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– Inorganic Photonics Materials –

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Scope of Research

In the laboratory, the main subject is to create novel functional amorphous materials such as organic-inorganic hybrids, polycrystalline and amorphous inorganic oxides. For obtaining such materials, the amorphous structure and the property are investigated by XRD, MAS NMR, thermal and optical analysis and quantum chemical calculations. Currently, we are trying to prepare novel amorphous-based optical functional materials such as proton conducting membrane, optical biosensor, and amorphous phosphor.

KEYWORDS
Glass
Photonics
Remediation
Organic-inorganic Hybrid
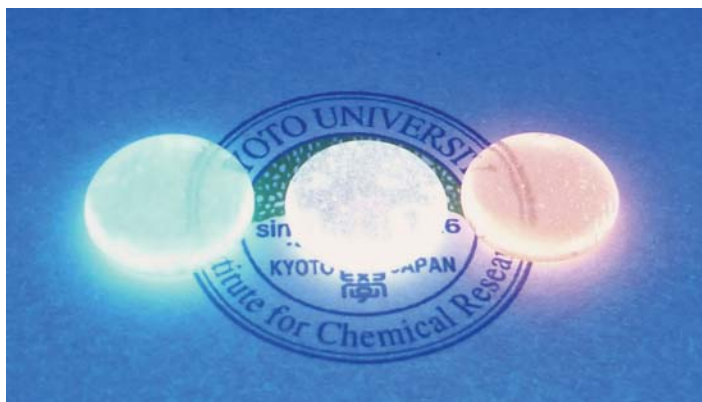
Selected Publications

Minami, T.; Tokuda, Y.; Masai, H.; Ueda, Y.; Ono, Y.; Fujimura, S.; Yoko, T., Structural Analysis of Alkali Cations in Mixed Alkali Silicate Glasses by 23Na and 133Cs MAS NMR", *J. Asian Ceram. Soc.*, doi:10.1016/j.jascer.2014.07.001 (2014).

Ueda, Y.; Tokuda, Y.; Goto, H.; Kobayashi, T.; Ono Y., Removal of Radioactive Cs from Nonwoven Cloth with Less Waste Solution Using Aqueous Sodium Metasilicate, *J. Soc. Remed. Radioact. Contam. Environ.*, **1,** 191-195 (2013).

Masai, H.; Takahashi, Y.; Fujiwara, T.; Matsumoto, S.; Yoko, T., High Photoluminescent Property of Low-Melting Sn-Doped Phosphate Glass, *Applied Physics Express*, **3,** [082102-1]-[082102-3] (2010).

Masai, H.; Fujiwara, T.; Matsumoto, S.; Takahashi, Y.; Iwasaki, K.; Tokuda, Y.; Yoko, T., White Light Emission of Mn-Doped SnO-ZnO-P_2O_5 Glass Containing No Rare Earth Cation., *Optics Letters*, **36,** 2868-2870 (2011).

Masai, H.; Yamada, Y.; Suzuki, Y.; Tearamura, K.; Kanemitsu, Y.; Yoko, T., Narrow Energy Gap between Triplet and Singlet Excited States of Sn^{2+} in Borate Glass, *Scientific Reports*, **3,** 3541 (2013).

Structural Analysis of Alkali Cations in Silicate Glasses

Structural analysis of alkali ions in glass is an important topic in glass science because of the mixed alkali effect (MAE) that originates when the composition of a glass is altered by gradual substitution of one alkali for another. More specifically, the MAE is characterized by the deviation from the linear additive properties of alkali silicate glasses, which can be attributed to structural, thermodynamic, electrodynamic, and other factors.

Recently, we investigated the heterogeneous distribution of Na^+ in mixed alkali silicate glasses (Na_2O-K_2O-SiO_2 glass) by performing ^{23}Na multiple-quantum magic-angle spinning (MQMAS) NMR studies. The results were also supported by the Na^+ elution analysis, which showed that Na^+ is extracted faster from more "aggregated" sites than from less aggregated sites. Nevertheless, in the previous study, the local structure of K^+ in Na_2O-K_2O-SiO_2 glass could not be investigated, as the ^{39}K sensitivity of NMR is extremely low. In order to understand the precise mechanism underlying the MAE, analyses of the local structure of both alkali ions are required.

