

# Photorefraction in lead-tin-fluorophosphate glasses

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Permanent grating patterns have been written directly in lead-tin-fluorophosphate glasses by use of UV radiation. The effect of photorefraction is studied in different tin-fluorophosphate compositions. Recorded gratings are found to be volume rather than surface elements. The induced index changes are comparable with those seen in  $\text{GeO}_2\text{-SiO}_2$  glasses. © 1998 Optical Society of America

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The main motivation of this Letter is to identify and characterize photosensitive materials having the potential for significantly higher optical nonlinearities than silica. Although  $\text{GeO}_2\text{-SiO}_2$  possesses a large index change and low loss, it is a poor nonlinear material [ $n^{(2)} \sim 2.2 - 3.4 \times 10^{-20} \text{ m}^2/\text{W}$ ]. Large optical nonlinearities have been observed in tin-fluorophosphate glasses<sup>1,2</sup> because of their unusual ability to dissolve molecular organic dopants, effectively allowing for a tailored nonlinear response. If periodic patterns in the refractive index could also be written in this material by use of UV light, then an unusual combination of properties would be available for building devices. A number of these novel device architectures for all-optical signal processing have been proposed and studied during the past decade.<sup>3-6</sup> The important configurations that have been used to demonstrate all-optical processing have relied on long interaction lengths<sup>7</sup> because of the small nonlinearities found in conventional glasses. Short interaction lengths, on the other hand, can be achieved in highly nonlinear materials.<sup>8,9</sup> The passive loss restrictions that limit most glasses, especially those that are not made by chemical-vapor deposition, can then be relaxed. The scale can be reduced still further by incorporation of resonant optical structures, which are characterized by very high internal intensities.<sup>10,11</sup> Subsequently, ideal all-optical structures will have a resonant architecture that provides high internal fields, so they must be fabricated by use of highly nonlinear photosensitive materials.

Low melting and transition temperatures of the host glass are a basic requirement that must be satisfied before doping with any organic material can be considered. This disadvantage common to many low-melting-temperature glasses is their vulnerability to attack from atmospheric water.<sup>1,12</sup> Lead-tin-fluorophosphate glasses, originally introduced by Tick,<sup>12,13</sup> have an unusual combination of properties, in which low melting temperature, relatively good durability, and high optical quality can all be found in a single glass. These glasses have also been fabricated into single-mode waveguides, with passive losses near 15 dB/m.

The glass used in these experiments, the composition of which was  $47\text{SnF}_2\text{-}47\text{PO}_{2.5}\text{-}4\text{PbO}\text{-}2\text{SnCl}_2$  (in mole

percent), was selected because of its ease of preparation and high optical quality. The glass was prepared by prereaction of lead metal and  $\text{NH}_4\text{H}_2\text{PO}_4$  at  $450^\circ\text{C}$  in a vitreous carbon crucible until completion of the reaction. The melt was momentarily cooled, and the remaining components were added and then held at  $400^\circ\text{C}$  for an additional hour. The samples were prepared in either bulk form or thin plates. The process for fabricating the thin plates required that the melt be transferred to a second crucible that had a small hole in the bottom and held at  $400^\circ\text{C}$ . The hole was sized so that the glass dripped out at a rate of a drop every 3–4 s. The drops were collected on a polished vitreous carbon substrate that was heated to  $80^\circ\text{C}$ . Heating the plate gave the bottom surface of the drops a polished appearance, and the top surface sagged; the result was that the top surface was rounded and the bottom surface perfectly flat. The vitreous carbon substrate was then cooled, and the hardened drops were released and used as preforms for molding the thin, flat test plates. The drop preforms were placed in a silicon carbide sleeve between two polished dies and heated to  $130^\circ\text{C}$ . Pressure was then applied to the dies, causing the glass to flow, forming a test plate with flat and parallel faces and with uniform thickness of 100–200  $\mu\text{m}$ .

