

Thermally poled silica samples are structurally heterogeneous: Electron diffraction evidence of partial crystallization

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Large structural modifications in *v*-SiO₂ are found to be induced by “thermal poling,” a treatment which makes the glass act as a frequency doubler of an impinging infrared light. The electron diffraction patterns of poled silica plates reveal the presence of a large amount (of order 10%) of crystallites showing patterns consistent with partial crystallization of the glassy matrix into the cristobalite polymorph of silica. © 2001 American Institute of Physics.

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It has been known since 1986 in GeO₂-doped SiO₂ glass,¹ that optical fibers may act as frequency doublers of infrared high-power laser light converting part of the radiation field into higher-frequency green light. The occurrence of second harmonic generation (SHG) is ruled out in centrosymmetric materials such as the amorphous core of an optical fiber and in fact, the bulk (amorphous silica) material shows no measurable second-order optical susceptibility $\chi^{(2)}$. The quest for a permanent $\chi^{(2)}$ in optical glasses led to a large research effort, since such materials may be used in the future for the development of inexpensive integrated optical frequency converters and electro-optic modulators. This effort has led to the discovery of alternative preparation schemes such as “thermal” poling² which are able to provide permanent conversion efficiencies comparable to those shown by the best inorganic crystals. Thermal poling consists of the application of a dc field (~5 kV, just below dielectric breakdown) to glass plates which are kept at moderate temperatures (~540–580 K, compared with ≈2000 K where the glass melts) for a few minutes.

The most widely accepted explanation for the phenomenon³ did not invoke structural modifications within the glass to accomplish the breakdown of its radial symmetry. Rather, it postulates the emergence of a dc field E_0 “frozen in” to a depth of a few microns below the anode surface. A static field such as this, induces, via a third-order nonlinearity [$\chi^{(3)}$], a second-order nonlinearity [$\chi^{(2)} \propto \chi^{(3)} E_0$], able to double the pump frequency. The estimate of the density of ionizable defects required to develop such a space-charge is a mere few parts per million. Recently, neutron diffraction and inelastic scattering⁴ have shown that the glass structure of “poled” silica plates as described by the $g(r)$ radial distribution functions, becomes anisotropic and significantly differs from that of native samples. From data on hand at the time, crystallization of part of the glassy matrix

into a cristobalite polymorph of silica appeared as a reasonable possibility.

The present letter reports some further steps into the clarification of this interesting puzzle. Here, we provide direct evidence of deep structural alterations induced by thermal poling in silica plates by means of inspection of poled and native samples by electron microscopy.

A JEOL 4000EX operating at an accelerating voltage of 400 keV was used for transmission electron microscopy (TEM). Thin glass plates were prepared following procedures described previously^{4,2} and samples for TEM were made by abrasion of the surface of the plates with a diamond scribe. Samples were taken from both, the anode and cathode surfaces. Fragments were collected on lacey carbon support films. Pieces several microns in size which extended over a hole were examined. In this fashion selected area electron diffraction patterns were collected from unsupported glass samples with a typical thickness of 1000 Å. The electron beam is incident approximately normal to the thin sample. Since the electron wavelength at 400 keV is 0.016 Å, the diffraction patterns closely approximate a two-dimensional slice through reciprocal space normal to the electron beam direction. Diffraction patterns were recorded on a cooled charge coupled device camera and then radially averaged. The reciprocal lattice coordinate Q was calibrated by assuming that the $S(Q)$ has peaks in the same positions for an amorphous standard silica rod. The experimental accuracy obtained in this fashion is ≈10%. Dark field microscopy, for example Fig. 1, was used to examine the shape and distribution of crystalline material found in some of the samples. This involved the use of an objective aperture placed on a powder diffraction ring. Bright field microscopy, where the aperture is placed on the unscattered beam, was used to examine the shape and thickness of the abraded amorphous fragments.

Native samples showed the expected diffuse rings from amorphous silica. After poling, all samples showed powder patterns containing crystalline rings on an amorphous back-

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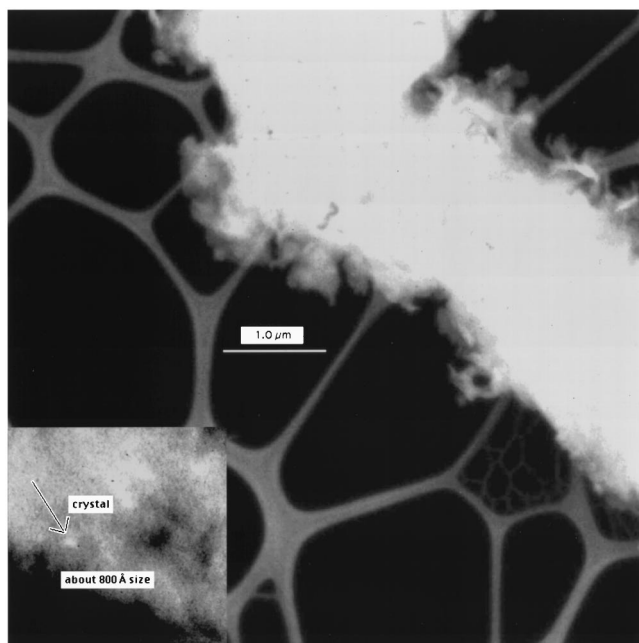


FIG. 1. A dark field image taken with a crystalline diffraction ring from a poled sample. The inset shows a magnified image of a typical crystal.

ground. An example diffraction pattern of a poled sample is shown in Fig. 2. The prominent diffraction rings were indexed and their position is listed in Table I together with the two known modifications of cristobalite. Given the 10% error bars, both the α - and β -cristobalite phases of silica are consistent with the data, the former appearing to be marginally closer to the present data. Note that intensities are not always reliable in electron diffraction due to dynamical scattering which would certainly be significant in crystals of 500–1000 Å thickness. Systematic absences could be a result of preferred orientation. We always observed symmetrical ring intensities in a randomly oriented set of samples, which would be highly coincidental if texture was present. Close examination of the diffraction patterns reveals the coexistence of crystallites with an amorphous phase which we assume to be silica. No evidence of an obvious difference be-



FIG. 2. Selected area diffraction pattern showing crystalline rings from a poled silica sample.

