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The System $BaO-SnO_2-Fe_2O_3$ with Less Than 50 Mol% BaO at 1200°C in Air, a Crystallographic Study

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The $BaO-SnO_2-Fe_2O_3$ system has been investigated after heating at 1200°C in air. The mol% BaO was less than 50%. In the part of the system examined five quaternary compounds were determined, $BaSn_2Fe_4O_{11}$, $Ba_3SnFe_{10}O_{20}$, $Ba_{.69}Sn_{2.62}Fe_{1.38}O_8$, $BaSn_{.90}Fe_{5.47}O_{11}$, and a compound of still unknown composition, the best approximation is $BaSn_{1.70}Fe_{2.75}O_{8.52}$. The compounds were recognized by their X-ray diffraction patterns. All X-ray powder diffraction patterns could be indexed. No indication was found for reduction of Fe^{3+} to Fe^{2+} at 1200°C. A solid solution of perovskite compounds was found in the system $Ba_2Fe_2O_5-BaSnO_3$, caused by oxidation of Fe^{3+} to Fe^{4+}. This oxidation was observed also in the area $Ba_2Fe_2O_5-BaFe_2O_4-BaSnO_3$. The triangulation found in the $BaO-SnO_2-Fe_2O_3$ system is discussed and the system is compared with the $BaO-TiO_2-Al_2O_3$ system.

Introduction

In an investigation of quarternary compounds in $Ba-M^{4+}-M^{3+}-O$ systems, the system $BaO-SnO_2-FeO_3$ has been explored more extensively. The reason for choosing this system is that the $BaO-SnO_2$ system is less complicated than the $BaO-TiO_2$ system. Moreover, there are no compounds in the $SnO_2-Fe_2O_3$ system, which reduces the number of possible ternary compounds. The system $BaO-SnO_2-Fe_2O_3$ is of particular interest because the Sn^{4+} ions are usually octahedrally coordinated and the Fe^{3+} ions can be coordinated both octahedrally and tetrahedrally by oxygen. Besides it was not expected that the valences of Sn and Fe would change at 1200°C in air. Because of the diversity of quarternary compounds it was decided to limit the investigation to a maximum of 50 mol% of BaO.

Experimental

The starting materials $BaCO_3$, SnO_2, and Fe_2O_3 were of AR quality. $BaCO_3$, SnO_2, and Fe_2O_3 were thoroughly mixed in an agate mortar in the appropriate ratios. The mixture was heated for one day at 1200°C in an Al_2O_3 crucible in air. After cooling, the reaction mixture was ground and heated again for several days. The total heating time was at least 1 week, but sometimes, when the reaction mixture was not in equilibrium, the heating time was extended to 1 or 2 months, with repeated grinding. It was observed that at the reaction temperature the sintering properties of most reaction mixtures were poor, with exception of the region near $BaFe_{12}O_{19}$. It was assumed that the mixture was in equilibrium if three or less compounds could be detected in the reaction mixture, according to the phase rule. Some mixtures showed four com-

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pounds in spite of a heating time of 2 months. The reaction mixtures were examined with a Philips PW 1050 X-ray diffractometer using graphite monochromated Cu$K\alpha$ radiation. The diffraction patterns were compared with those of compounds already known in this system. Several unknown compounds were traced in this way. The diffraction patterns of the new compounds were by trial and error indexed.

A reaction mixture was assumed to consist of one single compound if no other compounds could be traced in the diffraction pattern, and if the diffraction pattern could be completely indexed using the cell parameters of the compound. The unit cell parameters were determined from the diffraction patterns using the least-squares computer program T123 (*1*). One hundred and forty-two different compositions were studied in this system.

Results

In the pseudo-binary systems Fe_2O_3–SnO_2 and $BaSnO_3$–Fe_2O_3 no ternary compounds were found. In the system $Ba_2Fe_2O_5$–Fe_2O_3 only the compounds $BaFe_2O_4$(B) and $BaFe_{12}O_{19}$(M) could be detected after heating to 1200°C. Moreover five quarternary compounds were detected: $BaSn_2Fe_4O_{11}$(R), $Ba_3SnFe_{10}O_{20}$(X), $Ba_{.69}Sn_{2.62}Fe_{1.38}O_8$(H), $BaSn_{.90}Fe_{5.47}O_{11}$(K), and a compound of which the exact composition could not be determined. The cell parameters of all compounds found in the investigated part of the BaO–SnO_2–Fe_3 system are given in Table I. In the composition diagram (Fig. 1) the compounds have been indicated by the same symbol as given in Table I.

