ESRF	Experiment title: Local structural environment and valence state of Bi into bismuth-doped glasses	Experiment number: **HC-2264**
Beamline: ID26	Date of experiment: From: 03.12.2015 to: 09.12.2015	Date of report
Shifts: 18	Local contact(s): Lucia Amidani	
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Scientific background. Bi-doped glasses and optical fibers are promising candidates for the role of an active medium in lasers and amplifiers with tunable properties. For example, by selecting the composition and the concentration of dopants it is possible to change the spectral range of the luminescence and to create the refractive index difference for waveguide structures.

Despite the progress in bismuth lasers producing and large number of researches devoted to the bismuth-activated optical materials the nature of the bismuth active centers (BAC) has not been yet understood. At present, there are several hypotheses concerning the origin of the near infrared emission from Bi-doped glasses: Bi+, Bi-clusters, BiO, Bi^{2-}, Bi^{2}_{2}- point defects and others. But none of them has been directly confirmed.

The main aim of our investigation was to obtain precise information on the oxidation state of Bi centers and its local structural environment in Bi doped glasses. X-ray absorption spectroscopy (XAS) is the best method, allowing to get such information, while using of high-energy resolution helps to understand electronic structure of Bi-centers, but not only its oxidation state.

Samples and experimental techniques. There were several groups of samples, which are glasses and preforms for fiber optics. The latter were fabricated by modified chemical vapor deposition (MCVD) and furnace chemical vapor deposition (FCVD) methods. In all investigated preforms and fibers the cladding was the silica glass, and the core was the bismuth-activated silicate matrix co-doped with alumina, germanium or phosphorus. $MgO\text{-}Al_2O_3\text{-}SiO_2$ glasses were prepared by the traditional melting–quenching method at different temperature and atmosphere; chalcogenide glasses were prepared by means solid-phase synthesis. We have also measured metallic Bi, Bi_2O_3, $NaBiO_3$, $Bi_4(GeO_4)_3$ as reference samples.

High-Energy Resolution Fluorescence Detected (HERFD) XAS experiments were performed at ID-26 by using two energy ranges: Bi L_{III} (13.419 keV), scanned line: $L_{\alpha 1}$ (L_3-M_5) (10.839 keV) and Bi L_I (15.711 keV), scanned line: $L_{\beta 3}$ (L1-M_3) (13.211 keV). All the samples have been placed in multi-cell sample holder, which was mounted in 45° to the incident beam. Emitted x-rays were analyzed and focused onto a detector by spherically bent single crystal wafers (Ge(844) at 82.11° for L_{III} edge and Si(880) at 77.84° for L_I edge). The sample-wafers-detector geometry is defined by the Rowland circles.

Both Extended x-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) spectra have been recorded, but since the main interest concerns electronic structure, which XANES more sensitive to, EXAFS data were obtained only for few samples.

Results. As far as we know, the HERFD for Bi compounds have been measured in this experiment for the first time even for the reference samples. We have observed well resolved additional peak D (Fig.1) between peaks B and C ($2p^{3/2} \rightarrow 6d$ transition) for all references.

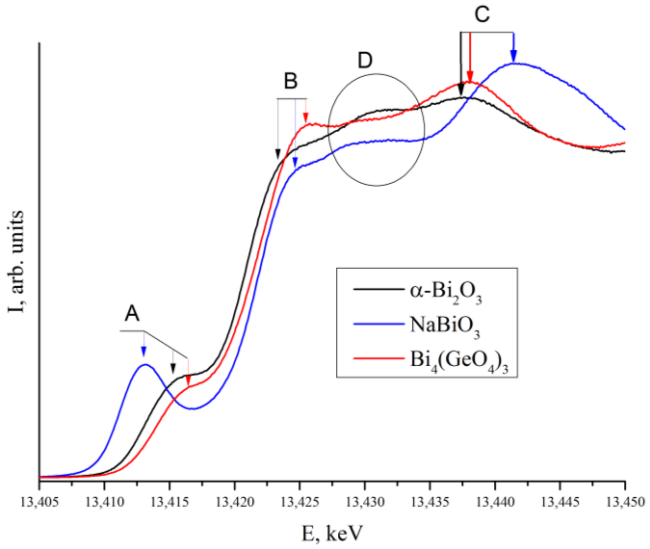

Fig.1. XANES spectra of references samples Bi_2O_3, $NaBiO_3$ and $Bi_4(GeO_4)_3$ Circle indicates the additional peak.

Concerning the other sample groups we have obtained the next preliminary results:

Al-Mg-silicate glasses

The glasses near cordierite ($Mg_2Al_4Si_5O_{18}$) composition: (22.2 mol% MgO- 22.2 mol.% Al_2O_3 – 55.6 mol.% SiO_2):xBi_2O_3 have been measured for x=0.01, 0.25, 0.5, 0.66, 1.0, 1.5, 2.0. According to obtained XANES spectra near L_{III}-edge intensity of pre-edge peak increases with increasing of bismuth concentration. At the same time bismuth concentration increase the absorption value of optical spectral lines at 500 nm and 700 nm [1,2]. This fact gives us a chance to link Bi centers electronic structure with the optical properties of these glasses.

Preforms for optical fibers with glass core composition: Bi : SiO_2; Bi : SiO_2 - Al_2O_3; Bi : SiO_2 - GeO_2; Bi : SiO_2 - Al_2O_3 - GeO_2; Bi : SiO_2 - Al_2O_3- P_2O_5. Сравнение результатов для этих образцов показывает существенное влияние состава сердцевин на XANES спектры висмута. For Bi : SiO_2 preform it was shown that addition of Ce strongly influence on the X-ray absorption spectrum, what can be a result of the bismuth oxidation state changing.

Chalcogenide glasses

Despite the fact, that structure of Bi-doped GeSx glasses should vary considerable with x [3,4] we have obtained identical XANES spectra for x from 1.35 to 1.5, what means that the structure changing does not influence on the local environment of Bi centers.

Currently, we are performing ab initio calculations to describe obtained data as precisely as possible.

References

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