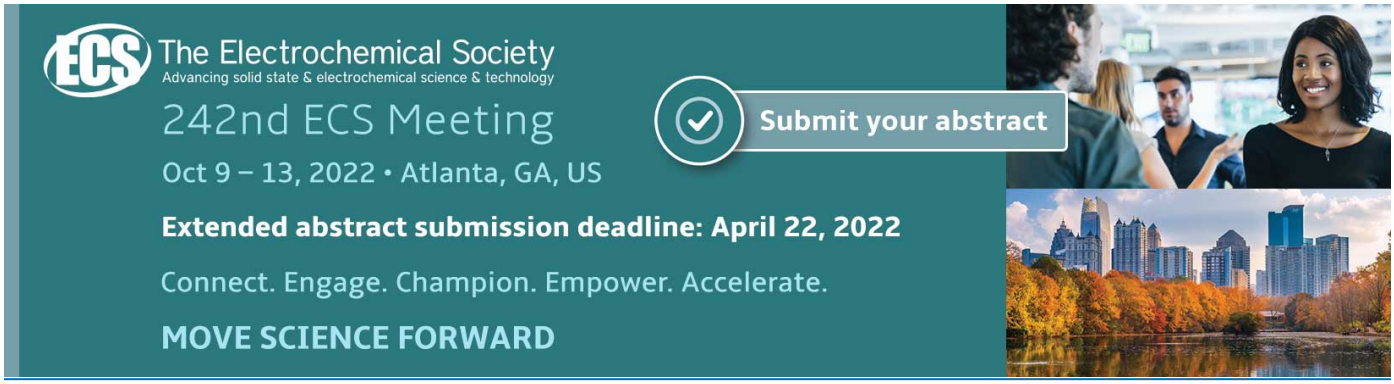
Ab initio calculation of the electronic structure of a solid solution of strontium-bismuth molybdat



Ab initio calculation of the electronic structure of a solid solution of strontium-bismuth molybdat

E V Sokolenko[1,*], E S Buyanova[2], Z A Mikhaylovskaya[3] and G V Slusarev[1]

[1] North Caucasian Federal University, 1, Pushkin str., Stavropol, 355009, Russian Federation
[2] Ural Federal University, 87, Mira str., Ekaterinburg, 620002, Russian Federation
[3] Institute of Geology and Geochemistry named after Academician A. N. Zavaritsky of the Ural Branch of the Russian Academy of Sciences, 7, Postal kane, Ekaterinburg, 620151, Russian Federation

E-mail: sokolenko-ev-svis@rambler.ru

Abstract. Scheelite-like compounds based on $SrMoO_4$ have been studied. Based on X–ray structural data, models of $Sr_{1-3x}Bi_{2x}MoO_4$ structures (x=0.2125) are constructed, at $x \geq 0.175$, a superstructural ordering is observed associated with the location of cationic vacancies. From the first principles, calculations of the density of states in the vicinity of the forbidden zone are performed. The calculated values of the band gap width were compared with the values obtained from the reflection spectra.

1. Introduction

Scheelite-like compounds with the general formula ABO4 (An+ - cationic sublattice, BOn- - anionic sublattice) are well studied, while the relative ease of replacing metal positions determines many variations in the chemical composition that allow fine adjustment of their functional characteristics. As a result, these compounds are still attractive from the point of view of finding new materials for scintillators, LED lasers [1, 2], ion conductors [3], phosphors [4], photocatalysts [5], microwave dielectrics [6], etc. It is possible to solve this problem of parameter optimization by using modern methods of structure modeling.