Figure 1 shows the idealized composition diagram of the system investigated. In this diagram the phase-width that can be expected for the compounds was not taken into account. $BaFe_{12}O_{19}$ shows a phase-width in the BaO–TiO_2–Fe_2O_3 system (*2*) and for hollandites comparable to $Ba_{.69}Sn_{2.62}Fe_{1.38}O_8$ a certain phase-width is reported too (*3*). The composition diagram has been subdivided into several triangles. Any composition within such a triangle will in equilibrium contain the three compounds at the angular points of this triangle. A different situation is found in the triangle $BaSnO_3$–$Ba_2Fe_2O_5$–$BaFe_2O_4$. Compositions within this triangle appear to contain only two phases, $BaFe_2O_4$ and a peroskite like phase, due to the oxidation of Fe^{3+} to Fe^{4+}. The compound $Ba_2Fe_2O_5$ was found to occur only when the reac-

TABLE I

LIST OF ALL COMPOUNDS DETERMINED IN THE INVESTIGATED PART OF THE $BaO–SnO_2–Fe_2O_3$ SYSTEM WITH UNIT CELL PARAMETERS AND THE SYMBOL USED IN FIG. 1

Compound	Symbol	a(Å)	b(Å)	c(Å)	α	β	γ	z	Reference
Fe_2O_3	F	5.038	5.038	13.772	90	90	120	6	A.S.T.M. index
SnO_2	S	4.738	4.738	3.188	90	90	90	2	A.S.T.M. index
$BaFe_{12}O_{19}$	M	5.892	5.892	23.198	90	90	120	2	*10*
$BaFe_2O_4$	B	19.05	5.390	8.448	90	90	90	8	*11*
$Ba_2Fe_2O_5$	Br	5.911	16.450	11.037	90	90	90	16	*5*
$BaSnO_3$	P	4.1163	4.1163	4.1163	90	90	90	1	A.S.T.M. index
$BaSn_2Fe_4O_{11}$	R	5.962(1)	5.962(1)	13.747(1)	90	90	120	2	This work
$Ba_{.69}Sn_{2.62}Fe_{1.38}O_8$	H	10.539	3.126	10.130	90	91.21	90	2	*3*
$Ba_3SnFe_{10}O_{20}$	X	15.359(4)	11.875(3)	5.227(2)	90	91.14(1)	90	2	This work
$BaSn_{.9}Fe_{5.47}O_{11}$	K	5.923(1)	5.923(1)	14.291(1)	90	90	120	2	This work
$BaSn_{1.70}Fe_{2.75}O_{8.52}$	Y	5.964(2)	5.964(2)	32.687(8)	90	90	120	?	This work

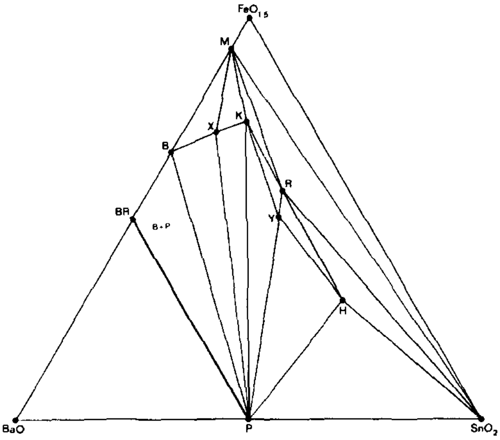

FIG. 1. Idealized composition diagram of the system BaO–SnO_2–Fe_2O_3 at 1200°C in air. The symbols used are explained in Table I. The thickened line P–BR indicates the solid solution $Ba(Sn,Fe)O_3$. N.B. Fe_2O_3 is considered as $FeO_{1.5}$.

tion mixture has the ideal composition, but this area has not been thoroughly investigated. Compositions on a line in the composition diagram contain two compounds, namely, the ones that are connected by this line.

We now discuss the compounds found and their occurrence in this system.

Fe_2O_3(F) and SnO_2(S): no sign was found for the occurrence of a solid solution area of these two compounds. As can be seen from Fig. 1, Fe_2O_3 only occurs in the triangle Fe_2O_3–$BaFe_{12}O_{19}$–SnO_2.

