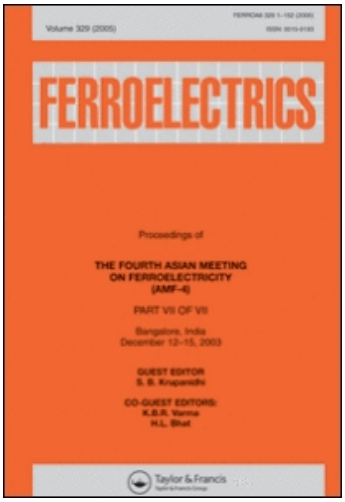

Ferroelectrics
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617887

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Yuhuan Xu[a]; F. Del Monte[a]; J. D. Mackenzie[a]; K. Namjoshi[b]; P. Muggli[b]; C. Joshi[b]
[a] Department of Materials Science and Engineering, University of California, Los Angeles, CA, USA [b] Department of Electrical Engineering, University of California, Los Angeles, CA, USA

To cite this Article Xu, Yuhuan , Monte, F. Del , Mackenzie, J. D. , Namjoshi, K. , Muggli, P. and Joshi, C.(1999) 'Nanocomposite of semiconducting ferroelectric antimony sulphoiodide dots-doped glasses', Ferroelectrics, 230: 1, 11 — 20
To link to this Article: DOI: 10.1080/00150199908214892
URL: http://dx.doi.org/10.1080/00150199908214892

Ferroelectrics, 1999, Vol. 230, pp. 11-20
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Nanocomposite of Semiconducting Ferroelectric Antimony Sulphoiodide Dots-Doped Glasses

YUHUAN XU[a], F. DEL MONTE[a], J.D. MACKENZIE[a], K. NAMJOSHI[b], P. MUGGLI[b] and C. JOSHI[b]

[a]*Department of Materials Science and Engineering and* [b]*Department of Electrical Engineering, University of California, Los Angeles, CA 90095, USA*

(Received December 8, 1998)

Antimony sulphoiodide (SbSI) is a semiconducting ferroelectric crystal. The SbSI possesses attractive properties, such as high pizoelectric constant, very high dielectric permittivity, and high electro-optic coefficient, but it is very difficult to grow a single crystal with bigger size. Currently, a method for synthesis of SbSI by liquid reaction has been developed in our laboratory. Nanocomposites of SbSI dots in sodium borosilicate glass as well as in organic modified silicate (ORMOSIL) matrix have been fabricated by the sol-gel technique. The dot size is controlled by processing conditions. The nanocomposites were characterized by x-ray diffraction and high resolution TEM. Quantum confinement effect was observed on optical spectra. Nonlinear optical property, the third order susceptibility $\chi^{(3)}$, of the SbSI dots-doped glasses was measured by four wave mixing method at 532 nm. The value of $\chi^{(3)}$ was found to be 6×10^{-11} esu at this non-resonant wavelength.

Keywords: semiconducting ferroelectric; antimony sulphoiodide(SbSI) dots-doped glass; sol-gel method; the third order susceptibility

INTRODUCTION

Nonlinear optical materials are required for a variety of applications including different electro-optical devices (such as directional couplers, guided-wave interferometers, and optical phase shifters, etc.)[1]. The third-order nonlinearity exists (third order susceptibility $\chi^{(3)} \neq 0$) in all crystalline and amorphous materials. The refractive index of a "$\chi^{(3)}$ material" is intensity-dependent. The index change $\Delta n = n_2 I$ is produces by a change in the intensity of the optical field itself. That is, for a waveguide switch the optical signal produces its own phase shift and hence determines its own output channel,

depending on its power. One of the potential advantages of $\chi^{(3)}$ materials is very fast optical response time(in the order of pico- or nano-second)[2]. An important sort of the third-order nonlinear optical materials is quantum confined semiconductor materials, including multiple-quantum well structures (QWS) and quantum dots (QD) materials[2]. Quantum-confinement effect in semiconductor micro-crystallites can result in novel optical properties, making these new materials attractive for applications in nonlinear optical devices, such as strong-weak beam switching, optical data storage, and lasers[3, 4]. QWS and QD materials are grown by MBE or MOCVD[5] methods and have been utilized in low-threshold or high power GaAS/AlGaAs QWS lasers. Present QWS and QDs materials are not transparent in visible region that makes their limitation for applications. Currently the nonlinear optical property of semiconductor QD-doped glasses has been enhanced[7]. However, the refractive index change Δn is not high enough for practical devices.

