Structural and Electrochemical Characterization of Columnar-Structured Mn-Doped Bi$_{26}$Mo$_{10}$O$_{69-d}$ Electrolytes

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Abstract—The present work is devoted to the investigation of two series of doped bismuth molybdates: Bi$_{26-2x}$Mo$_{10}$O$_{69-2d}$ and Bi$_{32}$Mo$_{10-2x}$Mn$_{2}$O$_{69-2d}$. Complex oxides were synthesized by conventional solid state technology and by co-precipitation method. The products were identified by powder diffraction. The powders and ceramic samples were examined by means of densimetry, laser diffraction, and electron microscopic methods. Porosity of the ceramic materials was estimated using the hydrostatic method. The electrical conductivity measurements were carried out using impedance spectroscopy method.

Keywords—Bismuth molybdate, columnar structures, impedance spectroscopy, oxygen ionic conductors.

INTRODUCTION

The Bi$_2$O$_3$-based complex oxides are rather interesting objects for fundamental and practical scientific research. They show ion-conductive, catalytic, ferroelectric, magnetic properties [1], [2] and different structural types, such as fluoride-related structures, pillar or layered Aurivillius phases or one-dimensional phases [1]-[4]. The last one includes columnar type compounds, such as Bi$_2$Mo$_6$O$_{19-4d}$-based solid solutions. The parent compound is a mono-dimensional oxide conductor built of covalent [Bi$_2$O$_4$]$_x$ columns extending along the [010] direction and separated by a highly disordered metal-oxygen polyhedra and isolated Bi ions [4], [5].

Bi$_{26}$Mo$_{10}$O$_{69-4d}$ (Bi$_{13}$Mo$_{12}$O$_{34.5}$) was first described by Buittery et al. [4] as a part of Bi-rich part of Bi-Mo-O system with Bi:Mo ratios ranging from 2.6 to 2.8. Vannier et al. [5] identified a Bi$_{23}$Mo$_6$O$_{19-4d}$ type in the Bi$_2$O$_3$-Mo$_2$O$_3$ system in a small solid solution range (2.57 ≤ Bi/Mo ≤ 2.77). More recently, [6] showed a number of room temperature stable bismuth molybdates with the Bi:Mo ratio 2.67 to 3.4 (i.e. 57.1% to 63.6% Bi$_2$O$_3$), which decay to the Bi$_{26}$Mo$_{10}$O$_{69-4d}$-type columnar structure at temperatures above ca. 920 K.

Bi$_{26}$Mo$_{10}$O$_{69-4d}$ crystallizes above 580-585 K in monoclinic symmetry; triclinic symmetry is observed below 585 K. The structure of the monoclinic form was described in [5] with the following unit cell parameters: \(a = 11.74\), \(b = 5.80\), \(c = 24.79\) Å, \(\beta = 102.84^\circ\) with \(P2/c\) space-group symmetry. The monoclinic model includes columns, Bi ions and MoO$_4$ tetrahedra, giving the total quantity of oxygen positions equal to 68 per one unit cell. The structure of the triclinic form with additional oxygen position was suggested in [7]. It includes MoO$_4$ polyhedra and Mo$_2$O$_3$-MoO$_4$ chains.

Bi$_{26}$Mo$_{10}$O$_{69-4d}$-based solid solutions can be obtained by substitution of Mo or Bi sites that leads to the formulae: Bi$_{26-2x}$Me$_x$Mo$_{10-2x}$Me$_{2x}$O$_{69-2d}$ (Me, Me" – substituting ions). They show fast oxygen ionic conduction and photocatalytic properties. The substitution of Bi$_{26}$Mo$_{10}$O$_{69-4d}$ may be carried out by doping of Bi-O sublattice or Mo-O sublattice or by double substitution. The Bi$_{26}$Mo$_{10-2y}$Me$_{2y}$O$_{69-4d}$ (Bi$_{13+y}$Mo$_{12}$Me$_{y}$O$_{34.5y}$) solid solutions were synthesized with 4 or 6 coordinated dopants [5] such as Me"= Li, Mg, Al, Si, Ge [8]; V, P, W [9]. The compounds with formulae Bi$_{26-2x}$Me$_x$Mo$_{10}$O$_{69-4d}$ (Bi$_{13+y}$Me$_{y}$Mo$_{12}$O$_{34.5y}$) were described for 8-coordinated dopants [5], such as Pb [10]; Ln [11]; Ca, Sr, Ba [9]. Double substituted Bi$_{26}$Mo$_{10}$O$_{69}$ was described for (Ca, Sr)$_2$Bi$_2$Mo$_6$(Cr, W)$_2$O$_{68}$ by [12]. In all described cases the substitution of isolated Bi ion occurred. The substitution in [Bi$_2$O$_4$]$_x$ sublattice was revealed only for the Te dopant [13], [14]. It can be observed only for high Te concentration and causes formation of additional [Bi$_{12-x}$Te$_x$O$_{34.5}$]$_x$ columns.

