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X-Ray Scattering Analysis of Complex Manganites $Bi_2Me\ Mn_4O_{10}$ (Me- Ca, Ba, Sr)

M.M. Mataev, N.O. Myrzahmetova, D.Z.H. Nuketaeva, N.A. Zhumanova, Z.H.K. Kuanysheva, M.A. Nurbekova and M.R. Abdraimova

Kazakh State Women`s Pedagogical University, Alma-Ata, Kazakhstan

Abstract: Complex oxide phases of compositions $Bi_2CaMn_4O_{10}$, $Bi_2SrMn_4O_{10}$ and $Bi_2BaMn_4O_{10}$ were synthesized by high temperature solid state reaction. The structure of the manganites, types of the crystal lattices, parameters of the unit cells, radiographic and pycnometric densities were identified by X-ray scattering for a first time: $Bi_2CaMn_4O_{10}$ – a=5,68, c=23,2 Å, $V_{un.cell}$= 748,2 Å^3, Z=2, ρ_{rad} = 4,52, ρ_{picn} =4,55 g/cm^3, $Bi_2SrMn_4O_{10}$ – a=7,56, b=8,56, c=5,72 Å, $V_{un.cell.}$= 370,2 Å^3, Z=2, ρ_{rad} = 7,93, ρ_{picn} =7,98 г/см^3, $Bi_2BaMn_4O_{10}$ – a=5,68, c=23,5 Å, $V_{un.cell}$= 757,8 Å^3, Z=4, ρ_{rad} = 7,16, ρ_{picn} =7,20 g/cm^3. Relationship between the crystalline lattice parameters of the manganites with electron configuration Mn^{3+} ion has been identified as well as electrophysical properties of manganites at room temperature.

Key words: Manganites · X-ray scattering analysis · Crystal lattice · Density

INTRODUCTION

Semiconductor materials which functionality is stipulated by electron charge are used in modern electronics. Increasing requirements to electronic devices expose the problem of search and implementation of alternative materials, working on non-classical principles. Spintronics devices using both electron charge and its spin can become a basis of future electronics [1].

Perovskite-like manganites are attractive as catalysts, cathodes of fuel elements and sensors of magnetic field. An unusual combination of properties in these compounds occurs at heterovalent doping, which results in stabilization of manganese cations in the mixed charge state and a significant change in the properties and first of all, the parameters of electron transport. The substitution of calcium by triply charged cations R^{3+} results in 1-2 times increase of $Ca_{1-x}R_xMnO_3$ conductivity and relatively high negative thermoEMF. The ratio of the manganese charge forms was affected by disproportionation processes enhanced with temperature increase [1-7].

In addition, the heat in the process of synthesis and subsequent heat treatment, inevitably results in a partial loss of oxygen, free vacancies in the oxygen sublattice and increase of manganese ion concentration with low charge [8]. Thus, oxygen vacancies play an important role in the charge balance and the formation of the complex properties of manganites. In the work [9], the magnetic and electrical properties of the anion-deficient compositions $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ (LSM) have been studied. It was found that a transition from rhombohedral (space group $R\bar{3}c$ Z = 2) to the orbital-ordered O'-orthorhombic (space group *Puma,* Z=4) structure occurs in the concentration range $0.075 \le \delta \le 0.1$ which is rather strange because the free oxygen vacancies must break the symmetry in the arrangement of d-orbitals of the manganese ions and suppress the orbital order. It is important that the regions of oxygen homogeneity in manganites are significantly narrow and often the authors describe only the synthesis conditions or measurements of the actual oxygen content in the samples, what complicates the analysis of the dependence of the properties on defect degree [10]. This study is to investigate the obtaining conditions and X-ray features of the new classes of complex mixed bismuth manganites where Bi^{+3} is substituted by bivalent ions.

Corresponding Author: Dr. Myrzahmetova, Kazakh State Women`s Pedagogical University, Aiteke bi 99, Alma-Ata, 050000 Kazakhstan.

MATERIALS AND METHODS

New polycrystalline complex bismuth manganites were synthesized by ceramic technology. Bismuth oxide (III) (mark "chemically pure"), sodium carbonate, strontium carbonate and barium carbonate (mark "high-pure") and manganese oxide (III) (mark "chemically pure") were used as the initial components. Solid-phase synthesis was carried using the thermal data of the initial components taking into account Tamman conditions for ceramic reactions [11, 12]. Stoichiometrically calculated mixtures of initial components preliminary annealed in a muffle furnace at 400°C for one hour, were thoroughly stirred and the calculated mixture of the starting components are thoroughly mixed and grinded in an agate mortar, placed in an alundum crucibles and annealed in a silite furnace. Annealing was performed by two stages: first stage at 600°C for 48 h and second stage at 800°C for 20 h [13, 14].