A theory for third-order optical nonlinearities in semiconductor microstructures was developed[6] and agreed with many experimental results. Based on the theory, the refractive index change

$$\Delta n/I = n_2 = K(r_B/R)^3[Re\chi^{(3)}] \quad (1)$$

where I is the intensity of light beam, r_B is the effective Bohr radius of the exciton, R is the dot size of the semiconductor micro-crystallite, and $[Re\chi^{(3)}]$ is the real parts of the "normalized" third-order susceptibility which depends only weakly on material parameters. In Eq.(1)

$$K = (3\pi 10^{13}/8c)(h^4\varepsilon^2)/(e^2\mu^{*2}E_g^2) \quad (2)$$

where ε is the dielectric constant of the semiconductor, μ^* is the reduced mass of electron-hole pair, E_g is the energy gap, e is electron charge, h is Planck constant, and c is light velocity in vacuum. The effective Bohr radius of the exciton

$$r_B = \varepsilon h^2/4\pi^2\mu^* e^2 . \quad (3)$$

From the Eqs.(1), (2) and (3), it is understood that the change of the optical index Dn is mainly proportional to the factor of $(r_B/R)^3$, and dielectric constantε plays a very important role. It is clear that semiconductor materials with large Bohr radii (or large ε) are the best candidates for strong nonlinearities. A possibility for increasing n_2 of a semiconductor QD doped

glass may be that looking for a semiconductor which has high dielectric constant and doping it in a glass matrix to form a new semiconductor quantum dots-doped glass.

Antimony sulfide iodide (SbSI)[8, 9] is the best candidate. This V-VI-VII compound SbSI and its family including BiSI, BiSBr, etc., are semiconducting ferroelectrics. They have relatively narrow energy gap (e.g., E_g ~ 1.9-2.0 eV, and absorption edge ~ 650-610 nm for SbSI). Semiconducting ferroelectrics SbSI have very high dielectric constant, very high electro-optical coefficient, photoconductivity, light-ferroelectric domain effect, photorefractive effect, etc.. The structural symmetry of SbSI crystal belongs to point group mmm (paraelectric phase) above 22°C and point group 2mm (ferroelectric phase) below 22°C.

The objective of this research is to develop a new semiconducting ferroelectric SbSI QD nonlinear optical material which have higher refractive index change Δn to be utilized for various nonlinear optical devices.

MATERIAL FABRICATION

SbSI crystal have good chemical stability and the melting point is 400°C. However, large size single crystal of SbSI cannot be obtained due to its strongly anisotropic structure. During past years, various growth techniques have been exploited to fabricate the SbSI crystal and thin film. By gas-phase reaction[9] very small needle-like (with length along c-axis) of crystals with a typical cross-sectional area < 1 mm^2 and a few mm in length are obtained and they are too small for any applications. Hot-pressed SbSI bulk ceramic was tried[10], but it cannot be used for applications because of their brittleness. SbSI thin films were deposited by electron-beam in Japan[11] and by vacuum thermal evaporation in USA[12]. However, these thin films were studied for their electrical but not optical properties. On the contrary to single bulk crystal growth, synthesis of very small crystallites of SbSI is not difficult. Recently, a method for synthesis of SbSI by liquid reaction was developed in our laboratory, UCLA.

