Atomic and electronic structures of interfaces in “K_2O-P_2O_5-MoO_3-Bi_2O_3 glass - $KBi(MoO_4)_2$ crystals” glass-ceramics

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Abstract

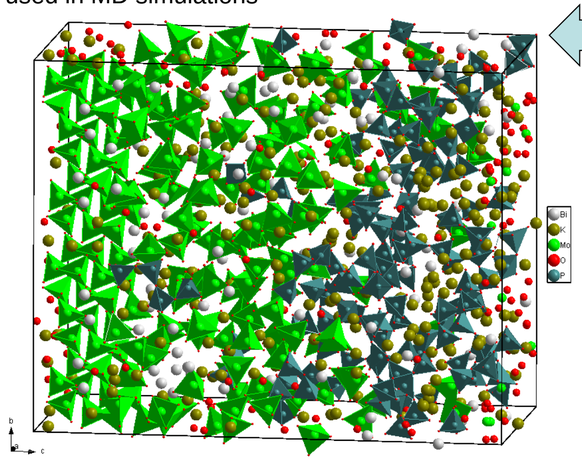
Oxide glass ceramics are composite materials perspective for various applications, in particular, in electronics, optical thermometry and biomedicine. The properties of oxide glass-ceramics are largely determined by processes in the "interface/interphase region", which has an atomic structure different from the structure of both crystalline and glass components. The mutual diffusion of component atoms can be effectively modeled in calculations using the molecular dynamics (MD) methods. Further application of the electronic structure calculation methods to the obtained atomic structures (when coordinates of atoms optimized in MD approach are input parameters of ES calculations) allows to calculate the most important micro- and macro-characteristics of the interphases layers.

In this report we present results of the computational studies of atomic and electronic structures of interfaces in “$KBi(MoO_4)_2$ crystal / K_2O-P_2O_5-MoO_3-Bi_2O_3 glass” glass-ceramic composite material. The atomic structures of interface layers of composites were calculated by MD methods implemented in Biovia Materials Studio program package [1]. The calculations were performed for ~20x20x45 Å three-dimensional periodic cells, which contained 300-500 atoms of composites. The electronic structure calculations were performed in the DFT approximation using the band-periodic plane wave pseudopotential method, for which the cells of smaller size ~12x12x12 Å were used. Calculations of the excited electronic states energies and optical absorption spectra of particular oxyanionic molecular groups of interface regions were performed by the TD-DFT method.

Relationships between atomic and electronic structures of interface (interphases) layers and optical characteristics of studied composites are discussed.

