Sheelite-related strontium molybdates: synthesis and characterization

The present research is devoted to the cationic-deficient SrMoO$_4$-based sheelite-related complex oxides. The doping with bismuth to A sublattice and codoping with bismuth and vanadium (to A and B sublattices, respectively) were discussed. The X-Ray powder diffraction and infrared spectroscopy were used to investigate structural characteristics of the complex oxides. In Sr$_{1-1.5x}$Bi$_x$MoO$_4$, a superstructural ordering was observed. Conductivity and dielectric loss of ceramic samples are measured using alternating current.

**Keywords:** sheelite; strontium molybdates; dielectric materials.


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**Introduction**

Sheelite-type complex oxides are quite interesting research objects because flexibility of substitutions in these systems leads to variety of their compositions, structure types and properties. Ideal sheelite-related oxides have a general formula ABO$_4$ and consist of A$^{n+}$ cations and (BO$_4$)$_{n^-}$ anions. A-site ions are coordinated with eight oxygen ions, and B-site ions are coordinated with four oxygen ion. Each site can be occupied simultaneously by different ions with various oxidation states; additional interstitial positions and vacancies lead to the deviation from the general formula. A lot of sheelite-type complex oxides are used as materials for scintillation detectors, lasers [1, 2], ionic conductors [3], phosphors [4], photocatalysts [5], and microwave dielectrics [6]. The regulation of the desired properties of sheelite-related materials can be provided by varying the quantity of the dopant, its nature, the ratios between dopants and the presence of additional vacancies or interstitial positions in the structure. For example, a substitution of A-site ions with Me$^{+3}$ in ABO$_4$ complex oxide can be described in two ways: (1) a formation of A$_{1-x}$Me$_x$BO$_{4+5x/2}$ phases, where electroneutrality is provided by the interstitial oxygen ions; (2) a formation of A$^{+2}_{1-1.5x}$Me$_x^+$BO$_{4+5x}$ (or A$^{+2}_{1-1.5x}$Me$_{0.5x}^+$MoO$_4$) phases containing cationic vacancies $\Phi$. The first way of substitution was detected for Pb(Mo/W)O$_4$ [7, 8] and Ca(Mo/W)O$_4$ [9] parent compounds. The second way was described for rare-earth substituted Ca(Mo/W)O$_4$, Sr(Mo/W)O$_4$ and Cd(Mo/W)O$_4$ [10–12].
As a result, cationic vacancies Ф and their ordering are additional structural factors influencing physico-chemical properties. Another way of the substitution of А positions is codoping with Me+3 and Me+1 or Me+5 ions, which leads to the formulae $A_{1-x}Me^{+1}_{0.5x}Me^{+3}_{0.5x}BO_4$ [13] and $A_{1-x}Me^{+3}_{1-x}Me^{+5}_{x}O_4$, respectively [14]. The present research is devoted to the Bi-doped strontium molybdate SrMoO$_4$. The existence of Sr$_{1-x}Bi_x$MoO$_4$ series was shown by Sleight and coauthors [15], who synthesized the complex oxide Sr$_{0.88}Bi_{0.08}$MoO$_4$ (tetragonal symmetry, Sp. Gr. I$4_1/a$) and described its good catalytic properties [15]. Sr$_{1-x}Bi_x$MoO$_4$ family has not been described yet, while Bi-doped calcium molybdates have been intensively researched as microwave dielectric [16] or pigments [14]. The basic characteristic and structure types of SrMoO$_4$ are similar to those of CaMoO$_4$, so the Bi-doped strontium molybdates should possess similarly promising properties. In addition, Bi-doping of strontium molybdates is expected to lead to decrease of the unit cell, resulting from the significant changes in B-sublattice. Therefore, the objects of the present work are Sr$_{1-x}Bi_x$MoO$_4$, Sr$_{1-x}Bi_xMo_{1-y}V_yO_4$, Sr$_{1-x}Bi_xMo_{1-y}O_yO_4$ solid solutions and their structure and properties.

**Experimental**

Synthesis of Sr$_{1-x}Bi_x$MoO$_4$ ($0 \leq x \leq 0.45$), Sr$_{1-x}Bi_xMo_{1-y}V_yO_4$ ($0 \leq x, y \leq 0.4$), Sr$_{1-x}Bi_xMo_{1-y}O_yO_4$ ($0 < x \leq 0.4, 0 < y \leq 0.2$) were synthesised by conventional solid state methods from SrCO$_3$ (98.5%), Bi$_2$O$_3$ (99.9%), V$_2$O$_5$ (98.5%) and MoO$_3$ (99.0%). Stoichiometric amounts of dried precursors were weighed and mixed in an agate mortar as dispersion in ethanol. Mixture powders were pelletized and heated at 550–650 °C with regrinding and repelletizing. Time of each heating was ~10 hours, the total time of heating was ~30 hours.

