Enhancing the second-order optical nonlinearity induced in bismuthate glasses by thermal poling

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The second-order optical nonlinearity induced in glass by thermal poling is proportional to the product of the glass' intrinsic third-order optical nonlinearity and the electrostatic field that is frozen inside the glass after poling. Therefore, bismuthate glasses, which exhibit intrinsically high third-order optical nonlinearity (with respect to e.g. silica), are attractive for enhancing the poling-induced second-order optical nonlinearity. Through careful optimization of both glass composition and poling conditions, we show that the second-order nonlinear coefficient can be enhanced significantly in Bi_2O_3–ZnO–B_2O_3 glasses, increasing from 0.2 pm/V in bismuth-free borate glass to 0.7 pm/V in 25-mol% Bi_2O_3 borate glass.

Introduction

Poled glass is an attractive material for making devices such as electro-optic switches and wavelength converters, in the form of either planar waveguides or optical fibres [1]. Among various glass poling techniques, thermal poling has proven to be both straightforward and reliable: the poling-induced second-order nonlinearity is of the order of $\chi^{(2)}$ = 1 pm/V in thermally poled silica, it possesses excellent long-term stability at room temperature and it is determined mainly by poling conditions [2]. The level of second-order nonlinearity does not change significantly with glass chemical composition but the stability of the nonlinearity is very much dependent on the latter [3]. Although the induced $\chi^{(2)}$ in thermally poled bulk silica is one or two orders of magnitude lower than the intrinsic $\chi^{(2)}$ in nonlinear crystals such as $LiNbO_3$, the conversion efficiency of nonlinear interactions can be kept at acceptable values by taking advantage of the longer interaction length and the higher damage intensity threshold available in periodically poled fibre waveguides [4] in comparison with their crystal planar waveguide counterparts. As far as building practical devices is concerned, however, enhancing the material's nonlinear coefficient is an obvious but still difficult task. Indeed, the underlying poling mechanism sets an upper limit to $\chi^{(2)}$ values achievable for a given glass. Briefly, thermal poling of glass involves the creation and then the storage of an extremely high electrostatic field (~10^8 V/m) in a near-surface layer underneath the anode, resulting in an effective second-order nonlinear optical susceptibility through the rectification of the intrinsic third-order nonlinear optical susceptibility by this frozen-in field: i.e. $\chi^{(2)} = 3\times\chi^{(3)}\times E_{dc}$ (note that alignment of dipoles along the direction of E_{dc} may contribute to the nonlinearity as

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well) [5]. This rectification model predicts that the maximum level of $\chi^{(2)}$ is set by the dielectric breakdown strength of the glass, i.e. $E_{dc} < E_b$. That is the bad news. But there is a good news: the rectification model predicts that $\chi^{(2)}$ should increase in proportion to $\chi^{(3)}$, for a given value of E_{dc}. According to this latter prediction, enhancement of $\chi^{(2)}$ can be achieved using the following strategy : 1) to search for a glass whose chemical composition gives a higher $\chi^{(3)}$ than in silica, 2) to pole it in such a way that the frozen-in field strength is at least as high as in silica. High-index glasses, such as Bi_2O_3–based ones, are potentially interesting for this purpose. Hereafter, we demonstrate that, following the above-mentioned strategy, the second-order nonlinearity can be enhanced significantly in Bi_2O_3–ZnO–B_2O_3 glasses. Details about the underlying physical mechanisms are not discussed here but can be found in [6].

