ABO$_4$ type scheelite phases in (Ca/Sr)MoO$_4$ - BiVO$_4$ - Bi$_2$Mo$_3$O$_{12}$ systems: synthesis, structure and optical properties

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Abstract
The cation deficient complex oxides of (Ca/Sr)MoO$_4$ - BiVO$_4$ - Bi$_2$Mo$_3$O$_{12}$ triple system are promising photocatalysts and pigments. Compounds with general formula of Ca$_{1-x}$$_2$Bi$_x$MO$_{4+y}$VO$_4$ and Sr$_{1-x}$Bi$_x$Mo$_{3+y}$O$_{12}$ were synthesized by conventional solid state technique in the range of 550-720 °C. Two wide regions of the solid solutions (ordinary and superstructured scheelite-type phases respectively) were found for each system. The diffuse scattering of homogeneous samples was investigated in the range of 190-1100 nm. Energy gaps calculated with linear approximation of Kubelka-Munk function decreases with bismuth and vanadium content.

1. Introduction
Materials based on CaMoO$_4$ and SrMoO$_4$ are of interest for science and technology as catalysts and photocatalysts, scintillation detectors, solid-state lasers, pigments as well as for using in photoluminescent and microwave devices due to a wide variety of functional properties [1-8]. The latter strongly depend on not only the nature of dopants [2-3] but also on synthesis techniques employed [2,3,8] and a place of doping. The doping in different sublattice (Ca/Sr or Mo) and varying parameters of synthesis (temperature, irradiation time, pH, speed of mixture, etc.) may cause distortion of MoO$_6$ polyhedra. This distortion, in turn, affects such physical and chemical properties as photocatalytic activity [8-10], optical and luminescence properties [2-3,11], conductivity [12], etc.

The most common way of substitution in ABO$_4$ complex oxides with scheelite structure is doping A-sublattice by trivalent Me$^{3+}$ cations [3,4,6-7,13]. In this case, three basic charge compensation mechanisms are possible in ABO$_4$ scheelites: (1) formation of oxide ion interstitials (A$_{1-x}$M$_{x}$BO$_4$+x/2) [12]; (2) co-substitution on A or B sites by subvalent cations (A$_{1-x}$Me$^{3+}$,Me$^{4+}$O$_4$ or A$_{1-x}$Me$^{3+}$B$_{2-x}$Me$^{5+}$O$_6$) [16-17,6]; (3) formation of cation vacancies (A$_{1-x}$M$_{x}$BO$_4$) [13-17]. Mechanism (3) was reported for rare earth molybdates Ln$_2$MoO$_{12}$ (Ln=La,MoO$_{4}$, $x=1/3$) with scheelite-type structure [14] and for a small number of completely investigated A$_{1-x}$M$_{x}$MO$_4$ series where $0 < x < 1/3$ [13,17]. But cation vacancies (Φ) and their ordering can influence not only structure, but also the physical and chemical properties of the molybdates, and, therefore, we pay close attention to them in the present work. The simultaneous use of mechanisms (2) and (3) have not been described yet. For this reason the present work is devoted to the synthesis and characterization of Bi and V co-doped CaMoO$_4$ and SrMoO$_4$ obtained by mechanisms (2) and (3).

