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Letter

Structural characterization of $Sm_{1-x}Ca_xFeO_{3-y}$ ($0 \leq x \leq 0.50$)

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Abstract

Samples of $Sm_{1-x}Ca_xFeO_{3-y}$ were synthesized in air by solid state reaction. The X-ray diffraction analysis on these samples shows that they are the one-phase perovskite-type compounds belonging to the *Pbnm* space group. The lattice parameters of $Sm_{1-x}Ca_xFeO_{3-y}$ are calculated by Cohen's least-squares method and the variation of the lattice parameters with increasing x is presented.

1. Introduction

The rare earth orthoferrites of chemical formula $RFeO_3$ were investigated intensively. Their crystallographic characteristics [1–3] and some properties [4–6] are fairly well known. In our work, the trivalent rare earths in $RFeO_3$ were partially substituted by the divalent metals with ionic radii near those of the rare earths, with the purpose to study the structures and properties of these new materials. In $La_{1-x}Ba_xFeO_{3-y}$, an orthorhombic phase and a cubic phase were observed, and the iron in the cubic phase was found to have an intermediate valence state between the trivalence and the tetravalence [7, 8]. $La_{1-x}Ca_xFeO_{3-y}$ prepared in normal pressure pure oxygen decreases linearly in the lattice constants of its orthorhombic perovskite-type structure with increasing x, and the isomer shift of the ^{57}Fe Mössbauer effect decreases gradually with increasing x, indicating a dynamic electronic structure of Fe in the compounds [9, 10]. In this work, the $Sm_{1-x}Ca_xFeO_{3-y}$ compounds were synthesized and characterized by X-ray powder diffraction.

2. Experimental procedure

Samples of $Sm_{1-x}Ca_xFeO_{3-y}$ employed in this study were synthesized in air for x ranging from 0 to 0.50 by solid state reaction. Dry Sm_2O_3, $CaCO_3$ and Fe_2O_3 of 99.5% purity or better were well mixed in the atom ratios of Sm:Ca:Fe$=(1-x)$:x:1 by grinding and preheated in air at 900 °C for 40 h. The mixtures were pressed into pellets and heated in air at 1300 °C for 72 h, followed by slow cooling at a rate of 60 °C h^{-1} down to 700 °C. The samples were tempered in air at 700 °C for a week and cooled slowly at a rate of 60 °C h^{-1} down to room temperature. The brown ceramics were pulverized for the X-ray powder diffraction.

The X-ray powder diffraction measurements were performed on a Rigaku D/max-rB diffractometer using Cu Kα radiation (50 kV, 100 mA), a receiving slit of 0.3 mm and a graphite monochromator for the diffracted beam. The positions of the observed diffraction peaks were obtained by a fitting process with the computer. The wave length of 1.54050 Å was used in all the calculations.

3. Results and discussion

The measured X-ray powder diffraction data on $Sm_{1-x}Ca_xFeO_{3-y}$ are listed in Table 1. Our diffraction result of the compound with $x=0$ is very similar to an early crystallographic study on $SmFeO_3$ [1]. All observed diffraction peaks of the $Sm_{1-x}Ca_xFeO_{3-y}$ samples were easily indexed on the basis of the orthorhombic unit cell consisting of four perovskite-like monoclinic pseudocells [1–3, 11]. As Ca substitutes for Sm from $x=0$ to $x=0.50$, some weak diffraction peaks became weaker and even disappeared. However, the intensity ratios of the main diffraction peaks changed minimally, and no additional peaks were observed, indicating that the samples synthesized are the one-phase perovskite-type compounds. All the compounds show the same systematic absences of the diffractions of the planes ($h0l$) with ($h+l$) odd and ($0kl$) with k odd, suggesting that the $Sm_{1-x}Ca_xFeO_{3-y}$ compounds with x between 0 and 0.50 belong to the same *Pbnm* space group as $RFeO_3$ [1, 12]. The interplanar distances d of the corresponding planes decrease as x increases from 0 to 0.20. The d-spacings increase a little as x increases from 0.20 to 0.30. The d values decrease again as x increases from 0.30 to 0.50.