2. Theoretical analysis

Strontium molybdate $SrMoO_4$ crystallizes in the structural type of scheelite (pr. gr. I41/a), it is constructed from molybdenum-oxygen etrahedron, between which eight-aligned strontium atoms are located [7]. The replacement of strontium positions in SrMoO4 with bismuth is possible by the formation of cation-deficient phases. The solid solution $Sr_{1-3x}Bi_{2x}MoO_4$ ($x \leq 0.4$) was first studied in [8], where its high catalytic activity was noted, but its detailed study was not carried out. Bismuth substitution leads to an improvement in the photocatalytic characteristics [8, 9], a decrease in the band gap width, melting temperature and sintering of samples. It was shown in [8, 10] that when doping with bismuth, a significant distortion of the structure and compression of the unit cell of strontium molybdate is observed, the presence of a superstructural ordering for compositions with a high content of vismut ($0.15<x<0.25$ $Sr_{1-3x}Bi_{2x}MoO_4$) is noted.

To refine the models of active centres given in the literature, obtained on the basis of experimental results, the calculation of the electronic structure of scheelite nanoclusters, including intrinsic and impurity defects, is of undoubted interest.

3. The experimental part

Initially, "$SrMoO_4$" clusters based on $SrMoO_4$ were studied, the coordinates of atoms from [7] were used to model the structure. Cells with a size of 2×2×1 are pre-constructed, the atoms connected to the rest of the structure by single bonds are removed. Then we considered "$SrMoO_4$-H": the previous cluster, whose surface bonds are saturated with hydrogen [11]. The next type is "$SrMoO_4$-BiH": clusters based on $SrMoO_4$, with the replacement of one strontium atom with bismuth, the cluster structure is optimized. During optimization, the coordinates of all atoms were fixed, except for Bi and the first coordination sphere around it. And finally "$BiSrMoO_4$" clusters based on structural data [12], cell 1×1×1. Atomic coordinates and crystallographic information for the composition of $Sr_{0.4}Bi_{0.4}MoO_4$ were used to construct a cluster model.

Calculations of the electronic structure of crystals using the DFT method were performed by the Q-chem program in the remote access mode on the North Caucasian Federal University server [11]. The use of the quantum-chemical approach makes it possible to model the necessary defective structure of any complexity, but the application to the elements in the lower half of the Periodic table due to the large number of electrons in heavy atoms is more difficult than to lighter atoms. Bismuth imposes certain restrictions on the choice of wave functions. Due to the presence of a large number of core electrons, which do not play a significant role in chemical behavior, we decided on the use of effective nuclear potentials (ECP).

The most applicable basis sets are compressed sets of atomically centered Gaussian functions: the universal basis (UGBS), the Christiansen-Ross-Ermler-Nash-Bursten set (CRENBL) and the Karlsruhe "def2" basis sets with ECP, which are recommended to be used from Na to Bi [13].

4. Results and discussion

To calculate the density of states in the vicinity of the forbidden zone, an effective nuclear potential was used, which makes it possible to significantly reduce the cost of machine time and use large nanoclusters.

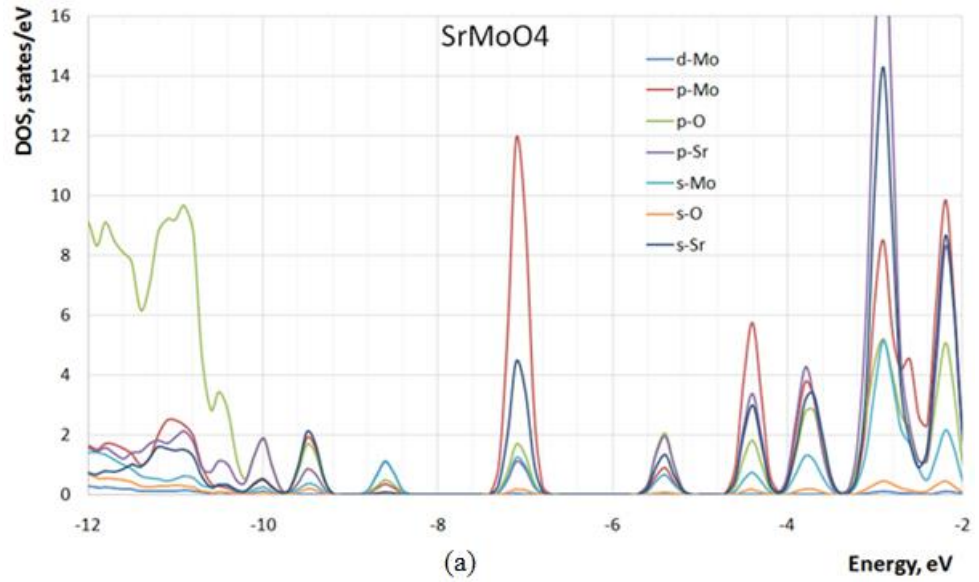
Figure 1 shows the PS (density of states) spectra in the vicinity of the ZZ for the clusters "$SrMoO_4$", "$SrMoO_4$-H", "$SrMoO_4$-BiH" and "$BiSrMoO_4$", the broadening parameter was assumed to be 0.1 eV. The values of ΔE_g (ZZ width) obtained experimentally and as a result of calculation by various methods are shown in table 1.

