High second-order nonlinearities induced in lead silicate glass by electron-beam irradiation

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A new technique for inducing a large permanent second-order susceptibility in lead silicate glass is reported. The procedure involves implanting electrons by irradiating the glass with an electron beam. Second-order nonlinearities $\chi^{(2)}$ as high as 0.7 pm/V are obtained.

It is clear that any technique that permits the creation of a large second-order nonlinearity in glass is of great interest both for practical reasons and from the standpoint of the underlying physics. The replacement of expensive nonlinear crystals with low-cost glasses would open up the prospect of parametric frequency converters and linear electro-optic modulators that are fully integrated into optical fibers or planar glass waveguides. In addition, the elucidation of the physical mechanism leading to the breakage of centrosymmetry in glass would be of considerable fundamental importance.

A host of techniques that lead to the creation of permanent second-order nonlinearity in glasses have been reported by several groups.[1–6] The most promising recent techniques are those reported by Myers *et al.*,[5] who created a second-order nonlinearity of 1 pm/V in the anodic surface of a silica glass sample by thermal poling at 250 °C under an applied electric field, and by Okada *et al.*,[6] who reported second harmonic (SH) generation in corona-poled glass waveguides.

An additional technique that has so far not been investigated is charge implantation by exposure to a low-energy electron beam. This method is already in use for poling polymers[7] and creating periodically inverting domains in lithium niobate[8] and tantalate[9] crystals. It has definite advantages over other poling techniques in that it offers the high resolution necessary for creating the complex periodic patterns needed in devices employing quasi-phase-matching. In this Letter we report what is to our knowledge the first successful use of electron implantation to create a large permanent second-order susceptibility in glass.

It has been known for a considerable time that the injection of electrons into dielectrics can lead to the formation of a space-charge electrostatic field directed perpendicular to the surface of the sample (the z direction). This field acts on the third-order susceptibility to create an effective second-order susceptibility. The SH polarization in an isotropic medium is then given by

$$P_z = \epsilon_0 d_{33} E_z^{\,2} + \epsilon_0 d_{31}(E_x^{\,2} + E_y^{\,2}),$$

$$P_y = 2\epsilon_0 d_{31} E_y E_z, \qquad P_x = 2\epsilon_0 d_{31} E_x E_z,$$

where the effective nonlinear coefficients are related by $d_{33} = 3d_{31}$ when conditions for Kleinman symmetry hold. In the case of a pump wave polarized in the plane of incidence (the $x-z$ plane), $P_y = 0$. It is the component of nonlinear polarization perpendicular to the propagation vector $k_{2\omega}$ that produces a SH polarization,

$$P_\perp = \epsilon_0 d_{33} E^2 n^{-1} \sin\alpha,$$

where E is the pump optical field, α is the angle of incidence, and n is the refractive index of the medium.

It is worth noting that if the P_x polarization component is omitted, this could lead to an overestimation by a factor of 2 of the nonlinear coefficient. This might also explain the disagreement in the ratio of the nonlinear tensor components observed in Ref. 5.

Experiments were carried out in samples of lead silicate glass (Pb ~ 45 wt.%) and commercial soda-lime glass coverslips. A scanning electron microscope was used for electron-beam irradiation of the samples. The beam currents used were in the range 0.3–10 nA, and the beam voltage ranged between 5 and 40 kV. The electron-beam spot size was 0.5 μm. The TV mode of a scanning electron microscope (horizontal scanning rate 0.064 ms/line, vertical scanning rate 0.017 s/frame) and a slower, SL-3, scanning mode (horizontal scanning rate 20 ms/line, vertical scanning rate 20 s/frame) were used. Two types of sample were prepared. In the first (type I) the dimensions were 2.5 mm × 20 mm × 30 mm, and the two 20 mm × 30 mm surfaces were polished. The other samples (type II) had dimensions of 1 mm × 7 mm × 30 mm. In the type II case, one 30 mm × 1 mm surface was also polished in addition to the two 7 mm × 30 mm surfaces. Areas of approximately 1 mm × 1 mm on one of the two 20 mm × 30 mm surfaces were irradiated in the electron microscope for type I samples; whereas, for type II samples areas of 1 mm × 1 mm on the polished 1 mm × 30 mm surface were irradiated. The duration of the irradiation ranged from 20 s to 30 min.