The absorption spectrum of a typical glass ( $47\text{SnF}_2\text{-}47\text{PO}_{2.5}\text{-}4\text{PbO}\text{-}2\text{SnCl}_2$ ) sample is shown in Fig. 1. Three UV laser sources were used for the recording experiments: tripled Nd:YAG (355 nm), excimer XeCl (309 nm), and quadrupled Nd:YAG (266 nm). The small absorption of the glass at 355 nm eliminates the tripled Nd:YAG source from consideration, leaving the option of recording in the moderate (309-nm) or the high (266-nm) absorption limit. The estimated penetration depth, which can be defined as the distance from the surface to the point at which the intensity falls to 1/10 of the incident level, for 266-nm radiation does not exceed 10  $\mu\text{m}$  and therefore only allows for the formation of a thin, low-efficiency grating. Another disadvantage at this wavelength was that it was easy to damage the glass irreversibly. The XeCl excimer laser proved to be the source of choice because it produced superior, damage-free optical gratings, which penetrated the entire thickness of the test plates. By use of an amplitude

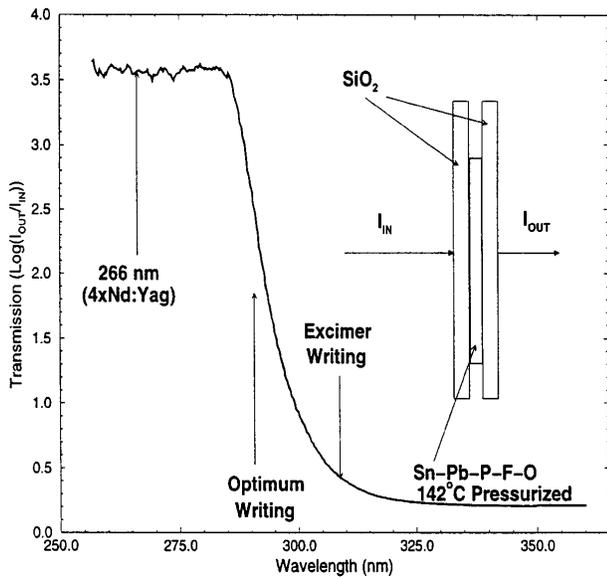


Fig. 1. Absorption spectrum of a  $47\text{SnF}_2\text{-}47\text{PO}_{2.5}\text{-}4\text{PbO}\text{-}2\text{SnCl}_2$  thin-plate sample. Instrument sensitivity did not allow for reliable measurement below 285 nm.

optical grating (Cr-on-quartz) mask with a  $13\text{-}\mu\text{m}$  pitch and 50% duty cycle, the thin-film sample was exposed to 309-nm radiation from the excimer source. This robust experimental exposure arrangement invariably produced optical gratings of very high quality, as illustrated in Fig. 2a. The image in Fig. 2a was photographed by use of a modified Schlieren technique, in which a source aperture is closed to produce an essentially collimated beam. The scanning electron micrograph of the identical grating, shown in Fig. 2b, does not indicate the presence of any recorded surface corrugation patterns, suggesting that the fringes are the result of an index change and not compaction of the glass.

Other compositions in the tin-fluorophosphate family of glasses were also examined for further study of the origin of the photorefractive effect. Figure 3a compares the strengths of the recorded patterns in lead-free  $44\text{SnF}_2\text{-}51.5\text{PO}_{2.5}\text{-}4.5\text{ZnF}_2$ ,  $35\text{SnF}_2\text{-}44\text{PO}_{2.5}\text{-}7.7\text{ZnO}\text{-}13.3\text{TlCl}$ , and the original  $47\text{SnF}_2\text{-}47\text{PO}_{2.5}\text{-}4\text{PbO}\text{-}2\text{SnCl}_2$  composition. The diffractive efficiency is defined here as the ratio of the power deflected into the first diffractive order and the total incident power. The grating efficiencies are permanent at room temperature, at least for as long as 8 months after the initial recording. However, the grating pattern can be erased when the temperature is raised to  $130^\circ\text{C}$ , which is above the glass-transition temperature. The data showed that the original glass ( $47\text{SnF}_2\text{-}47\text{PO}_{2.5}\text{-}4\text{PbO}\text{-}2\text{SnCl}_2$ ) exhibits by far the strongest effect. Some excursions were tested within this composition range by exchange of oxygen for fluorine and tin for phosphorous. The diffractive strengths of two examples,  $44\text{SnF}_2\text{-}3\text{SnO}\text{-}47\text{PO}_{2.5}\text{-}4\text{PbO}\text{-}2\text{SnCl}_2$  and  $43\text{SnF}_2\text{-}51\text{PO}_{2.5}\text{-}4\text{PbO}\text{-}2\text{SnF}_2$ , are compared with the original composition in Fig. 3b. The data show that no significant effect results from these chemistry changes. The diffraction pattern of the grating

