.8809	.8809	321

[a] Prepared at 1000 °C, 1 atm O_2.
[b] Interplanar spacing, Å.
[c] Observed intensity.
[d] Indexed on the basis of a tetragonal cell with $a=3.985$ Å, $c=4.005$ Å.

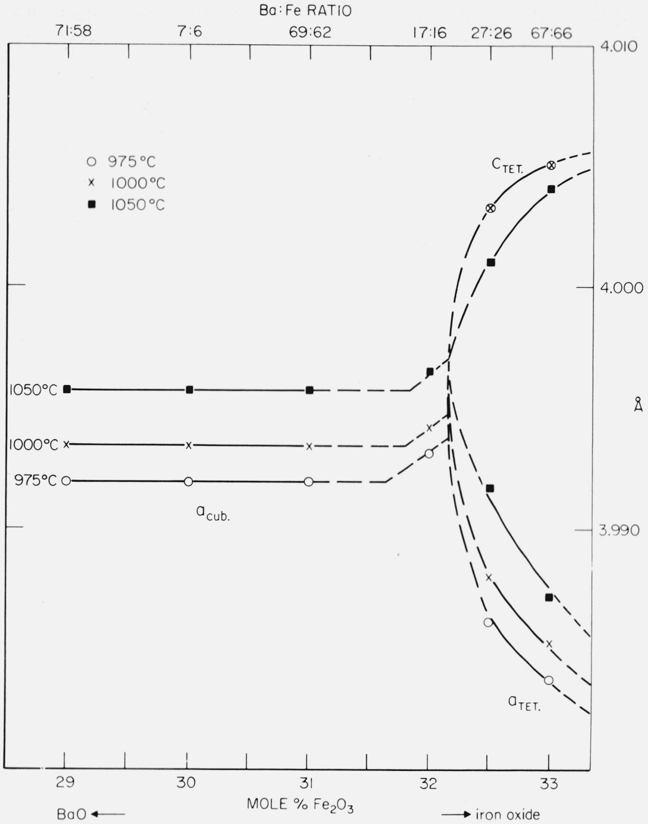

FIGURE 2. *Variation of room temperature-determined cell parameters with temperature and composition for cubic and tetragonal barium-iron perovskites.*

TABLE 6. *X-ray powder diffraction data for the cubic perovskite at the 17:16* Ba-Fe *ratio* [a]

d_{obs} [b]	I/I_o [c]	$\frac{1}{d^2_{calc}}$	$\frac{1}{d^2_{obs}}$	hkl [d]
3.994	13	0.0627	0.0627	100
2.824	100	.1254	.1253	110
2.306	23	.1880	.1880	111
1.9972	34	.2507	.2507	200
1.7862	8	.3134	.3134	210
1.6308	37	.3761	.3760	211
1.4122	17	.5014	.5015	220
1.3315	4	.5641	.5641	300
1.2631	12	.6268	.6268	310
1.2043	5	.6895	.6895	311
1.1530	6	.7522	.7522	222
1.0675	13	.8775	.8775	321
0.99858	3	1.0029	1.0029	400
.96875	3	1.0656	1.0656	410/322
.94146	5	1.1283	1.1282	411/330
.91635	3	1.1910	1.1909	331
.89313	5	1.2536	1.2537	420

[a] Prepared at 1000 °C, 1 atm O_2.
[b] Interplanar spacing, Å.
[c] Observed intensity.
[d] Indexed on the basis of a cubic cell with $a=3.994$, Å.

ratio and temperature in the limited homogeneity region is a complex feature which can be deciphered only with knowledge of accurate Fe^{4+}:Fe^{3+} ratios. At a fixed ratio, cell expansion with increasing temperature is probably a result of increased reduction of Fe^{4+} to Fe^{3+} with a corresponding decrease in oxygen content. Changes with cation-cation ratio at fixed temperature may be much more complicated than merely being due to variation in barium content. Increasing barium appears to cause expansion of a_{tet} and contraction of c_{tet} and a_{cubic} at fixed temperature in the single-phase region. Furthermore, it is highly unlikely that a stable perovskite structure can accommodate interstitial barium. At 1000 °C, the single-phase cubic perovskite, for example, contains an excess of about 1.3 mol percent BaO (in terms of $BaO:Fe_2O_3$) and its composition might be described as $Ba_{17}Fe_{16}O_N$ where $N=49-X$. This may be more appropriately written as $BaFe_{16/17}O_{N/17}$ which now indicates iron and oxygen vacancies rather than barium interstitials. The value of X will, of course, depend on the Fe^{4+}:Fe^{3+} ratio in the phase. Starting at the $BaFeO_{3-X'}$ phase, increasing amounts of barium at constant temperature will tend to increase the concentration of iron and oxygen vacancies. Increasing iron and $O^=$ vacancies should tend to expand the structure. Although unit cell volumes increase initially with increasing barium content, the apparent a cubic contraction associated with single phases from near the 17:16 ratio to the two phase region suggests a second mechanism operating simultaneously. A plausible hypothesis involves the general equilibrum