Changes in electrical conductivity and catalytic properties, both positive and negative, result from these substitutions. The present work is devoted to synthesis, investigation and comparison of new Mn-substituted Bi$_{26}$Mo$_{10}$O$_{69-4d}$-Manganese can show different oxidation state and coordination number and any of the two described types of substitution (Bi$_{26-2x}$Mn$_x$Mo$_{10}$O$_{69-4d}$ or Bi$_{32}$Mo$_{10-2y}$Mn$_y$O$_{69-4d}$).

II.EXPERIMENTAL

Polycrystalline samples of the compositions Bi$_{26-2x}$Mn$_x$Mo$_{10}$O$_{69-4d}$ and Bi$_{32}$Mo$_{10-2y}$Mn$_y$O$_{69-4d}$ (0 ≤ x, y ≤ 1) were synthesized by conventional solid state methods from the precursor oxides. Stoichiometric amounts of dried powders of Bi$_2$O$_3$ (99.9%), MoO$_3$ (99.5%), MnO (99.7%) were weighed and thoroughly grounded in an agate mortar with the ethanol as a homogenizer. The dried mixture was pelletized at 20 bar using a uniaxial press yielding pellets of 20 mm in diameter. The pellets were placed on an alumina plate on the “powder
bed” and heated at 823 K for 48 h, then quenched in water to room temperature. The samples were then regrinded in ethanol, dried, pelletized again and reheated to 1123 K for 24 h, followed by slow cooling in air to room temperature over a period of approximately 12 h.

The dopant concentration ranges of Bi26.25Mn12.5Mo10.0O69.4 and Bi25Mo10.25Mn12.5O69.4 solid solutions and crystal forms were determined by XRPD. X-ray powder diffraction data were obtained on a Bruker Advance D8 diffractometer with a VANTEC1 detector, Ni filtered Cu Kα radiation ($\lambda_1 = 1.54056$ Å and $\lambda_2 = 1.54439$ Å). Data were collected in flat plate $\theta$$\theta$ geometry and calibrated against external Si standards.

The grain size of the powders was estimated by a nanoparticle size analyzer (Shimadzu SALD-7101). The morphology of the obtained powders and their chemical composition were studied using a JEOL JSM 6390LA with EDX-analyzer JED 2300. Chemical analysis of the samples was realized by atomic emission and atomic absorption spectroscopy analysis of dissolved powders of bismuth molybdates on an iCAP 6500 Duo and Solaar M6 (Thermo Scientific) by both standard addition and calibration curve methods.

Hydrostatic weighting was used for investigation of the density of ceramic pellets coated with a moisture-resistant coating. The volume (geometric) porosity of ceramic samples was obtained by comparison of experimental and theoretical (X-ray) density values of the samples.

For the impedance measurements the synthesised samples were pelletized at 20 bar yielding pellets of 10 mm in diameter and ca. 2.5 mm thick. The pressed pellets were then heated to 1123 K for 24 h, and then slowly cooled in air to room temperature. Pt electrodes were applied by decomposition of NH4PbCl4 dispersion at ca. 673 K. The impedance measurements were carried out in the range of 523-1123 K on Elins Z-3000 impedance spectrometer over the frequency range of 3 MHz to 10 Hz. For the analysis of the impedance plots the equivalent electrical circuits method was used (Zview software, Version 2.6b, Scribner Associates, Inc.).