Glass samples and experimental conditions

Glass samples were fabricated by melting and quenching in the ternary Bi_2O_3–ZnO–B_2O_3 system and in the binary ZnO–B_2O_3 system. As the Bi_2O_3 content increased (from zero to 25.0 mol%), the glass transition temperature decreased (from ~550°C to ~419°C) while the glass density increased (from ~3.0 g/cm^3 to ~6.1 g/cm^3) and the refractive index increased (from ~1.62 to ~1.91). The $\chi^{(3)}$ enhancement factor (with respect to silica; refractive index: n_s), as estimated from Miller's rule by $F = \left[\left(n^2-1\right)/\left(n_s^2-1\right)\right]^4$, increased from 4.7 to 33.3 as n increased from 1.62 to 1.91. The refractive index was estimated from the Fresnel reflection contribution to measured optical transmission loss spectrum. The samples (thickness ranging from 0.2 mm to 1.0 mm) were poled inside an oven using pressed-contact electrodes. The poling procedure consisted in heating slowly the sample up to a prescribed temperature, applying the voltage (a few kilovolts) for a certain time (from a few minutes to more than one hour), cooling the sample slowly with the voltage still applied, and finally removing the voltage when the temperature became closer to room temperature. Various combinations of poling temperature and time were tested and different types of electrodes were used (see ref. [6] for details). Because of their relatively low glass transition temperatures, Bi_2O_3–ZnO–B_2O_3 glasses underwent large thermal stresses during poling. In order to avoid breaking of the sample, heating and cooling had to be carried out slowly and the maximum poling temperature had to be scaled according to T_g. The second-order optical nonlinearity induced after poling was evaluated through second-harmonic generation (SHG) Maker fringe experiments (details about the nonlinearity evaluation method can be found in ref. [6]).

Experimental results

Poling had to be carried out at temperatures relatively close to T_g in order to induce second-order optical nonlinearity in Bi_2O_3–ZnO–B_2O_3 glasses. On overall, the normalized SHG signal (η_{SHG}) was of the same order of magnitude as in silica ($\eta_{SHG} = 1$) when poling was carried out at temperatures ranging from $0.75\times T_{g,K}$ to $0.95\times T_{g,K}$, the optimal temperature depending on Bi_2O_3 content (Figure 1). Etching of poled samples in diluted nitric acid revealed that the nonlinearity was located in a thin layer underneath the sample surface which was in contact with the anode during poling. Like for silica, the SHG signal depended on the duration of poling (at a fixed poling temperature): the values of η_{SHG} displayed in Figure 1 are the peak values with respect to poling time. Like for silica, the SHG signal depended on the sample thickness but

the dependence was found to be much stronger than in silica: for instance, after poling of 12.5 Bi_2O_3 – 43.75 ZnO – 43.75 B_2O_3 glass, η_{SHG} was two orders of magnitude higher in 0.2-mm thick samples than in 1.0-mm thick samples, all poling conditions being the same (350 °C, 4 kV, 5 min). This dependence is too strong to be solely due to a change of the thickness of nonlinear layer with the sample thickness (η_{SHG} is actually proportional to the squared product of the nonlinear thickness and the spatially averaged nonlinear coefficient). More likely, it could be due to a possible influence of the sample thickness on the formation dynamics of the nonlinear layer [6].

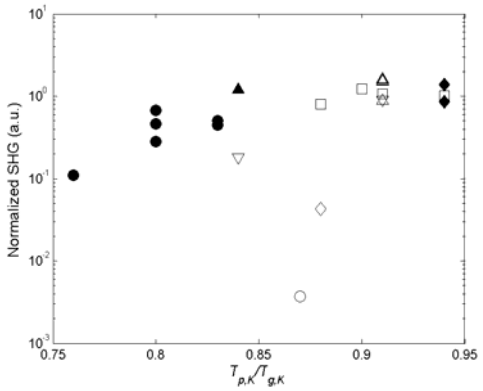

Fig. 1. Normalized SHG signal (pump wavelength: 1064 nm) as a function of the ratio between poling and glass transition absolute temperatures ($T_{p,k}/T_{g,k}$) in thermally poled glasses of various compositions (mol%): 55 ZnO – 45 B_2O_3 (◇,◆), 6.25 Bi_2O_3 – 46.88 ZnO – 46.88 B_2O_3 (□), 12.5 Bi_2O_3 – 43.75 ZnO – 43.75 B_2O_3 (△,▽,▲) and 25.0 Bi_2O_3 – 37.5 ZnO – 37.5 B_2O_3 (○,●). Samples were poled at 4 kV for different times. Highest values of SHG signal (with respect to poling time) are displayed for each glass. Samples thickness: 1.0 mm (◇,□,△,○), 0.9 mm (◆), 0.5 mm (▽), 0.2 mm (▲,●).