The accurate lattice constants of the $Sm_{1-x}Ca_xFeO_{3-y}$ compounds were calculated from the observed diffraction peaks by a program based on the Cohen analytical least-squares method. The lattice constants and the perovskite-like pseudo-cell dimensions of $Sm_{1-x}Ca_xFeO_{3-y}$ are listed in Table 2. The calculated

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TABLE 1. Powder diffraction data for $Sm_{1-x}Ca_xFeO_{3-y}$

$x=$	0			0.10			0.20			0.30			0.40			0.50			hkl
hkl	d_{obs} (Å)	d_{cal} (Å)	I/I_0	d_{obs} (Å)	d_{cal} (Å)	I/I_0	d_{obs} (Å)	d_{cal} (Å)	I/I_0	d_{obs} (Å)	d_{cal} (Å)	I/I_0	d_{obs} (Å)	d_{cal} (Å)	I/I_0	d_{obs} (Å)	d_{cal} (Å)	I/I_0	
110	3.887	3.885	21	3.883	3.882	15	3.867	3.872	16	3.887	3.875	13	3.870	3.874	14	3.863	3.863	13	110
002	3.853	3.851	12	3.851	3.849	8	3.847	3.845	9	3.856	3.850	6	3.844	3.843	7	3.841	3.839	6	002
111	3.469	3.469	19	3.469	3.466	14	3.458	3.459	15	3.468	3.461	13	3.463	3.460	12	3.455	3.451	9	111
020	2.798	2.798	31	2.789	2.795	20	2.783	2.786	20	2.789	2.784	8	2.781	2.782	14	2.776	2.771	12	020
112	2.735	2.735	100	2.734	2.733	100	2.728	2.728	100	2.734	2.731	100	2.730	2.728	100	2.720	2.723	100	112
200	2.698	2.699	23	2.701	2.697	26	2.696	2.693	32	2.707	2.698	37	2.702	2.699	20	2.693	2.695	27	200
021	2.628	2.630	9	2.623	2.627	9	2.617	2.619	10	2.624	2.618	9	2.619	2.616	8	2.597	2.606	5	021
103	2.318	2.319	5	2.317	2.317	4	2.313	2.314	4	2.318	2.318	4	2.317	2.314	4	2.312	2.312	3	103
211		2.318^{a}			2.317^{a}			2.312^{a}			2.316^{a}			2.315^{a}			2.311^{a}		211
022	2.263	2.264	8	2.257	2.261	8	2.254	2.256	8	2.258	2.256	8	2.255	2.254	6	2.249	2.247	5	022
202	2.209	2.210	17	2.211	2.209	10	2.208	2.206	11	2.212	2.210	11	2.210	2.209	11	2.207	2.205	8	202
113	2.142	2.142	6	2.142	2.141	5	2.137	2.137	5	2.141	2.140	5	2.139	2.137	4	2.130	2.133	4	113
122	2.088	2.088	2	2.079	2.085	1	2.078	2.081	2	2.079	2.081	1							122
220	1.943	1.943	23	1.939	1.941	20	1.936	1.936	22	1.939	1.938	21	1.936	1.937	24	1.931	1.932	21	220
004	1.925	1.926	22	1.925	1.924	14	1.922	1.922	15	1.926	1.925	14	1.889	1.921	7	1.918	1.919	12	004
023	1.894	1.892	5	1.891	1.890	4	1.887	1.886	4	1.889	1.887	3	1.886	1.885	2				023
221	1.884	1.884	11	1.883	1.882	8	1.878	1.878	9	1.882	1.879	8	1.880	1.878	9	1.872	1.873	6	221
213	1.765	1.765	1																213
114	1.719	1.725	18	1.714	1.724	12	1.710	1.722	10	1.713	1.724	11	1.710	1.721	8	1.702	1.719	5	114
131		1.719^{a}			1.717^{a}			1.712^{a}			1.711^{a}			1.710^{a}			1.704^{a}		131
311	1.673	1.672	3	1.671	1.671	2	1.670	1.668	2	1.672	1.671	3	1.668	1.671	3	1.663	1.668	2	311
132	1.603	1.603	9	1.5988	1.6014	8	1.5958	1.5971	8	1.5988	1.5971	7	1.5948	1.5957	6	1.5857	1.5903	7	132
024	1.5868	1.5864	6	1.5843	1.5850	8	1.5818	1.5823	9	1.5838	1.5834	10	1.5828	1.5810	10	1.5774	1.5778	13	024
204	1.5661	1.5676	28	1.5657	1.5666	24	1.5632	1.5646	22	1.5661	1.5670	24	1.5642	1.5652	25	1.5710	1.5633	17	204