TABLE I. Indexed diffraction rings and their position together with the two known modifications of cristobalite.

Measured d (Å)	Alpha d (Å)	X-ray intensity	Beta d (Å)	X-ray intensity
3.8	4.0	100	4.1	100
2.2	2.5	13	2.5	16
1.9	1.9	4	1.9	4
1.4	1.4	2	1.4	3
1.3	1.3	1	1.3	2
1.1	1.1	1	1.1	2

tween the anode and the cathode sides was detected.

The distribution of crystallites is best examined in real space. Figure 1 shows a dark field image taken from one of the diffraction rings in a poled sample. Diffuse scattering makes a shard of glass visible in the upper right corner with the lacy carbon support in the background. Crystallites such as those indicated with the arrow in the inset of Fig. 1 are revealed as localized brighter regions of the order of 500–1000 Å in size. From the image, it is clear that the crystallites are embedded in an amorphous matrix. Crude estimates of the crystalline volume fraction show it to be of order of magnitude 0.1. Unfortunately, the plates were too thin for a cross section study of the crystallite distribution. In this respect, from the measurements we can only conclude that the formation of crystallites is not restricted to the surfaces (i.e., to the last or few last atomic layers). The possibility that the crystallites observed are a consequence of either electron beam radiation damage or specimen preparation is ruled out because they were never seen in the native material.

With regard to the precise mechanism which leads to devitrification under thermal poling, the data at hand only enable us to speculate. From knowledge pertaining to other glassy systems⁵ we expect that partial-ordering transformations breaking the isotropy of the glass may be triggered by the combined effects of the perturbing dc field and temperature. In fact, electric field enhancement of crystallization from solid amorphous phases has been recently demonstrated.⁶ Other athermal mechanisms, such as UV radiation have also been found to produce small crystallites in glass.^{7,8} This comes as a consequence of the metastable nature of glassy matter which makes it prone to relax into structures having similar stability. For SiO_2 the β -cristobalite form of crystalline silica appear as a feasible candidate⁹ at temperatures comparable to those needed to heat the sample up for the ‘‘poling’’ to be efficient (≈ 560 K). It has a macroscopic density (2.20 g cm^{-3}) matching that of the glass, a highly symmetric cubic $Fd\bar{3}m$ structure and a large disorder of dynamic nature.¹⁰ Further support for this scenario is lent from a recent interpretation¹¹ of the phase transformations between SiO_2 in which the whole set of stable crystal structures may be derived from a common body centered cubic structure. Precisely, the optimal ‘‘poling temperatures’’ $T_{\text{pol}} \approx 540\text{--}580$ K correspond to an interval where β -cristobalite is the most stable form of SiO_2 at such densities. Later on, as the material is left to cool down to ambient and the poling fields are finally removed, one expects that a first-order phase transition occurs centered at ≈ 533 K. Below the transition temperature α -cristobalite becomes the stablest form. Symmetrywise, this crystal may be described as a tetragonal

$P4_12_12$ chiral (noncentrosymmetric) form.^{10,12} Its formation from the β -cristobalite cubic structure involves a substantial shrinkage of some of the unit cell parameters,¹³ a fact that may well explain the large brittleness shown by most materials after poling. In this respect, it should be mentioned that the possibility of partial crystallization in thermally poled fused quartz has been previously reported.¹⁴ The presence of nanocrystals were inferred only by a small peak and a peak precursor in x-ray diffraction patterns tentatively assigned to cristobalite and quartz, respectively. The phenomenon then was explained in terms of inhomogeneous heating of the sample by the Joule effect during poling. If such an effect is confined to within a few microns below the anode face it could lead to high enough temperatures to surpass the glass transition temperature. Our present findings rule out this possibility because of the presence of nanocrystals also in the cathode side. Distributing the Joule effect along the whole sample can never heat it so much.

The extent upon which the presence of crystallites within the glassy matrix affects the optical properties of the material making it able to sustain SHG still needs to be clarified. As mentioned above, α -cristobalite is noncentrosymmetric and may well, at least in part, lead to the emergence of the optical nonlinearity.¹⁵ Furthermore, the nonlinearity of the nanocrystals can be enhanced by finite size effects. A preferential orientation of the crystallites would also be relevant. Although they appear randomly oriented in our measurements, the absolute orientation is lost during the abrasion process. The anisotropy previously observed by neutron diffraction⁴ lends support to the possibility of a preferential orientation. However, the fact that the nonlinearity is mostly located a few microns below the anode surface makes it unlikely that the intrinsic $\chi^{(2)}$ of the nanocrystals is the sole cause of the effect. On the other hand, the possibility that the $\chi^{(3)}$ third-order nonlinearity of the samples is largely enhanced by partial crystallization seems plausible. This, in turn, would enhance the induced $\chi^{(2)}$ by the frozen-in field postulated in the usual explanation of the effect. Notice that in this case,

both types of cristobalite would contribute to the enhancement. In any case, the present finding demonstrates that, contrary to previous beliefs,³ the glass structure is deeply altered when it is subjected to thermal poling. Furthermore, our findings are on a well characterized material such as high-purity silica glass, an important issue regarding the clarification of the basic mechanisms leading to the effect.

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