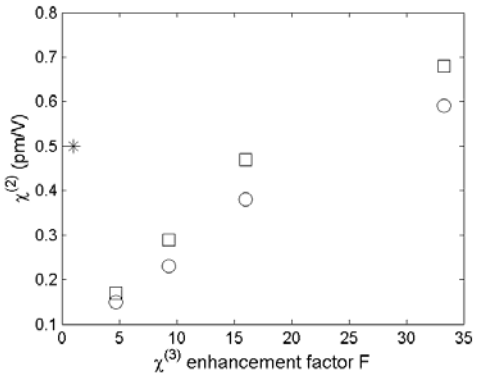

Fig. 2. Values of the second-order nonlinear coefficient $\chi^{(2)}$ (spatially averaged across the nonlinear layer) in thermally poled glasses under study as a function of $\chi^{(3)}$ enhancement factor F (with respect to silica). The values of $\chi^{(2)}$ are calculated from Maker fringe measurements performed on samples and calibrated using a quartz plate. For calculation, refractive indexes at pump and SH wavelengths were either taken from reported data for Bi_2O_3 – B_2O_3 glasses [7] (circles) or estimated from Fresnel reflection measurements (squares). The typical level of $\chi^{(2)}$ in thermally poled silica (F = 1) is indicated by a star.

The values of $\chi^{(2)}$ were found to increase with increasing Bi_2O_3 content, and therefore with increasing $\chi^{(3)}$ of the glass (Figure 2). On overall, $\chi^{(2)}$ was of the same order of magnitude as in thermally poled silica. For the glass with the highest Bi_2O_3 content (25.0 mol%), $\chi^{(2)}$ reached 0.7 pm/V for the present poling conditions. Regarding the evaluation of $\chi^{(2)}$, it is worth to note that 1) only the lower limit of $\chi^{(2)}$ was obtained in some cases (when instead of measured values of the nonlinear thickness, the coherence length was used as an upper limit), 2) slightly underestimated $\chi^{(2)}$ was obtained using refractive index values taken from reported data for Bi_2O_3 – B_2O_3 glasses [7], 3) the determination of the nonlinearity depth profile should improve the evaluation of the nonlinearity, possibly revealing local value of $\chi^{(2)}$ higher than the spatially average one. Finally we would like to mention that higher local values of $\chi^{(2)}$ were obtained recently by modifying the poling procedure [8].

Discussion

The experimentally determined relationship between $\chi^{(2)}$ and $\chi^{(3)}$ is sub-linear and has an offset with respect to $\chi^{(2)}$ level in poled silica (Figure 2). Assuming that the $\chi^{(2)} = 3\times\chi^{(3)}\times E_{dc}$ rectification model is still valid here and that the frozen-in field has reached the limit set by dielectric breakdown ($E_{dc} \cong E_b$), this result implies that the dielectric breakdown strength E_b is lower in Bi_2O_3–ZnO–B_2O_3 glasses than in silica and decreases slightly with increasing Bi_2O_3 content. The incorporation of bismuth in the matrix increases the $\chi^{(3)}$ of the glass but, we believe, reduces E_b because electrons in bismuth orbitals are less tightly bonded. If it is the case that high-index glasses have intrinsically low dielectric breakdown strengths, then the enhancement of $\chi^{(2)}$ will not be directly proportional to the increase of $\chi^{(3)}$ and the limit $E_{dc} < E_b$ must be considered seriously. In practice, a trade-off has to be made between $\chi^{(3)}$ and E_b when one selects glass candidates for enhancing $\chi^{(2)}$ by the rectification model strategy.

Conclusion

We have demonstrated for the first time that the second-order nonlinearity $\chi^{(2)}$ induced by thermal poling in high-index Bi_2O_3–ZnO–B_2O_3 glasses increased with increasing values of the intrinsic third-order nonlinearity $\chi^{(3)}$, as predicted by the rectification model. Experimental results suggest that the dielectric breakdown strength was lower in these glasses than in silica and decreased with increasing Bi_2O_3 content. The latter result showed the importance to select glass compositions on the basis of *both* the intrinsic $\chi^{(3)}$ and dielectric breakdown strength for the purpose of enhancing $\chi^{(2)}$.

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