Previously, Sleight et al. [18] reported the $x = 0.04$ compositions of (Ca/Sr)$_{1-x}$Bi$_{2x}$MO$_4$ series with the tetragonal scheelite structure (sp. g. I4/a). Sleight assumed that solid solution limit could apparently go all the way to 0.333. The structure, microwave dielectric properties, conductivity and photocatalytic activity of Ca$_{1-x}$Bi$_2$MO$_4$ series were investigated in [13,19]. Guo et al. [13] synthesized series of solid solutions Ca$_{1-x}$Bi$_2$MO$_4$ (0.005 ≤ x ≤ 0.20), using a conventional ceramic method, and examined their microstructure and microwave dielectric properties. The 0 ≤ x ≤ 0.15 compositions were found to be single-phase and to have scheelite structure with cationic vacancies [13,19] (the structural model of Sr$_{0.88}$Bi$_{0.12}$MoO$_4$ [18] was used). It was shown that Bi-doped samples exhibit improved values of the mi-
crowave quality factor (Qf). Vibrational spectroscopy results revealed large distortions of MoO₄ and BiO₈ polyhedra [13], with a strong correlation between substitutions in the cation (A²⁺) sublattice and microwave dielectric properties of the Ca₁₋xBiₓMo₃O₁₂ series. Later, the powder X-ray and neutron diffraction patterns for compositions with 0.15 < x ≤ 0.225 were shown to exhibit a tetragonal supercell with a_{44} = \sqrt{5}a, c_{44} = c where a and c are the tetragonal scheelite cell parameters [19]. This superstructural ordering results in the additional reflections on XRPD patterns detected by Guo et al. [13] and provided by ordering of Bi atoms and cationic vacancies [19]. Samples described with supercell showed maximal photocatalytic activity due to complex microstructure at grain surface and also showed a decrease of total conductivity as compared to samples with normal scheelite structure [19]. The conductive properties and structure of Sr₁₋xBiₓMo₃O₁₂ compositions (0.025 ≤ x ≤ 0.225) were described in [20]. The superstructural ordering was also observed for 0.15 ≤ x ≤ 0.4. In Fourier-transformed infrared spectra of Sr₁₋xBiₓMo₃O₁₂ the general shifting of absorption bands caused by deformation of MoO₄ tetrahedra was observed. An increase of overall electrical conductivity with x was also observed. The activation energy decreased with x insignificantly (from ~1.2 to ~1.1eV), indicating that the charge carriers and conduction mechanism in Sr₁₋xBiₓMo₃O₁₂ generally were the same as in the parent compound SrMoO₄. Probably, the increase of conductivity was caused by the increase in the oxygen ion mobility provided by the distortion of MoO₄ polyhedra [20].

Synthesis of Sr₁₋xBiₓMo₃₋yVₙO₄ results in the two-phase samples consisting of BiVO₄ (monoclinic) and SrMoO₄ phases [20]. In contrast, Ca₁₋xBiₓMo₃₋yVₙO₄ single-phase solid solutions are observed for 0 ≤ x ≤ 0.9 [6]. One possible reason of such discrepancy is that the dopants influence differently the composition and structure of strontium and calcium molybdates. The simultaneous presence of Bi and V in Ca₁₋xBiₓMo₃₋yVₙO₄ oxide leads to the simultaneous expansion and contraction of its unit cell due to the replacement of calcium with bismuth and molybdenum with vanadium, respectively; as a result, the unit cell volume changes slightly [6]. In contrast, in Sr₁₋xBiₓMo₃₋yVₙO₄ doping with both Bi and V leads to the contraction of unit cell and by that means makes this oxide unstable. It can be assumed that such contraction decreases the distance between [BO₄]^{−} (B = Mo, V) clusters and, consequently, increases the repulsion between them. As a result, decomposition of Sr₁₋xBiₓMo₃₋yVₙO₄ oxide is observed [20]. In general, Bi- and (Bi+V) doped CaMoO₄ and SrMoO₄ show the decreasing melting point temperature and, as a consequence, lower sintering temperature, as well as increasing conductivity, catalytic and photocatalytic activity. In addition, the shift of absorbance bands from UV to violet and blue parts of spectra was observed, and the energy gap decreases [6,22]. The last mentioned characteristics are important factors for such technical areas as photocatalytic oxidation under visible light or pigment technology.

Thus, the priority goal of the present work was to show the effects of bismuth and vanadium co-doping on the UV-VIS spectral characteristics and E_{g} values of the Ca₁₋xBiₓMo₃₋yVₙO₄ and Sr₁₋xBiₓMo₃₋yVₙO₄ complex oxides.

2. Experimental

Samples of Ca₁₋xBiₓMo₃₋yVₙO₄ and Sr₁₋xBiₓMo₃₋yVₙO₄ (0 < x ≤ 0.4, 0 < y ≤ 0.5) were synthesised by conventional solid state methods from SrCoO₃ (99.5%) or CaCoO₃ (99.5%), Bi₂O₃ (99.9%), V₂O₅ (98.5%) and MoO₃ (99.0%) as starting materials. Stoichiometric amounts of dried precursors were weighed and mixed in an agate mortar as dispersions in ethanol. Mixed powders were then pelletized and calcined in steps at 550–720 °C with duration about 10 hours at each step followed by regrinding and re-pelletizing. The overall time of calcination was about 30 hours. X-ray powder diffraction (XRD) data were obtained using a Bruker Advance D8 diffractometer with a VANTEC1 detector (Ni filtered Cu Ka radiation, θ/0 geometry). XRD data were collected in the 2θ range of 6–120°, with steps of 0.02103° and an effective scan time of 200 s per step.