$BaFe_{12}O_{19}$(M): this compound occurs in a considerable area (Fig. 1). Striking changes were found in the intensities of some X-ray reflections on increasing Sn content. The 0 0 8 reflection decreased in intensity while it increased for the 1 0 6 reflection. The cell parameters slightly increase with increasing Sn content. The changes are probably due to incorporation of Sn^{4+} in $BaFe_{12}O_{19}$, as was reported for Ti^{4+} (*2*).

$BaFe_2O_4$(B): in accordance with the results of Meriani (*4*), only the low temperature form of $BaFe_2O_4$ was found, for the samples were air cooled from 1200°C. In this compound too changes in the intensities of X-ray reflections were found on increasing Sn content. These changes were not studied in detail.

$Ba_2Fe_2O_5$(BR): this compound has not been found outside its ideal composition. The brown color of the compound suggests that no formation of Fe^{4+} took place at 1200°C, in accordance with the results of Lucchini *et al.* (*5*).

$BaSnO_3$(P): compositions in the pseudobinary system $BaSnO_3$–$Ba_2Fe_2O_5$ yielded one phase only, due to the already mentioned oxidation of Fe^{3+} to Fe^{4+}. The Fe^{4+} ions are incorporated in the perovskite structure, thus forming a solid solution of $BaFeO_3$ and $BaSnO_3$. The X-ray diffraction pattern of $Ba(Sn,Fe)O_3$ is slightly different from that of pure $BaSnO_3$. The 1 0 0 reflection has increased in intensity and all reflections are slightly broadened.

$BaSn_2Fe_4O_{11}$(R): this hexagonal compound is isostructural with $BaTi_2Fe_4O_{11}$ (*6*). The X-ray powder diffraction pattern is given in Table II; absent reflections are *h h l* with $l = 2n + 1$. No indication for a phase width was found. The structure of this compound has been determined using neutron powder diffraction (Cadée, to be published).

$Ba_{.69}Sn_{2.62}Fe_{1.38}O_8$(H): this monoclinic compound was reported to be isostructural with the hollandite structure (*3*). The X-ray diffraction pattern (Table III) has been indexed for the space group $I2/m$. The reason for using this space group instead of $C2/m$ is that it demonstrates the link with the tetragonal hollandite and simplifies the indexing. The reflections $3\ 0\ \bar{1}$, $3\ 0\ 1$, $1\ 0\ \bar{3}$ and $1\ 0\ 3$ are characteristic for this compound and have been used to determine its presence in the reaction mixtures. The composition of this hollandite can be written as $Ba_xSn_{4-2x}Fe_{2x}O_8$ (*3*). This formula suggests a phase width, but the variation has been found to be small, $x = 0.69 \pm 0.01$. No tripling of the short axis of this compound

TABLE II

LIST OF OBSERVED AND CALCULATED *d*-VALUES OF $BaSn_2Fe_4O_{11}$(R)

h k l	*d*(calc.)	*d*(obs.)	*I*
0 0 2	6.930	6.94	<1
1 0 0	5.195	5.19	3
1 0 1	4.862	4.86	9
1 0 2	4.149	4.15	4
0 0 4	3.451	3.449	16
1 0 3	3.441		
1 1 0	2.992	2.993	44
1 0 4	2.870	2.871	100
1 1 2	2.744	2.744	68
2 0 0	2.589	2.591	17
2 0 1	2.545	2.548	5
1 0 5	2.434	2.425	41
2 0 2	2.424		
1 1 4	2.258	2.256	30
2 0 3	2.255		
1 0 6	2.099	2.100	7
2 0 4	2.069	2.068	1
2 1 0	1.956	1.955	<1
2 1 1	1.936	1.936	1
2 0 5	1.886	1.886	1
2 1 2	1.881		
1 0 7	1.839	1.839	2
1 1 6	1.820	1.820	3
2 1 3	1.799	1.798	1
3 0 0	1.724	1.717	85
0 0 8	1.722		
2 0 6	1.717		
2 1 4	1.700	1.700	49
3 0 2	1.673	1.673	16
2 1 5	1.594	1.594	2
2 0 7	1.566	1.565	1
3 0 4	1.541	1.542	1
2 2 0	1.493	1.494	43
1 0 9	1.467	1.467	1
3 1 0	1.434	1.433	8
2 0 8	1.433		
3 1 2	1.404	1.404	<1
2 1 7	1.386	1.386	1
3 0 6	1.378	1.378	1
0 0 10	1.377		
2 2 4	1.369	1.469	1
3 1 3	1.369		
1 0 10	1.330	1.330	4
3 1 4	1.324	1.324	17
2 0 9	1.316	1.316	3
4 0 0	1.293	1.292	2
2 1 8	1.291		
4 0 2	1.270	1.270	4
1 1 10	1.250	1.250	11
4 0 3	1.244	1.244	2

