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Temperature dependent nonlinear coefficients and second harmonic generation in quaternary glass system doped with TiO_2

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The paper reports the effect of poling temperature (120 °C to 200 °C in the step of 40 °C for 1 hour) on the second order nonlinear coefficient for quaternary glass (54.04 P_2O_5 -30.02 Bi_2O_3-7.38 ZnO-8.55 K_2O) doped with X percentage of TiO_2 (X = 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1) determined by Maker's fringe patterns. Corresponding coherent second harmonic generation (SHG) in the forward direction is also studied. A 400 dc voltage was applied for the glass samples of thickness 1mm at the poling temperature. It is observed that the coherent SHG intensity increases with increase in TiO_2 percentage, reaches maximum at 0.4% TiO_2 and decreases for further increase in TiO_2. SHG intensity increases with the increase in poling temperature. It is observed that value of d-coefficients (d_{31} and d_{36}) change with the poling temperature.

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1. Introduction

The measurement of the nonlinear optical (NLO) coefficients of materials is of interest. Two different experimental techniques have been widely used to measure NLO coefficients. The first one is concerned with the possibility of obtaining phase matching between the fundamental and the harmonic waves while the second, irrespective of the phase matching, can be used for all the materials. The technique was used by Maker et al. [1] on quartz to demonstrate the interference between the bound and free harmonic waves. By varying the angle of incidence of a laser beam on the plane parallel sample of NLO material, the intensity of the generated second harmonic in the forward direction is found to oscillate in a periodic fashion.

The nonlinear optical properties of materials have received an increasing importance since the invention of a laser. The optical nonlinear devices are useful as optical modulators, optical switches, memories etc. Much attention has been focused on glassy materials because of their large optical nonlinearity and fast response time [2]. Glasses are widely used in optical applications due to their good optical quality and low transmission loss in the region of interest. Large second order nonlinearity (SON) in thermally poled glasses is of great interest since it opens new frontiers in optical material research. The SON is not expected in glass because of its inversion symmetry. However, in 1991 it was observed that a permanent and large SON can be generated in fused silica using thermal poling [3]. Since then a large number of investigations were done on the physical mechanism and potential applications of the SON in glassy materials, [4-8]. To the best of our knowledge TiO_2 doped quaternary glass is not yet explored for SON. Phosphate glasses are substrates of choice because they can incorporate a large concentration of rare-earth ions to work as a lasing material. Waveguide lasers based on phosphate glasses have been reported by several groups [3,4,9].

In this paper we report a detailed Maker fringe investigation to find the nonlinear coefficients on thermally poled 54.04 P_2O_5 -30.02 Bi_2O_3-7.38 ZnO-8.55 K_2O quaternary glass system doped with different percentage of TiO_2 as a function of poling temperature along with coherent second harmonic generation.

2. Experimental

A quaternary glass system 54.04 P_2O_5-30.02 Bi_2O_3-7.38 ZnO-8.55 K_2O (in mol %) was prepared from analytically pure powders of $NH_4H_2PO_4$, Bi_2O_3, ZnO and K_2CO_3 and with variable % of TiO_2 (0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1). The mixture of raw materials was thoroughly mixed in a mixer/ grinder at its highest speed (14,000 RPM) for 5 minutes to get uniform mixture of the above powders. This mixture was melted in an alumina crucible at 750 °C and soaked at the same temperature for 3 hours. The glass was quenched into preheated stainless steel moulds and annealed close to the glass transition temperature (T_g). T_g in the above proportion determined by differential thermal analysis (Rigaku, TG-DTA 8112BH). The poling was performed on $10 \times 10 \times 1 mm^3$ size samples sandwitched in between two flat electrodes made up of stainless steel. A dc voltage of 400V was applied across the glass sample with poling temperature of 120 °C, 160 °C and 200 °C respectively for 1 hour, followed by gradual cooling to room temperature in the presence of poling voltage.

