Fullerene doped glasses

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Optical glasses doped with a fullerene mixture of C_{60}/C_{70} were made in our lab. Three peaks, corresponding to C_{60}, C_{70}, and a modified fullerene (possibly its oxide), respectively, were found in the chromatogram of high performance liquid chromatography (HPLC) analysis of the 0.1-wt % fullerene doped phosphate glass. Depending on the doping procedure and impurity, weak to strong interacting between C_{60} and its environment was found by the nuclear magnetic resonance study. For both phosphate and fluorophosphate glasses with 0.01-wt % fullerene mixture doping, the eigen UV absorption edge showed a significant blueshift, indicating that the bonding between the nonbridging oxygen in these glasses was subjected to a strong change due to the fullerene doping. © *1994 American Institute of Physics.*

Fullerenes and their derivatives in the condensed phase may find many new applications because of their unique caged structures. Some of them have already been verified to be superconductors.[1] Further studies on the condensed phase may also relate it to the semiconductor industry, like the films grown on the GaAs surface for microelectronics.[2] In their work of first isolation of a macroscopic quantity of C_{60}/C_{70}, Kratschmer and co-workers found that a fullerene crystal had disordered hcp/fcp packing and the distances between the center of fullerenes were about 1 nm.[3] Soon after that experiment, nuclear magnetic resonance (NMR) was used to characterize the structure of fullerenes. ^{13}C NMR experiments on C_{60} and C_{70} in organic solvents showed that there was one NMR line for C_{60}, contributed from 60 equivalent carbon atoms in the icosahedron structure, and five NMR lines for C_{70}, which corresponded to five sets of equivalent carbon atoms in the rugby ball structure.[4,5] Similar ^{13}C NMR measurements[6] on solid C_{60}/C_{70} showed that there was also one line for C_{60} at room temperature even when the sample was not spinning, which indicated that C_{60} itself probably was spinning at high frequency and the anisotropy was averaged out. On the other hand, C_{70} seemed not to be taking this reorientation, at least not at high frequency, so the C_{70} sample had to spin at the magic angle to observe all five lines. Meanwhile, the IBM group was able to determine that the correlation time for C_{60} rotation to be 10^{-9} s at room temperature and the components of the chemical shift tensor were 200, 186, and 40 ppm in the crystal.[7]

As one of the condensed phases of fullerene, its doped optical glasses may have some new potential applications. The fullerenes are now trapped in the matrix of glasses, and being stabilized and isolated from outside environments, they may withstand higher laser power than the coated fullerene films or fullerene-doped polymers in the nonlinear optical experiments. It is also interesting to know the interaction of fullerenes and the matrix of the optical glasses that will modify the properties of both fullerenes and optical glasses. In the following, the procedure of making fullerene doped optical glasses, the hardness measurement, the NMR studies, the high performance liquid chromatography (HPLC) analysis, and the optical absorption studies of these glasses are presented.

The C_{60}/C_{70} used to dope the glasses in this work was extracted from the carbon soot produced by the dc contact arc vaporization of graphite rod. The composition of the phosphate laser glass is (wt %):BaO(14.47); SrO(10.33); K_2O(9.54); Al_2O_3(6.47); P_2O_5(41.86); Er_2O_3(0.21); Nd_2O_3(0.21); Yb_2O_3(16.9); and C_{60}/C_{70}(0.01). The composition of the fluorophosphate laser glass is the same with that of the phosphate laser glass, except that 4.14 wt % of LiF was added and P_2O_5 was reduced to 37.72 wt %. The fullerenes, together with the powders of either pure optical glasses (phosphate and fluorophosphate) or rare-earth elements (Nd, Er, and Yb) doped laser glasses, were mixed and heated to 1200 K for 1 h in a sealed device. The device was then cooled down to room temperature at a rate of 10 K per hour. It is necessary to use a sealed device since it prevents the escape of fullerenes at high temperature and the oxidation of fullerenes.[8] It is difficult to dope the fullerenes with its concentration higher than 0.1 wt % because the glasses will crack during the cooling process and show some opaque particles in the inhomogeneous black–brown matrix. For 0.01-wt % fullerene doping glasses, the color is darker than that of the organic solvents with the same fullerene concentration. It is easy to obtain a large volume ($5 \times 5 \times 5$ mm^3) in which no particles are visible either to the naked eye or to an optical microscope with $100 \times$ magnification. To one's surprise, the mechanical property of these glasses has a significant change due to such a small doping. For example, the Vickers-hardness (scratch hardness) H_v has been used widely by the glass technologist that indicates the strength of the chemical bonds. The H_v value for the silica glass is 710 kg/mm^2.[9,10] In our case, the H_v value of the fullerene-doped
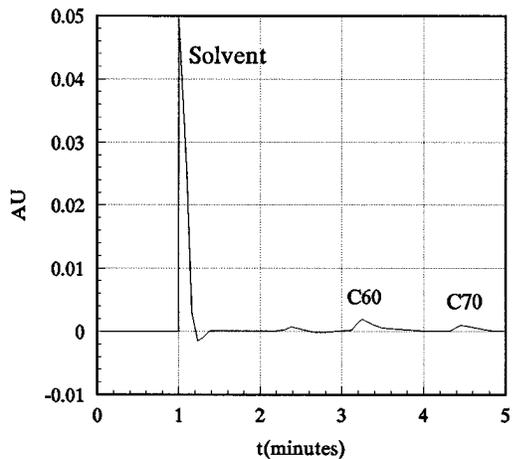
FIG. 1. Liquid chromatography signal of 0.56-g phosphate glass doped 0.1-wt % fullerenes. The signals in sequence are solvent, an unidentified modified fullerene, C_{60} and C_{70}.