was found in the X-ray diffraction pattern, in accordance with the results reported for $Ba_{.7}Sn_{2.6}Cr_{1.4}O_8$ (*7*).

$Ba_3SnFe_{10}O_{20}$(X): the unit cell parameters of this monoclinic compound (a = 15.359 Å, b = 11.875 Å, c = 5.227 Å, β = 91.14°) show a striking resemblance with the ones of $Ba_3TiAl_{10}O_{20}$, a = 14.854 Å, b = 11.356 Å, c = 4.986 Å, β = 90.00° (*8*), and of $Pb_3GeAl_{10}O_{20}$, a = 14.39 Å, b = 11.44 Å, c = 5.004 Å, β = 90.00° (*9*). This resemblance and the noteworthy overall formulas suggest the compounds to be isostructural. Using the atomic parameters of $Pb_3 GeAl_{10}O_{20}$ (*9*) as starting parameters an attempt was made to refine the neutron powder diffraction pattern of $Ba_3SnFe_{10}O_{20}$ which was recorded at 873 K in order to avoid magnetic reflections. $Ba_3SnFe_{10}O_{20}$ is antiferromagnetic, TN = 710 K. This refinement was only successful if the *z*-parameters reported by Vinek *et al.* (*9*) were taken as negative. The same was found for the refinement of the X-ray diffraction data of a single crystal of $Pb_3GeGa_{10}O_{20}$ (Cadée and Verschoor, to be published). For the indexing of the X-ray powder diffraction pattern (Table IV) a body-centered space lattice was used to demonstrate the similarity with $Pb_3 GeAl_{10}O_{20}$ and $Ba_3TiAl_{10}O_{20}$. By heating $Ba_3SnFe_{10}O_{20}$ for 2 months at 1200°C it was possible to grow very small crystals, but these crystals were too thin for X-ray single crystal diffraction. The compositions studied yielded not any indication for a phase width of $Ba_3SnFe_{10}O_{20}$.

$BaSn_{.90}Fe_{5.47}O_{11}$(K): this hexagonal compound has unit cell parameters that are almost identical to those of $BaSn_2Fe_4O_{11}$(R). Consequently it is not easy to distinguish the X-ray diffraction patterns of the two compounds. The pattern of $BaSn_{.90}Fe_{5.47}O_{11}$ shows no systematically absent reflections, unlike that of $BaSn_2Fe_4O_{11}$. Moreover, the reflections 1 1 3, 2 0 3, 3 0 3/2 1 5, and 2 0 7 of $BaSn_{.90}Fe_{5.47}O_{11}$ have a considerable intensity, whereas the pattern of $BaSn_2Fe_4O_{11}$ shows only weak intensities at the same diffraction angles. The X-ray powder diffraction of $BaSn_{.90}Fe_{5.47}O_{11}$ is given in Table V. The unit cell of $BaSn_{.90}Fe_{5.47}O_{11}$ contains two formula units, like $BaTi_2Fe_4O_{11}$ (*6*). The composition given here appeared to consist of one phase after heating at 1200°C during 1 week. A slight alteration of the composition resulted in more than one

