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Report on the DSc thesis titled

„Photostimulated processes in the volume and on the surface of alkaline earth metal bismuthates in heterogeneous systems“

submitted by Mr. Dmitry Sergeevich Shtarev in partial fulfilment of the degree of Doctor of Physical-Mathematical Sciences (DSc)

The dissertation of Dmitry Sergeevich Shtarev is devoted to the study of photostimulated processes in alkaline earth metals bismuthates, such as photocatalytic processes, photostimulated defect formation and luminescence. The exploration of the interconnection between these photochemical and photophysical processes is a distinctive feature and advantage of the studies presented in the thesis by D.S. Shtarev.

The novelty of the presented studies is confirmed by the fact that alkaline earth metals (Mg, Ca, Sr, Ba) bismuthates represent a new class of visible light active materials. Many of them were synthesized in this work for the first time. Also, the photocatalytic properties of these materials as well as their luminescence and photostimulated defect formation were established and studied for the first time. All samples were characterized using experimental methods and techniques corresponding to the high modern standards including analysis of the crystal structure (Raman spectroscopy and XRD including Rietveld X-rays analysis), morphology (SEM, BET) and energy structure (XPS, DRS), mass-spectrometry (ICP- MS) analysis of chemical composition of dispersed samples, as well as DTA, electrochemical impedance spectroscopy and so on.

The photocatalytic activity of the samples was evaluated using model reactions of phenol and acetaldehyde decomposition for photocatalyst–solution and photocatalyst–gas heterogeneous systems in accordance with ISO standards, as well as the CO₂ photoreduction. The photoactivity of the samples was evaluated on the basis of experimental results obtained by different experimental methods (chromatography, diffuse reflectance spectroscopy, luminescence) under the same conditions of irradiation of the samples in a given spectral range that confirmed the reliability of the obtained results and conclusions. Remarkably, that the author proposed and successfully implemented a

technique for measuring the spectra and kinetics of luminescence *in situ* under continuous actinic irradiation of the samples using the features of excitation and registration of luminescence. In general, from a methodological point of view, the work of Dmitry Sergeevich Shtarev is fully consistent with modern standards in the area of photoactive materials exploration and includes the synthesis of new materials, their comprehensive characterization, experimental studies by various complementary methods and interpretation of the results using modern theoretical concepts, as well as the results of quantum chemical calculations using the DFT approach.

The main results of the work are of a fundamental nature and can be formulated as following:

- Alkaline earth metal bismuthates of complex composition are a new subclass of visible light photocatalysts
- The photocatalytic activity of alkaline earth metal bismuthates with various alkaline earth metal cations increases with an increase of the atomic number of the cation
- Photocatalytic activity of alkaline earth metal bismuthates increases with an increase of the content of alkaline earth metal cations in the cationic substructure
 - Bismuthates of alkaline earth metals are characterized by a competition between the efficiencies of their luminescence (as a radiative physical pathway of excitation decay) and photocatalytic activity (as a chemical pathway of excitation decay)
- The variability of the conditions for the formation of alkaline earth metal bismuthate structures allows to control their composition, band structure, the degree of defectiveness of the cationic and anionic sublattices, and, as a result, the efficiency of photostimulated molecular processes on their surface.
- Bismuthates of alkaline earth metals are characterized by an atypical relationship (asymmetric Matsumoto plot) between the value of the band gap energy determined by the type of the metal and the position of the potentials of the top of the valence band and the bottom of the conduction band.

Thus, again, the experimental results obtained by D.S. Shtarev are reliable and the conclusions drawn on their basis are substantiated. However, while reading the text of the dissertation, the following questions arose:

- 1) During the study of the relationship between the intensity of luminescence and photocatalytic activity of strontium bismuthates $\text{Sr}_2\text{Bi}_2\text{O}_5$, $\text{Sr}_3\text{Bi}_2\text{O}_6$, and $\text{Sr}_6\text{Bi}_2\text{O}_{11}$, it was found that the last bismuthate, for which photoluminescence was not detected, demonstrates the highest photocatalytic activity. Could it be that the reason for this observation is a temperature quenching of the luminescence, which is strongest for $\text{Sr}_6\text{Bi}_2\text{O}_{11}$ comparing to $\text{Sr}_2\text{Bi}_2\text{O}_5$ and $\text{Sr}_3\text{Bi}_2\text{O}_6$ (Figure 85, page 183)
- 2) One of the most interesting and valuable results to predict the photocatalytic activity of new class photocatalysts is a new trend in the dependence of the position of the potentials of the bottom of the conduction band and the top of the valence band and the bottom of the conduction band on the band gap energy of alkaline earth metal bismuthates (Figure 143, page 168). These dependences are characterized by a slope of the straight lines $E_c(E_g)$ and $E_v(E_g)$ of the same sign, which is typical for similar dependences. At the same time, for all dependencies, there is a convergence of lines at $E_g = 0$. Which physical meaning can be given to a hypothetical structure of materials at the point $E_c(E_g = 0)$ and $E_v(E_g = 0)$?

As a summary I can conclude that the dissertation of Shtarev Dmitry Sergeevich on the topic "Photostimulated processes in the volume and on the surface of alkaline earth metal bismuthates in heterogeneous systems" meets the main requirements established by Saint-Petersburg State University for Doctor of Science degree, and Dmitry Sergeevich Shtarev deserves the award of the degree of Doctor of Physical and Mathematical Sciences in specialty 1.3.8. Condensed Matter Physics.



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