exhibits features associated with the intermediate rather than Raman-Nath or the Bragg regime. The magnitude of the index change that produced these gratings was directly measured by interferometry and found to be of the order of 0.001. By use of transmissive interferometric measurement, the optical path difference between the exposed and the unexposed regions was calculated with a large circular amplitude mask (not shown here). The index decreases in the exposed regions.

The preparation conditions also play an important role in this process. If the glass is melted at too high a temperature, above  $450^\circ\text{C}$ , the photorefractive effect disappears. This suggests that the melt has a thermally dependent threshold structure. Cycling a hot melt from low ( $<450^\circ\text{C}$ ) to high temperature ( $>450^\circ\text{C}$ ) and then back to low temperature ( $<450^\circ\text{C}$ ) ensured that this was not simply a consequence of volatilization of some of the glass components. The low-temperature samples at the beginning and end of this experiment were photorefractive, but the middle high-temperature glass was not.

After exposure all the lead-containing glasses became slightly yellow owing to a small redshift in the position of the UV-absorption edge. This yellowing occurred whether or not the glass was photorefractive, hence the color centers associated with this shift are probably not the source of the refractive-index decrease. When lead was replaced with zinc no yellowing was observed, even though these glasses were weakly photorefractive.

The investigation of the photorefractive effect in a lead-tin-fluorophosphate host is still in the early stages, so a reliable physical model has not yet been developed. One of the first effects that was noticed was that the magnitude of the index change was very dependent on the melting temperature just before

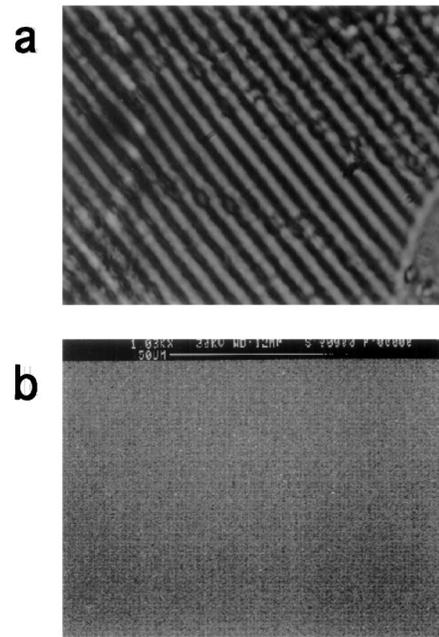


Fig. 2. a, Pseudo-schlieren micrograph of the recorded  $13\text{-}\mu\text{m}$  grating, indicating the strong volume-index modulation. b, Scanning electron micrograph of the grating.