TABLE III

LIST OF OBSERVED AND CALCULATED *d*-VALUES OF $Ba_{.69}Sn_{2.62}Fe_{1.38}O_8$

h k l	*d*(calc.)	*d*(obs.)	*I*	*h k l*	*d*(calc.)	*d*(obs.)	*I*
1 0 $\bar{1}$	7.376	7.36	5	1 1 $\bar{4}$	1.940	1.939	10
1 0 1	7.221	7.21	4	1 1 4	1.928	1.928	19
2 0 0	5.266	5.26	6	4 0 $\bar{4}$	1.845	1.845	4
0 0 2	5.062	5.06	14	4 0 4	1.806	1.806	5
2 0 $\bar{2}$	3.689	3.690	13	5 0 $\bar{3}$	1.805		
2 0 2	3.612	3.614	14	3 0 $\bar{5}$	1.771	1.770	10
3 0 $\bar{1}$	3.339	3.344	38	5 0 3	1.771		
3 0 1	3.296	3.299	72	6 0 0	1.756	1.755	26
1 0 $\bar{3}$	3.234	3.238	71	3 0 5	1.739	1.739	1
1 0 3	3.195	3.195	29	3 1 $\bar{4}$	1.728	1.729	1
1 1 0	2.996	2.989	3	4 1 3	1.717	1.717	1
0 1 1	2.986			0 1 5	1.700	1.700	2
4 0 0	2.634	2.637	20	0 0 6	1.688	1.688	17
2 1 $\bar{1}$	2.605	2.606	100	6 0 $\bar{2}$	1.670	1.671	2
2 1 1	2.591	2.589		5 1 $\bar{2}$	1.661	1.660	9
1 1 $\bar{2}$	2.585			5 1 2	1.643	1.643	21
1 1 2	2.572	2.573		2 1 $\bar{5}$	1.626	1.626	18
0 0 4	2.531	2.533	7	2 0 6	1.597	1.597	2
3 0 $\bar{3}$	2.460	2.462	12	0 2 0	1.563	1.563	12
3 0 3	2.408	2.411	7	1 2 $\bar{1}$	1.529	1.529	5
4 0 $\bar{2}$	2.357	2.359	9	6 1 $\bar{1}$	1.518	1.518	4
3 1 0	2.335	2.336	10	2 2 0	1.498	1.498	5
4 0 2	2.317	2.317	8	7 0 $\bar{1}$	1.493	1.493	4
2 0 $\bar{4}$	2.301	2.302	17	0 2 2	1.493		
0 1 3	2.293	2.295		7 0 1	1.484	1.484	2
2 0 4	2.263	2.265	7	1 1 6	1.467	1.467	1
3 1 $\bar{2}$	2.131	2.131	3	5 1 $\bar{4}$	1.450	1.450	20
2 1 3	2.092	2.092	2				
5 0 $\bar{1}$	2.072	2.071	4				
1 0 $\bar{5}$	1.997	1.996	1				
4 1 $\bar{1}$	1.981	1.981	17				
1 0 5	1.981						
4 1 1	1.969	1.969	12				

TABLE IV

LIST OF OBSERVED AND CALCULATED *d*-VALUES OF $Ba_3SnFe_{10}O_{20}$ (X)

h k l	*d*(calc.)	*d*(obs.)	*I*	*h k l*	*d*(calc.)	*d*(obs.)	*I*
1 1 0	9.416	9.41	5	7 1 0	2.158	2.154	28
2 0 0	7.692	7.67	1	3 5 0	2.155		
0 2 0	5.945	5.94	8	1 3 2	2.155		
0 1 1	4.788	4.79	9	2 5 $\bar{1}$	2.087	2.085	6
3 1 0	4.706	4.70	2	2 5 1	2.078	2.076	
2 2 0	4.702			4 2 $\bar{2}$	2.048	2.047	19
4 0 0	3.842	3.819	6	4 0 $\bar{1}$	2.038		
1 3 0	3.836			3 3 $\bar{2}$	2.019	2.013	18
1 2 $\bar{1}$	3.818			4 2 2	2.014		
3 0 $\bar{1}$	3.697	3.697	2	7 0 1	2.009		
3 0 1	3.624	3.622	3	3 3 2	1.995	1.994	5
4 2 0	3.227	3.225	61	5 1 $\bar{2}$	1.983	1.978	12
0 3 1	3.157	3.154	100	0 6 0	1.980		
3 2 $\bar{1}$	3.139	3.136		6 3 1	1.977		
3 3 0	3.133			0 4 2	1.962	1.960	3
3 2 1	3.093	3.091	46	5 1 2	1.945	1.943	5
4 1 $\bar{1}$	3.023	3.021	27	6 4 0	1.939		
5 1 0	2.975	2.970	43	7 2 $\bar{1}$	1.928	1.927	2
0 4 0	2.971			8 0 0	1.920	1.919	11
4 1 1	2.970			7 3 0	1.920		
2 3 $\bar{1}$	2.933	2.932	26	2 6 0	1.917		
2 3 1	2.908	2.907	17	7 2 1	1.903	1.903	5
5 0 $\bar{1}$	2.673	2.673	2	4 5 $\bar{1}$	1.891	1.890	6
0 0 2	2.614	2.615	44	4 5 1	1.878	1.877	1
6 0 0	2.561	2.543	36	6 0 $\bar{2}$	1.848	1.848	3
1 4 $\bar{1}$	2.551			6 0 2	1.811	1.811	7
1 4 1	2.543			8 1 $\bar{1}$	1.793	1.793	1
1 1 $\bar{2}$	2.527			5 3 $\bar{2}$	1.793		
1 1 2	2.511	2.509	2	4 6 0	1.760	1.760	10
2 0 2	2.460	2.460	1	4 4 $\bar{2}$	1.758		
4 3 $\bar{1}$	2.453			1 5 2	1.744	1.743	19
5 2 $\bar{1}$	2.437	2.437	1	3 6 1	1.737	1.737	
5 3 0	2.428	2.424	3	4 4 2	1.737		
4 3 1	2.425			1 0 $\bar{3}$	1.735		
0 2 2	2.393	2.394	4	6 2 2	1.732		
4 4 0	2.350	2.348	5	3 5 $\bar{2}$	1.670	1.670	31
1 5 0	2.348			1 2 $\bar{3}$	1.666	1.644	
3 4 1	2.297	2.296	12	7 4 1	1.664		
2 2 $\bar{2}$	2.296			3 0 $\bar{3}$	1.660		
4 0 $\bar{2}$	2.181	2.180	4	6 5 1	1.659		
				1 2 3	1.659		