X-ray powder diffraction data were obtained on a DRON-3 with Cu Kα monochromatic radiation in the range of 5–75° of 2θ. IR FT spectrometry measurements were carried out at Nicolet 6700 with attenuated total reflection attachment. Density of powder samples was measured by hydrostatic weighting. For conductivity measurements, the ceramic pellets of 10 mm in diameter and ca. 2.5 mm thickness were covered by Pt. Impedance spectra were obtained in two-electrode measurement cell on LCR-819 and Elins Z-3000 impedance spectrometers, over the frequency ranges 1 Hz and 3 MHz to 10 Hz, respectively, at stabilised temperatures from ca. 25 °C to ca. 625 °C. Data presented correspond to the second cooling run. Data were modelled using equivalent electrical circuits with the Zview software (Version 2.6b, Scribner Associates, Inc.).

**Results and discussion**

Synthesis of Sr$_{1-x}Bi_x$MoO$_4$ yielded samples with the structure of Sr$_{0.88}Bi_{0.08}$MoO$_4$ [15], up to $x = 0.2$ (Sp.gr. I$4_1/a$). At $0 < x < 0.4$ additional peaks in the small angle range are evident; for the $x > 0.45$ composition additional peaks in the pattern can be identified as Bi$_3$MoO$_{12}$. We supposed that $0.2 < x \leq 0.4$ compositions have superstructural ordering caused by ordering of cationic vacancies (Fig. 1).

As a result, in the XRPD data for $0.2 < x \leq 0.4$ compositions all peaks can be successfully indexed using a tetragonally ordered supercell $a_{sup} = \sqrt{5}a_{sub}$.
$c_{\text{sup}} = c_{\text{sub}}$ (where sup and sub subscripts denote the super- and subcell, respectively) in $I4_1/a$ space group (Fig. 2). Compositional dependence of the unit cell parameters for $\text{Sr}_{1-x}\text{Bi}_x\text{MoO}_4$ compositions are shown in Fig. 2, where the linear chemical compression is caused by the substitution of the bigger cation with the smaller one (ionic radii $r_{\text{Sr}^{2+}} = 1.26$ Å, $r_{\text{Bi}^{3+}} = 1.17$ Å [17]). The measurements of density showed that experimental density is equal to the theoretical (X-ray) one to within the 2–3% of absolute values.

Synthesis of $\text{Sr}_{1-x}\text{Bi}_x\text{Mo}_{1-x}\text{V}_x\text{O}_4$ results in the two-phase samples that consist of BiVO$_4$ (monoclinic) and SrMoO$_4$ phases. In contrast, Ca$_{1-x}\text{Bi}_x\text{Mo}_{1-x}\text{V}_x\text{O}_4$ solid solutions are observed for $0 \leq x \leq 0.9$ [14]. One possible reason was that the dopants influence differently the composition and structure of strontium and calcium molybdates. The simultaneous presence of Bi and V in Ca$_{1-x}\text{Bi}_x\text{Mo}_{1-x}\text{V}_x\text{O}_4$ leads to the expansion of the unit cell of a complex oxide due to the replacement of calcium with bismuth and compression of the unit cell due to the replacement of molybdenum with vanadium; as a result, the unit cell changes slightly [14] (ionic radii $r_{\text{Ca}^{2+}} = 1.12$ Å, $r_{\text{V}^{5+}} = 0.54$ Å, $r_{\text{Mo}^{6+}} = 0.41$ Å [17]). In contrast, in Sr$_{1-x}\text{Bi}_x\text{Mo}_{1-x}\text{V}_x\text{O}_4$ both of Bi and V lead to compression of the unit cell, making it unstable. It can be assumed that such compression of the unit cell leads to the decrease of the distance between $[\text{BO}_4]^{n-}$ ($B = \text{Mo, V}$) clusters and, consequently, to the increase of repulsion between them. As a result, the destruction of Sr$_{1-x}\text{Bi}_x\text{Mo}_{1-x}\text{V}_x\text{O}_4$ system is observed. Creating an oxygen deficiency in the crystal lattice provides distortion in BO$_4$ tetrahedra and formation of $[\text{BO}_4]^{-}[\text{BO}_3]^{n-}$-type bonds through common oxygen atoms. This can be realized by changing...
the composition of strontium molybdate to Sr$_{1-1.5x}$Bi$_x$Mo$_{1-y}$V$_y$O$_{4-d}$.

It was expected that low concentration of bismuth would not provide a proper compression of the unit cell and single-phase samples would not be observed even at small $y$. But high concentration of bismuth can provide an efficient compression of the unit cell and the possibility of doping with vanadium. In fact, we observed such trend. For $x = 0.1$ in Sr$_{1-1.5x}$Bi$_x$Mo$_{1-y}$V$_y$O$_{4-d}$ no single-phase samples was obtained, for $x = 0.2$ only $y = 0.05$ composition is single phase, for $x = 0.3$ and $x = 0.4$ single-phase compositions were observed at $y = 0.05–0.1$ and $0.05–0.2$, respectively. In this research, the maximum concentration of vanadium was not determined exactly, but the general trend is clear.