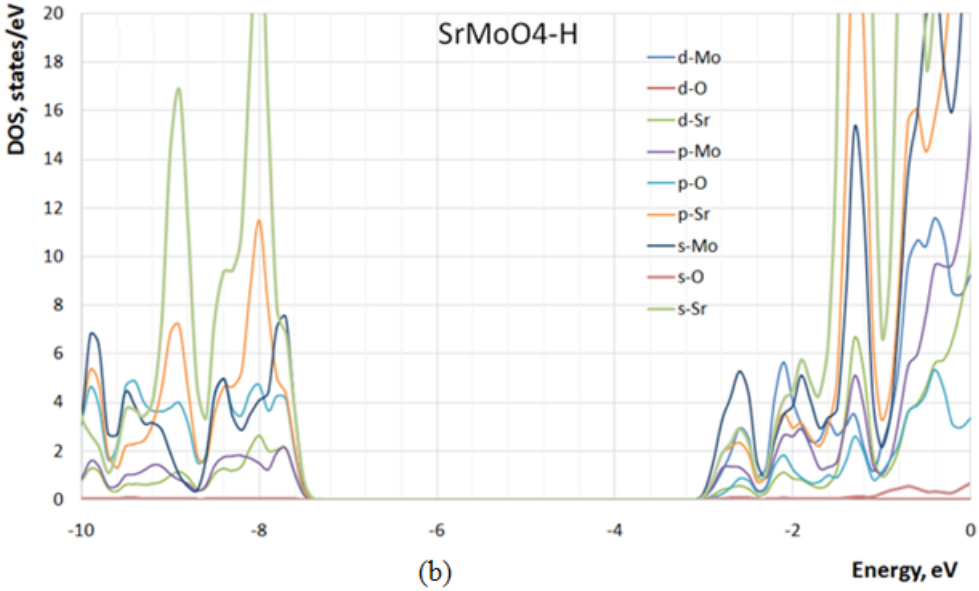
The distribution of the density of states in the vicinity of the SrMoO4 ZZ includes a number of additional local energy levels in the forbidden zone (figure 1(a)), which are eliminated when the broken bonds are saturated with hydrogen (figure 1(b)). The introduction of bismuth does not lead to the formation of local levels in the ZZ, a decrease in the value of ΔE_g occurs due to an overexpression of the electron density.

Table 1. Values of the forbidden zone width $Sr_{1-3x}Bi_{2x}MoO_4$.

Composition	Method	E_g, eV	Research data, eV
$SrMoO_4$	calculation	5.1	submitted work
	experiment	4.4	[12]
	calculation	5.35	[14]
	calculation	4.2	[14]
	experiment	3.26	[12]
$Sr_{0.925}Bi_{0.05}MoO_4$	experiment	3.27	[12]
$Sr_{0.85}Bi_{0.10}MoO_4$	experiment	3.26	[12]
$Sr_{0.70}Bi_{0.20}MoO_4$	experiment	3.17	[12]
$Sr_{0.55}Bi_{0.30}MoO_4$	experiment	3.01	[12]
$Sr_{0.40}Bi_{0.40}MoO_4$	experiment	4.32	[9]

