Excited states of luminescence centers in "$KBi(MoO_4)_2$ @phosphate-molybdate glass" ceramics

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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 MoO_4 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.

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