The reflection spectra were obtained in the range of 190–1100 nm by using a spectrophotometer Evolution 300 (Termo Sci) equipped with an integrating sphere. The absorption coefficient curves were derived from reflection curves using Kubelka-Munk model. Energy gaps for direct interband transitions were calculated with linear approximation of Kubelka-Munk function [21].

3. Results and Discussion

As-prepared samples of nominal composition Ca₁₋xBiₓMo₃₋yVₙO₄ and Sr₁₋xBiₓMo₃₋yVₙO₄ (0 < x ≤ 0.5, 0 < y ≤ 0.5) were found to contain one phase for y ≤ 0.05 (x = 0) and y ≥ 0.2 (x = 0) for CaMoO₄- and SrMoO₄-based systems, respectively, although the solubility limit of vanadium in Ca₁₋xBiₓMo₃₋yVₙO₄ is reported to be y = 0.9 [6,22]. BiVO₄ was also detected in CaMoO₄-based samples with x = 0 and 0.2 < y ≤ 0.5. Presence of BiVO₄ was also found in Ca₁₋yBiₓMo₃₋yVₙO₄ (0.4 < y ≤ 0.9) [22], but this fact was disregarded by authors during solid solution limits discussion. At low x concentration the scheelite structure are observed. But for oxides with higher x values the additional peaks in the XRD patterns are evident. These oxides were found to have the tetragonal supercell with a_{44} = \sqrt{5}a, c_{44} = c, where a and c are the tetragonal scheelite cell parameters, like it was found earlier for Ca₁₋xBiₓMo₃O₄ [19] and Sr₁₋xBiₓMo₃O₄ [20]. The areas of solid solutions (ordinary scheelite and superstructured scheelite) and investigated fields of triple phase diagram are shown at Fig. 1. It is seen that continuation of solid
solutions areas can be expected for $0.5 < x \leq 0.7$, $0.5 < y \leq 0.6$) values. Compositions without solid solutions areas contain additional Bi$_3$MoO$_9$ and monoclinic BiVO$_4$.

Previously, free refinement of the occupancies in superstructured Ca$_{1-3x}$Bi$_2$Mo$_2$O$_9$ solid solutions showed the 4$b$ site positions to be fully occupied by bismuth, the 16$f$ site positions are partially occupied by both Ca$^{2+}$ and Bi$^{3+}$[19]. In the present work, the refinement of the occupancies of 4$b$ and 16$f$ sites revealed the same pattern of doping.

It can be clearly observed that high concentration of bismuth only (i.e. $x+y$ values) does not lead to the superstructural ordering, but relatively high concentration of cationic vacancies accompanying high concentrations of bismuth provide the ordering of bismuth at 4$b$ position. Samples with superlattice ordering contain plains which along z axis. High concentration of cationic vacancies in $x-y$ compositions areas contain additional Bi$^{4b}$ positions show the ordering of bismuth only (i.e. $x+y$ values) does not lead to the super- transitions areas can be expected for $0.5 < y \leq 0.5$.

The dependencies of the unit cell parameters for Ca$_{1-1.5x}$Bi$_{1-x}$Mo$_{1-y}$V$_{1-y}$O$_{4}$ and Sr$_{1-1.5x}$Bi$_{1-x}$Mo$_{1-y}$V$_{1-y}$O$_{4}$ compositions are shown in Fig. 3. The compression and enlargement are caused by substitution by smaller of bigger cation, respectively (ionic radii $r_{Ca^{2+}} = 1.12$ Å, $r_{Sr^{2+}} = 1.26$ Å, $r_{Bi^{3+}} = 1.17$ Å [23]).

