Division of Materials Chemistry
– Inorganic Photonics Materials –

http://noncry.kuicr.kyoto-u.ac.jp/

Prof
YOKO, Toshinobu
(D Eng)

Assoc Prof
TOKUDA, Yomei
(D Eng)

Assist Prof
MASAI, Hirokazu
(D Eng)

Students

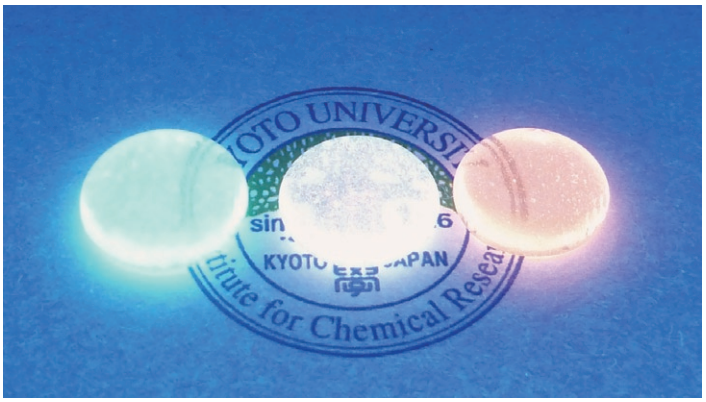
HINO, Yusuke (M2)
HORII Akinori (M2)
OGAWA, Tadahiro (M2)
SHIRAI, Ryota (M2)
SUZUKI, Yuto (M2)
TANIMOTO, Toshiro (M2)
MINAMI, Tomohiro (M1)
MIYATA, Hiroki (M1)
UTSUMI, Nihiro (M1)
MATSUKI, Hiroaki (UG)
OKUMURA, Shun (UG)

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

Amorphous Oxide Phosphor
Low Melting Glass
Organic-Inorganic Hybrid Materials
Optical Microbiosensor
Proton Conducting Membrane



Selected Publications

Tokuda, Y.; Oka, T.; Takahashi, M.; Yoko, T., Inhomogeneous Distribution of Na^+ in Alkali Silicate Glasses, *J. Ceram. Soc. Japan*, **199,** 909-915 (2011).

Tokuda, Y.; Nishioka, S.; Ueda, Y.; Koyanaka, H.; Masai, H.; Takahashi, M.; Yoko, T., Preparation of Proton-Conductive Organic–Inorganic Hybrid Titanophosphite Membranes, *Solid State Ionics*, **225,** 232-235 (2012).

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.; Tanimoto, T.; Fujiwara, T.; Matsumoto, S.; Tokuda, Y.; Yoko, T., Correlation between Emission Property and Concentration of Sn^{2+} Center in the SnO-ZnO-P_2O_5 Glass, *Optics Express*, **20,** 27319-27326 (2012).

Preparation of Proton Conductive Membranes with Graded Monomer Conversion

Future advances in fuel cell technology are contingent on the development of new materials. One such material is the Nafion membrane (DuPont); it is a proton-conducting membrane and has been employed in polymer electrolyte fuel cells (PEFCs). However, the PEFC faces problems including poor carbon monoxide tolerance and heat rejection in temperatures between 60 and 80°C. In order to overcome these drawbacks, a proton-conducting membrane is required to operate at intermediate temperatures around 100–150°C and should possess good durability and thermal stability.

In this study, we describe a novel technique to prepare a membrane with a graded monomer conversion using ultraviolet light (UV) irradiation during radical photopolymerization. A schematic procedure is shown in Figure 1. High conversion at the surface of the membrane enhanced durability while low conversion at the inner part of the membrane facilitated proton conductivity. This incremental change in the proton conductivity is possible because pK_{a1} of vinylphosphonic acid (VPA) is 2.74 and pK_{a2} is 7.34, while pK_a of PVPA is around 5–6. Copolymerization of VPA with an additive monomer of hydrophobic nature having a low chain transfer constant leads to an increase in the conversion of the additive polymer.

