X-Ray Scattering Analysis of Complex Manganites

\( \text{Bi}_2\text{Me Mn}_4\text{O}_{10} \) (Me- Ca, Ba, Sr)


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Abstract: Complex oxide phases of compositions \( \text{Bi}_2\text{CaMn}_4\text{O}_{10} \), \( \text{Bi}_2\text{SrMn}_4\text{O}_{10} \) and \( \text{Bi}_2\text{BaMn}_4\text{O}_{10} \) 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: \( \text{Bi}_2\text{CaMn}_4\text{O}_{10} \) – \( a=5.68, c=23.2 \, \text{Å} \), \( V=748.2 \, \text{Å}^3 \), \( Z=2 \), \( \rho_{\text{rad}}=4.52, \rho_{\text{picn}}=4.55 \, \text{g/cm}^3 \), \( \text{Bi}_2\text{SrMn}_4\text{O}_{10} \) – \( a=7.56, b=8.56, c=5.72 \, \text{Å} \), \( V=370.2 \, \text{Å}^3 \), \( Z=2 \), \( \rho_{\text{rad}}=7.93, \rho_{\text{picn}}=7.98 \, \text{g/cm}^3 \), \( \text{Bi}_2\text{BaMn}_4\text{O}_{10} \) – \( a=5.68, c=23.5 \, \text{Å} \), \( V=757.8 \, \text{Å}^3 \), \( Z=4 \), \( \rho_{\text{rad}}=7.16, \rho_{\text{picn}}=7.20 \, \text{g/cm}^3 \). Relationship between the crystalline lattice parameters of the manganites with electron configuration \( \text{Mn}^{3+} \) 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 \( \text{R}^{3+} \) results in 1-2 times increase of \( \text{Ca}_{1-x}\text{R}_x\text{MnO}_3 \) 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 \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_4 \) (LSM) have been studied. It was found that a transition from rhombohedral (space group 16R, \( Z=2 \)) to the orbital-ordered O'-orthorhombic (space group Puma, \( Z=4 \)) structure occurs in the concentration range 0.075 \( \leq \delta \leq 0.1 \) 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 \( \text{Bi}^{3+} \) is substituted by bivalent ions.
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

<table>
<thead>
<tr>
<th>d_002 Å</th>
<th>d_exp Å</th>
<th>10°d_exp</th>
<th>hkl</th>
<th>10°d_exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi,CaMnO_2</td>
<td>5,808</td>
<td>296,5</td>
<td>004</td>
<td>297,5</td>
</tr>
<tr>
<td>8</td>
<td>4,552</td>
<td>295,9</td>
<td>006</td>
<td>297,9</td>
</tr>
<tr>
<td>10</td>
<td>4,037</td>
<td>295,2</td>
<td>100</td>
<td>298,2</td>
</tr>
<tr>
<td>12</td>
<td>3,725</td>
<td>295,0</td>
<td>010</td>
<td>296,0</td>
</tr>
<tr>
<td>16</td>
<td>3,461</td>
<td>294,8</td>
<td>112</td>
<td>296,8</td>
</tr>
<tr>
<td>20</td>
<td>2,946</td>
<td>294,0</td>
<td>200</td>
<td>296,0</td>
</tr>
<tr>
<td>25</td>
<td>2,429</td>
<td>293,8</td>
<td>102</td>
<td>295,8</td>
</tr>
<tr>
<td>30</td>
<td>2,038</td>
<td>293,3</td>
<td>012</td>
<td>295,3</td>
</tr>
<tr>
<td>Bi,SrMnO_2</td>
<td>4,004</td>
<td>623,8</td>
<td>002</td>
<td>632,0</td>
</tr>
<tr>
<td>15</td>
<td>3,718</td>
<td>723,4</td>
<td>110</td>
<td>732,4</td>
</tr>
<tr>
<td>18</td>
<td>3,371</td>
<td>880,0</td>
<td>111</td>
<td>887,0</td>
</tr>
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<td>21</td>
<td>3,186</td>
<td>985,2</td>
<td>102</td>
<td>994,3</td>
</tr>
</tbody>
</table>

Formation of new phases was controlled by X-ray scattering analysis performed using the radiologic diffractometer X’Pert MPD PRO (PANalytical). Analysis conditions included: CuKα - 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.
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 ($10^4d^2$) and significant correlation between radiographic and pycnometric densities.

**CONCLUSIONS**

Configuration 3$d^4$ electrons of Mn$^{3+}$ ion in octahedral symmetrical field of O$^2-$ are $d^g \mu d^h$ states i.e. they characterize by $d_{x^2}$ or $d_{y^2}$ 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 $c \geq a$ parameters.

If $d_{x^2}$ state are occupied then MnO$_6$ octahedron reduces along C-axis and dependence of $c \geq a$ states behaves similarly to strontium phase.

Study of electrophysical characteristics of 15kg/sm$^3$ manganite tablets compacted at a pressure and room temperature has showed the following results of dielectric permittivity (ε) and resistance (R): Bi$_2$CaMnO$_{10}$ $\varepsilon=165,9$; R=69 kOhm and Bi$_2$SrMnO$_{10}$ $\varepsilon=78,5$; R=3,4 Mohm. Probably, the high values of $\varepsilon$ 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.

**REFERENCES**