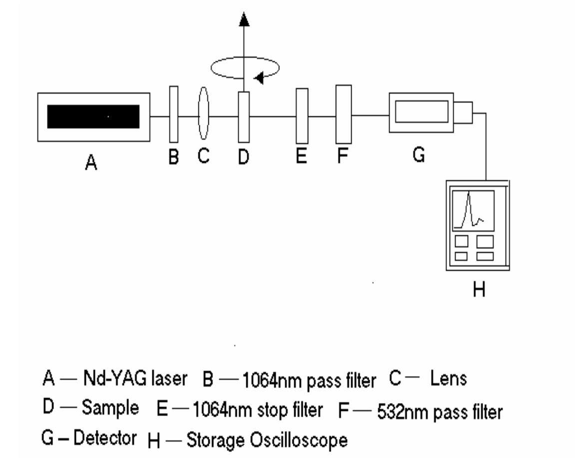

Fig. 1. Experimental setup for measuring Maker fringe patterns and coherent SHG in poled glasses.

The Maker fringe and coherent SHG setup, shown in Fig. 1, was used to analyze the nonlinear profile induced in the poled samples. The pump beam from a 1064 nm Q-switched Nd-YAG laser having a pulse width of 20 ns, pulse energy of 15mJ and repetition rate of 1Hz was focused onto the poled sample mounted on a sample holder through a lens 14 cm of focal length. The incident laser radiation was filtered by a 1064 nm pass filter (Melles Griot) to minimize the background intensity. The generated second harmonic signals from the poled sample were measured as a function of incident angle for determining the Maker's fringe pattern, while for coherent SHG the poled sample was set with its surface facing a pump beam. The measurements were repeated at least six times and were found to be reproducible with the accuracy of ± 4 % SHG inensity. The signal generated was focused onto a detector fast photodiode (FND100) through 532 nm pass filter (Melles Griot). The SHG signal was measured using a fast storage oscilloscope (THS 730 A) and coherence was confirmed by using a polarizer.

3. Results and discussion

Coherent second harmonic generation in quaternary glass system 54.04 P_2O_5 -30.02 Bi_2O_3-7.38 ZnO-8.55 K_2O doped with TiO_2 has been carried out for samples poled at 120 ^oC, 160 ^oC, 200 ^oC with 400V dc during poling of 1hour is shown in Fig. 2, (a), (b) and (c) respectively. The SHG intensity varies as square of the input intensity, the pulse width of fundamental beam and 2ω (second harmonic) beam was found to be the same confirming the second harmonic generation (measured on FND-100 with appropriate filters). Fig. 3 shows a quadratic dependence on fundamental laser intensity. SHG signal in 0.4% TiO_2 doped sample, poled at 200 ^oC. Inset shows the second harmonic signal in KDP. The straight line fit to the experimental data points with slope 1.99 $\pm$ 6 and 2.0 $\pm$ 0.1 for poled sample and KDP respectively.

The sample could not be poled at higher applied voltages due to formation of the corona discharge on the sample. The SH signal increases as the poling temperature increases. Fig. 4 shows the SH signal of quaternary glass system 54.04 P_2O_5 -30.02 Bi_2O_3-7.38 ZnO-8.55 K_2O doped with different % of TiO_2. It is observed that coherent SHG increases as the % of TiO_2 increases, reaches its maximum at 0.4% of TiO_2 and then decreases with further increase in the % of TiO_2. The behavior can be attributed to the absorption of the fundamental wave at higher concentration of TiO_2.The same samples were used to determine the Maker fringe pattern.

