Division of Materials Chemistry
– Inorganic Photonics Materials –

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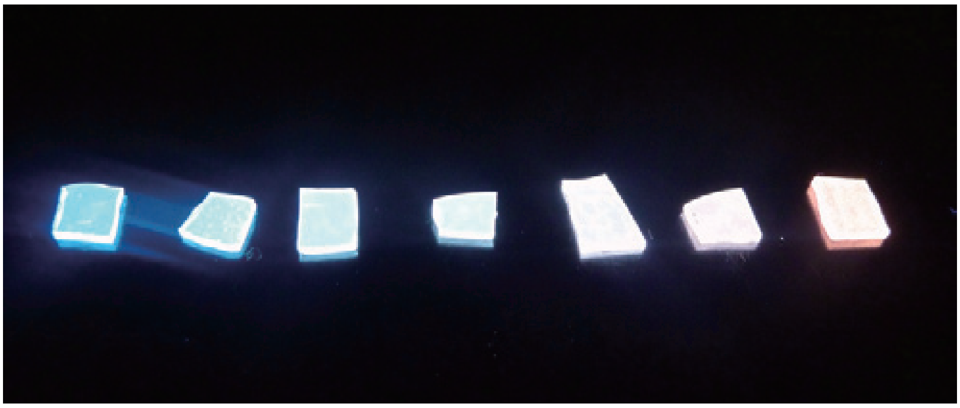
Scope of Research

In this laboratory, amorphous, polycrystalline inorganic materials and organic-inorganic hybrid materials with various optical functions such as photorefractivity, photolumionescence and photocatalysis are the target materials, which are synthesized by metathesis, sol-gel, melt-quenching and sintering methods and so on. Aiming at highly functional materials the structure-property relationship is investigated by X-ray diffraction techniques, high-resolution NMR, thermal analysis, various laser spectroscopies and quantum chemical calculations.

KEYWORDS
Organic-inorganic Hybrid Materials
Low Melting Glass
Proton Conducting Membrane
Optical Microbiosensor
White Glass Phosphor



Selected Publications

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).
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Takahashi M, Suzuki M, Miyagawa Y, Ihara R, Tokuda Y, Yoko T, Nemoto T, Isoda S: Photo-Curable Organically Modified Silicate-Phosphate Alternating Copolymer for Photonics Applications, *J. Sol-Gel Sci. Technol.*, **54,** 319-324 (2010).
Menaa B, Takahashi M, Tokuda Y, Yoko T: Characterization and Solventless Growth of Salicylic Acid Macro-Crystals Involving a Nitrogen Gas Flow, *Cryst Res Tech.*, **45,** 341-346 (2010).

D-1 Structure Engineering of Organic-inorganic Hybrid Material by Solventless Synthesis

Organic-inorganic hybrid materials are potential candidates for use in the fabrication of electronic and photonic devices with high functionality because these materials can be processed easily and have a high solubility of functional molecules. Such materials are frequently prepared by using a sol-gel method because of their composition selectivity and low-temperature process. However, the sol-gel process is sometimes complicated, and it is difficult to obtain a monolith because of the crack formation during solvent evaporation.

Recently, another synthesis route for organic-inorganic hybrids, involving solventless reactions using orthophosphoric acid and organically modified silanes, has been developed. In this process the following metathesis occurs on heating: Si–X + P–OH $\rightarrow$ Si–O–P + HX$\uparrow$ (X = Cl, ethoxy), where groups that do not participate in this reaction are omitted from the reaction formula. This reaction proceeds with eliminations of HX because the reaction temperature is near/above the boiling point of HX. Because of the absence of solvent evaporation, a transparent, crack-free, large, hybrid monolith can be produced simply by mixing the starting reagents, followed by heat-treatment.

We have developed a new class of proton-conducting organic–inorganic hybrid silicophosphite membranes, produced by ethanol condensation under solventless and one-pot conditions. The membranes exhibit good thermal stability up to intermediate temperatures (~218 °C). Structural analyses using ^{29}Si and ^{31}P NMR spectroscopy and IR measurements have revealed that ethanol condensation produced an inorganic alternating copolymer structure, Si–O–P, with a phosphole group, and successive polymerization enabled these structures to connect with each other. In this way, it is possible to achieve structure engineering of inorganic–organic networks. The proton conductivities of the hybrids are as high as 5.2×10^{-3} S cm^{-1} at 85 °C under 80% relative humidity.

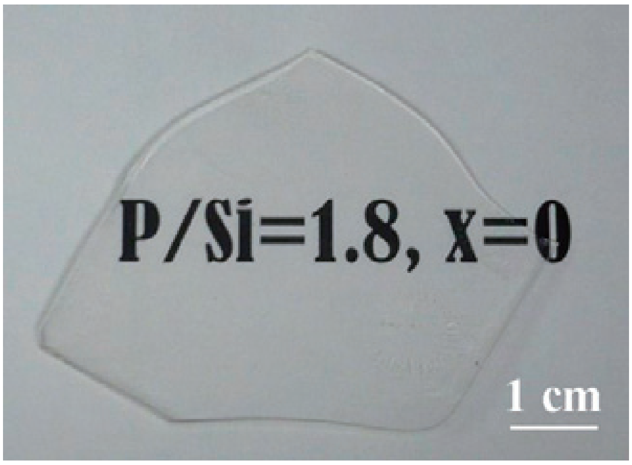

Figure 1. Photograph of an organic-inorganic hybrid phosphosilicate membrane. Crack-free and large-sized membranes can be prepared.

D-2 Fabrication of Rare Earth Free White Glass Phosphor

Recently, the three-band lamps consisting of rare earth (RE)-doped blue, red, and green phosphors and the white light emitting diode (LED) basically consisting of blue-LED and yellow phosphor, such as $Y_3Al_5O_{12}:Ce^{3+}$ have been commercially available. However, these white emitting devices consisting of sharp emission bands possess lower colour rendering than the conventional broad band emission device. In addition, RE-free material will be required from a view point of uneven distribution of RE on earth. Here, our group has emphasized that white emission constituted of various kinds of wavelength can be attained by RE-free phosphor, such as Sb^{3+},Mn^{2+}-doped calcium halophosphate, ($Ca_5(PO_4)_3(F,Cl):Sb^{3+},Mn^{2+}$). Although the emission of the calcium halophosphate possesses two broad emission bands, these emission bands are inherently fixed because of the crystal structure. On the other hand, it is more hopeful that amorphous oxide glass material will show white light without RE cation, because it is possible to tune the various coordination fields of the emission centre. If a glass material without RE cation shows the high emission property comparable to the crystalline phosphor, it will become a novel emitting material possessing wide chemical composition or good formability that can be applied to the industrial manufacturing. Such an emitting material is quite different from the conventional RE-doped crystalline phosphor. Recently, we have succeeded in preparing the Sn-doped transparent glass possessing high quantum efficiency ever reported. Our group is aiming at developing a novel white glass phosphor for UV LED.