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Preparation of Thin Film of Layer Structured Bismuth Iodide with a Long Chain Alkylammonium and its Nonlinear Optical Property

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We have examined to prepare a hybrid thin film consisting of bismuth triiodide and alkylammonium iodide by the conventional spin-coating technique. Their X-ray diffraction profiles and UV-Vis-NIR absorption spectra showed that the two-dimensional $(Bi_2I_9^{3-})_x$ layer was sandwiched between alkylammonium layers by the molecular fastener effect. The third order nonlinear property of the thin film was estimated by the third harmonic generation (THG) measurements. Strong THG signals were observed from the hybrid thin film with stearylammonium iodide, which gave 10^{-11} esu order of $\chi^{(3)}$ values.

Keywords: layer structured bismuth iodide; alkylammonium cation: excitonic band; nonlinear optical property

INTRODUCTION

Recently, perovskite-type layered complexes $(C_nH_{2n+1}NH_3)_2MX_4$ (M=Cd(II), Cu(II), Pb(II), Sn(II), etc; X=I, Br, Cl) have attracted much attention due to their unique optoelectronic properties as well as the ease for their film preparation.[1] They naturally form a two-dimensional quantum well structure of halogen-bridged $(MX_4^{2-})_x$ layer with support of alkylammonium cations. Especially, it has been known that PbI_2-based layered complexes have very stable excitons with large binding energy and oscillator strength at room temperature, and thus, show several unique optical properties such as a strong photo- and electroluminescence[2] or the third order optical nonlinearity.[3]

Some trivalent metal halide / methylammonium complexes $(CH_3NH_3)_3M_2X_9$ (M=Bi(III), Sb(III); X=Br, Cl) have much interest in their phase transition behaviors and ferroelectric properties.[4] A MX_6 octahedra in the complex shares three *cis*-vertices with other octahedra to form a two-dimensional

network $(M_2X_9^{3-})_x$ as shown in Figure 1. Methylammonium cations occupy the vacancies inside the corrugated layer. Furthermore, it has been well known that absorption spectrum of semiconductive BiI_3 crystal showed a strong excitonic band and large third-order optical nonlinearity around the bandgap wavelength. Therefore, BiI_3-based hybrid complex with long chain alkylammonium was greatly expected as the third-order nonlinear optical material with ease for the film processing.

In this study, we examined to prepare a thin film of hybrid complex consisting of bismuth triiodide and alkylammonium. The characterizations of obtained films were performed by the X-ray diffraction (XRD) and UV-Vis-NIR absorption spectroscopy. Their third-order nonlinear optical properties were investigated by third harmonic generation (THG) measurements.

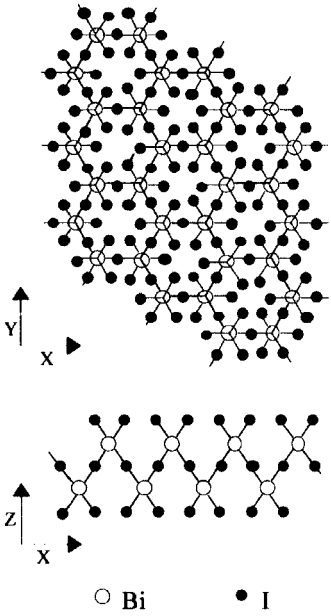

Figure 1 Two-dimensional network structure of $(Bi_2I_9^{3-})_x$.

EXPERIMRNTAL

Bismuth triiodide BiI_3 and n-alkylammonium iodides $C_nH_{2n+1}NH_3I$ (n=1, 2, 4, 8, 18), with 2:3 of the molar ratio were dissolved in ethanol. A crystalline solid of their hybrid materials was obtained by the slow evaporation of the solvent from the mixed solution. The elemental analysis: Calculated for $(C_{18}H_{37}NH_2)_3Bi_2I_9$: C, 27.4; H, 5.10; N, 1.77; I,48.2. Found: C, 27.4; H, 5.19; N, 1.71; I, 48.4. The thin film was prepared on a quartz substrate using a conventional spin-coating technique from acetonitrile solution. Almost saturated solutions were dropped onto the substrate and spread with the spinning rate of 3500-7000 rpm. All prepared films have their thickness of about 20-30nm.

XRD patterns of the films were obtained by a Mac Science MXP-18 X-ray diffractometer with the use of Cu-Kα radiation. UV-Vis-NIR absorption spectra of the films were taken by Shimadzu UV-3100PC spectrophotometer in the wavelength range of 200-2400 nm. THG Maker-fringe measurements were carried out between 1.5 and 1.8 μm of the fundamental wavelength with wavemixing of a Q-switched Nd:YAG laser and a tunable dye laser. Third-order nonlinear susceptibilities $\chi^{(3)}$ were calculated by the procedure reported elsewhere.[5]

RESULTS AND DISCUSSION

The spin-coated films prepared from $(C_nH_{2n+1}NH_3)_3Bi_2I_9$ (n=4, 8, 18) has high transparency with a reddish orange color. However, in the case of n=1, 2, their film has poor quality with light scattering. Figure 2 shows X-ray diffraction profiles of the films of $(C_nH_{2n+1}NH_3)_3Bi_2I_9$ (n=2, 4, 18). All profiles are characteristic of the hybrid complexes; which are different from those of alkylammonium iodide or bismuth triiodide themselves. A strong peak at 2θ=3.1° and a quite weak peak at 6.2° were observed in the profile of $(C_{18}H_{37}NH_3)_3Bi_2I_9$, corresponding to a long-period spacing of 28.5 Å and its 2nd reflection, respectively. The obtained long spacing were plotted against the number of carbon of alkylammonium cation in figure 3. This shows the long spacing is setting linearly longer with the number of carbon, indicating that alkylammonium cation oriented perpendicular to the surface in the film. On the other hands, a noticeable difference on the XRD profile could not be found in the