III. RESULTS AND DISCUSSION

A Crystal Structure

The XPRD measurements showed formation of the single-phase Bi26.25Mn12.5Mo10.0O69.4 and Bi25Mo10.25Mn12.5O69.4 complex oxides up to $x=0.8$ and $y=0.2$. SEM measurement confirmed these homogeneity ranges. The high dopant content ($x=0.40$ and $y=0.2$) leads to stabilization of the monoclinic form of Bi26.25Mn12.5Mo10.0O69.4. The unit cell parameters of Bi26.25Mn12.5Mo10.0O69.4 show a good correlation with the Vegard's law (Table I, Fig. 1).

| TABLE I |
|-----------------|-----------------|-----------------|
| CELL PARAMETERS OF Mn-DOPED Bi25Mo10.0O69.6 (PRESENT WORK) AND SOME Bi25Mo10.0O69.6-BASED SOLID SOLUTIONS [5] | | |
| Composition | $a=0.002$, $b=0.001$, $c=0.005$, $\alpha=0.02$, $\beta=0.02$, $\gamma=0.02$, $V$ ($\AA^3$) |
| Bi25Mn12.5Mo10.0O69.4 | 11.774 | 5.801 | 24.744 | 89.8 | 102.63 | 89.88 | 1649.10 |
| Bi25Mn12.5Mo10.0O69.4 | 11.734 | 5.800 | 24.734 | 89.8 | 102.19 | 89.92 | 1645.40 |
| Bi25Mn12.5Mo10.0O69.4 | 11.728 | 5.793 | 24.693 | 90.0 | 102.17 | 89.85 | 1639.90 |
| Bi25Mn12.5Mo10.0O69.4 | 11.703 | 5.787 | 24.680 | 90.0 | 102.17 | 90.00 | 1633.90 |
| Bi25Mn12.5Mo10.0O69.4 | 11.693 | 5.780 | 24.672 | 90.0 | 102.17 | 90.00 | 1630.00 |
| Bi25Mn12.5Mo10.0O69.4 | 11.681 | 5.775 | 24.652 | 90.0 | 102.18 | 90.00 | 1625.50 |
| Bi25Mn12.5Mo10.0O69.4 | 11.669 | 5.769 | 24.638 | 90.0 | 102.24 | 90.00 | 1620.89 |
| Bi25Mn12.5Mo10.0O69.4 | 11.654 | 5.763 | 24.615 | 90.0 | 102.27 | 90.00 | 1615.43 |
| Bi25Mn12.5Mo10.0O69.4 | 11.749 | 5.800 | 24.789 | 89.9 | 102.68 | 89.92 | 1648.00 |
| Bi25Mn12.5Mo10.0O69.4 | 11.735 | 5.801 | 24.793 | 90.0 | 102.77 | 90.00 | 1645.75 |
| Bi25Mo10.0O69.6 [5] | 11.771 | 5.801 | 24.772 | 89.96 | 102.91 | 89.93 | 1648.76 |
| Bi17.5Mo10.0O69.6 [5] | 11.741 | 5.801 | 24.782 | 90.00 | 102.81 | 90.00 | 1645.90 |

As a result, we observe the formation of single phase powder samples by using either of the two substitution ways. It can be explained from two points of view:

(1) Mixed oxidation state of Mn in complex oxide provides different types of coordination (4 and 8);

(2) Only doping of Bi-O sublattice occurs, the existence of the Bi25Mo10.02Mn12.5O69.4 ($y=0.2$) is a result of forming the Bi25(Mo10.02Bi1.5)O69.2-based solid solutions [5].

