Computational investigation of atomic and electronic structures of phosphate-based crystal-glass composites

V. Chornii[1,2,*], V. Boyko[1], S.G. Nedilko[2], V. Borysyuk[2], Yu. Hizhnyi[2], Ya. Zhydachevskyy[3]

[1]National University of Life and Environmental Sciences of Ukraine, 15 Geroiv Oborony st., Kyiv, Ukraine

[2]*Taras Shevchenko National University of Kyiv, 64/13 Volodymyrska st., Kyiv, Ukraine*

[3]*Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, Warsaw 02-668, Poland*

* vchornii@gmail.com; vchornii@nubip.edu.ua

Abstract

Motivation

The interphase layers greatly determine the physical characteristics of composite materials, particularly, such as nanostructured glass-ceramics. These characteristics are difficult to predict using only general knowledge about atoms, ions or molecules interactions. At the same time, the mutual diffusion of component atoms can be effectively modeled in the molecular dynamics (MD) calculations. The further electronic structure calculations for the obtained atomic structures allow obtaining relevant micro and macro-characteristics of such layers.

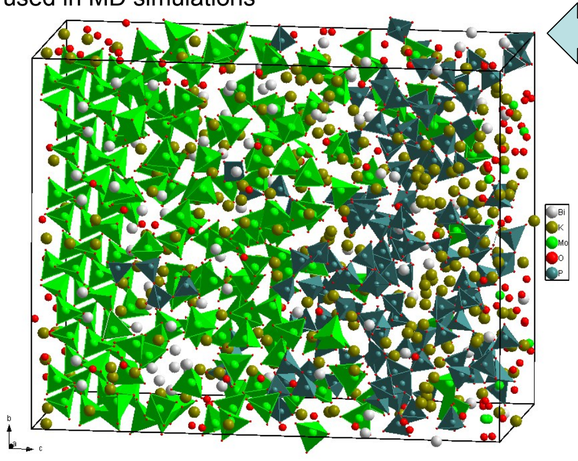
Methods of calculations

The computational studies of the atomic and electronic structures of glasses and crystal-glass interphases were carried out using Materials Studio 2019 package [1]. Two types of composites were considered: a) $KBi(MoO_4)_2$ crystal - K_2O-P_2O_5-MoO_3-Bi_2O_3 glass; and b) $K_2Eu(PO_4)(WO_4)$ crystal - K_2O-P_2O_5-WO_3-V_2O_5 glass. The atomic structures of initial glasses and interphases were calculated by MD methods implemented in Amorphous Cell and Forcite programs. The electronic structure calculations were performed in the DFT approximation using the band-periodic plane wave pseudopotential method CASTEP for which the cells of smaller sizes were used. The partial densities of states, spatial distributions of electron densities were calculated with use of GGA-PBE exchange-correlation functional.