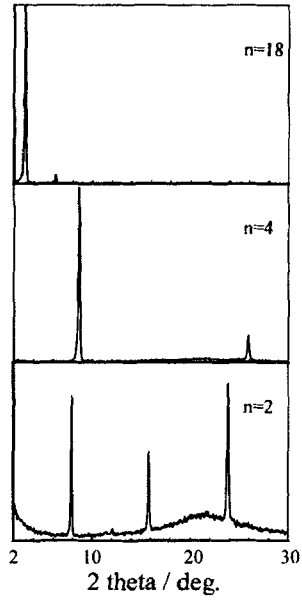

Figure 2 X-ray diffraction profiles of $(C_nH_{2n+1}NH_3)_3Bi_2I_9$.

case of n=1 and n=2. Their long spacing were almost constant ca. 1.1nm, as plotted in figure 3. R. Jakubas et al.[4] reported that, in the crystal of $(CH_3NH_3)_3Bi_2I_9$, the $CH_3NH_3^+$ cations occupied cavities on the rigid polyanions $(Bi_2I_9^{3-})_x$. This means that small size cations such as $CH_3NH_3^+$ and $C_2H_5NH_3^+$ are trapped between the $(Bi_2I_9^{3-})_x$ layers, thus can not work as the molecular fastener to establish them in the thin film. This is the reason why their thin films with a high transparency could not be prepared.

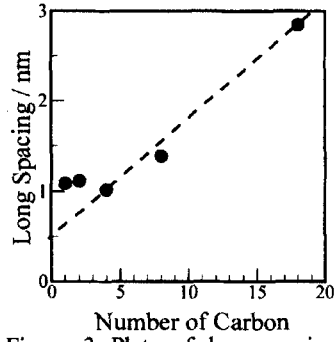

Figure 3 Plots of long spacing length against number of carbon n of alkylammonium.

An absorption spectrum of $(C_nH_{2n+1}NH_3)_3Bi_2I_9$ (n=18) thin film is shown in figure 4. Three major absorption peaks could be observed at 244, 350 and 498 nm. The alkylammonium cations itself do not have any absorption peaks in this range. So it is thought that they come from those of $(Bi_2I_9^{3-})_x$ polyanions. Similar spectral pattern could be observed for n=4, 8. Colloidal solution of BiI_3 cluster prepared in acetonitrile and vapor deposited film of bulk BiI_3 were also displayed in figure 4. An excitonic band of bulk BiI_3 could be observed near the bandgap at 590nm. The spectrum of BiI_3 colloid reveals three peaks at 290, 360, and 475nm, which are blue-shifted from the bulk bandgap. The lowest energy peak at 475nm is thought to be originated in the quantum well structure.[6] On the analogy of the spectral pattern,

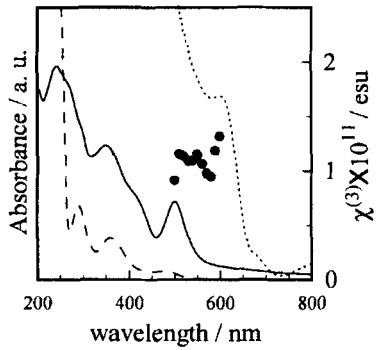

Figure 4 absorption spectra of $(C_{18}H_{37}NH_3)_3Bi_2I_9$ (solid line), colloidal BiI_3 (broken line), and vapor deposited film of BiI_3 (dotted line). $\chi^{(3)}$ values for $(C_{18}H_{37}NH_3)_3Bi_2I_9$ are also plotted against third harmonic wavelength.

from the bulk bandgap. The lowest energy peak at 475nm is thought to be originated in the quantum well structure.[6] On the analogy of the spectral pattern,

the sharp band at 498nm in the spectra of $(C_nH_{2n+1}NH_3)_3Bi_2I_9$ is thought to be also the excitonic band from the low-dimensional quantum well structure of $(Bi_2I_9^{3-})_x$. The red shift and increment of absorption intensity of the excitonic band compared with those of BiI_3 colloid might derive from the anisotropically expansion effect of their quantum well structure.

Third-order nonlinear susceptibilities $\chi^{(3)}$ were also plotted against their third harmonic wavelength in figure 4. 10^{-11} esu order of $\chi^{(3)}$ could be obtained between 500 and 600 nm of the third harmonic wavelength. This seems to be enhanced by three-photon resonance on the excitonic band at 498nm. These relatively large $\chi^{(3)}$ values may be originated from delocalized electron in the layered $(Bi_2I_9^{3-})_x$. On the other hand, the largest $\chi^{(3)}$ value in our study was observed at 600nm, which is shifted toward lower energy region than excitonic absorption at 498nm. Such behavior is resembled to those of the glassy semiconductor.

CONCLUSION

We prepared the hybrid thin film consisted from BiI_3 and $C_nH_{2n+1}NH_3I$ by the conventional spin coating technique. Reddish orange thin films with high transparency were obtained in the case of $n \geq 4$. It was indicated that long chain alkylammonium cations play an important role as the molecular fastener to fabricate inorganic-organic hybrid thin film with high quality. From their THG measurements, it was suggested that $(C_nH_{2n+1}NH_3)_3Bi_2I_9$ ($n \geq 4$) have a high potential as a nonlinear optical material, even though it is off resonance condition. This result is related to the existence of corrugated two-dimensional network structure of $(Bi_2I_9^{3-})_x$ with delocalized electron.

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