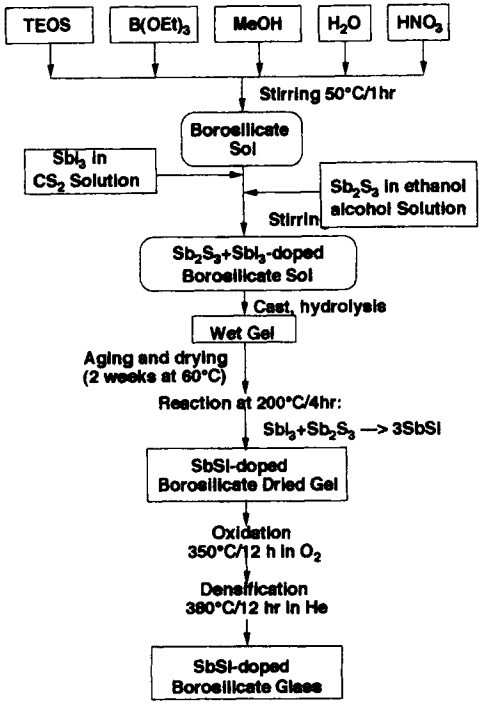

Figure 1 A flow chart for fabrication of SbSI dots-doped borosilicate glass

The sol-gel method was chosen for fabrication of the SbSI quantum dots embedded in the sol-gel derived glasses. A flow chart is shown in Fig. 1. The processing for fabrication of SbSI dots-doped glass includes: 1) preparation of the Na_2O-B_2O_3-SiO_2 gel matrix by the sol-gel route proceeds; 2) mixing the Na_2O-B_2O_3-SiO_2 wet gel with the solution of antimony tri-iodide SbI_3 in solvent (e.g., CS_2) and stirring the mixture at 50°C for few hours, SbI_3 doped a Na_2O-B_2O_3-SiO_2 wet gel is formed; 3) casting or dipping the wet gels and

aging the samples at room temperature by 1 week and thendrying them at 60°C for 2 weeks; 4) sulfidation of the dried gel in H_2S at 180°C by 2 hours. By the chemical reactions:

$SbI_3 + H_2S$ ----> $SbSI + H_2 + I_2$(gas)

H_2 + O(in the gel matrix) ----> H_2O(gas)

a SbSI dots-doped Na_2O-B_2O_3-SiO_2 dried gel is formed. The dried gel samples are heat-treated at 350°C under O_2 flow for 12 hours, and then at 380°C in air for 12 hours. Finally, SbSI dots-doped glasses (bulk or thin film) are obtained. The bulk materials are dark brown color and transparent for red light. Fabrication of SbSI QDs-doped in an ORMOSILs (organic modified silicates) matrix by the sol-gel technique is similar to the processing for SbSI QD/glass, except different starting chemicals for the matrix and lower temperature (around 200°C) for heat-treatment. SbSI QDs doped ORMOSILs materials in both bulk and film have been fabricated.

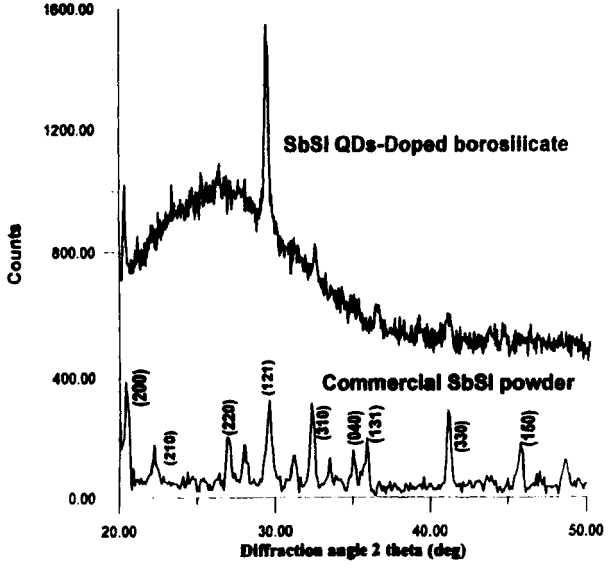

Figure 2 X-ray diffraction pattern of the same SbSI dots doped-glass in comparison with that of commercial SbSI powder.