phase in the reaction product, e.g., the composition $BaSn_{.875}Fe_{5.50}O_{11}$ contained $Ba_3SnFe_{10}O_{20}$ in the reaction product. No evidence was found for a solid solution of R and K.

It was assumed that the unit cell of $BaSn_{.90}Fe_{5.47}O_{11}$ contains 22 O-atoms and 2 Ba-atoms, which results in two formula units pro unit cell. They form a close packed stacking of four O_4 and two BaO_3

TABLE V

LIST OF CALCULATED AND OBSERVED *d*-VALUES OF $BaSn_{.9}Fe_{5.47}O_{11}$ (K)

h k l	*d*(calc.)	*d*(obs.)	*I*
0 0 1	14.242	14.3	1
0 0 2	7.136	7.14	1
1 0 0	5.124	5.12	3
1 0 1	4.823	4.83	8
1 0 2	4.163	4.16	2
0 0 4	3.570	3.572	6
1 0 3	3.488	3.489	10
1 1 0	2.960	2.960	65
1 0 4	2.930	2.932	100
1 1 1	2.898	2.901	15
0 0 5	2.857	2.858	6
1 1 2	2.734	2.736	9
2 0 0	2.563	2.564	9
1 1 3	2.514	2.516	68
1 0 5	2.495	2.497	4
2 0 2	2.413	2.414	19
0 0 6	2.381	2.381	<1
1 1 4	2.279	2.279	1
2 0 3	2.257	2.258	30
1 0 6	2.159	2.159	2
2 0 4	2.083	2.084	10
1 1 5	2.056	2.054	<1
0 0 7	2.041	2.040	1
2 1 0	1.938	1.937	<1
2 1 1	1.920	1.920	1
2 0 5	1.908	1.908	21
1 0 7	1.896	1.896	4
2 1 2	1.870	1.870	1
1 1 6	1.855	1.855	1
2 1 3	1.795	1.795	5
0 0 8	1.786	1.786	3
2 0 6	1.745	1.745	2
3 0 0	1.709	1.709	3
2 1 4	1.703	1.704	58
3 0 1	1.697		
1 0 8	1.686	1.686	9
3 0 2	1.662	1.662	2
3 0 3	1.609	1.609	14
2 1 5	1.604	1.604	
2 0 7	1.597	1.597	29
3 0 4	1.542	1.542	<1
1 1 8	1.529	1.529	3
1 0 9	1.516	1.516	2
2 1 6	1.503	1.503	2
2 2 0	1.480	1.481	35
3 0 5	1.467	1.467	33
2 0 8	1.465		
3 1 1	1.415	1.415	<1
2 2 3	1.414		
2 1 7	1.405	1.405	3
1 1 9	1.399	1.399	2
3 1 2	1.395		
1 0 10	1.376	1.377	<1
2 2 4	1.368	1.368	2
3 1 3	1.363	1.363	1
2 0 9	1.350	1.350	1
3 1 4	1.321	1.321	16
2 2 5	1.314	1.314	9
2 1 8	1.313		