Table 1: Indexing of radiographs of synthesized phases

I/I_0	d_{exp}, Å	$10^4/d^2_{exp}$	hkl	$10^4/d^2_{theor}$
$Bi_2CaMn_4O_{10}$				
46	5,808	296,5	004	297,5
13	5,077	387,9	102	383,9
8	4,552	483,4	103	476,8
10	4,037	614,4	110	619,0
15	3,869	668,0	006	669,0
16	3,790	696,2	112	693,0
31	3,553	792,3	113	786,0
33	3,187	985,8	106	978,0
100	3,050	1075	115	1083
25	2,888	1190	008	1190
13	2,839	1241	200	1238
16	2,753	1319	202	1312
46	2,667	1406	203	1405
23	2,575	1508	009	1506
21	2,420	1708	213	1715
20	2,356	1802	118	1809
20	2,292	1904	206	1907
51	2,233	2006	215	2012
21	2,034	2421	208	2428
38	1,937	2669	001	2678
25	1,8991	2771	224	2773
16	1,846	2934	225	2940
33	1,795	3104	310	3096
11	1,755	3243	305	3250
11	1,712	3385	314	3393
26	1,703	3447	306	3455
30	1,675	3566	315	3560
$Bi_2SrMn_4O_{10}$				
28	4,004	623,8	002	632,0
15	3,718	723,4	110	723,0
18	3,371	880,0	111	881,0
21	3,186	985,2	102	943,0
35	3,118	1029	012	1026
100	2,812	1265	200	1280
48	2,722	1350	112	1355
25	2,643	1432	201	1438
8	2,490	1613	020	1612
10	2,429	1695	210	1685
8	2,327	1827	013	1825
25	2,292	1904	202	1912
15	2,222	2085	121	2090
11	2,134	2146	113	2145
11	2,080	2311	212	2315
30	1,989	2528	004	2528
$Bi_2BaMn_4O_{10}$				
46	5,869	290,3	004	290,0
26	3,782	699,1	112	692,0
20	3,625	760,9	105	762,5
16	3,576	781,9	113	782,0
46	3,302	917,0	114	909,0
93	3,062	1066	115	1072
100	2,940	1157	008	1160
63	2,853	1228	200	1238
23	2,754	1318	202	1311
30	2,565	1520	204	1528
33	2,429	1695	205	1691
30	2,411	1719	213	1711
20	2,338	1829	214	1838
26	2,296	1897	206	1891
50	2,233	2006	215	1998
26	2,128	2210	216	2201
20	2,045	2390	208	2398
26	1,961	2600	0012	2610
40	1,943	2648	223	2639
30	1,898	2775	224	2766
30	1,851	2920	225	2929
50	1,798	3093	310	3095
20	1,721	3375	314	3385
26	1,680	3543	0014	3552
16	1,635	3740	316	3748
56	1,583	3990	317	3983
26	1,561	4105	322	4097

Formation of new phases was controlled by X-ray scattering analysis performed using the radiologic diffractometer X'Pert MPD PRO (PANalytical). Analysis conditions included: CuK_α - radiation, Ni - filter, U=30 kV, I=10 mA, rotation rate - 1000 pulses/s and time constant τ=5 s, 2θ= 10° - 90°. Diffraction peaks were evaluated using hundred-point scale. Radiographs of the synthesized polycrystalline powders were indexed by the homology method (homologue is distorted structure type of perovskite). Pycnometric density of manganites was determined by the method described in [15]. Toluene served as indifferent liquid. The density of each manganite was measured 4 - 5 times and the data were averaged. Table 1 shows the results of indexing of radiographs of manganites.

Table 2: Crystalochemical characteristics of manganites

Compound	Type of symmetry	a, Å	b, Å	c, Å	$V_{unit.cell}$, Å^3	Z	ρ_{rad} ---------- g/sm^3 --------	ρ_{picn}
$Bi_2CaMn_4O_{10}$	Tetragonal	5,68		23,2	748,2	2	4,52	4,55
$Bi_2BaMn_4O_{10}$	Tetragonal	5,68		23,5	757,8	4	7,16	7,20
$Bi_2SrMn_4O_{10}$	Rhomboidal	7,56	8,56	5,72	370,2	2	7,93	7,98

Indexing of radiographs of synthesized phases has showed that barium and calcium manganites crystallize in the tetragonal system and strontium manganite in the orthorhombic lattice.

Accuracy of data for indexing of manganites are confirmed by the significant correlation of the experimental and calculated inverse values of the interplanar spacing squares ($10^4/d^2$) and significant correlation between radiographic and pycnometric densities.

CONCLUSIONS

Configuration $3d^4$ electrons of Mn^{3+} ion in octahedral symmetrical field of O^{2-} are $d\varepsilon^3$ и d_a^1 states i.e. they characterize by $d_{x^2.y^2}$ or d_{z^2} functions. If $d_{x^2-y^2}$ state are free then a cation is strongly shielded along *Z*-axis that will results in Coulomb interaction with ligands along *X*- and *Y*- axes. This results in extension of MnO_6 octahedron along *Z*-axis and correlation of *c* ε *a* parameters.

If $d_{x^2.y^2}$ state are occupied then MnO_6 octahedron reduces along *C*-axis and dependence of *c* ε *a* states behaves similarly to strontium phase.

Study of electrophysical characteristics of 15kg/sm^2 manganite tablets compacted at a pressure and room temperature has showed the following results of dielectric permittivity (ε) and resistance (R): $Bi_2CaMn_4O_{10}$ ε=165,9; R=69 kOhm and $Bi_2SrMn_4O_{10}$ ε=78,5; R=3,4 Mohm. Probably, the high values of ε can be explained by the influence of Bi^{+3} ions on the local polarization of Mn^{3+} ions. As a result, they have a high refraction index and high electrical stability in optical environment.

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