After irradiation, the samples were tested for evidence of SH generation. Q-switched (1-kHz repetition rate, 200-ns envelope duration) mode-locked (76-MHz repetition rate, 3-ns pulse duration) Nd:YAG

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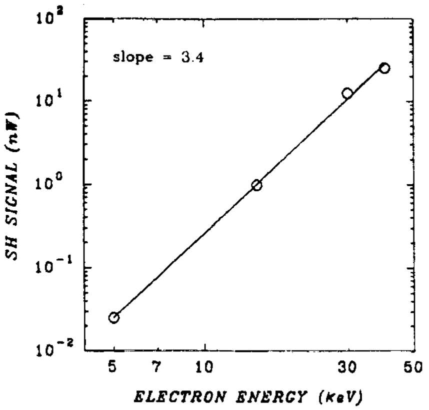

Fig. 1. SH signal as a function of electron-beam energy. The current was kept constant at 3 nA for an electron-beam spot diameter of 0.5 μm, a frame size of 1 mm × 1 mm, a horizontal scanning rate of 0.064 ms/line, and a vertical scanning rate of 20 s/frame. The solid curve is the best straight-line fit, yielding a slope of 3.4 on the log–log plot.

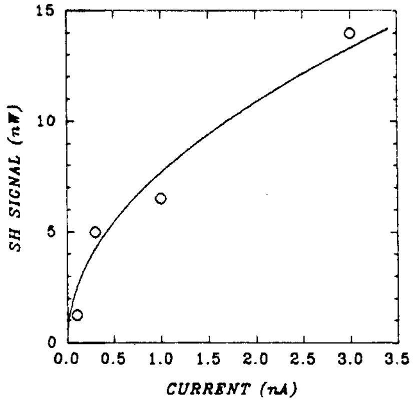

Fig. 2. SH signal as a function of electron-beam current. The electron energy was fixed at 40 keV. The scanning conditions were identical to those in Fig. 1.

laser pulses at 1064 nm were used as a pump source, with an average power of 1.2 W.

The pump laser beam, polarized in the plane of incidence, was focused (by using a lens of focal length 10 cm) onto the electron-beam-irradiated areas of the type I samples. The angle of incidence (approximately 60°) was chosen to lie close to the Brewster angle, and the diameter of the pump beam in the focal spot was approximately 40 μm.

No visible SH signal was observed in the treated samples of coverslip glass. In contrast, relatively efficient SH generation (visible to the naked eye) was observed from the irradiated lead silicate glass samples, which had been exposed for approximately 1 min to the electron beam. Longer exposures did not lead to any significant increase in the SH signal.

The dependence of SH power on electron-beam energy and current was explored. The SH efficiency was found to increase exponentially with the electron energy to as high as the limit of 40 keV imposed by the scanning electron microscope (Fig. 1). It also increased with the electron-beam current (Fig. 2). However, strong inhomogeneities in the SH signal from different irradiated regions of glass were present at high currents (approximately 10 nA). Such behavior appears to be due to inhomogeneous distributions of charge near the surface, caused perhaps by electrical breakdown of the glass at high electron currents. It was also observed that the SH signal at the edge of the irradiated regions was approximately twice as high as in the middle of the regions, which may be due to the fringing fields at the edges.

The value of nonlinear interaction length (related to the layer depth over which the space-charge field is present) has to be known if the value of the nonlinearity is to be accurately estimated. The geometry illustrated in Fig. 3 was used for this purpose. Type II samples were used, and the optical pump beam, which was perpendicular to the 7 mm × 30 mm surface, was focused close to the edge near the polished 1 mm × 30 mm surface so that the beam passed through the region irradiated by the electron microscope. The near-field pattern of the SH was imaged by using a microscope objective and

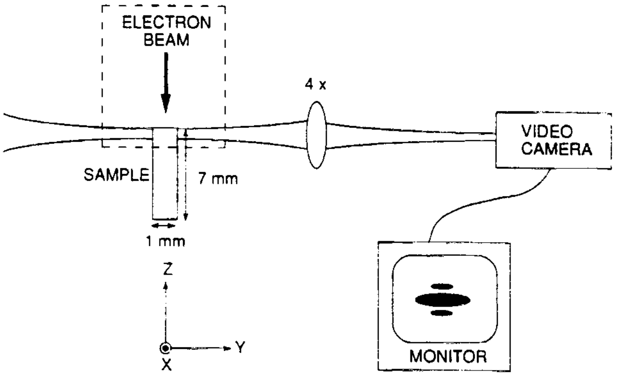

Fig. 3. Geometry used for imaging the depth profile of the induced second-order nonlinearity. The dashed box indicates the surface that had been previously exposed to the electron beam from the scanning electron microscope in the SL-3 mode.