phosphate/fluorophosphate glass is 550 kg/mm^2, compared to 440 kg/mm^2 of the undoped glasses. This indicates that some stronger bonds replace the former weaker ones in the phosphate/fluorophosphate glasses due to the fullerene doping.

In order to verify that C_{60}/C_{70} are intact in the glasses after being heated at 1200 K for 1 h and annealed for several days, a glass pellet of 0.1-wt % fullerene doping was analyzed by the high performance liquid chromatography (Millipore 2010) at Rice University. The 0.56-g glass pellet was grounded to powder and dissolved in 15-ml toluene (HPLC grade). The solution was then filtered through 0.2-mm filter paper (GELMAN, Super) and evaporated down to 2 ml in a rotor-vapor. 25 μl of the solution was injected through a Water U6K injector into the HPLC system to carry out the analysis. Water's PDA996 photodiode array detector was used to record the absorption spectrum. Figures 1 and 2 are
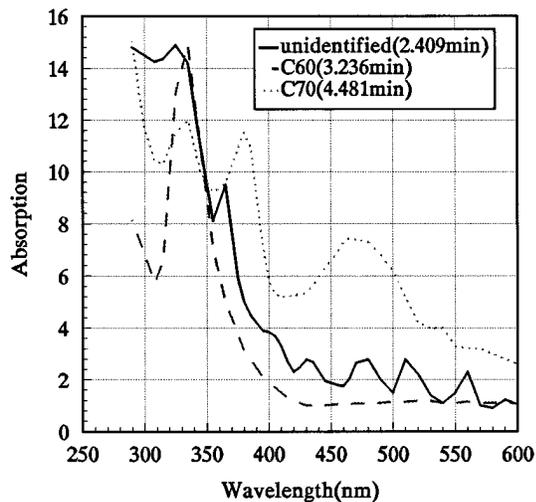

FIG. 2. Absorption spectrum of the first, second, and third peaks after the peak of the solvent in Fig. 1.

the redrawing of the output of HPLC to show the results of one of the repeatable analyses. In Fig. 1, there are three peaks after the strong solvent signal and the signal-to-noise ratio is about 100:1. Figure 2 shows the absorption spectrum of these peaks. It is obvious that C_{60} and C_{70} were doped into the glass intact since the last two peaks possess the same retention times and the same absorption spectra of the standard C_{60} and C_{70} isomers, respectively. The total amount of C_{60} and C_{70} in the grounded powder is about 5 μg. Since the grounding was conducted in an ordinary mortar to avoid any chemical attack on the samples, it is believed that the current measurement only gave the low bound of the doping percentage, which is 0.001% by this measurement. It is also worth noticing that an unidentified peak at 2.38 min is very close to the features representing $C_{60}O$. The total area ratio of these three peaks is 1:6:2 for the $C_{60}O(?)$, C_{60}, and C_{70}, respectively.

The existence of fullerene in optical glasses was further confirmed from the NMR study by a Brucker MSL-400 NMR spectrometer. Two samples were prepared for the NMR experiment, and both contained 0.1-wt % fullerene. The first sample was from a container sealed in air and prepared several months before the experiment. The chemical shift of ^{13}C in this sample was 146.14 ppm. The linewidth full width at half-maximum (FWHM) was 614 Hz without the sample spinning and became 84 Hz when the sample was spinning at the magic angle with 4063 rps. Compared to the 488-Hz linewidth of pure C_{60} at the same chemical shift position, such a small deviation of NMR data seems to indicate that C_{60} in the glass matrix was subjected to little influence from its environment. It is worth noticing that C_{60} reorientates rapidly also in the glass to contribute a single NMR line without sample spinning. The second sample was prepared in a container sealed in the vacuum and measured several days after the preparation. The NMR linewidth is so broad that one cannot obtain the signal without sample spinning and is 341 Hz with sample spinning. It seems that C_{60} was subjected to strong influence from the glass matrix. The reason for this different appearance of NMR is still not clear. Nevertheless, the NMR experiments confirmed the result from HPLC that fullerene was doped into the glass intact.