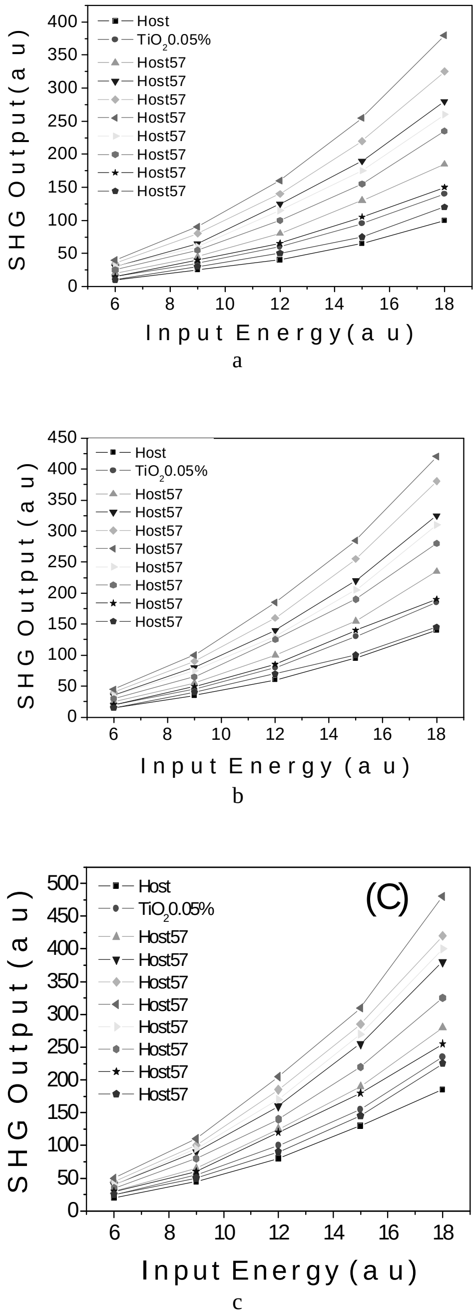

Fig. 2 Second harmonic generation of quaternary glass X different % of TiO2 poled at (a) 120 ^oC (b) 160 ^oC (c) 200 ^oC.

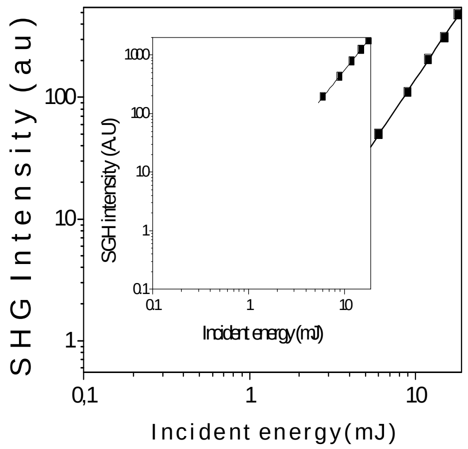

Fig. 3. SHG signal in 0.4% TiO_2 doped sample. Poled at 200 °C. Inset shows the second harmonic signal in KDP. The straight line fit to the experimental data points with slope 1.99 ± 6 and 2.0 ± 0.1 for poled sample and KDP, respectively.

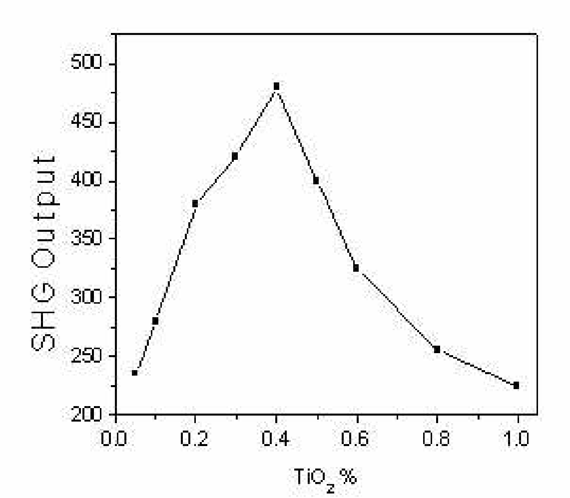

Fig. 4. SHG output of quaternary glass system as a function of TiO_2 % doped.

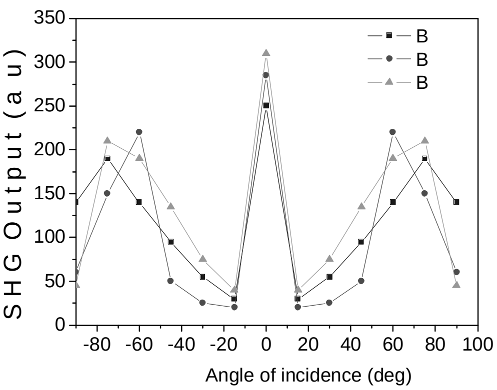

Fig. 5. Maker fringe patterns of quaternary glass systems doped with 0.4 % of Tio_2 poled at 120 °C, 160 °C and 200 °C with an applied voltage 400 V.