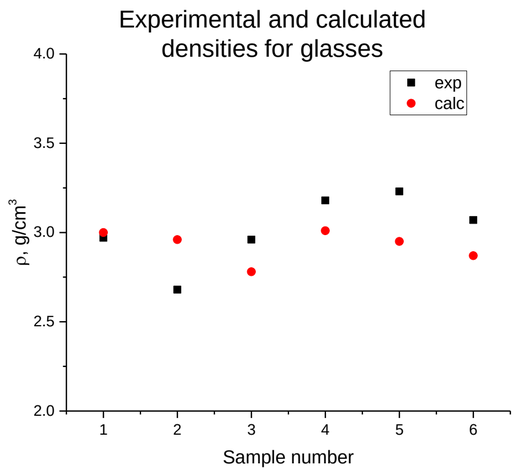
Results

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

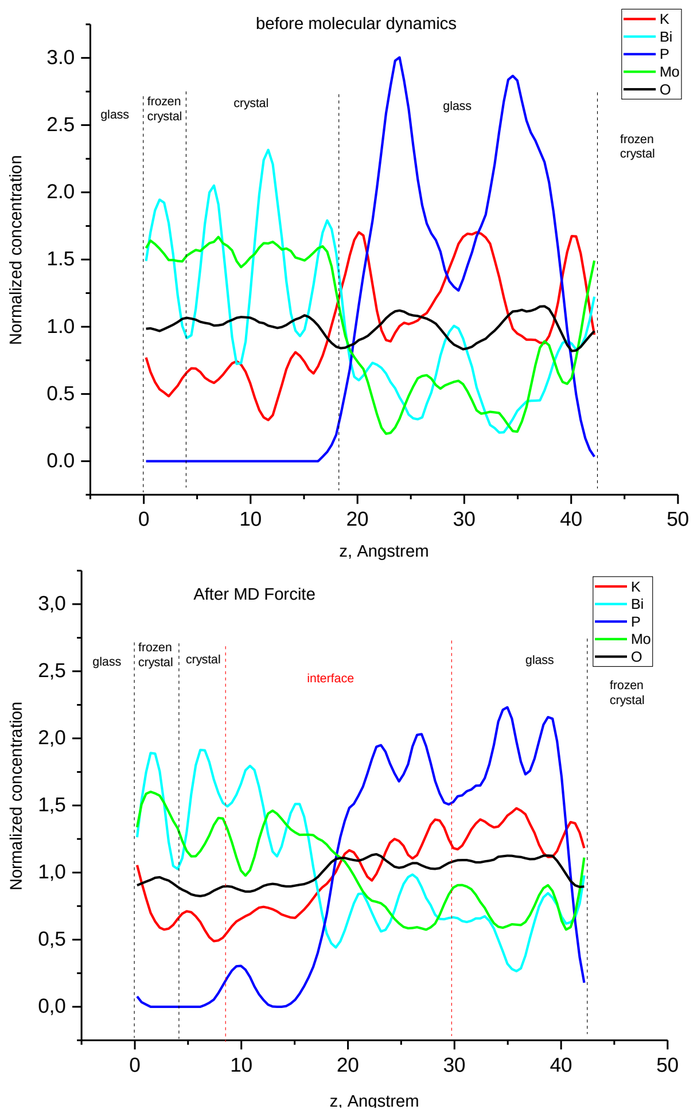


Atomic structure of glasses and glass ceramics in K_2O-P_2O_5-MoO_3-Bi_2O_3 system was simulated with using of combinations of P_2O_7, P_3O_9, P_3O_{10}, P_4O_{13}, MoO_4 and Mo_2O_7 fragments, while K and Bi were introduced to cell as separate atoms according to experimental compositions of glasses.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

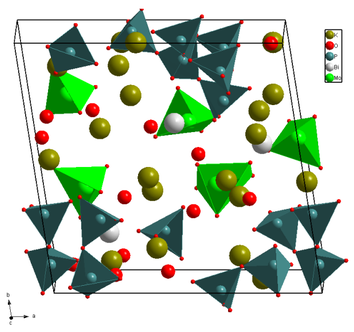
Experimental and calculated densities for glasses



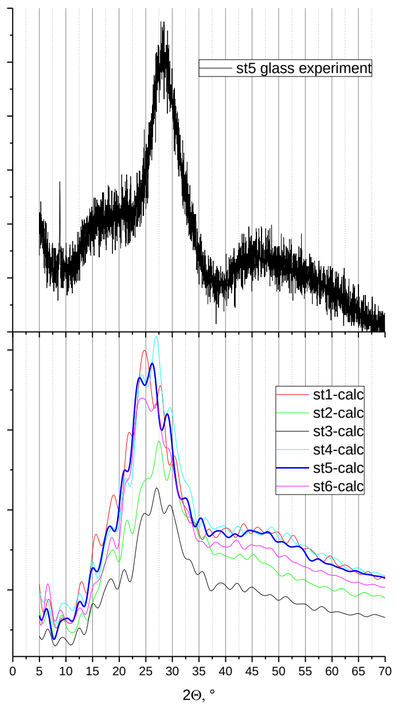
Elements concentration profiles of the interface cells before and after MD simulations



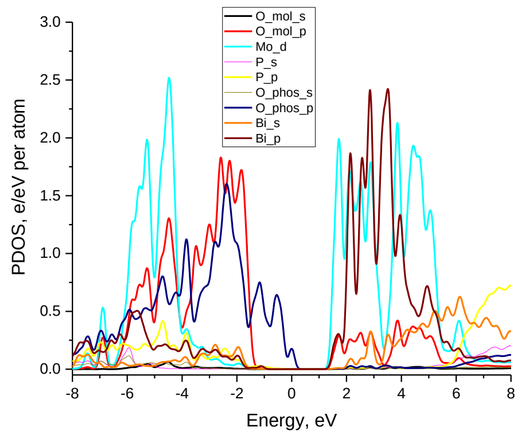
Periodic cell of crystal/glass interface used in DFT calculations

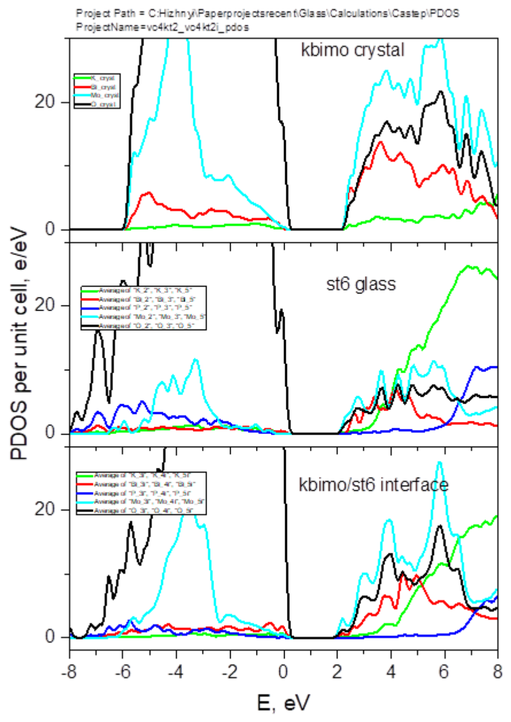


Experimental and calculated XRD patterns for glasses of K_2O-P_2O_5-MoO_3-Bi_2O_3 system

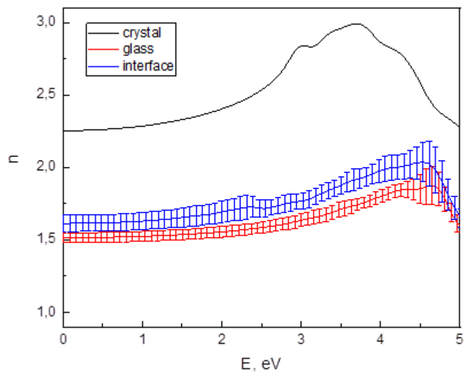


Partial densities of electronic states of crystal/glass interface calculated by DFT method





Calculated PDOS of glass, crystal and interface regions of studied glass-ceramics



Calculated refraction indexes of glass, crystal and interface regions of studied glass-ceramics

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.
- 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.