Supplementary Material

Luminescent P_2O_5-MoO_3-Bi_2O_3-K_2O glasses and glass ceramics on their basis: insights from experimental and computational studies

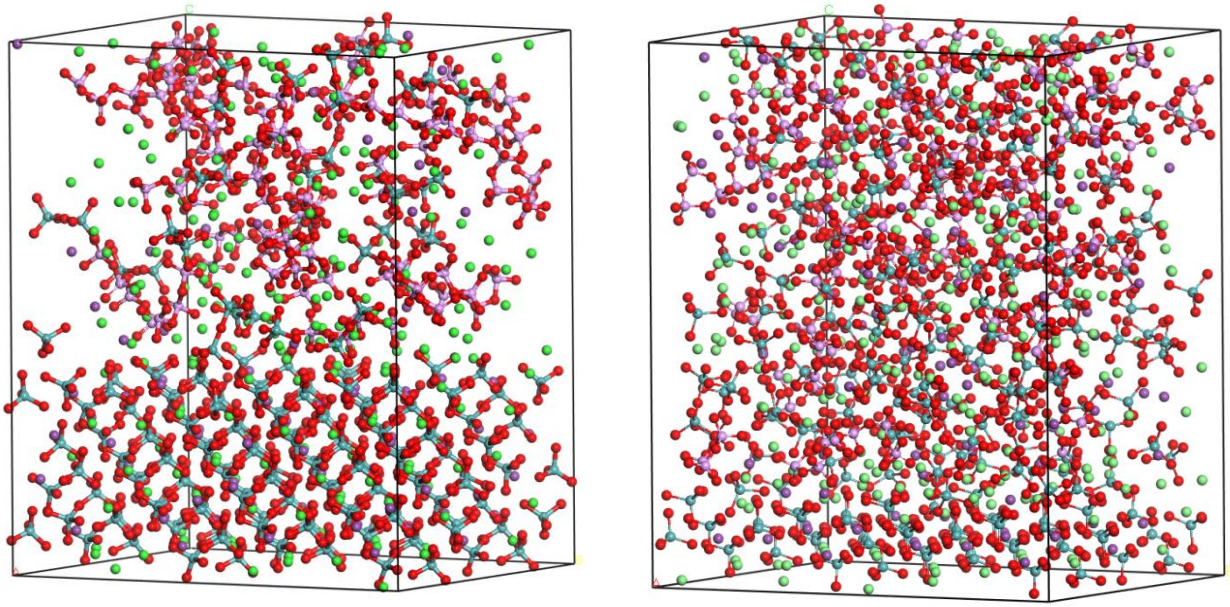
Yu. Hizhnyi[1,2], V. Borysiuk[1], V. Chornii[1,3*], A. Suchocki[4], K. Terebilenko[1], Ya. Zhydachevskyy[4], S. Nedilko[1]

[1]*Taras Shevchenko National University of Kyiv, 64/13 Volodymyrska st., 01601 Kyiv, Ukraine*
[2]*Donetsk Institute for Physics and Engineering of NAS of Ukraine, 03028, Kyiv, Ukraine*
[3] *National University of Life and Environmental Sciences of Ukraine, 03041 Kyiv, Ukraine*
[4]*Institute of Physics Polish Academy of Sciences, 32/46 al. Lotników, 02-668 Warsaw, Poland*

*Corresponding author, email: vchornii@gmail.com

1. Procedure of atomic structure modeling

To calculate the atomic structure of the interfacial layer, a three-dimensional periodic cell was constructed by adding a vacuum layer to the layer of cleaved crystal. To construct the crystal layer, the CleaveSurface procedure was applied to the unit cell of $KBi(MoO_4)_2$ crystal (structure parameters were taken from the literature [1]) with the following parameters selected: the direction of the normal to the cleavage surface (1 1 1), surface vectors U = (1 -1 0) and V = (1 2 -2). The thickness of the crystal layer was taken as 15.115 Å, and the thickness of the vacuum layer was 25.00 Å. Then, the vacuum layer was filled with glass fragments. With this choice of structural parameters, a quasi-orthogonal (α = β = 90°, γ = 95.09°) three-dimensional periodic cell with lattice parameters a = 26.2033, b = 34.1704, c = 42.3828 Å is formed. An example of the structure is shown in Fig. S1.



a) b)

Figure S1. Periodic cell constructed for interphase of $KBi(MoO_4)_2$@G5.69 system: initially filled (a) and after MD calculations (b) (K - green, Bi - violet, Mo - dark cyan, P - magenta, O – red color).

To calculate the atomic structure of glass, crystal atoms were removed from the specified cell and the entire cell was filled with glass of the appropriate composition. The experimental glass density (Table S1) was chosen as the initial parameter for modelling by the Amorphous Cell utility [2]. The choice of fragments for filling was based on the analysis of experimental FTIR spectra. The filling was carried out at a temperature of 300 K with the relative coordinates of the atoms within the individual molecular fragments frozen (to simplify further analysis). The rest of the Amorphous Cell utility options were set default.

