TD-DFT computational studies of the optical properties of luminescence centers in Bi-containing glass-ceramics

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Abstract

Theoretical modeling of the electronic structure of interphases in heterostructure composites is powerful tool in elaboration of novel technologically perspective optical materials [1]. This report presents results of the excited electronic states and optical spectra calculations of molybdate groups MoO4 and Bi ions, which are currently considered as possible centers of luminescence of glass-ceramic composite material "$KBi(MoO_4)_2$ crystal@phosphate-molybdate glass of K_2O-P_2O_5-MoO_3-Bi_2O_3 system". The atomic and electronic structures of the crystal, glass and interphase layers of composites were obtained in earlier studies using molecular dynamics and band-periodic DFT methods.

The calculations were carried out at the Time-Dependent Density Functional Theory (TD-DFT) within molecular cluster approach. The geometry-optimized calculations were carried out using Gaussian software package [2]. Excited electronic states of molybdate groups MoO_4 or Bi ions in crystal, glass and interphase layers were calculated using the two-level ONIOM-2 approach. The quantum mechanical (QM) region comprised the atoms of molybdate groups MoO_4 or Bi ions, while the mechanical (MM) region comprised all atoms of crystal, glass and interphase layers (~2500 atoms). The electronic embedding was used in order to take into account electrostatic interaction between the QM and MM regions, i.e., the atoms of the QM region were treated by TD-DFT calculations, while the atoms of the MM region were treated as partial charges contributing to the quantum-mechanical Hamiltonian.

Calculations were carried out for 10 structures of glass and interphace regions of the composite and then averaged to obtain statistically valuable results. The excited states of the MoO_4 groups and Bi ions in $KBi(MoO_4)_2$ crystal were also calculated using the same approach, method and approximations.

Results on the optical spectra for three different components of composite material (crystal, glass and interphase) are compared with experimental data in order to outline the properties inherent to each component. The origin of intrinsic luminescence in phosphate-molybdate glass-ceramics is discussed.

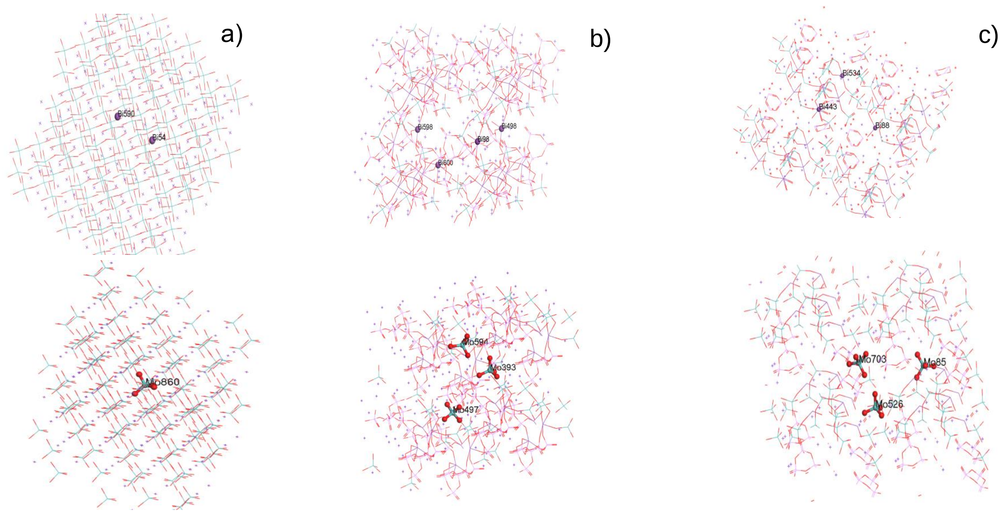


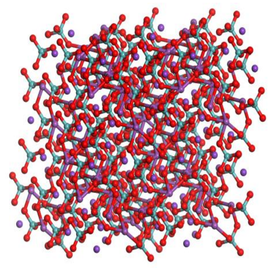
Fig.1. QM (ball and stick) and MM (stick) regions of $KBi(MoO_4)_2$ crystal clusters (a), phosphate-molybdate glass of a certain composition (b) and their interface (c) used in calculations of spectra of bismuth ions (top row) and molybdate groups (bottom row).

Calculation method

The computational modelling of excited electronic states and optical spectra of bismuth ions in phosphate-molybdate glass ceramics was performed using the quantum chemical method in the molecular cluster approach. Molecular clusters of $KBi(MoO_4)_2$ crystal, phosphate-molybdate glass of a certain composition and their interface.

