Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Tae-Dong Kim [a], Kwang-Sup Lee [a], So Young Lee [b], Young Joe Kim [b] & Jae Won Song [b]

[a] Department of Polymer Science & Engineering, Hannam University, Taejon, 306-791, Korea

[b] School of Electronic and Electrical Engineering, Kyungpook National University, Taegu, 702-701, Korea

Version of record first published: 24 Sep 2006

To cite this article: Tae-Dong Kim, Kwang-Sup Lee, So Young Lee, Young Joe Kim & Jae Won Song (2001): Organic-Inorganic Hybrid Material for Electro-Optic Modulator, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 371:1, 337-340

To link to this article: http://dx.doi.org/10.1080/10587250108024755

Mol. Cryst. and Liq. Cryst., 2001, Vol. 371, pp. 337-340

Organic-Inorganic Hybrid Material for Electro-Optic Modulator

TAE-DONG KIM[1], KWANG-SUP LEE[1], SO YOUNG LEE[2], YOUNG JOE KIM[2] and JAE WON SONG[2]

[1] *Department of Polymer Science & Engineering, Hannam University, Taejon 306-791, Korea and* [2] *School of Electronic and Electrical Engineering, Kyungpook National University, Taegu, 702-701, Korea*

Abstract Organic-inorganic hybrid material (SIAZO-VP2) for nonlinear optics was prepared by the sol-gel processable monomer derived from 3-isocyanatopropyltriethoxysilane with hydroxy-functionalized nonlinear optical chromophores. The measured value of NLO coefficient strongly depended on conditions such as poling temperature, poling time and heating rate. The maximum value of SIAZO-VP2 film which was heated at 200°C exhibited d_{33} = 64 pm/V in Maker-fringe measurement. It was found that the thermal stability of the film was greatly enhanced as poling time increased and a poling temperature became higher. Using this hybrid material, we fabricated a vertically asymmetric coupled electro-optic modulator. The resulting device exhibited a good performance with the extinction ratio of ca. 9 dB, the half wave voltage of 5 V, and the bandwidth of 1.5 MHz at the wavelength of 633 nm.

INTRODUCTION

Nonlinear optics is expected to play a major role in the fields of optical information processing, optical sensing, and telecommunications [1]. A wide variety of materials can be used as nonlinear optical (NLO) systems. Those are inorganic crystals, organic crystals, Langmuir-Blodgett compounds, polymers, organic-inorganic hybrids, etc. Among them, organic-inorganic hybrid materials composed of silica glass and photo-functional organic molecules can be considered as one of the best candidates to develop optical materials with large optical nonlinearity and low optical losses [2, 3]. Here, the use of highly cross-linked silica

matrix can be remarkably reduced the thermal relaxation of the molecular dipoles. Thus, some organic-inorganic hybrid materials have been extensively investigated for photonic devices such as optical switches, optical fibers for use in communications, and frequency modulators [4].

Taking advantages of these, we have recently developed a novel hybrid system (SIAZO-VP2) having four bonding sites between chromophore and silica matrix. Its physical properties and nonlinear optical activity in terms of poling conditions is investigated. Also, using this hybrid material, we have fabricated a vertically asymmetric-coupled electro-optic modulator, which involved new device design concept that operates by the upper clad perturbation.

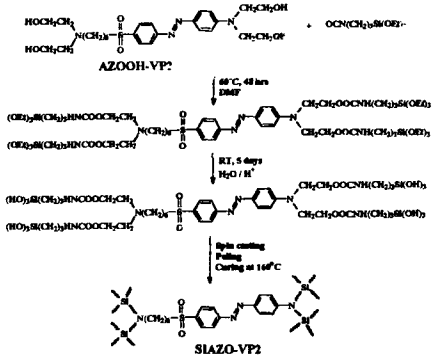
SOL-GEL PROCESS FOR ORGANIC-INORGANIC HYBRIDS

The alkoxysilane containing the second-order NLO dye (AZOOH-VP2) was synthesized by the coupling reaction between an alcoholic NLO chromophore and 3-isocyanatopropyltriethoxysilane at 60°C for 48 hrs in *N,N*-dimethylformamide solvent. To the resulting solution, a slight excess amount of 1N HCl was added. The solution was stirred for 6 days at room temperature, providing a homogeneous solution. The viscosity of reaction solutions increased after the hydrolysis and polycondensation reaction. The sol-gel process is outlined in Scheme 1.

