

# Division of Materials Chemistry

## – Inorganic Photonics Materials –

<http://mizuochilab.kuicr.kyoto-u.ac.jp/websites/>



Assoc Prof  
TOKUDA, Yomei  
(D Eng)



Assist Prof  
MASAI, Hirokazu  
(D Eng)

### Students

UEDA, Yuki (M2)  
USUI, Takaaki (M2)

TAKAHASHI, Yuya (M1)  
KANEKO, Shunichi (M1)

TORIMOTO, Aya (M1)  
DANJO, Takuya (UG)

## Scope of Research

In this laboratory, the main subject is to create novel functional amorphous materials, such as organic–inorganic hybrids, polycrystalline, and amorphous inorganic oxides. The amorphous structure and its properties 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 a proton conducting membrane, optical biosensor, and amorphous phosphor.



### KEYWORDS

Organic-inorganic Hybrid      Solid State NMR  
Oxide Glass      Photoluminescence

### Selected Publications

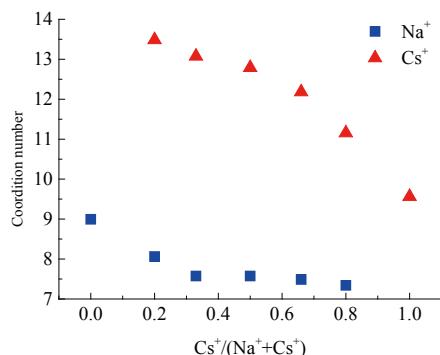
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- Masai, H.; Miyata, H.; Yamada, Y.; Okumura, S.; Yanagida, T.; Kanemitsu, Y., Tin-Doped Inorganic Amorphous Films for Use as Transparent Monolithic Phosphors, *Scientific Reports*, **5**, 11224 (2015).

## 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 arises 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, and electrodynamic factors, among others.

Recently, we investigated the heterogeneous distribution of  $\text{Na}^+$  in mixed alkali silicate glasses ( $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{SiO}_2$  glass) by performing  $^{23}\text{Na}$  multiple-quantum magic-angle spinning (MQMAS) nuclear magnetic resonance (NMR) studies. The results were also supported by  $\text{Na}^+$  elution analysis, which showed that  $\text{Na}^+$  is extracted faster from more aggregated sites than from less aggregated sites. Nevertheless, in the previous study, the local structure of  $\text{K}^+$  in  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{SiO}_2$  glass could not be investigated, as the  $^{39}\text{K}$  sensitivity of NMR is extremely low. In order to understand the precise mechanisms underlying the MAE, analyses of the local structure of both alkali ions are required.

Here, we report structural analysis of  $\text{Na}^+$  and  $\text{Cs}^+$  in sodium cesium silicate glass by using  $^{23}\text{Na}$  and  $^{133}\text{Cs}$  magic-angle spinning (MAS) NMR spectroscopy. In the NMR spectra of cesium silicate crystals, the peak position shifted to a higher magnetic field for structures with larger  $\text{Cs}^+$  coordination numbers and to lower magnetic field for smaller  $\text{Cs}^+$  coordination numbers. The MAS NMR spectra of  $x\text{Na}_2\text{O}-y\text{Cs}_2\text{O}-2\text{SiO}_2$  ( $x = 0, 0.2, 0.33, 0.5, 0.66, 0.8$ , and  $1.0$ ;  $x+y = 1$ ) glass reveal that the average coordination number of both alkali cations decreases with an increasing  $\text{Cs}^+/\text{(Na}^++\text{Cs}^+\text{)}$  ratio. In addition, the coordination number of  $\text{Na}^+$  in  $x\text{Na}_2\text{O}-y\text{Cs}_2\text{O}-2\text{SiO}_2$  glass is smaller than that of  $\text{Cs}^+$ . This difference between the average coordination numbers of the alkali cations is considered to be one structural reason for the mixed alkali effect.



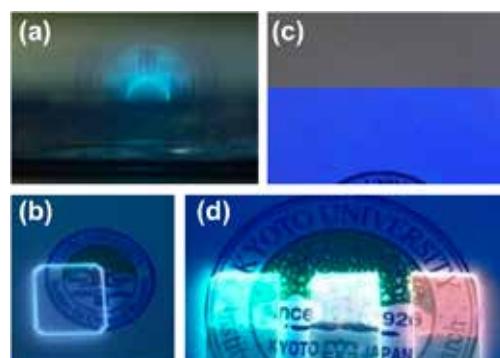
**Figure 1.** Average coordination numbers of  $\text{Na}^+$ ,  $\text{Cs}^+$  in  $x\text{Na}_2\text{O}-y\text{Cs}_2\text{O}-2\text{SiO}_2$  glasses ( $x = 1.0, 0.8, 0.66, 0.5, 0.33$ , and  $0.2$ ;  $x+y = 1$ ).

## 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 have random networks that allow diversity in local structure. This diversity is the origin of various functionalities of inorganic glass.

Emitting solid-state matter is one of the main applications of transparent amorphous materials. Since oxide glass consists of a random network structure, metastable species can be introduced easily, compared with ordered crystals. We have recently focused on the  $\text{ns}^2$ -type emission center as an activator in amorphous materials. The emission centers take the metastable valence state of each element, and their emissions are strongly affected by the coordination field because of the electrons in the outermost shell. However, there is no detailed understanding of the dispersion and energy diagram in oxide glasses, although it is expected that the random networks of the glasses have strong influence on the emission property of the  $\text{ns}^2$ -type emission centers.

Recently, we have reported the highest quantum efficiency (QE) for amorphous  $\text{Sn}^{2+}$ -doped  $\text{ZnO}-\text{P}_2\text{O}_5$  glass (Figure 2a). In addition, photoluminescence of the metastable  $\text{In}^+$  centers (non-conventional  $\text{ns}^2$ -type center) is demonstrated (Figure 2b). On the other hand, the photoluminescence of the  $\text{Sn}^{2+}$  center can be demonstrated in amorphous film prepared by a liquid phase reaction (Figure 2c and 2d). It is notable that an energy transfer from  $\text{Sn}^{2+}$  (donor) to  $\text{Mn}^{2+}$  (acceptor) is observed even in the film shape (Figure 2d). Because some glasses show luminescence with a high value of quantum efficiency comparable to crystalline phosphor, RE-free glass phosphor is a fascinating material from the viewpoint of unique emission mechanisms in a random matrix.



**Figure 2.** Amorphous materials containing  $\text{ns}^2$ -type emission centers. (a)  $\text{Sn}^{2+}$ -doped bulk glass, (b)  $\text{In}^+$ -doped bulk glass, and (c), (d)  $\text{Sn}^{2+}$ -doped films. The emission color of the film can be controlled by co-doping of  $\text{Mn}^{2+}$  cations.