Comparison of Maker fringe patterns between poled samples at different poling temperatures 120 °C, 160 °C and 200 °C and applied voltage 400 V during poling is shown in Fig 5. It should be pointed out that the Maker fringe pattern of the sample poled at 120 °C and 200 °C show similar pattern [10-15]. This type of fringe pattern can be found in two cases; (i) a thin nonlinear susceptibility ($\chi^{(2)}$) layer in combination with the presence of a bulk $\chi^{(2)}$; i.e., a $\chi^{(2)}$ which is a extended throughout the entire bulk sample, or (ii) a thin $\chi^{(2)}$ layer on the anode surface with an additional layer of $\chi^{(2)}$ near the cathode surface.

The objective of Maker fringe pattern method is to measure the second harmonic power generated by a sample as a function of the angle of rotation (i.e., as a function of the angle of incidence of the fundamental beam), and compare this measurement with Potassium dihydrogen phosphate (KDP) well characterized material to obtain the d_{eff} of the sample [16]. The second order nonlinear coefficients are given in Table 1.

Table 1.

Poling temp.	d_{36} pm/V	d_{31} pm/V
120	111	317
160	90	335
200	117	349

For finding the planes Miller's rule was used (17). The nonlinear coefficients d_{31} and d_{36} were considered on the basis of sample rotation axis and fundamental beam axis (18).

The equation (1) gives the nonlinear coefficients.

$$d_{eff} = \left[\frac{P_m(\theta)\eta}{P_m^{ref}(\theta)\eta^{ref}} \right]^{1/2} \left[\frac{L_c^{ref}(\theta)}{L_c(\theta)} d_{eff}^{ref} \right] \qquad (1)$$

Where $Lc(\theta)$ is the coherence length of corresponding angle obtained from fringe spacing, $Pm(\theta)$ is the envelope of peaks in the fringe pattern.

Where

$$\eta = \left[\frac{(n_\omega + 1)^3 (n_{2\omega} + 1)^3 (n_{2\omega} + n_\omega)}{128 n_{2\omega} R(\theta)} \right] \qquad (2)$$

Where n_ω and $n_{2\omega}$ are the refractive indices of the prepared glass at the fundamental and second harmonic frequency respectively, $R(\theta)$ is the multiple reflection factor.

Fig. 5 corresponds to Maker fringe pattern of the sample poled at different temperatures, where the near surface becomes small. The bulk effect seems strongly sensitive to uncontrolled effects during poling but it is always induced in more or less degree [19]. The very different depth of the two nonlinear profiles allows us to associate the short period fringes with the bulk effect. The rising of the envelope of the fringe minima is due to the near surface effect as well as the exponential distribution of the bulk nonlinearity. The coherent second harmonic generation was observed for samples poled at 0.3-0.5 kV, no second harmonic signals were detected from the specimens heat treated with a voltage in the range of 0-0.3 KV applied. This observation indicates that in the present experiments the surface crystallization is necessary for the SH signal [20], which might be occurring at 400 V. There is a less SH output in the angle range 15^o -45^o may be due to the stress caused during the cooling process from heat treatment temperature to room temperature because of difference in thermal expansion coefficient of different components of glass and precipitated crystals. However, this kind of stress leads to symmetry in poled glass materials which show less SH signal at these angles but have maximum intensity at larger angle [21].

4. Conclusions

We have considered KDP as the standard reference sample to find nonlinear coefficients of quaternary glass system 54.04 P_2O_5 -30.02 Bi_2O_3-7.38 ZnO-8.55 K_2O doped with TiO_2 (0.4%) by using Maker fringe pattern. Sample poled at 200 ^oC exhibited higher second order nonlinear coefficient value for the plane 010. We have shown that the quaternary glass system nonlinear coefficient can be maximized by an appropriate choice of doping material and percentage. Coherent SHG has increased in 0.4% TiO_2 doped sample. As the poling temperature increases there is a increase in coherent SHG, no SHG response for samples poled at below 120 ^oC.

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