The proton conductivity of the present membrane was 6.3×10^{-4} Scm^{-1} at 150°C even under dry conditions. The durability of the membrane VET-ht was much higher than that of polyvinylphosphonic acid, PVPA. The membrane was also thermally stable up to 200°C. These properties contribute to overcome the conventional problems associated with decreases in proton conductivity of polymer electrolytes at intermediate temperatures between 100 and 150°C.

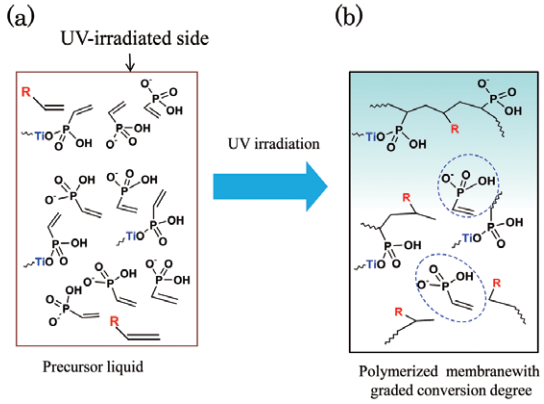


Figure 1. Schematic representation of membrane with graded degrees of polymerization:
(a) titanophosphite precursor.
(b) copolymerized membrane with graded degrees of polymerization.

Fabrication of Rare Earth-free Amorphous Oxide Phosphor

Nowadays, rare earth (RE)-containing materials have been used as white-emitting devices. However, these white-emitting devices consisting of sharp emission bands of RE possess lower color rendering than the conventional broad band emission device. Moreover, since there is uncertainty about the stable supply of RE over the future, it is worthwhile to examine RE-free emitting material. We have focused on the RE-free phosphors that have been used for white fluorescent lamp. It is expected that white light emission can be attained by RE-free phosphor, for example Sb^{3+}, Mn^{2+}-doped calcium halophosphate. On the other hand, if glass material without the RE cation shows white light emission comparable to the crystalline phosphor, it will be considered a novel emitting material capable of much broader emission and good formability that is quite important in the industrial manufacturing process.

Recently, we have reported the highest quantum efficiency (QE) for amorphous SnO-ZnO-P_2O_5 low-melting glass. It is notable that the transparent oxide glass containing no RE cation shows high UV-excited emission that is comparable to crystal phosphor such as $MgWO_4$; further, this was the largest efficiency of glass material without RE cation ever reported. The broad emission is brought about by Sn^{2+}, which is the most conventional and harmless ns^2 type center. Our group has also demonstrated white light emission of RE-free Mn-doped SnO-ZnO-P_2O_5 glass. The transparent glass showed blue ~ white ~ red emission, which depended on the amount of MnO (Figure 2). In particular, some glasses showed white light emission with a high value of quantum efficiency comparable to $MgWO_4$ crystalline phosphor, which suggests that RE-free glass phosphor is very fascinating material from the viewpoint of unique emission mechanisms in a random matrix.

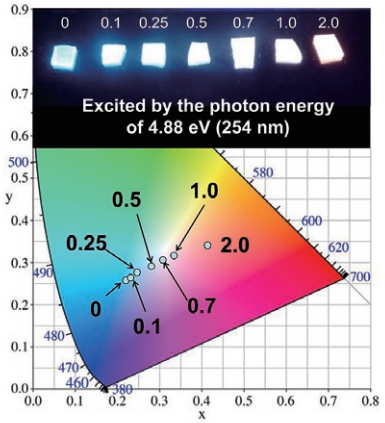


Figure 2. Chromaticity coordinates of the xMnO-2.5SnO-57.5ZnO-40P_2O_5 glasses. Inset shows a photograph of these glasses under exposure to the photon energy of 4.88 eV (254 nm).