RESULTS AND DISCUSSION

The thermal properties of the SIAZO-VP2 were examined by the differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). We did not observe clearly the glass transition temperature. The TGA data under the nitrogen atmosphere exhibited initial decomposition temperature due to the thermal breaking of azo-group at 265°C for SIAZO-VP2.

The SIAZO-VP2 gives an absorption maximum at 446 nm and its absorption edge at 565 nm. Under 5 kV poling voltage applied to the corona needle at 200°C for 1 hr, the order parameter value (ϕ = 1-A_1/A_0, A_0 and A_1 are the absorbances of the film before and after corona poling, respectively) for SIAZO-VP2 was estimated to be 0.35.



SCHEME 1. Sol-gel process for SIAZO-VP2

The second-order NLO properties of the poled film were characterized by the second harmonic generation (SHG) at 1064 nm fundamental wavelength with Y-cut quartz crystal (d_{11} = 0.5 pm/V) as the reference. Fig. 1 shows the relationship between the SHG intensity and the incident angle of an exciting beam of SIAZO-VP2 by using a standard Maker fringe technique. From the calculation, we obtained d_{33} value of 64 pm/V for SIAZO-VP2. It was found that the thermal stabilities of NLO activity were greatly enhanced as poling time increased and a poling temperature became higher. Fig. 2 shows that the SHG signal remained stable for the hybrid material until reaching about 120°C. This result indicates that the lattice hardening of this hybrid system with 4-bonding sites can clearly contribute for thermal stability.

Using this hybrid material, we have fabricated a vertically asymmetric-coupled electro-optic modulator, which involved new device design concept that operates by the upper clad perturbation. The far field image at the output of the vertical asymmetric coupler is shown in Fig.4a. Fig. 4b represents the intensity modulation response and applied voltage. The resulting device exhibited a good performance with the extinction ratio of ca. 9 dB, the half wave voltage of 5 V, and

the bandwidth of 1.5 MHz at the wavelength of 633 nm.

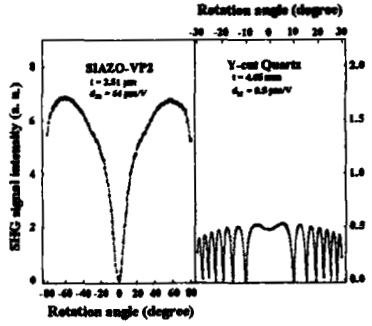


FIGURE 2. Comparison of angular SHG dependence between poled SIAZO-VP2 film and quartz as reference (t : thickness).

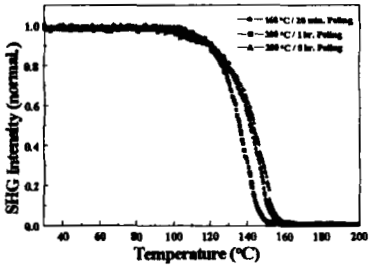


FIGURE 3. Thermal stability of NLO activities for four organic-inorganic hybrid materials.

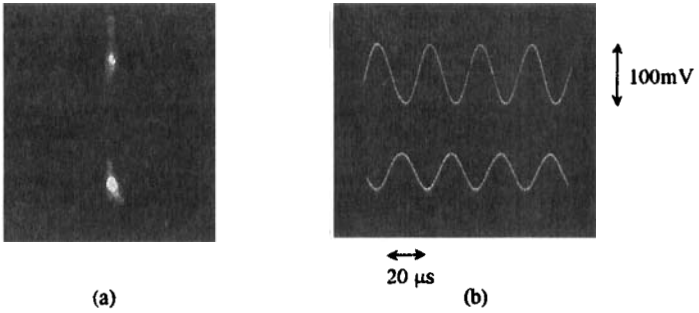


FIGURE 4. Far field mode pattern (a) and intensity modulation response (b) of vertical asymmetric EO Modulator

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