We believe that here only substitution of Bi atoms occurs. This hypothesis is corroborated by the ranges of Bi25Mo10.02O69.4 solid solution e.g. $y=0.2$ composition results in Bi25Mn12.5Mo10.02O69.4 composition that corresponds to the ratio (Bi+Mn)/Mo=2.67. Both mentioned ratios are in the solid solution range described by [5] (2.57 ≤ Bi/Mo ≤ 2.77). The compositions mentioned ($y=0.1$ and $y=0.2$) also show unit cell parameters similar to that of the Bi/Mo=2.6 solid solutions (Table I, [5]). The same phenomenon was observed for Mg-doping, when solid solutions ranges was determined up to $x=0.4$ [15] and $y=0.25$ [8] and Co (to $x$, $y=0.21$ [16]). It should be noted that in spite of the difference of ionic radii of Bi, Mo and any dopant element the compression of the unit cell is observed. The Rietveld analysis is not effective for the occupancy calculation due to proximity of Bi and Mn mass attenuation coefficient for CuKα radiation. Thus we can say that x-doping leads to substitution of Bi, but the way of substitution of y-doping is not obvious, therefore in the present...
In this paper we consider mostly the x-doped compositions.

The concentrations of the manganese obtained from EDX measurements were found to be similar to the corresponding theoretical values. The variations in manganese content from one grain to another may be attributed to normally higher error of EDX analysis for low concentration of the elements. The concentration of Bi and Mo couldn't be determined correctly because of overlapping of their spectral lines.

The results of chemical analysis realized by AAS and AES-ICP methods are shown in Table II. The concentrations of all dopants confirm the theoretical formulae within the experimental errors. The method of calibration curves was determined to be not suitable for Mn determination because of large Bi concentration in the solution. The standard addition methods compensated Bi and can be recommended for chemical analysis of such materials.

Hydrostatic weighting study showed high density of the sintered pellets, experimental density reaches values more than 97% of theoretical (X-ray) density (Table III).

![Fig. 1 The Unit cell parameters visualization for the Bi\textsubscript{26-x}Mn\textsubscript{x}Mo\textsubscript{10}O\textsubscript{48-6} compositions](image)

![Fig. 2 SEM images for Bi\textsubscript{26-x}Mn\textsubscript{x}Mo\textsubscript{10}O\textsubscript{48-6}: (a) x=0.2, powder, secondary electrons imaging, scale 1:1000; (b) x=0.6, ceramic pellet surface, backscattering electrons imaging, scale 1:2500; (c) x=0.6, ceramic pellet cross-section, backscattering electrons imaging, scale 1:1700](image)
C. Electrical Conductivity

The impedance spectroscopy was used for investigation of electro-conductive properties of the ceramic samples of Mn-substituted Bi$_{25.3}$Mn$_{0.7}$O$_{60.4}$. For the analysis of impedance plots the equivalent electrical circuits method was used (Zview software, Version 2.6b, Scribner Associates, Inc.). Figs. 3 (a) and (b) show examples of complex plane plots of Bi$_{25.3}$Mn$_{0.7}$O$_{60.4}$ at different temperatures. In general, this shape of complex plane plots is typical for all studied compositions. Equivalent electrical circuits were obtained by using a complex nonlinear least square. For every temperature it gave the good agreement of calculated and experimental impedance curves (Figs. 3 (a) and (b)). It can be seen that the shape of the complex plane plots appears to be different in different temperature regions. In general, two types of complex plane plots can be described, at relatively high temperatures and at relatively low temperatures. High temperature spectra were characterized by depressed unsymmetrical semi-circle (Fig. 3 (a)). The total resistivity of the sample corresponds to the high frequency intercept of it. The depressed semi-circle can be described by two linked parallel R-CPE connections (R is resistor; CPE is constant phase element). The CPE capacity parameters are about 10$^{-2}$ - 10$^{8}$ F, therefore R-CPE parallel connections correspond to electrochemical processes at the electrodes [17] (they are named as R el1, CPE el1 and R el2, CPE el2 at equivalent electrical circuits at Fig. 3 (a)).