Results

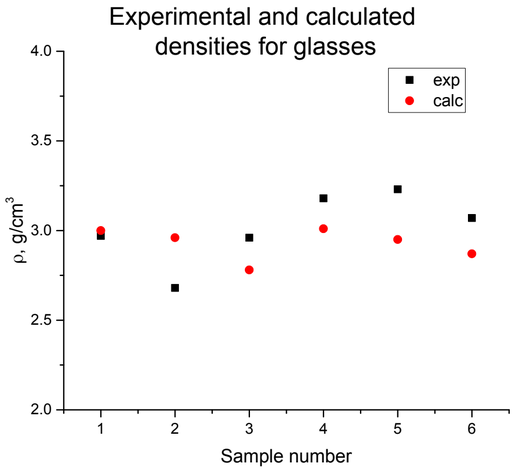
K_2O-P_2O_5-MoO_3-Bi_2O_3 system

Periodic cell of $KBi(MoO_4)_2$ crystal/glass interface used in MD simulations

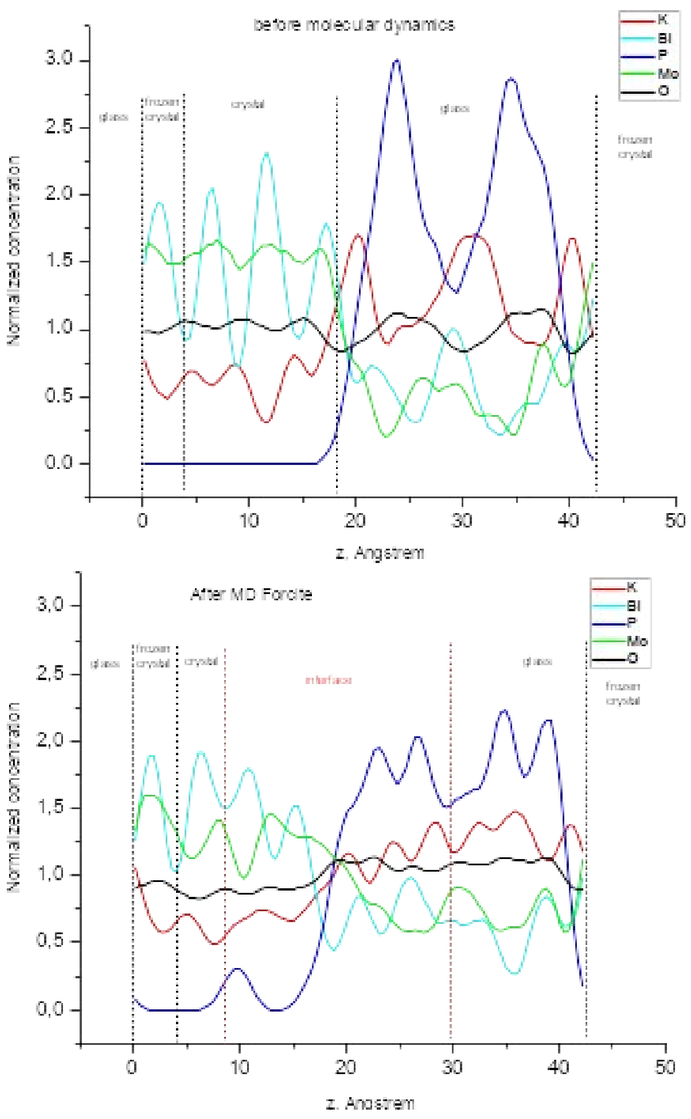


Atomic structure of glasses and glass ceramics in K_2O-P_2O_5-MoO_3-Bi_2O_3 system was simulated with using of combinations of P_2O_7, P_3O_9, P_3O_{10}, P_4O_{13}, MoO_4 and Mo_2O_7 fragments, while K and Bi were introduced to cell as separate atoms according to experimental compositions of glasses.
Satisfactory correlation between experimental and calculated densities and XRD patterns was found.

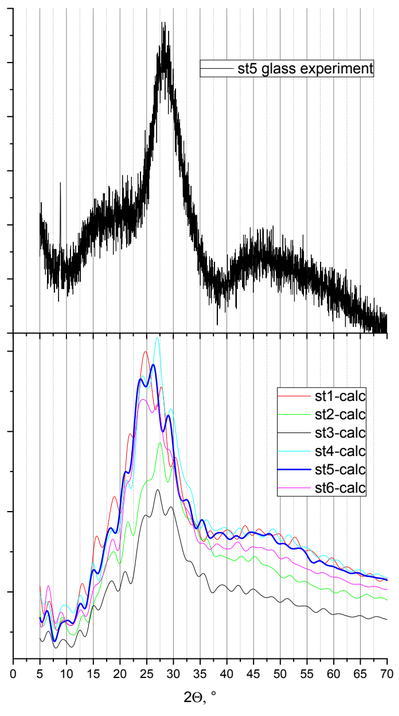
Experimental and calculated densities for glasses



Elements concentration profiles of the interface cells before and after MD simulations

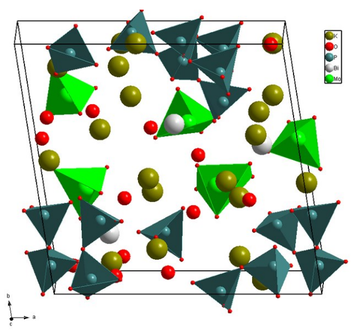


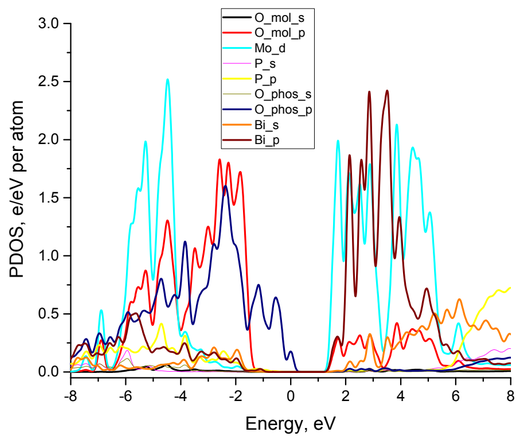
Experimental and calculated XRD patterns for glasses of K_2O-P_2O_5-MoO_3-Bi_2O_3 system



Partial densities of electronic states of crystal/glass interface calculated by DFT method