312		1.5651^{a}			1.5641^{a}			1.5614^{a}			1.5640^{a}			1.5638^{a}			1.5611^{a}		312
223	1.5489	1.5491	4	1.5452	1.5479	3	1.5428	1.5449	2	1.5489	1.5464	4	1.5452	1.5452	2	1.5359	1.5418	2	223
133	1.4539	1.4535	7	1.4495	1.4520	5	1.4471	1.4486	3	1.4503	1.4489	5	1.4467	1.4474	4	1.4395	1.4430	3	133
115	1.4312	1.4321	1	1.4312	1.4311	1													115
313	1.4238	1.4249	1																313
040	1.3981	1.3991	1	1.3941	1.3973	1													040
041	1.3767	1.3766	3																041
224	1.3682	1.3676	10	1.3665	1.3665	9	1.3623	1.3642	5	1.3658	1.3656	9	1.3634	1.3642	8	1.3595	1.3615	7	224
025	1.3500	1.3496	4	1.3496	1.3485	3	1.3459	1.3464	2	1.3499	1.3476	4	1.3496	1.3455	5	1.3473	1.3430	2	025
400		1.3494^{a}			1.3487^{a}			1.3463^{a}			1.3490^{a}			1.3494^{a}			1.3473^{a}		400
411	1.2922	1.2932	1																411
330		1.2950^{a}																	330
142	1.2772	1.2776	4	1.2757	1.2762	4	1.2728	1.2726	2	1.2757	1.2723	3	1.2748	1.2712	3	1.2696	1.2666	2	142
331		1.2771^{a}			1.2760^{a}			1.2730^{a}			1.2739^{a}			1.2736^{a}			1.2700^{a}		331
402		1.2735^{a}			1.2728^{a}			1.2707^{a}			1.2731^{a}			1.2732^{a}			1.2712^{a}		402
043	1.2266	1.2285	8	1.2258	1.2272	4	1.2205	1.2239	4	1.2247	1.2237	5	1.2208	1.2225	6	1.2208	1.2183	4	043
332		1.2275^{a}			1.2264^{a}			1.2237^{a}			1.2246^{a}			1.2241^{a}			1.2209^{a}		332
241		1.2263^{a}			1.2249^{a}			1.2215^{a}			1.2215^{a}			1.2208^{a}			1.2165^{a}		241
116	1.2195	1.2190	10	1.2184	1.2182	6	1.2166	1.2167	4	1.2189	1.2183	7	1.2174	1.2162	7	1.2140	1.2147	5	116
420	1.2161	1.2155	8	1.2148	1.2146	2	1.2132	1.2122	2										420
225	1.2074	1.2071	3																225
234	1.2003	1.2001	2	1.1990	1.1991	2													234
421		1.2006^{a}			1.1998^{a}														421
143		1.1979^{a}			1.1966^{a}														143
135	1.1601	1.1601	6	1.1586	1.1586	4	1.1567	1.1569	1										135
206		1.1593^{a}			1.1583^{a}			1.1572^{a}											206
422		1.1591^{a}			1.1583^{a}			1.1561^{a}											422
333	1.1567	1.1563	5	1.1552	1.1553	4	1.1545	1.1529	2	1.1549	1.1538	3	1.1552	1.1532	3	1.1507	1.1504	2	333
315	1.1430	1.1454	1																315
243	1.1188	1.1181	3	1.1159	1.1170	2	1.1139	1.1142	1	1.1155	1.1145	3	1.1120	1.1136	3	1.1070	1.1100	2	243
404	1.1052	1.1051	4	1.1046	1.1045	2	1.1034	1.1028	1	1.1054	1.1047	2							404
423	1.0989	1.0986	3																423
151	1.0851	1.0850	4	1.0805	1.0837	2	1.0786	1.0805	2	1.0797	1.0799	2							151
250	1.0360	1.0339	6	1.0357	1.0327	1													250
045		1.0357^{a}			1.0347^{a}														045
136		1.0378^{a}			1.0370^{a}														136
316	1.0278	1.0273	7	1.0272	1.0266	5	1.0250	1.0253	3	1.0268	1.0268	5	1.0259	1.0256	6	1.0246	1.0242	4	316
424		1.0278^{a}			1.0271^{a}			1.0254^{a}			1.0269^{a}			1.0264^{a}			1.0246^{a}		424
027	1.0253	1.0241	4																027
512	1.0221	1.0220	5																512