The ionic radius of vanadium is smaller than that of molybdenum ($r_{Mo^{6+}} = 0.41$ Å, $r_{V^{4+}} = 0.355$ Å), and V-doping impedes expansion of the unit cell in the case of Ca$_{1-1.5x}$Bi$_{1-x}$Mo$_{1-y}$V$_{1-y}$O$_{4}$ and promotes the decrease of cell volume in the case of Sr$_{1-1.5x}$Bi$_{1-x}$Mo$_{1-y}$V$_{1-y}$O$_{4}$. In both cases, the superstructural ordering is a “growth factor” of c-parameter. It leads to the sharp rise of c-parameter or local plateau on c-parameter dependence in the cases of Ca$_{1-1.5x}$Bi$_{1-x}$Mo$_{1-y}$V$_{1-y}$O$_{4}$ and Sr$_{1-1.5x}$Bi$_{1-x}$Mo$_{1-y}$V$_{1-y}$O$_{4}$ respectively. Probably, it is caused by stereochemical activity of 6$S$ lone pair of bismuth in the planes parallel to (xoy) plane.

Typical diffuse scattering spectra of (Ca/Sr)$_{1-1.5x}$Bi$_{1-x}$Mo$_{1-y}$V$_{1-y}$O$_{4}$ compositions are similar (Fig. 4). The scattering in the range of ~500–1100 nm is close to 100%. The spectra for CaMoO$_4$ and SrMoO$_4$ contain a broad band in the range of wavelengths ~200–300 nm that corresponds to electronic transition within the MoO$_6^{2-}$ complex [24]. For Bi-doped and (Bi+V) -doped samples this band is located in higher wavelengths (see Fig. 4). The separate absorbance bands that correspond to transitions in the vanadium-oxygen complex are not observed. The band gap calculations for (Ca/Sr)$_{1-1.5x}$Bi$_{1-x}$Mo$_{1-y}$V$_{1-y}$O$_{4}$ were carried out by using Kubelka-Munk theory and Tauc relation. Fig. 5 shows the Tauc plot for some compositions. The graph consists of non-linear and linear regions. The value of $E_g$ can be obtained by drawing a tangent on the linear part. The point of inflection on the X-axis provides the value of band gap for the prepared powders.

**Fig. 1** The areas of scheelite-type solid solutions (red), superstructured scheelite solid solutions (blue) and tree-phases areas (gray) in CaMoO$_4$ - BiVO$_4$ - Bi$_2$Mo$_3$O$_9$ (a) and SrMoO$_4$ - BiVO$_4$ - Bi$_2$Mo$_3$O$_9$ (b) ternary diagram. White regions are unstudied areas ($x > 0.5$, $y > 0.5$).

**Fig. 2** Planes including Bi 4$b$ positions show the ordering of bismuth atoms in tetragonal supercell. “SrBi” 16$f$ positions are mixed with Sr, Bi and $\Phi$. 

![Diagram](Image-89x91 to 245x227)
Fig. 3 The unit cell parameters depending on \( x \) and \( y \) parameters in \( \text{Ca}_{1.5x+y} \text{Bi}_{x+y} \text{Mo}_{1-y} \text{V}_y \text{O}_4 \) (a,c,e) and \( \text{Sr}_{1.5x+y} \text{Bi}_{x+y} \text{Mo}_{1-y} \text{V}_y \text{O}_4 \) (b,d,f) solid solutions.
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**Fig. 4** The diffuse scattering spectra for some Ca$_{1-1.5x-y}Bi_{x+y}Mo_{1-y}V_yO_4$ (a) and Sr$_{1-1.5x-y}Bi_{x+y}Mo_{1-y}V_yO_4$ (b) compositions.

**Fig. 5** Tauc plots for some Ca$_{1-1.5x-y}Bi_{x+y}Mo_{1-y}V_yO_4$ (a) and Sr$_{1-1.5x-y}Bi_{x+y}Mo_{1-y}V_yO_4$ (b) compositions.