Here, we report the structural analysis of Na^+ and Cs^+ in sodium cesium silicate glasses by using ^{23}Na and ^{133}Cs magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. In the NMR spectra of cesium silicate crystals, the peak position shifted to higher magnetic field for structures with larger Cs^+ coordination numbers and to lower magnetic field for smaller Cs^+ coordination numbers. The MAS NMR spectra of xNa_2O-yCs_2O-$2SiO_2$ ($x = 0$, 0.2, 0.33, 0.5, 0.66, 0.8, 1.0; $x+y = 1$) glass reveal that the average coordination number of both the alkali cations decreases with increasing $Cs^+/(Na^++Cs^+)$ ratio. In addition, the coordination number of Na^+ in xNa_2O-yCs_2O-$2SiO_2$ glass is smaller than that of Cs^+. This difference between the average coordination numbers of the alkali cations is considered to be one structural reason of the mixed alkali effect.
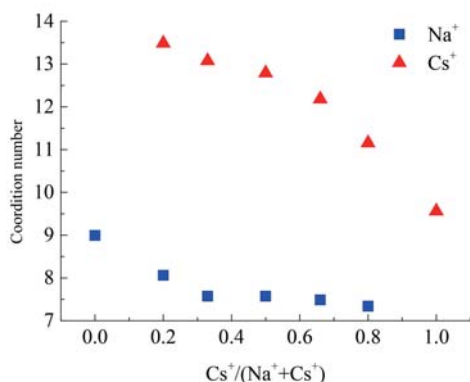

Figure 1. Average coordination number of Na^+, Cs^+ in xNa_2O-yCs_2O-$2SiO_2$ glasses ($x = 1.0, 0.8, 0.66, 0.5, 0.33, 0.2$; $x+y = 1$).

Oxide Glasses: the Structure, Physical Property, and Functionalization

Glass is a solidified liquid that can possess characteristics of both solid and liquid. Although glass is an isotropic material from macroscopic viewpoint, it is indeed anisotropic in terms of microscopic scale. Various compositions of inorganic glasses bring a random network that allows diversity in local structure. The diversity is the origin of various functionalities of inorganic glass.

Phosphate glass is one of important oxide glass materials and P_2O_5 is generally classified into a network former (NWF) group from the viewpoint of glass forming ability. However, P_2O_5 is indeed different from other NWF oxides, such as SiO_2, and B_2O_3, because of P=O bond, which allows to take non-bridging ortho- or pyro-phosphate units by delocalized electrons. Although it is predicted that the connectivity of PO_4 units in the glasses have strong influence on the network formation (in other words, the chemical composition of the glass), there is no universal understanding of atomistic and electronic structure in phosphate glasses even for simple binary phosphate glasses due to the lack of detailed information on the behavior of P=O bond.

Recently, we have examined the 3-dimentional (3D) atomistic and electronic structures in a combination with synchrotron X-ray total scattering, Extended X-ray Absorption Fine Structure (EXAFS), and solid state NMR. Furthermore, we construct 3-D structure model by reverse Monte Carlo (RMC)-modelling method on the basis of total scattering and XAFS data, and try to understand not only atomic ordering in the glasses. It has found that the ZnO_x network is formed instead of phosphate chains with increasing ZnO amount in binary ZnO-P_2O_5 glass (Figure 2). (This work has done by collaboration with Dr. S. Kohara, Spring-8).

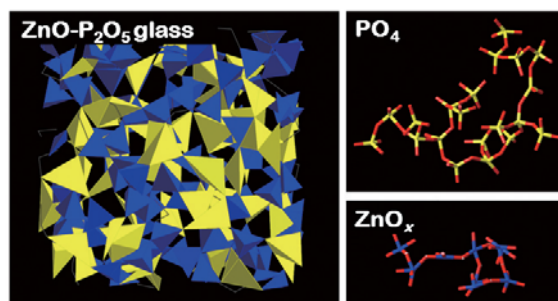**Figure 2.** 3D modeling of a ZnO-P_2O_5 glass obtained by RMC modelling. (blue pyramid: PO_4 tetrahedron, yellow pyramid: ZnO_x tetrahedron). The connectivity of PO_4 and ZnO_x tetrahedra in the ZnO-P_2O_5 glass is also shown.