In the Table 1, the unit cell parameters of the single-phase samples are shown. When $x$ is fixed and $y$ increases or when $y$ is fixed and $x$ increases, a general compression of the unit cell is observed. The presence of vanadium in the structure leads to the absence of cationic ordering, and no additional peaks in X-ray diffraction profiles of $x = 0.3–0.4$ are observed. Unfortunately, it has proved impossible to accurately refine the oxide ion positions in the unit cell using a Rietveld approach, due to dominance of the X-ray scattering by the cations in this system and only neutron diffraction can refute or confirm the specified theory about the [BO$_4$]–[BO$_3$]$^{n-}$-type bond formation.

Powders of the Sr$_{1-1.5x}$Bi$_x$MoO$_4$ compositions were characterized by IR FT spectroscopy (Fig. 3). Several adsorption bands in the range of 950–500 cm$^{-1}$ were detected. According to Basiev [18] scheelite-related compound ABO$_4$ consists of [MoO$_4$]$^{2-}$ clusters and isolated A$^{2+}$ ions and, as a result, characteristic absorption bands can be assigned only to the vibrations in [MoO$_4$]$^{2-}$ clusters [19]. Strong absorption bands in the range 940–550 cm$^{-1}$ are related to O–Mo–O stretches of the

![Fig. 3. IR FT spectra of the Sr$_{1-1.5x}$Bi$_x$MoO$_4$ compositions](image_url)

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<td>Unit cell parameters of Sr$_{1-1.5x}$Bi$<em>x$Mo$</em>{1-y}$V$_y$O$_4$ (0.1 $&lt;$ x $&lt;$ 0.4, 0.05 $&lt;$ y $&lt;$ 0.2) compositions</td>
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<td>Composition</td>
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<td>Sr$<em>{0.7}$Bi$</em>{0.2}$Mo$<em>{0.95}$V$</em>{0.05}$O$_4$</td>
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MoO₄ tetrahedron. Additional absorption band near 425–400 cm⁻¹ can also be assigned to the deformational vibrations of O–Mo–O bands. In the IR FT spectra, the general shifting of absorption bands is observed. The same trend was observed for Ca₁₋₋ₓₓₓₓ Biₓ MoO₄ [16]; in both cases it is caused by the deformation of MoO₄ tetrahedra resulting from the presence of cationic vacancies.

Conductivity measurements of Sr₁₋₋ₓₓₓₓ Biₓ MoO₄ ceramic showed very high resistivity of samples (Fig. 4). A slight increase of conductivity is observed for the samples with superstructural ordering (0.2 < x < 0.45) and two-phase samples (x > 0.45).

Changing of dielectric loss tangent (tgδ) was measured at the range of 303–903 K at cooling at the fixed frequency of 1 kHz using the parallel R_p + C model (series connected R_s and Ls were shown to be negligible). The tgδ vs temperature curves of Sr₁₋₋ₓₓₓₓ Biₓ MoO₄ compositions are shown at Fig. 5. The acceptable dielectric losses (tgδ < 0.1) of Sr₁₋₋ₓₓₓₓ Biₓ MoO₄ compositions were observed for temperatures below ~573 K, while tgδ decreases with x values until x = 0.3. Then, at x > 0.3, tgδ increases, probably because of structural ordering of the samples.

For Sr₁₋₋ₓₓₓₓ Biₓ Mo₁₋ᵧᵧᵧᵧ O₄₋ₐ₋₋₋ compositions we observed a significant growth in conductivity in comparison with Sr₁₋₋ₓₓₓₓ Biₓ MoO₄. As a result, in the range of ~303–573 K the tgδ rises by approximately one order (Fig. 6). It is consistent with the increase of oxygen ion conductivity associated with structural changes.

The tgδ vs frequency dependences of all compositions of substituted SrMoO₄ indicate that effective dielectric properties are observed at frequency above 1 MHz, i.e. in the microwave range, as well
as CaMoO$_4$ — based dielectric materials [16] (the example is given in Fig. 7).

### Conclusions

Thus, the present research demonstrates the existence of cationic-deficient scheelite-related complex oxides of Sr$_{1-1.5x}$Bi$_x$MoO$_4$ series and Sr$_{1-1.5x}$Bi$_x$Mo$_{1-y}$V$_y$O$_4$-$d$ series. In Sr$_{1-1.5x}$Bi$_x$MoO$_4$, superstructural ordering is observed for $0.2 < x \leq 0.4$. For Sr$_{1-1.5x}$Bi$_x$Mo$_{1-y}$V$_y$O$_4$-$d$ series a changing in oxygen sublattice is assumed. Both of the complex oxide series show dielectric properties at temperatures below 503 K and frequencies above 1 MHz. Conductivity and tangent of dielectric loss for Sr$_{1-1.5x}$Bi$_x$Mo$_{1-y}$V$_y$O$_4$-$d$ compositions is greater than for Sr$_{1-1.5x}$Bi$_x$MoO$_4$. It is consistent with the increase of oxygen ion conductivity associated with mentioned structural changes.

### Acknowledgements

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### References


