# Bi-doped silica glass - analysis of luminescent center

**Yasushi Fujimoto**
*Institute of Laser Engineering Osaka University, 2-6 Yamada-oka, Suita, Osaka, 565-0871 Japan*

Recently, we have discovered a new infrared emission from a bismuth-doped silica glass (BiSG)[1]. The emission of BiSG at 1.25 μm with 0.8-μm excitation has a very wide spectrum, which is 300 nm of full width at half maximum (FWHM) and long lifetime (630μs), and, therefore, we have pointed out the possibilities that this new infrared emission would be useful as a core-material of an optical amplifier at zero-dispersion wavelength and a ultra-short pulse generation. The optical amplification and the laser oscillation phenomena are reported by several researchers [2,3], however, the luminescent mechanism is still being discussed. In this paper, we propose the structural model of Bi luminescent center expected by examining the local environment of Bi ions in BiSG using several analytical methods.

1) The quality of glass and fluorescence intensity (roles of aluminum ions) [4]

$Al_2O_3$ addition is effectively afects to increase the fluorescence intensity. The intensity of BiSG (BiSG_A ;$Bi_2O_3$ :1.0mol%, $Al_2O_3$ :2.3mol%) emmits around three orders of magnitude larger than that of BiSG (BiSG_B ;$Bi_2O_3$ :1.0mol% without $Al_2O_3$). BiSG_A have glassy wetting while BiSG_B did not show glassy wetting. Therefore, it is considered that both Bi and Al atoms should be close together, and the roles of aluminum ions are summarized into following two points; a) to assist the configuration of the peculiar luminescent center of Bi ion with some coupling effect, b) to increase the compatibility with silica network.

2) Electron spin resonance (ESR)[1]

There is no unpaired electrons in BiSG sample by measuring electron spin resonance. This result show that the possible valence states of Bi ions in BiSG are $Bi^{3+}$ or $Bi^{5+}$.

3) X-ray absorption fine structure (XAFS) [5]

The distance between Bi ion and neighboring ion (oxygen) is evaluated by Bi-$L_{III}$ edge XAFS analysis. The Bi-O distances in BiSG are calculated to be 2.1Å and 2.3Å by using FEFF8.2. 2.1Å is the same value of $Bi^{5+}$-O in LiBi(5+)$O_3$.

4) X-ray photoelectron spectroscopy (XPS)

The peak binding energy in XPS spectrum is sensitive to the local environment of an ion, especially, valence state. We observed the binding energies of $Bi_{5/2,7/2}$ in Bi metal, $Bi_2O_3$, and BiSG. These peaks are shifted to higher energy in order of Bi metal (0)-> $Bi_2O_3$ (3+)-> BiSG. The BiSG valence state is expected to be higher ($Bi^{5+}$) than that of $Bi_2O_3$.

5) $^{27}$Al-NMR [4]

The $^{27}$Al-NMR peak on BiSG exists at the same as α-$Al_2O_3$. Therefore, Al ions of 6-fold corundum structure are dominant in BiSG.

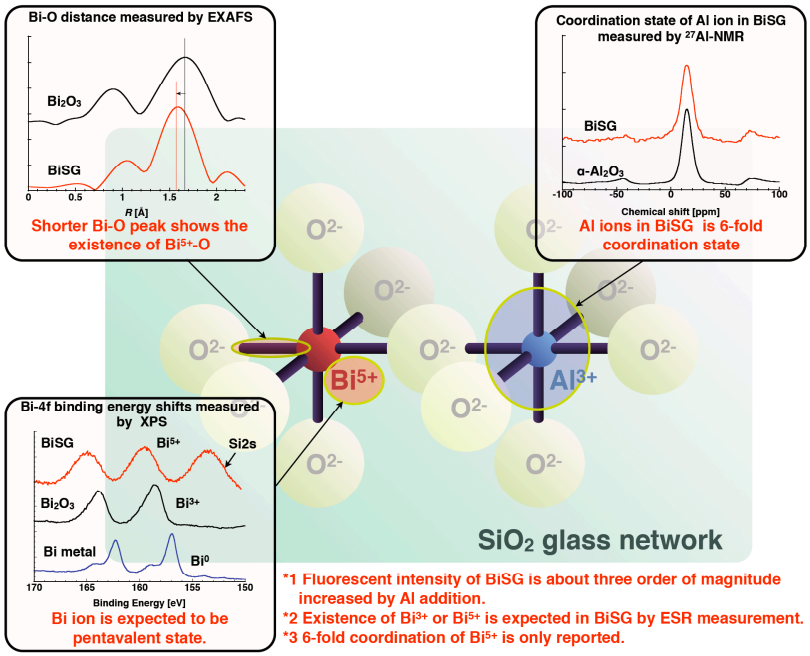


Fig. 1 The expected local structure of Bi ion in BiSG.

In conclusions, we propose that the local structure of Bi ion in BiSG shown in Fig.1. These results will help to study out the luminescent mechanism on the peculiar Bi infrared luminescent center.

## References

[1] Y. Fujimoto and M. Nakatsuka, Jpn. J. Appl. Phys., **Vol.40** (2001) No.3B pp.L279 - L281, "Infrared fluorescence from bismuth doped silica glass"

[2] Young-Seok Seo, Yasushi Fujimoto, Masahiro Nakatsuka, IEEE Photon. Tech. Lett., **Vol.18,** No.18 (2006) pp1901-1903, "Simultaneous amplification at two wavelengths near 1300 nm in a 6.5 cm long bismuth-doped silica glass"

[3] E.M. Dianov, V.V. Dvoyrin, V.M. Mashinsky, A.A. Umnikov, M.V. Yashkov, A.N. Gur'yanov, Quantum Electronics, **35** (2005) 1083-1084, "CW bismuth fibre laser"

[4] Y. Fujimoto and M. Nakatsuka, J. Non-Cryst. Solids, **352**(2006) p2254-2258, "$^{27}$Al-NMR Structural Study on Aluminum Coordination State in Bismuth Doped Silica Glass"

[5] T. Ohkura, Y. Fujimoto and M. Nakatsuka, J. Am. Ceram. Soc., **90** [11] (2007) p3596 – 3600, "Local structures of bismuth ion in bismuth doped silica glasses analyzed by using Bi $L_{III}$ X-ray absorptions fine structure"