The intensity with the background subtracted is relative to the strongest peak.

[a] This calculated diffraction peak overlaps the peak above.

TABLE 2. Crystallographic constants of $Sm_{1-x}Ca_xFeO_{3-y}$

x	Unit cell constants			Unit cell vol. (Å^3)	Density (g/cm^3)	Pseudo-cell parameters		
	a (Å)	b (Å)	c (Å)			a' (Å)	b' (Å)	β (°)
0	5.397(6)	5.596(3)	7.702(9)	232.68	7.26	3.887(6)	3.851(4)	92.07
0.10	5.394(6)	5.589(3)	7.697(9)	232.11	6.94	3.884(0)	3.848(9)	92.03
0.20	5.385(3)	5.572(0)	7.689(8)	230.75	6.64	3.874(6)	3.844(9)	91.95
0.30	5.395(9)	5.568(6)	7.700(0)	231.37	6.28	3.877(0)	3.850(0)	91.80
0.40	5.397(5)	5.564(4)	7.685(8)	230.82	5.95	3.876(0)	3.842(9)	91.74
0.50	5.389(0)	5.541(3)	7.677(5)	229.27	5.65	3.964(4)	3.838(7)	91.60

interplanar distances are listed with the measured data in Table 1.

The variation of the lattice constants a, b and c of $Sm_{1-x}Ca_xFeO_{3-y}$ is shown in Fig. 1. The parameters $a'(=c')$ and b' of the monoclinic pseudo-cell $vs.$ x are plotted in Fig. 2. The unit cell volumes and the X-ray densities are shown in Fig. 3. a maintains minimal change except two minima at $x=0.20$ and 0.50, whereas b decreases almost linearly, as x increases from 0 to 0.50. c and the pseudo-cell parameters a' and b' and the unit cell volume V decrease as x increases from 0 to 0.20. c, a', b' and V increase a little with x increasing from 0.20 to 0.30. c, a', b' and V decrease again as x increases from 0.30 to 0.50. The β angle between the a' and c' axes in the pseudo-cell decreases linearly from 92.07° to 91.60° with x increasing from 0 to 0.50 (Fig. 2), implying the tendency of an increasing symmetry of $Sm_{1-x}Ca_xFeO_{3-y}$ with an increasing substitution of Ca for Sm. The linear decrease in the X-ray density with increasing x may give rise to the disappearance of some weak diffraction peaks.