$$2Fe^{3+}+\tfrac{1}{2}O_2\rightarrow 2Fe^{4+}+O^{2-}.$$

Physically, this mechanism would operate in the following manner. As iron and $O^=$ vacancies are created by addition of barium, the concentration level of the $O^=$ vacancies would be decreased if some of the available Fe^{3+} is oxidized to Fe^{4+}. The total number of iron vacancies would not be affected but the Fe^{4+}:Fe^{3+} ratio, and consequently $O^=$ concentration, would increase. Cell contraction, as observed, might result.

Data pertinent to temperatures above 1050 °C could not be obtained in this study because of problems with container materials. Above the melting point of Au, platinum tubes were used as containers for equilibration runs. In gold, hex-$BaFeO_{3-X}$ is not stable above 960 °C and 1 atm O_2. In platinum, however, a hexagonal $BaFeO_{3-X}$-like phase does exist above 960 °C and persists at elevated temperatures to at least 1300 °C. The phase is normally admixed with perovskite-like material but tends to predominate with increasing firing time. Consistent and reproducible equilibria data are difficult to obtain. It is hardly likely that hex-$BaFeO_{3-X}$ converts at 960 °C to perovskite-like $BaFeO_{3-X'}$ which in turn transforms at some temperature > 1050 °C back to a hex-$BaFeO_{3-X''}$ phase. This is apparent, especially in view of the data of MacChesney et al. [1], suggesting the existence of an orthorhombic brownmillerite-like $Ba_2Fe_2O_5$ which might be expected to form at sufficiently elevated temperatures in O_2. Goto and Takada [7] using Pt containers and 1 atm O_2 reported a cubic $2BaO\cdot Fe_2O_3$ phase with a melting point near 1370 °C. As pure $Ba_2Fe_2O_5$ is not cubic and the reported $a=8.07$ Å parameter is approximately $2\times a_{\text{cubic}}$ perovskite, a value which may be used to index a hexagonal $BaTiO_3$-like phase, the compound was probably erroneously identified. It is likely that the phase observed was of the hex-$BaFeO_{3-X}$ type. More interesting, however, is the stability of the compound to a congruent melting point in 1 atm O_2 and the exclusion of a stability range for a perovskite-like $BaFeO_{3-X'}$. These reported data and the inconsistent data above 1050 °C in this study have but one common denominator, platinum containers. It is, therefore, suggested that in the presence of Pt, a reaction occurs resulting in the stabilization of a hexagonal $BaTiO_3$-like phase containing Pt^{4+}. Hexagonal phases containing Pt^{4+} are not unusual and have been reported by Dickinson et al. [10], Blattner et al. [11], and Stratton [12]. If platinum does indeed tend to stabilize the hexagonal form, it is not surprising that the cubic and tetragonal high temperature perovskites herein reported have not been previously observed, as most experiments involving synthesis of materials are conducted using Pt-containers. Furthermore, chemical analyses for Fe^{4+}:Fe^{3+} ratios, when Pt is present, would lead to erroneous oxygen ion concentrations.

4. Summary

Phase relations in the BaO-"iron oxide" pseudobinary in the vicinity of the 1:1 cation-cation ratio were determined in 1 atm O_2 and between 800 to 1050 °C. Below 960 °C a hex-$BaTiO_3$-like phase, $BaFeO_{3-X}$ exists. Above 960 °C, this phase transforms to a perovskite-like $BaFeO_{3-X'}$. Specimens quenched from the 960 to 1050 °C range and having Ba:Fe ratios of 67:66 and 27:26 yield single-phase tetragonal perovskite at room temperature. Single-phase cubic perovskite can be quenched from this temperature range at the 17:16 ratio. Hex-$BaTiO_3$-like phases were observed in specimens heated above 1050 °C in Pt-containers. These are considered to be products of a Pt-specimen reaction.

5. References

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