The strangest behavior of fullerene-doped optical glasses is their optical absorption. The doping level of two samples was limited to 0.01 wt % to obtain the homogeneous samples. The first sample is the phosphate laser glass containing Nd, Er, and Yb. The optical transmission spectra with (solid line) and without (dotted line) fullerene doping for 1-mm-thick samples were shown in Fig. 3. Fullerene doping induces a broad additional absorption in the visible near-infrared region and a 15-nm blueshift of the edge of eigen absorption. The second sample is fluorophosphate laser glass containing the same rare-earth elements. The optical transmission spectra of 1.56-mm-thick samples were showed in Fig. 4. The optical transmission spectrum is quite similar to Fig. 3: A broad additional absorption band in the visible near-infrared region and a 40-nm blueshift of the eigen absorption edge for this thickness.

In conclusion, we have successfully doped fullerenes into the high-temperature optical glasses for the first time to
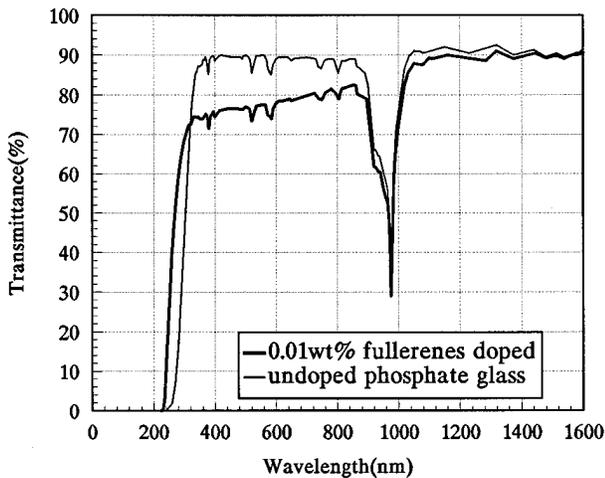
FIG. 3. Optical transmission of 1-mm thickness phosphate laser glasses without fullerene doping (dotted line) and with 0.01-wt % fullerene doping (solid line). The sharp peaks are from the rare-earth ions Nd, Er, and Yb. The doped fullerene induces a broad additional absorption band in the visible and near infrared region and a 15-nm blueshift of the eigen absorption edge.

our knowledge. The liquid chromatography experiment confirmed the existence of both the fullerene feed and its derivation (may be $C_{60}O$) in the glasses after the glass-forming process. NMR experiment showed that fullerenes are subjected to different influences from the glass matrix depending on the preparing and the after-processing. The Vickers-hardness experiment and the optical absorption measurements showed the influence on the glass matrix from the doped fullerenes. It is well known that the eigen absorption edge of oxide glasses is determined by the energy gap between the bonding and antibonding orbital of the nonbridging oxygen in these glasses;[11,12] the blueshift observed above means a larger gap or a less number of this bonding due to the fullerenes doping. The increase of the Vickers hardness of the fullerene doped glasses may be related to the formation of microcrystal in the glasses which corresponded to the cracking in heavier doping. A more careful study using other methods (Raman, electronic microscope, etc.) is needed. The search for the potential applications of fullerene-doped glasses has begun in our group. For example, we have successfully demonstrated the suppression of the self-mode locking of a YAG laser using its nonlinear absorption property.[13] More recently, Liu and Jia also observed the third-order optical nonlinearity in our sample.[14]
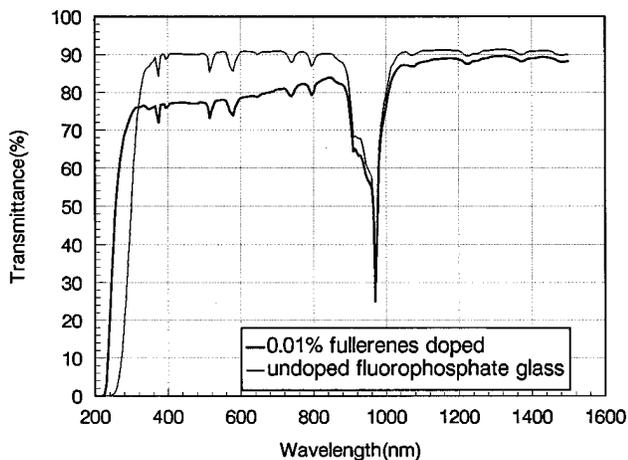
FIG. 4. Optical transmission of 1.56-mm thickness fluorophosphate laser glasses without fullerene doping (dotted line) and with 0.01-wt % fullerene doping (solid line). The blueshift of the eigen absorption edge is about 40 nm.

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