Periodic cell of crystal/glass interface used in DFT calculations

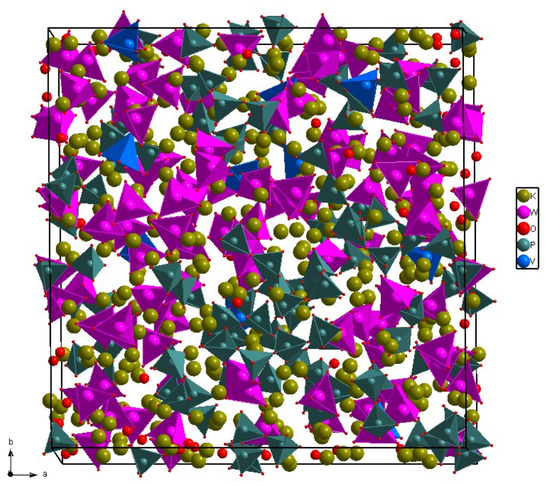


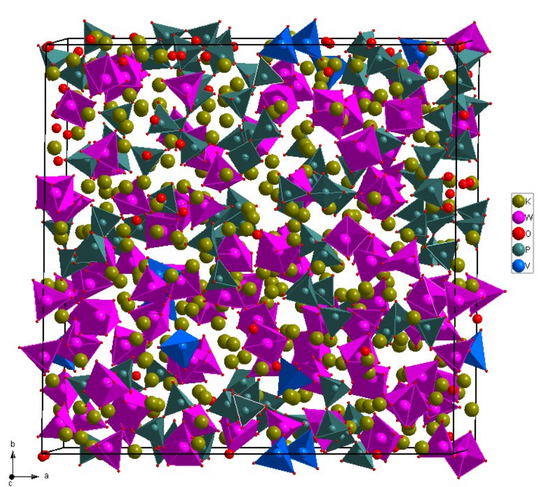


K_2O-P_2O_5-WO_3-V_2O_5 system

Molecular fragments used for initial packing of periodic cells of K_2O-P_2O_5-WO_3-V_2O_5 glasses used in MD simulations:

1) K, WO_4, VO_4, P_2O_7, P_3O_{10}, P_4O_{13} 2) K, WO_4, WO_6, VO_4, P_2O_7, P_3O_{10}, P_4O_{13}

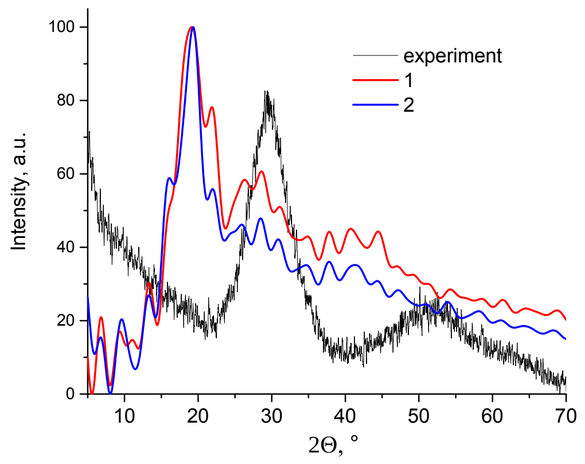




ρ_1^{calc} =3.35 g/cm^3 ρ_2^{calc} =3.26 g/cm^3

ρ^{exp} =3.73±0.04 g/cm^3

Experimental and calculated XRD patterns for glass of K_2O-P_2O_5-WO_3-V_2O_5 system



Conclusions

- Molecular dynamic methods allow to obtain the atomic structures of phospho-molybdate glasses and glass-ceramics.
- Correlation between calculated and experimental data for density and XRD patterns can serve as criteria for choice of glass and glass-ceramics initial composition and other calculation parameters.
- Content of K, WO_4, WO_6, VO_4, P_2O_7, P_3O_{10}, P_4O_{13} fragments greatly determines the calculated XRD patterns for K_2O-P_2O_5-WO_3-V_2O_5 system in contrast to K_2O-P_2O_5-MoO_3-Bi_2O_3, one.
- Spatial width of the interface region can be determined from element concentration profiles calculated by MD method.
- Diffusion of phosphate groups into molybdate crystal region is clearly observed in case of phospho-molybdate system.
- Calculated PDOSes show that the optical processes in the interface (interphase) region take place in complex PO_4 + MoO_4 centers.

Acknowledgements

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References:

[1] BIOVIA, Dassault Systèmes, Materials Studio 2019 (version 19.1.0.5), San Diego: Dassault Systèmes, 2018.