$SrMoO_4$	experiment	3.70	[9]
$SrMoO_4$:2.5%Bi^{3+}	experiment	3.52 -	[9]
$SrMoO_4$:5.0%Bi^{3+}	experiment	3.42 -	[9]
$SrMoO_4$:7.5%Bi^{3+}	calculation	4.1	submitted work
$Sr_{0.70}Bi_{0.20}MoO_4$	calculation	2.5	submitted work
$Sr_{0.40}Bi_{0.40}MoO_4$	calculation	4.93	[15]
$BaMoO_4$	calculation	4.10	[15]
$BaMoO_4$ distortion	calculation	4.92	[16]





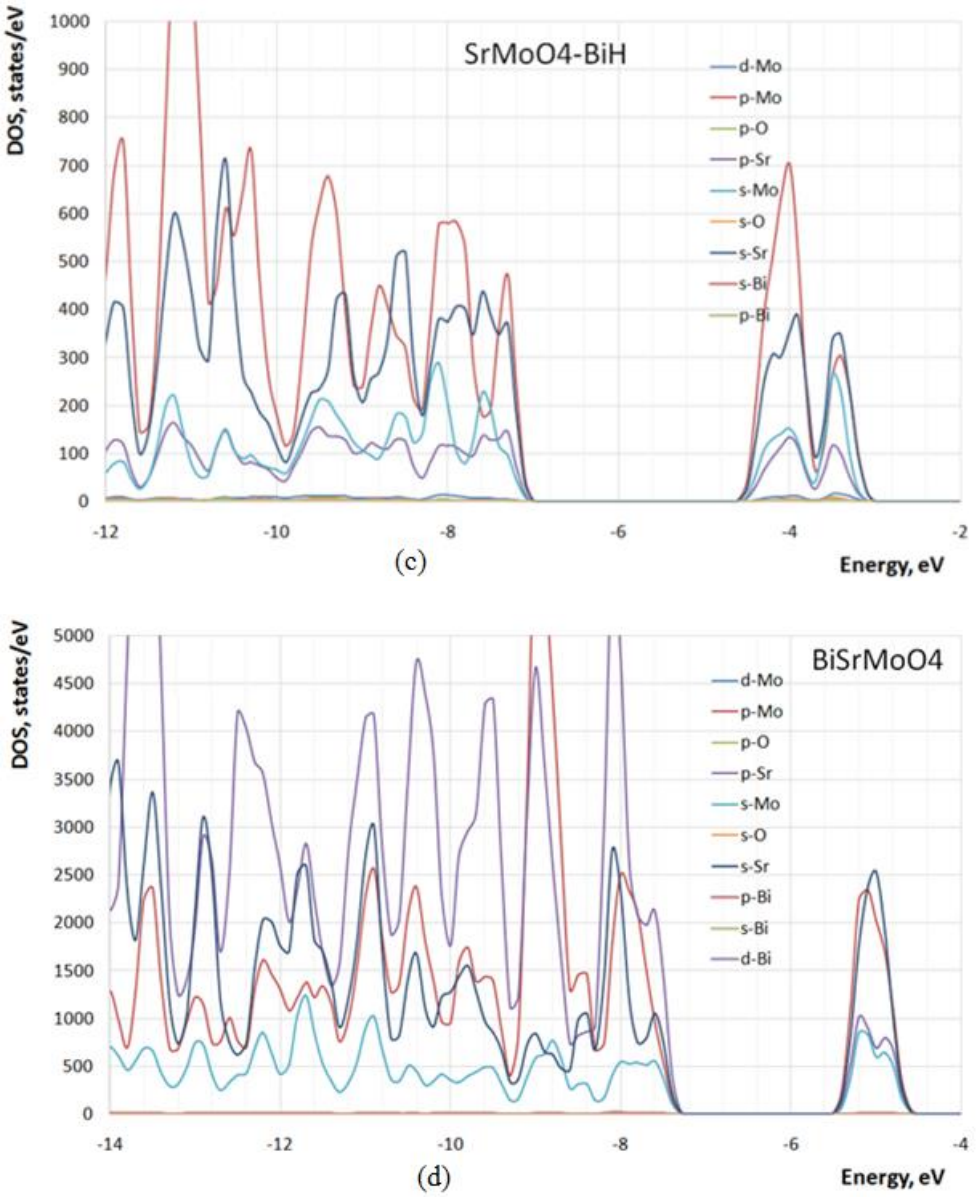


Figure 1. Partial electron density of states: for a cluster "$SrMoO_4$" (a), for a cluster "$SrMoO_4$-H" (b), for a cluster "$SrMoO_4$-BiH" (c), for a cluster "$BiSrMoO_4$"(d).

The decrease in ΔEg when bismuth is introduced into the structure of strontium molybdate is shown for the Sr1-xBixMoO4+x/2 series in [8] from the reflection spectra, by approximating the linear sections of the Tautz function. The analysis of DOS [14, 15, 16, 17] indicates that the upper part of the valence band consists mainly of O orbitals ($2p_x$, $2p_y$ and $2p_z$), the smaller contribution is made by the Ca and Mo orbitals. The lower part of the conduction band is obtained mainly from the Mo 4d orbital. Comparison with our results (figure 1) can be associated with a large contribution of the interelectron interaction in quantum chemical methods: oxygen makes an insignificant contribution to the formation of the boundary levels of the ZZ.

The introduction of bismuth (figures (1c) and (1d)) leads to a significant narrowing of the band gap (table 1), which can be associated with a distortion of the crystal lattice. The same effect was found in [15], where theoretical calculations gave a value of ΔE_g=4.93 eV for BaMoO4, which does not contain dislocations, and in a distorted structure, ΔE_g=4.10 eV was obtained. The effect of surface treatment