layers, comparable to $BaTi_2Fe_4O_{11}$ (*6*). Searching for the best composition the Sn–Fe ratio was varied, while the Ba–O ratio remained the same. Because of the dark red color of well-powdered reaction products, Fe was assumed to remain in the trivalent state. The importance of heating the reaction mixtures for at least 1 week at 1200°C was demonstrated with the composition $BaSnFe_4O_9$. After heating at 1200°C for 1 day, a complete X-ray diffraction pattern of $BaSn_{.90}Fe_{5.47}O_{11}$ was found, with a few impurities. After heating the reaction product for a week, also $BaSnO_3$ and a compound denoted by Y (see below) could be detected in the X-ray diffraction pattern. This indicates that the Ba–Sn ratio in compound K is greater than 1, which was supported by several other experiments.

The exact composition of this compound

may slightly differ from the empirical one given here. the correct composition can only be determined from single crystals. So far, however, attempts to grow single crystals remained unsuccessful. Meanwhile the structure of this compound has been determined by interpretation of the neutron powder diffraction pattern (Cadée, to be published).

$BaSn_{1.70}Fe_{2.75}O_{8.52}$ (Y): the exact composition of this compound could not be determined. The composition given here yielded the reaction product with the least contaminants, the heating time was 3 weeks, contaminants are $BaSnO_3$ and $BaSn_2Fe_4O_{11}$ (R).

The diffraction pattern given in Table VI was observed in the diffraction pattern of the composition $BaSn_{1.5}Fe_{2.0}O_7$, after a heating time of 3 weeks. The main contaminant was $BaSnO_3$, only a trace of $BaSn_2Fe_4O_{11}$ was present. The composition $BaSn_{1.5}Fe_{2.0}O_7$ was chosen for observing the diffraction pattern of the compound

TABLE VI

LIST OF OBSERVED AND CALCULATED *d*-VALUES OF THE COMPOUND Y ($BaSn_{1.70}Fe_{2.75}O_{8.52}$)[a]

h k l	*d*(calc.)	*d*(obs.)	*I*	*h k l*	*d*(calc.)	*d*(obs.)	*I*
0 0 4	8.116	8.12	<1	1 0 16	1.897	1.897	2
1 0 0	5.143	5.11	3	2 1 4	1.896		
1 0 1	5.080	5.08		2 0 12	1.871	1.871	<1
1 0 2	4.905	4.90	3	1 1 14	1.836	1.835	1
1 0 3	4.649	4.65	<1	2 1 6	1.835		
1 0 4	4.350	4.34	<1	0 0 18	1.813	1.813	3
1 0 5	4.039	4.04	2	1 0 17	1.799	1.798	10
1 0 7	3.454	3.456	3	2 0 13	1.799		
0 0 10	3.260	3.260	8	2 1 7	1.799		
1 0 8	3.196	3.195	3	2 1 8	1.759	1.759	1
1 1 0	2.975	2.974	100	2 0 14	1.730	1.729	1
1 1 4	2.795	2.796	22	3 0 0	1.719	1.718	28
1 0 10	2.756	2.757	8	2 1 9	1.717		
1 1 6	2.610	2.610	13	3 0 1	1.717		
1 0 11	2.570	2.571	11	1 1 16	1.683	1.682	2
2 0 1	2.569			3 0 4	1.683		
2 0 2	2.546	2.547	<1	2 0 15	1.663	1.663	8
2 0 3	2.508	2.507	1	3 0 5	1.663		
2 0 4	2.458	2.456	1	3 0 6	1.640	1.640	3
2 0 5	2.397	2.398	18	2 0 16	1.600	1.601	3
0 0 14	2.330	2.330	8	2 1 12	1.585	1.585	2
2 0 6	2.229			3 0 8	1.585		
1 0 13	2.257	2.256	6	1 0 20	1.556	1.556	6
2 0 7	2.256			3 0 9	1.554		
2 0 8	2.179	2.179	3	1 1 18	1.549	1.549	
1 0 14	2.124	2.121	<1	2 0 17	1.541	1.540	
2 0 9	2.101	2.101	2	2 1 13	1.540		
1 1 12	2.008	2.009	10	2 2 0	1.489	1.489	21
1 0 15	2.005	2.005		1 0 21	1.489		
2 0 11	1.946	1.945	4	3 0 11	1.488		
2 1 1	1.946						

[a] This diagram was observed in the diffraction pattern of the composition $BaSn_{1.5}Fe_{2.0}O_7$, that contained Y, $BaSnO_3$ (P) as main contaminant, and a trace of $BaSn_2Fe_4O_{11}$(R).

denoted by Y, because the simple diffraction pattern of $BaSnO_3$ can easily be recognized.