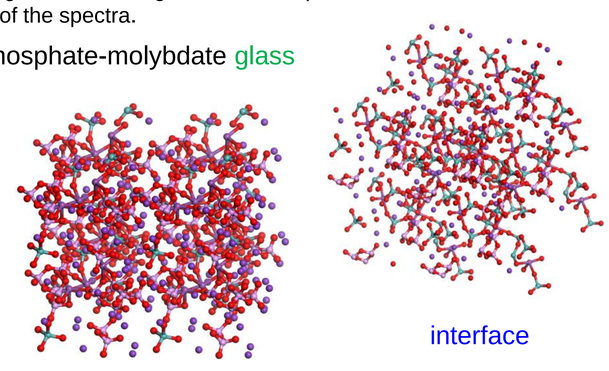
The energies of the excited electronic states and optical absorption spectra of bismuth ions were calculated by the TD-DFT method in the basis of Gaussian atomic functions using the quantum chemical software package Gaussian 09. The influence of the immediate environment on the calculated characteristics was taken into account using the ONIOM procedure, which is one of the variants of the QM/MM approach. In this approach, the system under consideration is divided into two parts - the domain of quantum mechanics (QM) and molecular mechanics (MM). For the atoms included in the QM domain, a quantum mechanical calculation of the electronic properties is performed, and all other atoms in the system are included in the MM domain and approximated in the calculation by point charges or dipoles on the nuclei. When calculating the spectra of bismuth in the KBi(MoO4)2 crystal, the QM region included two bismuth ions located in the central part of the cluster, and the MM region included all other atoms in the crystal cluster. Similarly, the QM and MM regions of the phosphate-molybdate glass clusters and the interface.

The LANL2DZ basis set and the B3LYP functional for approximating the exchange-correlation potential were used in the calculations of the spectra.