[18] (a change in the surface state contributes to an increased concentration of small defects) on the PL spectra in $CaMoO_4$ is observed. The influence of the disordering of the structure on the width of the ZZ was also noted in [14]. Consequently, the substitution of strontium bismuth in SrMoO4 molybdenum, accompanied by the generation of catonic vacancies, affects the energy parameters of polycrystalline samples $Sr_{1-3x}Bi_{2x}MoO_4$.

5. Conclusion

The large variation in the estimation of the band gap width is not so much due to the unreliability of experimental and computational methods, it's about the object itself. The plastic structure of the neck allows generating its own or introducing impurity bulk and surface defects that affect the electronic structure, redistribute the electron density and create local levels in the band gap. Thus, there is a way to control the properties of materials by regulating the electron density.

Acknowledgments

The synthesis, certification and experimental determination of the functional characteristics of the materials was carried out with the support of the grant of the Russian Research Foundation 20-73-10048.

The work was carried out using the equipment of the Centre for Collective Use of the North Caucasus Federal University with the financial support of the Ministry of Education and Science of Russia, the unique identifier of the project RF----2296.61321X0043 (agreement No. 075-15-2021-672).

References

[1] Danevich F A, Georgadze A Sh, Kobychev V V, Kropivyansky B N and Nagorny S S 2006 Application of $PbWO_4$Crystal Scintillators in Experiment to Search for 2β Decay of 116cd *Nuclear Instruments and Methods in Physics Research A* **556** 259-65

[2] Shimamura K, Sato H, Bensalah A, Machida H, Sarukura N and Fukuda T 2002 Growth of Ce-Doped Colquiriite- and Scheelite-Type Single Crystals for Uv Laser *Applied Optics Materials* **19(1)** 109-16

[3] Neiman A Ya, Pestereva N N, Sharafutdinov A R and Kostikov Yu P 2005 Conduction and Transport Numbers in Metacomposites $MeWO_4 \cdot WO_3$ (Me=Ca, Sr, Ba) *Russian Journal of Electrochemistry* **41(6)** 598-611