The substitution of divalent Ca for trivalent Sm in $Sm_{1-x}Ca_xFeO_{3-y}$ may result in either variation of electronic structure of Fe or oxygen deficiency in the lattice. The electronic structure of Fe may affect the ionic radius of Fe and further the lattice dimension [8, 9]. However, the $Sm_{1-x}Ca_xFeO_{3-y}$ compounds were synthesized in air, and all the samples were brown, which may indicate the existence of only trivalent iron in the compounds. Thus, the variation of the lattice constants and the unit cell volume of $Sm_{1-x}Ca_xFeO_{3-y}$ may depend mainly on the increasing oxygen deficiency caused by the increasing substitution of divalent Ca for trivalent Sm and on the distribution of the oxygen defects in the lattice.

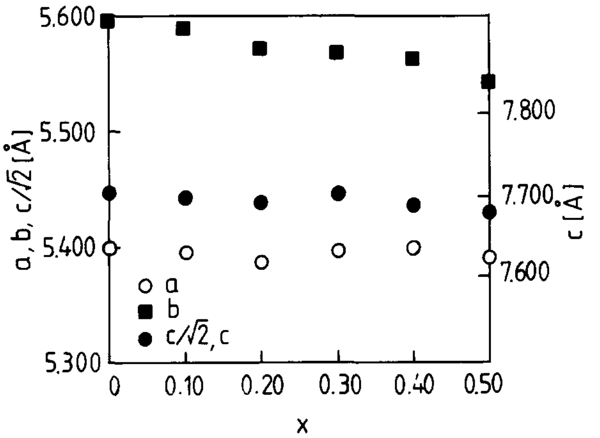

Fig. 1. Lattice constants a, b and c and $c/\sqrt{2}$ of $Sm_{1-x}Ca_xFeO_{3-y}$ $vs.$ x.

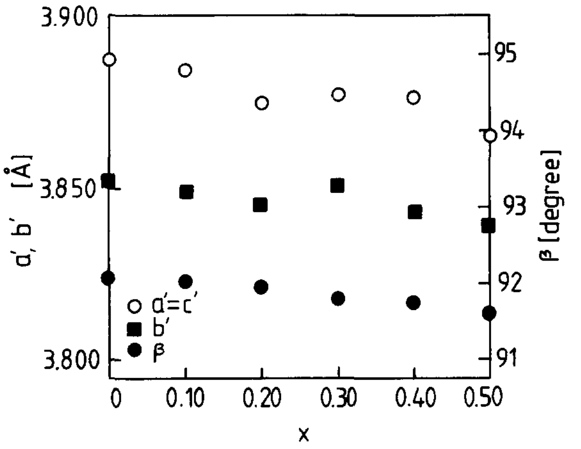

Fig. 2. Pseudo-cell parameters a' $(=c')$, b' and β of $Sm_{1-x}Ca_xFeO_{3-y}$ $vs.$ x.

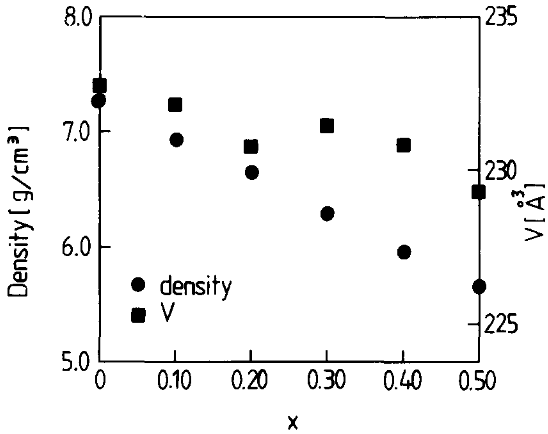

Fig. 3. Unit cell volume and X-ray density of $Sm_{1-x}Ca_xFeO_{3-y}$ $vs.$ x.

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