Molecular clusters of $KBi(MoO_4)_2$ crystal

phosphate-molybdate glass



interface

Results

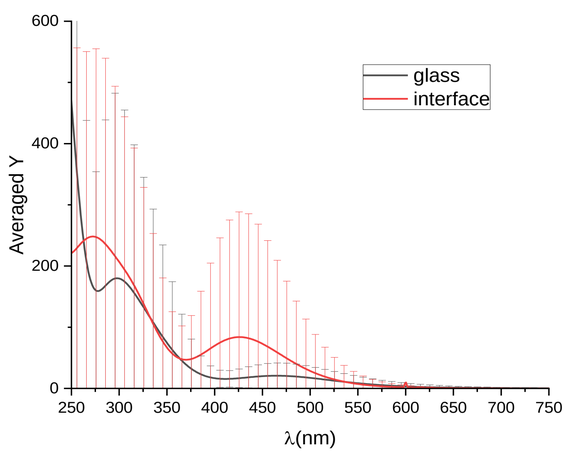


Fig.2. Averaged absorption spectra of bismuth atoms

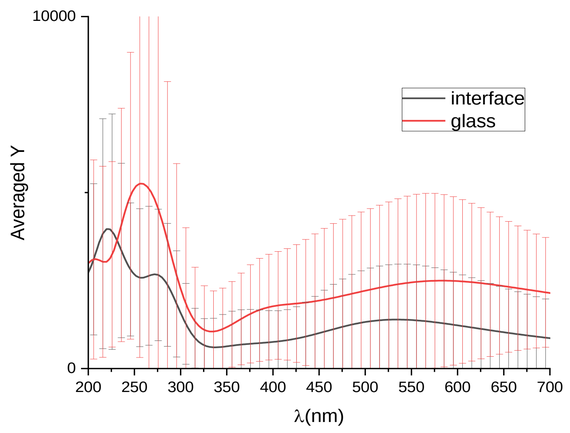


Fig.3. Averaged absorption spectra of molybdate group atoms

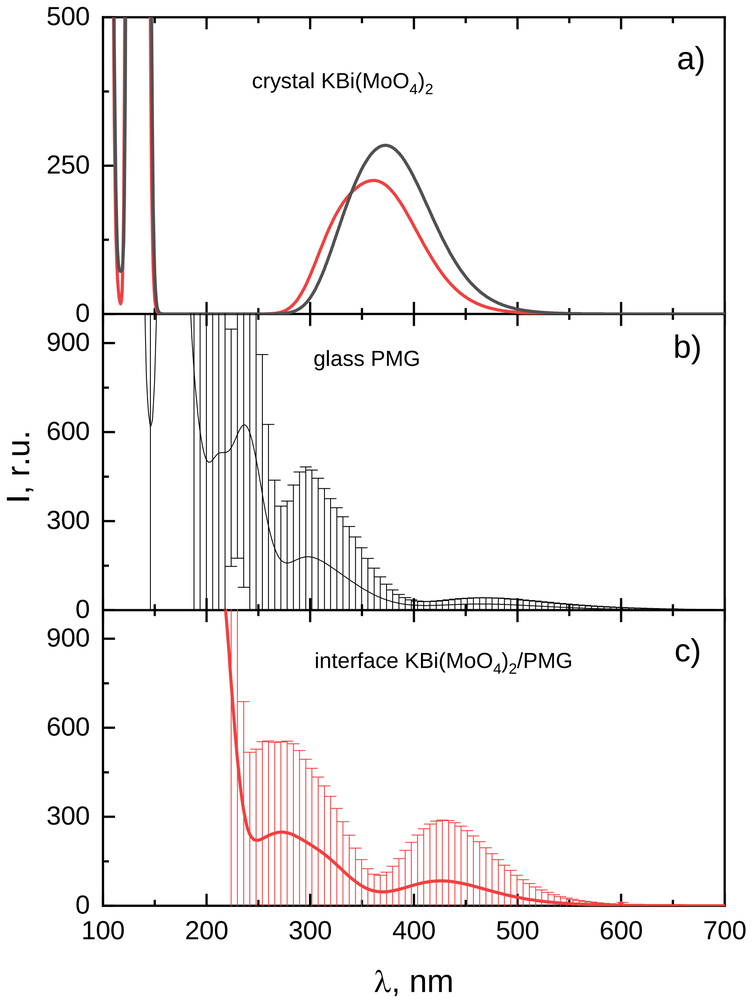


Fig.4. Absorption spectra of bismuth atoms in different parts of the composite: crystal (a), glass (b) and interface (c)

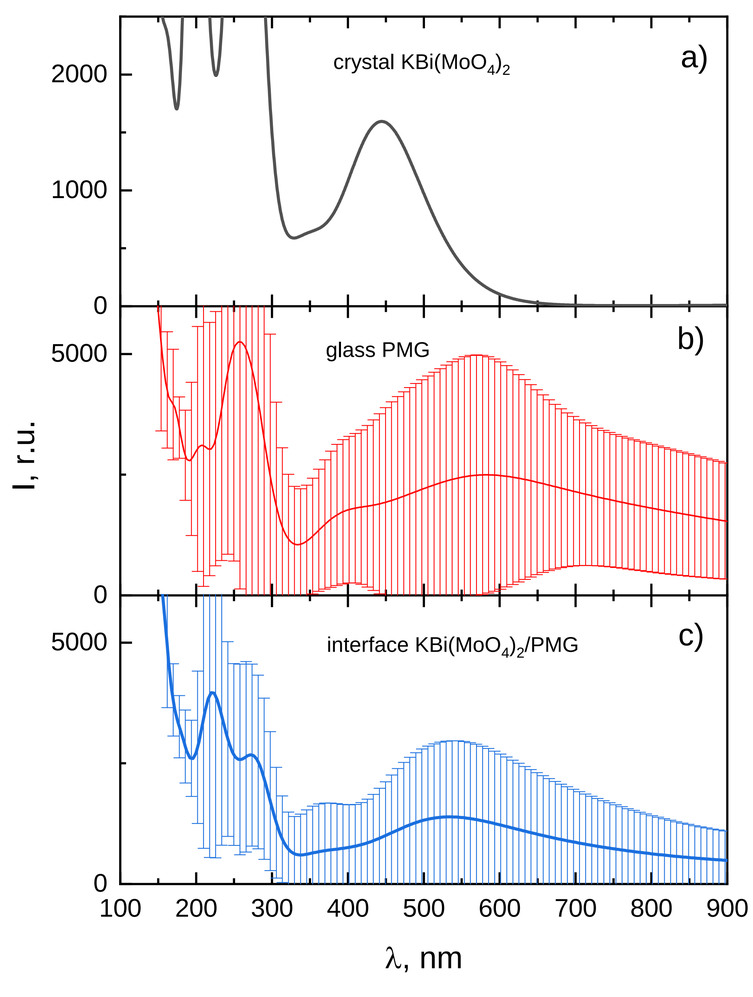


Fig.5. Absorption spectra of molybdate group atoms in different parts of the composite: crystal (a), glass (b) and interface (c)

Conclusions

According to the results of calculations, it was found that the optical absorption spectra of bismuth atoms and molybdate groups, which are possible luminescence centres of such glass ceramics, are significantly different in different areas of the composite material. In particular:

1) In the transition from glass to interface, the average value of the spectral position of the long-wavelength band maximum of bismuth atoms shifts towards shorter wavelengths, from 374 nm (in the case of glass) to 297 nm in the case of interface.
2) When moving from glass to the interface, there is also a shift in the average value of the maximum of the long-wave band of molybdate groups towards short wavelengths, from 589 nm (in the case of glass) to 377 nm in the case of the interface.
3) The calculated spectra of bismuth in the $KBi(MoO_4)$ crystal are characterised by a band in the region of 350-400 nm, which generally coincides with the experimental data.
4) The averaged spectra of bismuth atoms in glass are characterised by a band at 300 nm and a low-intensity band in the region of 400-550 nm. In contrast, in the interface, the calculated average spectra of bismuth atoms have distinct maxima at 270 and 430 nm.
5) In the case of molybdate groups, a significant difference in the averaged spectra exists when comparing the cases of crystal and amorphous components (glass or interface).

Acknowledgements

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References:

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