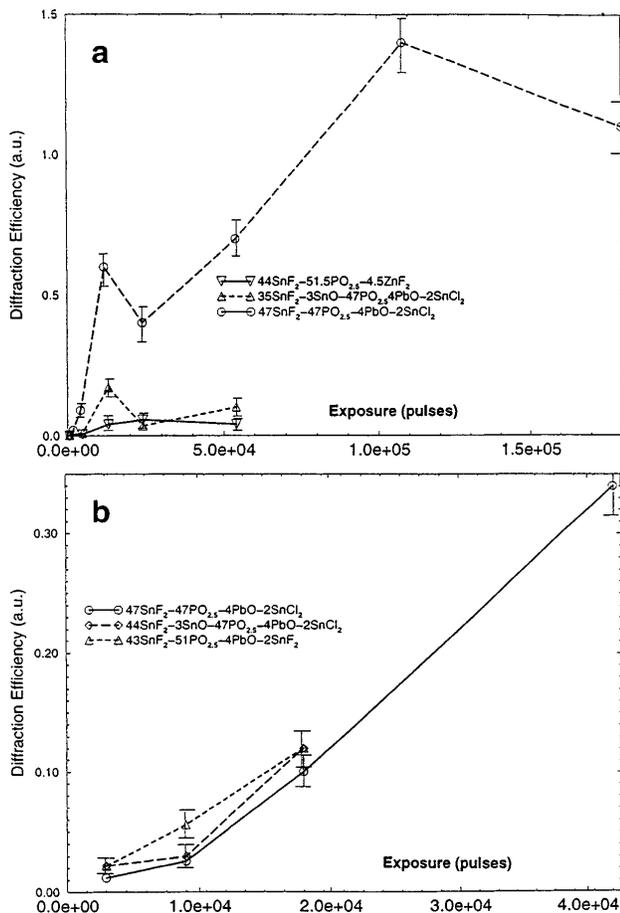


Fig. 3. Relative diffraction efficiencies of the gratings recorded in lead and zinc glass compositions. The error bars indicate the maximum fluctuation of the diffracted efficiency across the exposed region. Each pulse corresponds to approximately  $8 \text{ mJ/cm}^2$ . Average beam energy was  $200 \text{ mW}$  with a  $30\text{-Hz}$  repetition rate. b, Relative diffraction efficiencies of the gratings recorded in compositions with varying oxygen ratio.

quenching. If the temperature is raised from  $400$  to  $450^\circ\text{C}$ , the effect becomes negligible.

The induced index change increases initially and eventually saturates after extended exposure at  $309 \text{ nm}$ . At  $266 \text{ nm}$  the absorption is so strong that saturation is inevitably preceded by permanent damage to the glass and does not offer any further insights into the dynamics of the mechanism. At high beam energies (more than  $1000 \text{ J/cm}^2$  total at  $309 \text{ nm}$ ), it is conceivable that the local temperature of the sample is raised above the glass-transition temperature, at which rapid structure relaxation could occur. At lower energies (less than  $10 \text{ J/cm}^2$  total at  $309 \text{ nm}$ ), however, this may not be true. Also, attempts to induce an index change with continuous exposure from a  $1000\text{-W}$  mercury arc lamp were unsuccessful.

The internal changes of the structure, induced by the radiation close to the absorption edge, are likely to explain the index difference between the exposed and the unexposed domains. The structure of  $\text{Sn-P-Pb-O-F}$  glass is believed to be a complex double-chain ladder arrangement with weak interchain bonding at  $\text{F-Sn}$

sites.<sup>14</sup> One possibility is that these interchain sites are destroyed by the incident UV radiation. The net result of this structure is an effective decrease of the chain lengths, which could reduce the refractive index. Similar optically induced structural changes have been observed in some chalcogenide systems.<sup>15</sup> It appears that small variations of the  $\text{F-O}$  content has little effect on the ability to write gratings, as demonstrated by the composition excursion experiments. An encouraging consequence of this is that the durability can be increased by reducing the  $\text{F:O}$  content without sacrificing the strength of the photorefractive effect. Lead, however, seems to represent a crucial part of the composition, since neither zinc nor  $\text{Zn-Tl}$  compositions produced comparable changes in the index.

In conclusion, direct grating writing onto different glasses in the tin-fluorophosphate family has been demonstrated. Optical gratings were written by exposure of the samples to  $309\text{-}$  and  $266\text{-nm}$  pulsed UV radiation, which resulted in an index change of  $10^{-3}$ . The recorded pattern remained stable at room temperature, showing no signs of degradation after more than 8 months. The recorded gratings are identified as a volume rather than as surface patterns. The mechanism of the refractive-index change is not known and will be the focus of further studies.

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