[4] Bin J, Liu H, Mei L, Liang L, Gao H, Li H and Liao L 2019 Multi-Color Luminescence Evolutionand Efficient Energy Transfer of Scheelite-Type $LiCaGd(WO_4)_3:Ln^{3+}$ (Ln=Eu, Dy, Tb) Phosphors *Ceramics International* **45(2)** 1837-45

[5] Yao W F and Ye J H 2006 Photophysical and Photocatalytic Properties of $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$ Solid Solutions *The Journal of Chemical Physics B* **110(23)** 11188-95

[6] Vidya S, John A, Solomon S and Thomas J K 2012 Optical and dielectric properties of $SrMoO_4$ Powders Prepared by the Combustion Synthesis Method *Advanced Materials Research* **1(3)** 191-204

[7] Gürmen E, Daniels E, King J S 1971 Crystal Structure Refinement of $SrMoO_4$, $SrWO_4$, $CaMoO_4$, and $BaWO_4$ by Neutron Diffraction *The Journal of Chemical Physics* **55** 1093-7

[8] Mikhaylovskaya Z A, Buyanova E S, Petrova S A, Kuznetsova Yu A and Piankova D V 2019 Synthesis and Properties of$(Ca/Sr)_{1-3x}Bi_{2x}MoO_4$SolidSolutions *Inorganic Materials* **55(10)** 1020-6

[9] Wang Y, Xu H, Shao C and Cao J 2016 Doping Induced Grain Size Reduction and Photocatalytic Performance Enhancement of $SrMoO_4:Bi^{3+}$ *Applied Surface Science* **392** 649-57

[10] Mikhaylovskaya Z A, Buyanova E S, Sokolenko E V, Sliusarev G V, Petrova S A and Zatsepin A F 2020 Effect of Bismuth Addition on the Crystal and Electronic Structure of Strontium Molybdate *Russian Journal of Physical Chemistry A* **94(12)** 2502-9

[11] Sokolenko E V and Slyusarev G V 2019 Modeling of Structural Defects in Silicon Carbide *Inorganic Materials* **55(1)** 19-31

[12] Mikhaylovskaya Z A, Buyanova E S, Petrova S A and Nikitina A A 2018 Sheelite-Related

Strontium Molybdates: Synthesis and Characterization *Chimica Techno Acta* **5(4)** 189-95
[13] Wadt W R and Hay P J 1985 Ab Initio Effective Core Potentials for Molecular Calculations - Potentials for main group elements Na to Bi *The Journal of Chemical Physics* **82** 284-98
[14] Errandonea D, Gracia L, Lacomba-Perales R, Polian A and Chervin J C 2013 Compression of Scheelite-Type $SrMoO_4$ Under Quasi-Hydrostatic Conditions: Redefining the High-Pressure Structural Sequence *Journal of Applied Physics* **113(12)** 123510
[15] Sczancoski J C, Cavalcante L S, Marana N L, da Silva R O, Tranquilin R L, Joya M R, Pizania P S, Varela J A, Sambrano J R, Siu Li M, Longo E and Andrés J 2010 Electronic Structure and Optical Properties of $BaMoO_4$ Powders *Current Applied Physics* **10** 614-24
[16] Oliveira F K F, Oliveira M C, Gracia L, Tranquilin R L, Paskocimas C A, Motta F V, Longo E, Andres J and Bomio M R D 2018 Experimental and Theoretical Study to Explain the Morphology of $CaMoO_4$ Crystals *Journal of Physics and Chemistry of Solids* **114** 141-52
[17] Rabuffetti F A, Culver S P, Suescun L and Brutchey R L 2014 Structural Disorder in $AMoO_4$ (A = Ca, Sr, Ba) Scheelite Nanocrystals *Inorganic Chemistry* **53(2)** 1056-61
[18] Paradelasa S M V, Gonçalvesa R F, Mottab F V, Limac R C, Lid M S, Longoe E, de Marquesa A P A 2017 Effects of Microwave-Assisted Hydrothermal Treatment and of Use of Cappingreagent on the Photophysical Properties of $SrMoO_4$ phosphors *Journal of Luminescence* **192** 818-26