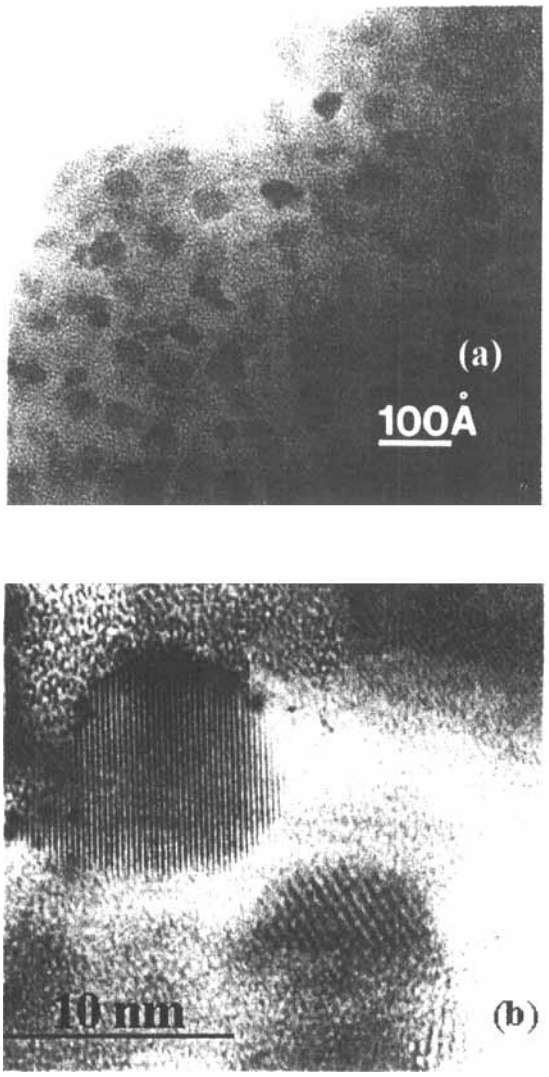

Figure 3 HRTEM image of SbSI dots-doped glass. Crystallites with size around 60Å are distributed in the glass matrix(a), and some large particles present lattice fringes(b).

CHARACTERIZATION

Figure 2 shows the X-ray diffraction pattern of the same SbSI dots doped-glass in comparison with that of commercial SbSI powder. Both the samples have the same diffraction peaks except stronger amorphous background presented on the pattern of SbSI-doped glass.

The micro-structure of the SbSI dots(concentration 8 wt%)-doped sodium borosilicate glass (with the composition of 5 mole% Na_2O-20 mole% B_2O_3-75 mole% SiO_2) was observed by high resolution transmission electron microscope (HRTEM). Figure 3(a) and (b) is the HRTEM image of the material. SbSI crystallites with size around 60 Å are distributed in the glass matrix(a) and some large particles present lattice fringes(b). Electron diffraction pattern of these particles are matched with that of commercial SbSI crystalline powder.

OPTICAL MEASUREMENTS

Linear absorption spectra of SbSI dots (8 wt%)-doped glasses annealed at different temperatures were measured by SHIMADZU UV-260 spectrum Photometer. It was observed that the absorption edge shifts from 530 to 350 nm which were corresponding to annealing temperature decreasing from 380 to 280°C. It can be understood that the lower annealing temperature, the smaller SbSI crystalline size, and the stronger quantum confinement effect. A typical exciton absorption peak at 350 nm was observed(see Figure 4).

Photoluminescence effect for SbSI dots-doped glasses was measured with shinning of Argon ion laser (488 and 515 nm). Both bulk and film samples have light-emitting in a range from 520 to 900 nm with a maximum of intensity around 600 nm. Figure 5 shows a typical photoluminescence-intensity spectrum for a bulk sample.

The third order nonlinear optical susceptibility of the SbSI dots-doped glasses was determined by degenerate four wave mixing (DFWM) at 532 nmusing a frequency doubled Nd:YAG laser beam with a pulsewidth of around 10ns (intensity of 100 MW/cm^2, and repeating frequency of 1 Hz).

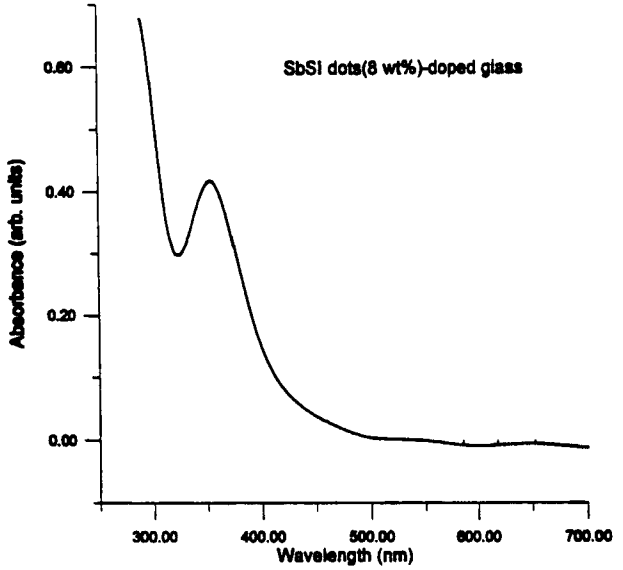

Figure 4 Exciton absorption peak at 350 nm of SbSI dots-doped glass.