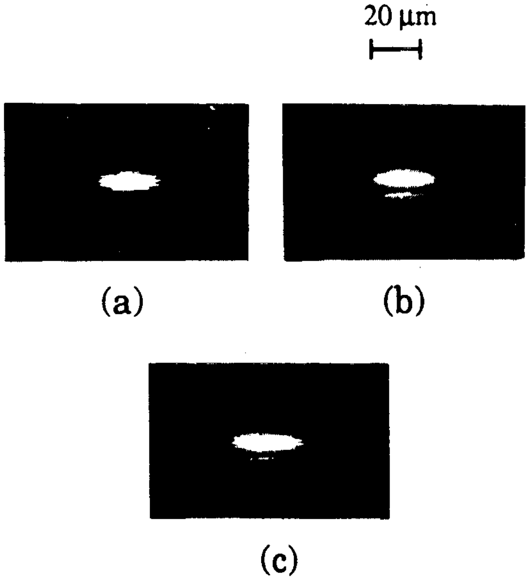

Fig. 4. Near-field pattern of the SH signal. (a), (b), and (c) show changes in the intensity of the sidelobes as the sample was scanned along the x axis within the 1-mm distance corresponding to the irradiated region.

a video camera. The SH field distribution [Fig. 4(a)] consisted of a central lobe of width 6 μm together with two weak sidelobes. The width of the near-field spot did not depend perceptibly on the electron-beam energy. By comparing the near and far-field patterns, the SH field in the sidelobes was found to be π out of phase with the SH field in the central lobe. In some regions of the glass samples the SH intensity of the sidelobes increased, while the main lobe intensity decreased [Figs. 4(b) and 4(c)].

These results provide evidence for an electrostatic space-charge field concentrated near the electron-beam-irradiated surface, which is caused by macroscopic charge separation. The minima in the observed SH intensity distribution clearly coincide with the locations of implanted charge. The negative charge is concentrated at the electron implantation depth, given by $0.01E_0^{1.8}$ in micrometers, where E_0 is the electron energy in kilo-electron-volts.[10] The positive charge, which is located near the surface, arises from the emission of secondary electrons.[7] It is well known that when two oppositely charged layers exist side by side, the electrostatic field is localized in the region in between; the main lobe in the near-field SH intensity distribution coincides with this region. It is likely that the sidelobes in the SH distribution arise from inhomogeneities in the charge distribution, which themselves may be caused by the stepwise scanning of the electron beam. Indeed, the intensity of sidelobes was smaller after irradiation in the SL-3 microscope mode when the distance between the scan lines was smaller (1 μm compared with ~4 μm in the TV mode).

It should be noted that photoinduced SH generation has already been observed in this glass.[11] The observation of a second-order nonlinearity in the same glass by different methods is of great interest from the point of view of elucidation of the underlying mechanism in both cases. Indeed, the existence of out-of-phase regions in the SH near-field patterns in the photoinduced case, as well as in the present case gives convincing evidence that one and the same mechanism—macroscopic charge separation—operates in each case.

Taking into account the oblique transmission angle of the pump beam through the glass substrate, one obtains a nonlinear interaction length of approximately 7 μm (the pump-to-SH coherence length of the lead silicate glass was approximately 30 μm). Finally, we obtained a value of the effective second-order susceptibility $\chi^{(2)} = 2d_{33} \sim 0.7$ pm/V, which yields an electrostatic field of magnitude 10 V/μm, taking $\chi^{(3)} = 1.6 \times 10^{-21}$ (m/V)^2. This value of nonlinear susceptibility is approximately 40 times higher than the one reported in Ref. 11.

An extremely important practical advantage of the electron-beam technique is the ease with which quasi-phase-matching can be achieved. Quasi-phase-matching requires a tightly controlled periodic modulation in the induced nonlinearity, which may be obtained by simply programming the electron-beam machine to expose the material in steps of the required period. Unlike thermal poling there is no need to deposit a periodic electrode pattern, which represents not only a significant technological complication but is also difficult to implement directly on conventional optical fibers. Electron-beam implantation at the mega-electron-volt level, by contrast, can easily penetrate to the core region of an optical fiber. The optimization of the parameters of electron-beam irradiation and the precise composition of the lead silicate glass will be needed to increase the induced dc field and make the fullest use of the advantages of the high third-order nonlinearity in these glasses. Although the technique has so far been tried successfully only in lead silicate glass, other glasses are not precluded. Conductivity and dielectric breakdown of glasses may ultimately limit the levels of nonlinearity that are attainable. Failure to see SH signals from commercial coverslips may be due to the high conductivity of such impure samples and their low third-order nonlinearity.

In conclusion, we have created a large second-order nonlinearity in glass by electron-beam irradiation. The mechanism has been found to be the generation of high electrostatic space-charge fields in the glass. The great flexibility offered by high-resolution electron-beam direct-write machines suggests that this technique may have important applications in glass-based optoelectronic devices.

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