The diffraction patterns of R, K, and Y are very similar, because their *a*-axes are nearly equal and they all have hexagonal symmetry. The compound denoted by Y can be traced by its reflections 0 0 10, 1 0 8, 1 1 4, 1 1 6 and 2 0 6, which have a considerable intensity whereas the patterns of the two other compounds show no reflections at the same diffraction angle. It should be noted that the reflections 0 0 10 and 1 0 8 practically coincide with the 1 0 $\bar{3}$ and 1 0 3 reflections of the phase $Ba_{.69}Sn_{2.62}Fe_{1.38}O_8$ (H).

According to the unit cell parameters, the compound denoted by Y can be considered as a close packed structure of Ba and O atoms. This implies a stacking sequence of 14 layers in the direction of the *c*-axis, resulting in a mean distance between the layers of 2.335 Å. This distance is 2.312 Å in $BaFe_{12}O_{19}$, 2.291 Å in $BaSn_2Fe_4O_{11}$, and 2.3765 Å in $BaSnO_3$. The position of Y in the composition diagram (Fig. 1) suggests the possibility that this compound is an intergrowth of $BaSnO_3$ and $BaSn_2Fe_4O_{11}$. Electron microscopy experiments showed some stacking faults in the compound Y, that can be interpreted into $BaSnO_3$ intergrowths (to be published). The electron diffraction pattern showed systematic absent reflections for $h\ h\ l$ with $l = 2n + 1$. The X-ray diffraction pattern can be explained with this diffraction condition. Observed $h\ h\ l$ reflections with $l = 2n + 1$ are overlapped by other reflections.

The reaction rate in this part of the composition diagram is sluggish; several compositions contained four compounds even after a heating time of 2 months, thus hampering a determination of the exact composition of compound Y. Moreover, $BaSnO_3$, $BaSn_2Fe_4O_{11}$, and compound Y are found to occur simultaneously in the reaction mixtures of a considerable number of compositions, in contradiction with the results obtained from the other compositions. This also hindered the determination of the exact composition of compound Y.

Discussion

In the studied part of the BaO–SnO_2–Fe_2O_3 system five quaternary compounds could be detected. From the BaO–TiO_2–Al_2O_3 system, the only comparable system studied in detail, only three quaternary compounds were reported (*8*). From two compounds, the hollandite phase (*3*) and the compound $Ba_3TiAl_{10}O_{20}$, isomorphs have been found in the present studied system. No isomorph was found of the third compound, $BaTiAl_6O_{12}$, although the compound $BaSn_{.90}Fe_{5.47}O_{11}$ has a comparable composition. The X-ray powder diffraction pattern of $BaTiAl_6O_{12}$, prepared by heating the reaction mixture for 3 weeks at 1250°C, shows no similarity with the pattern of $BaSn_{.90}Fe_{5.47}O_{11}$. Besides, the reported indexing of the diffraction pattern of $BaTiAl_6O_{12}$ was found to be doubtful.

The hollandite phase has been found in many other ternary systems too (*3*). Besides the reported occurrence of the R- and X-phase their occurrence has been found in many other ternary systems too (Cadée, to be published). The triangulation shown in Fig. 1 is only questionable in the area around compound Y. There is no triangle for the three compounds P, Y, and R, although a considerable number of compositions contained these three compounds in their reaction mixture. The present triangulation was chosen because it better fitted the results obtained from the other compositions. All triangles shown in Fig. 1 are supported by at least one composition in the triangle with the three compounds at the angular points detected in the reaction mixture. The simultaneous occurrence of compounds P, Y, and R in the reaction mixture may be caused by not reaching equilibrium. The area wherein P, Y, and R are found simultaneously is bounded to the two areas where four compounds are found in the reaction mixtures, which also means that equilibrium was not reached. It might be interesting to investigate comparable systems and to extend the investigations to other temperatures.

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