![Impedance plots](image)

**Fig. 3 Impedance plots and equivalent electrical circuits of x=0.3 compound: (a) high temperature region; (b) low temperature region**

Low temperature spectra are characterized by a slightly depressed symmetrical (model I) or unsymmetrical (model II) semi-circle in the high and medium frequency part, which represents the total resistivity of the sample, associated to straight lines at low frequencies. These straight lines generally describe the complicated ionic transport and processes at the electrodes interface (Fig. 3 (b)). The symmetry of high-frequency semi-circle shows the strong dependence from dopant concentration (Fig. 4). For compounds with low Mn-content only one semi-circle is observed, but for the samples with larger Mn concentration the semi-circle becomes unsymmetrical and can be described by two semi-circles (Fig. 4). Therefore, two equivalent models were suggested (I and II in Fig. 3 (b)). Model I describes the total resistivity of Bi$_{26.2}$Mn$_{0.8}$O$_{60.4}$ with low Mn content (x<0.5), while model II describes combination of the bulk and grain boundary resistivity of Mn-rich complex oxides (0.5<x<0.8) (Fig. 3 (b)). The corresponding CPE capacity values in R-CPE connections are about 10$^{-11}$ F for “CPE bulk” and 10$^{-10}$ F for “CPE grain boundary”, which are typical capacity values for polycrystalline samples [17]. Possible explanations of this phenomenon are 1) the presence of the second phase thin layer is not detected at room temperature (e.g. triclinic Bi$_{25}$Mo$_{10}$O$_{60}$ can cover grains of monoclinic Bi$_{25}$Mo$_{10}$O$_{60}$). 2) the preferred orientation of the grains (it can be indirectly confirmed by specific profile function at X-Ray diffractograms).

![Complex plane plots](image)

**Fig. 4 High and medium frequency parts of the complex plane plots of Bi$_{26.2}$Mn$_{0.8}$O$_{60.4}$ with T=673K. Evolution of the spectra shape vs. Mn concentration is shown**

According to the results of the impedance measurements the temperature and concentration curves of electrical
conductivity of $\text{Bi}_{26.2\pm3}\text{Mn}_{25.26}\text{Mo}_{10}\text{O}_{9.4}$ ceramic samples were plotted. The characteristic Arrhenius plots (log (σ)–1000/T) have linear shape and activation energy values (0.5–0.95 eV) which is typical for oxygen-ion conductors. Figs. 5 (a) and (b) show characteristic temperature, dopant concentration and conductivity relationship of the Mn-substituted $\text{Bi}_{25}\text{Mn}_{6}\text{Mo}_{10}\text{O}_{9.4}$. Two significant drops of the electrical conductivity associated with monoclinic-triclinic phase transition are observed only for the parent compound Fig. 5 (a). The temperature of the phase transition of triclinic $\text{Bi}_{26.2\pm3}\text{Mn}_{25.26}\text{Mo}_{10}\text{O}_{9.4}$ is below the range of measurement temperature thus only conductive properties of monoclinic form are observed. The activation energy of Mn-substituted $\text{Bi}_{25}\text{Mn}_{6}\text{Mo}_{10}\text{O}_{9.4}$ increases with $x$ from 0.5 to 0.80 eV. The concentration plots of the total electrical conductivity of $\text{Bi}_{26.2\pm3}\text{Mn}_{25.26}\text{Mo}_{10}\text{O}_{9.4}$ represent a parabolic dependence (Fig. 5 (b)). The highest conductivity in the series at all temperatures is detected for the $\text{Bi}_{25.4}\text{Mn}_{6.6}\text{Mo}_{10}\text{O}_{9.4}$ compound: $\sigma_{293K} = 2.8*10^{-3} \text{S cm}^{-1}$ at 973 K and $\sigma_{623K} = 1.3*10^{-3} \text{S cm}^{-1}$ at 673 K.

IV. CONCLUSION

As a result of the present work the formation of single-phase $\text{Bi}_{26.2\pm3}\text{Mn}_{25.26}\text{Mo}_{10}\text{O}_{9.4}$ and $\text{Bi}_{25}\text{Mn}_{10.25}\text{Mn}_{25.26}\text{Mn}_{10.25}$ complex oxides up to $x=0.8$ and $y=0.2$ was shown. Dense and massive ceramics samples with low porosity ($\leq$3%) were obtained. The electrical conductivity measurements were carried out using impedance spectroscopy and showed high ionic conductivity at $\text{Bi}_{26.2\pm3}\text{Mn}_{25.26}\text{Mo}_{10}\text{O}_{9.4}$. The maximum of conductivity in all temperatures is detected for $\text{Bi}_{25.4}\text{Mn}_{6.6}\text{Mo}_{10}\text{O}_{9.4}$.

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