For the case of cells with crystal/glass interphases, in order to more adequately account for the influence of the inner regions of the crystal on the properties of the interphase region, the atomic coordinates in the lower layer of the crystal (see Fig. S1) were "frozen". The thickness of such "frozen" layers was the same for all considered variants of glass components and was approximately 4 Å.

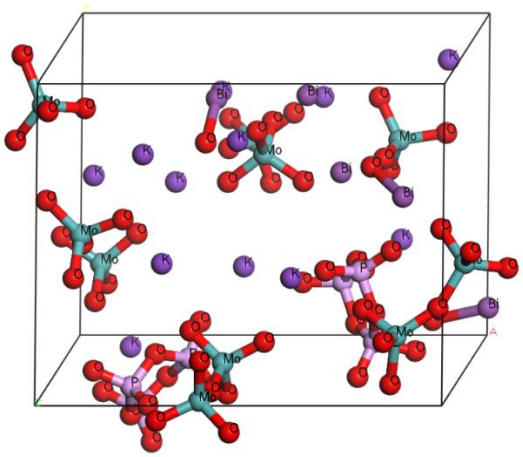


Figure S2. The view of 12x12x12 Å periodic cell of G5.69 glass, used in the DFT-based geometry optimizations.

Table S1. Chemical composition, experimental and calculated densities of synthesized and modeled samples of P_2O_5 - MoO_3-Bi_2O_3-K_2O glass system.

Glass number	Sample name	Chemical composition of the experimental glass samples (in mol %)				[O]/[P] ratio	ϱ_{exp} (g/cm³)	ϱ_{calc} (g/cm³)	Ratio of elements in the cell	
		x(P_2O_5)	y(MoO_3)	z(Bi_2O_3)	(1-x-y-z)(K_2O)				Type and quantity of atoms and molecular fragments used to fill unit cell	Chemical composition of modeled glass "cell" after MD
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
1	G1	36.49	11.17	1.00	51.54	3.71	2.91	2.82	51K, 1Bi, $4P_3O_9$, $4P_3O_{10}$, $3P_4O_{13}$, $2MoO_4$, $2Mo_2O_7$	$K_{45}P_{31}Mo_5Bi_1O_{121}$
2	G1.48	40.3 1	16.53	1.48	41.68	3.69	2.96	2.78	42K, 2Bi, $4P_3O_9$, $4P_3O_{10}$, $4P_4O_{13}$, $4MoO_4$, $2Mo_2O_7$	$K_{42}P_{40}Mo_8Bi_2O_{158}$
3		34.45	13.55	3.60	48.41	3.95	2.68	2.96	48K, 4Bi, $5P_3O_9$, $4P_3O_{10}$, $2P_4O_{13}$, $3MoO_4$, $2Mo_2O_7$	$K_{48}P_{35}Mo_7Bi_4O_{170}$
4	G4.12	23.01	46.02	4.12	26.85	6.35	2.97	3.00	27K, 4Bi, $2P_3O_9$, $3P_3O_{10}$, $2P_4O_{13}$, $11MoO_4$, $6Mo_2O_7$	$K_{27}P_{23}Mo_{23}Bi_4O_{160}$
5		27.18	36.24	4.86	31.71	5.35	3.23	2.89	64K, 9Bi $8P_3O_9$, $6P_3O_{10}$, $3P_4O_{13}$, $10MoO_4$, $4Mo_2O_7$,	$K_{65}P_{55}Mo_{36}Bi_9O_{314}$
6		29.89	29.89	5.35	34.87	4.85	3.18	3.01	70K, 11Bi, $6P_3O_9$, $6P_3O_{10}$, $6P_4O_{13}$, $10MoO_4$, $10Mo_2O_7$	$K_{70}P_{60}Mo_{30}Bi_{11}O_{302}$
7	G5.69	31.79	25.43	5.69	37.09	4.55	3.07	2.87	37K, 6Bi $5P_3O_9$, $4P_3O_{10}$, $4P_4O_{13}$, $5MoO_4$, $4Mo_2O_7$,	$K_{37}P_{33}Mo_{13}Bi_6O_{185}$

Table S2. Parameters of interatomic interaction (Forcefield Types [2]) used in MD calculations.

Елемент	**Forcefield type, description**
Mo	Mo3+6, molybdenum tetrahedral, +6 oxidation state
O	O_3_z, oxygen, tetrahedral, in zeolites
P	P_3+5, phosphorous tetrahedral, +5 oxidation state
Bi	Bi3+3, bismuth tetrahedral, +3 oxidation state
K	K_, potassium

References

[1] Klevtsov, P.V.; Vinokurov, V.A.; Klevtsova, R.F. Double Molybdates and Tungstates of Alkali Metals with Bismuth, $M^{+}Bi(TO_4)_2$. *Kristallografiya*, **1973**, *18*, 1192–1197.

[2] BIOVIA Materials Studio. An Integrated, Multi-scale Modeling Environment. https://www.3ds.com/products-services/biovia/products/molecular-modeling-simulation/biovia-materials-studio (accessed: 22.01.2025).