Division of Materials Chemistry
- Inorganic Photonics Materials -

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Scope of Research

In this laboratory, amorphous and polycrystalline inorganic materials and organic-inorganic hybrid materials with various optical functions such as photorefractivity, optical nonlinearity, phptolumionescence and photocatalysis are the target materials, which are synthesized by 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.

Research Activities (Year 2009)

Publications

Kakiuchida H, Takahashi M, Tokuda Y, Yoko T: Rewritable Holographic Structures Formed in Organic-Inorganic Hybrid Materials by Photothermal Processing, *Adv. Funct. Matter*., **19**, 2569-2576 (2009).

Tokuda Y, Tanaka Y, Takahashi M, Ihara R, Yoko T: Silicophosphate/silicophosphite Hybrid Materials Prepared by Solventless Ethanol Condensation, *J. Ceram. Soc. Japan*, **117**, 842-846 (2009).

Teixeira LAV, Tokuda Y, Yoko T, Morita K: Behavior and State of Boron in CaO-SiO2 Slags during Refining of Solar Grade Silicon, *ISIJ INTERNATIONAL*, **49**, 777-782 (2009).

Presentations

Oka T, Tokuda Y, Takahashi M, Yoko T, "Quantitative Structure Analysis of Quadrupolar Nuclei in Amorphous Materials", Annual Meeting of the Ceramic Society of Japan 2009, Japan, 16–18 March 2009.

Oku S, Tokuda Y, Takahashi M, Yoko T, Yamada T, Kitagawa H, "Solvent-free Synthesis and Application of Proton-conducting Organic-inorganic Hybrid Phosphosilicate Membranes", The 47th Symposium on Basic Science of Ceramics, Japan, 8–9 January 2009.

Grants

Yoko T, Grants-in-Aid for the Scientific Research from Japan Society for the Promotion of Science, No. 20613007.

Tokuda Y, Murata Science Foundation, July 2008–March 2009.

Tokuda Y, Iketani Science and Technology Foundation, April 2009–March 2010.

Tokuda Y, The Kyoto University Foundation, April 2009–March 2010.

Structure Engineering and Material Function Controlling of Organic-inorganic Hybrid Materials

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 processibility. However, the sol-gel process is sometimes complicated, and it is difficult to obtain monolithic material because of crack formation during solvent evaporation.

Recently, an organic-inorganic silicophosphate hybrid has been obtained under a solventless, catalyst-free, low-temperature, one-pot condition by using orthophosphoric acid and organically modified chlorosilane. The following acid-base reaction (metathesis) took place: Si–Cl + P–OH → Si–O–P + HCl↑. The resultant viscous liquid was cooled down to an ambient temperature, producing a transparent monolithic hybrid material that contained an almost complete alternating polymer consisting of silicate and phosphate units and a high homogeneity in an intermolecular scale. The crack-free monolithic hybrid material was easily obtained because of the absence of solvent evaporation.

One can easily introduce organic dyes into the abovementioned hybrid material as it melts at temperatures less than 100 °C and possesses various organic groups. Additionally, rare earth ions and Au nanoparticles can be easily dispersed in this hybrid material because the present material has copolymer structure consisting of silicate and phosphate units. This high solubility of both the organic and the inorganic functional centers is one of the advantages of the optical host material application. Another advantage of this organic-inorganic hybrid material is related to the low-temperature processibility of the material because the melting temperature of the material is less than 100 °C, the material can be used in a hot-emboss technique or photothermal fabrication in order to obtain photonic devices (Figure 1).

In this study, we developed another class of silicophosphate hybrid formation reaction that is based on solventless alcohol condensation without HCl production: Si–OEt + P–OH → Si–O–P + EtOH↑. The hybrid material shows low-melting property, as melting temperatures ranged from 50 to 110 °C where the organic dyes do not degrade. The functional centers such as the rare earth ions will disperse homogeneously in the alternating copolymer of silicate and phosphate as reported previously. Additionally, the chemical durability was much higher than that of the hybrids prepared by the acid-base reaction. Therefore, the present hybrid material is a good candidate of the optical host material for the organic and/or inorganic functional centers.

We also developed proton-conducting organic-inorganic hybrid phosphosilicate membranes using organically modified alkoxysilane and anhydrous vinylphosphonic acid (Figure 2). The membranes synthesized in the present study are crack-free, large-sized, and flexible, and they exhibit good thermal stability up to intermediate temperatures (~218 °C). The proton conductivities of the hybrids are as high as 5.2×10^{-3} S/cm at 85 °C under 80% RH.

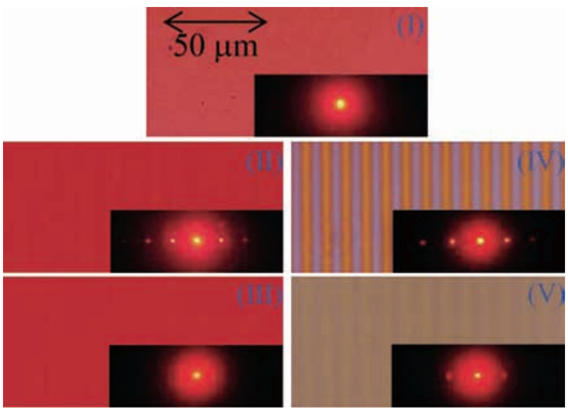

Figure 1. Snapshots of the optical grating images and diffraction patterns during the grating formation/decay process at lower (I, II–III) and higher (I, IV–V) irradiation intensities

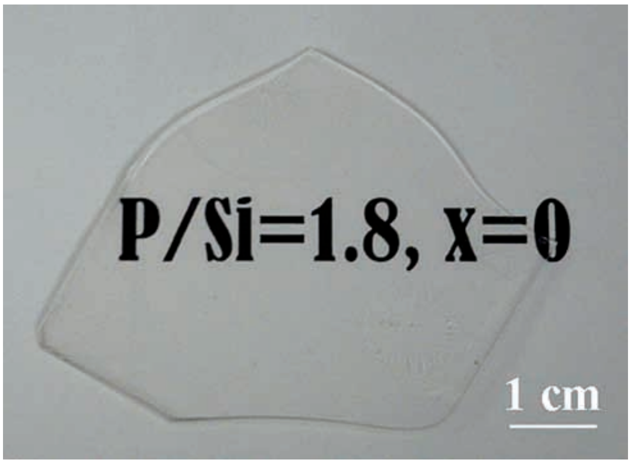

Figure 2. Photograph of an organic-inorganic hybrid phosphosilicate membrane. Crack-free and large-sized membranes were obtained.