Calculated values of the band gap ($E_g$) for Ca$_{1-1.5x-y}Bi_{x+y}Mo_{1-y}V_yO_4$ were found to be 3.83–2.64 eV for $\{x = 0, y = 0\}$ – $\{x = 0.1, y = 0.5\}$ compositions. $E_g$ values for Sr$_{1-1.5x-y}Bi_{x+y}Mo_{1-y}V_yO_4$ were 4.25–2.87 eV for $\{x = 0, y = 0\}$ – $\{x = 0.2, y = 0.3\}$ compositions. It is seen that the band gap value decreases with $x$ and $y$ (Fig. 6), and it reduces not only with bismuth content ($x+y$ value) but with vanadium content ($y$) as well. For CaMoO$_4$-based solid oxides, $E_g$ value slowly decreases with $x$ and rapidly decreases with $y$, while for SrMoO$_4$-based solid oxides we observed the opposite trends (Fig. 6). In general, the energy gap in (Ca/Sr)$_{1-1.5x-y}Bi_{x+y}Mo_{1-y}V_yO_4$ is reduced by additional bands of Bi 6p electrons and by modification of states of Mo 4d electrons caused by distortion of MoO$_4$ polyhedra. Bands of Bi 6p electrons lead to the significant decrease of $E_g$ even for low concentration of bismuth for both series of molybdates. In the case of distortion of MoO$_4$ polyhedra for SrMoO$_4$-based solid oxides, the sufficient contraction of the unit cell is observed, while for CaMoO$_4$-based solid oxides the cell volume grows. Therefore, the distortion of MoO$_4$ polyhedra caused by the formation of cation vacancies (represented by $x$ while $y = 0$) is generally smaller for CaMoO$_4$-based compounds than that for SrMoO$_4$-based compounds. Strongly distorted MoO$_4$ polyhedra in SrMoO$_4$-based compounds do not change significantly at vanadium doping ($y > 0$), but weakly distorted MoO$_4$ polyhedra in CaMoO$_4$-based compounds show a sharp alteration at the same time. Meanwhile, some special effects for superstructured phases are not observed. For the purpose of $E_g$ minimization, therefore, the best compositions are found to be $\{x = 0.1–0.2, y = 0.4–0.5\}$ and $\{x = 0.2–0.4, y = 0.1–0.2\}$ for CaMoO$_4$.
Fig. 6 The \( E_g \) changing in \( \text{Ca}_{1-1.5x-y} \text{Bi}_{x+y} \Phi_x \text{Mo}_{1-y} \text{V}_y \text{O}_4 \) (a) and \( \text{Sr}_{1-1.5x-y} \text{Bi}_{x+y} \Phi_x \text{Mo}_{1-y} \text{V}_y \text{O}_4 \) (b) series

based and \( \text{SrMoO}_4 \)-based compounds, respectively. These compositions are expected to be the most effective photocatalysts in \( \text{(Ca/Sr)}_{1-1.5x-y} \text{Bi}_{x+y} \Phi_x \text{Mo}_{1-y} \text{V}_y \text{O}_4 \) series because of absorption of energy in both UV and vis (i.e. blue) parts of spectra.

4. Conclusions

Compounds with general formulae of \( \text{Ca}_{1-1.5x-y} \text{Bi}_{x+y} \Phi_x \text{Mo}_{1-y} \text{V}_y \text{O}_4 \) and \( \text{Sr}_{1-1.5x-y} \text{Bi}_{x+y} \Phi_x \text{Mo}_{1-y} \text{V}_y \text{O}_4 \) were synthesized by conventional solid state technique in the temperature range of 550–720 °C. The areas of solid solutions (ordinary scheelite and superstructured scheelite) were determined. It was observed that relatively high concentration of cationic vacancies accompanying high concentrations of bismuth provide the ordering of bismuth at \( 4b \) position. The diffuse scattering spectra of homogeneous samples contain a broad band in the range of ~200–450 nm. Energy gaps, calculated with linear approximation of Kubelka-Munk function, decrease with bismuth content. The compositions with minimal \( E_g \) are found to be \( \{ x = 0.1–0.2, y = 0.4–0.5 \} \) and \( \{ x = 0.2–0.425, y = 0.1–0.2 \} \) for \( \text{CaMoO}_4 \)-based and \( \text{SrMoO}_4 \)-based compounds, respectively. These compositions are expected to be the most effective photocatalysts in \( \text{(Ca/Sr)}_{1-1.5x-y} \text{Bi}_{x+y} \Phi_x \text{Mo}_{1-y} \text{V}_y \text{O}_4 \) series.

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