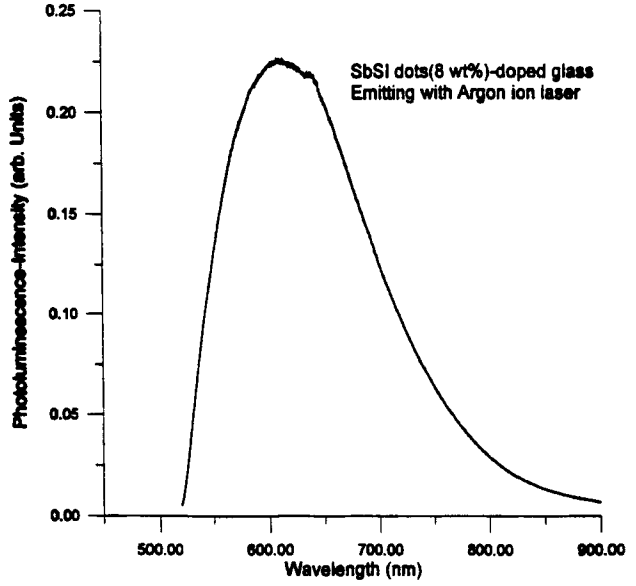

Figure 5 Photoluminescence spectrum of SbSI dots-doped glass.

Three beams were sent along three edges of a symmetric 3-D pyramid[13] and focused separately so that their focal points lay near the apex of the pyramid. When the sample was placed at the apex of the pyramid, a beam came out along the fourth edge of the pyramid which could clearly be seen on a piece of paper. This beam went away when any of the three beams was blocked, indicating nonlinear behavior. The signal was detected using a photodiode connected to a computer for acquiring data. Then a CS_2 cell and a CdS filter were also put at the same position and the values of the nonlinear signals were measured. Using these comparative data[12]. The value of $\chi^{(3)}$ of 3 μm thick thin film of SbSI (8 wt%)-doped glass sample was found to be 6×10^{-11} esu. The laser frequency was away from the resonant frequency of the exciton for the sample.

DISCUSSION

1) Based on the optical absorption results, it is understood that the exciton peak and absorption edge are strongly related with controlling annealing temperature and the doping concentration. Obviously, if the crystallites have uniform small size and high concentration, the material will has better nonlinear optical properties. 2) For our SbSI dots-doped glass samples the exciton absorption peak was observed at 350 nm, and the $\chi^{(3)}$ was measured by the light at 532 nm. Therefore, the measured data represents that effect which worked in a non-resonant mode, and hence the data is certainly much smaller than that in a resonant mode. 3) Since SbSI is a ferroelectric crystal, it is expected that when an a.c. electrical field applied on SbSI dots-doped glasses, the dipoles in the dots will be switched, which means that exciton-recombination will be controlled by the field, and hence optical emission can be controlled by electrical signals.

CONCLUSION

1) A new kind of quantum dots-doped glass, semiconducting ferroelectric SbSI dots-doped glass was successfully fabricated by liquid reaction method.

By XRD and TEM techniques, it was identified that SbSI crystallites with size around 60 Å were distributed uniformly in the glass matrix. 2) Strong quantum confinement effect including exciton peak, edge blue shift, and light emitting was observed from optical absorption and photoluminescence experiments. 3) The third order nonlinear optical susceptibility, $\chi^{(3)}$, was found to be 6×10^{-11} esu. at 532 nm. This wavlength was away from the exciton resonance wavelength.

Acknowledgments
The authors wish to express their appreciation's to Mr. R. T. Nielsen for the photoluminescence measurement. This work was supported by the AFOSR/ BMDO.

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