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Pulsed laser deposited lead-germanate glass systems

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ABSTRACT Lead-germanate glasses of composition $x\text{PbO}-(1-x)\text{GeO}_2$ (x ranging from 0.1 to 0.4) have been synthesized and used as ablation targets for reactive pulsed laser deposition (PLD) at various oxygen pressures. The bulk glassy materials and the PLD-produced films were investigated by Fourier-transform infrared spectroscopy to reveal the effects of the bulk stoichiometry and of the reactive atmosphere employed for film preparation on the structural characteristics of the studied bulk glasses and thin-film forms.

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1 Introduction

Lead-germanate optical glasses are attractive systems for photonics applications owing to their intrinsic infrared transmission ($\sim 5 \mu\text{m}$) and suitability as laser hosts in the near infrared (T_m : $1.9 \mu\text{m}$), their large refractive index (~ 1.8) and $\chi^{(3)}$ non-linearity, and, finally, their significant photosensitivity that may lead to efficient optical grating and feedback structures for waveguide applications [1, 2]. The localized photorefractivity of such pulsed laser deposited (PLD) multi-component systems has been studied and it was shown that refractive-index changes as large as $\Delta n \sim 10^{-3}$ can be achieved [3]. Furthermore, the behavior of the photosensitivity, such as, for example, the sign of Δn , can be controlled [4] by the growth conditions.

In the present work, binary $x\text{PbO}-(1-x)\text{GeO}_2$ glasses were developed to investigate their fundamental behavior. The bulk glasses were characterized by Fourier-transform infrared (FTIR) spectroscopy with emphasis placed on the most stable compositions ($0.1 \leq x \leq 0.4$). These materials were used as targets in pulsed laser deposition experiments using ArF (193 nm) laser pulses. Thin films grown at room temperature and at various reactive atmosphere conditions were found to exhibit excellent optical quality, high mechanical strength, and excellent adherence to glassy and metal substrates. Materials growth was studied in connection with thin-film structural properties, as revealed by FTIR spectroscopic measurements [5, 6]. Preliminary results are reported here aiming at

the understanding of fundamental structural properties of the layered structures. A correlation of the reactive environment to the structural properties, thickness, and uniformity of the developed film structures is also attempted.

2 Materials preparation

Five glass compositions were prepared in the system $x\text{PbO}-(1-x)\text{GeO}_2$ with $x = 0.10, 0.20, 0.25, 0.30$, and 0.40 . Stoichiometric amounts of GeO_2 and PbO were mixed and melted in a platinum crucible at $900\text{--}1100^\circ\text{C}$ for 1 h. Cylindrical glass specimens, with a thickness of $\sim 2 \text{ mm}$ and 15 mm in diameter, were prepared by casting the homogenized melts in a stainless steel mold. The as-prepared specimens were subsequently annealed at 450°C to remove residual internal stresses. Bulk glasses were subjected to optical polishing before spectroscopic measurements.

Thin films were produced from the bulk lead-germanate glasses by irradiation in a stainless steel vacuum chamber, which was evacuated to a residual pressure of $5 \times 10^{-4} \text{ Pa}$ prior to each deposition experiment. A nanosecond excimer laser source (ArF, 193 nm) operating at a pulse-repetition rate of 10 Hz was used for the ablation of the lead-germanate glasses. A focusing quartz lens with 45-cm focal length was placed outside the vacuum chamber and the laser beam incidence angle onto the target surface was set at 60° . With this arrangement the energy fluence of the laser beam was 4.5 J/cm^2 at the target. Film deposition was performed for about 60 min. The target was mounted on a vacuum-compatible and computer-controlled XY translator. The ablated material was collected on the surface of a rotating stainless steel or glass slide collector, which was placed parallel to the target surface. The oxygen pressure in these PLD experiments ranged from $2 \times 10^{-3} \text{ Pa}$ to 75 Pa .

3 Spectroscopic measurements

Infrared spectra of bulk materials and of thin films deposited on stainless steel substrates were recorded in the specular reflectance mode and in the transmission–reflectance mode, respectively. For this purpose, a Fourier-transform vacuum spectrometer (Bruker 113v) equipped with a 11° off-normal reflectance attachment was employed. Appropriate sources and detectors were used to cover the entire infrared region. The spectrum of a high-reflectivity aluminum mirror was used as reference. All spectra were measured with 2-cm^{-1}

resolution at room temperature and represent the average of 200 scans.

The measured reflectance spectra of bulk glasses were analyzed by Kramers–Kronig transformation [5, 6] to obtain the absorption coefficient spectra presented in this work. The measured transmission–reflectance spectra of thin films were converted into the absorbance formalism to allow comparison with spectra of the corresponding bulk glassy materials.

4 Results and discussion

Figure 1 shows the absorption coefficient spectra of bulk $x\text{PbO}-(1-x)\text{GeO}_2$ glasses prepared in the composition range $0.10 \leq x \leq 0.40$, including the spectrum of glassy GeO_2 for comparison [5, 6]. As the lead oxide content increases, the strongest absorption band in the infrared shifts progressively to lower wavenumbers. For pure GeO_2 glass ($x = 0$) the dominant infrared feature peaks at 915 cm^{-1} and arises from the asymmetric stretching vibration of $\text{Ge}-\text{O}-\text{Ge}$ bridges connecting germanate tetrahedral units [5, 6]. Breaking the $\text{Ge}-\text{O}-\text{Ge}$ bridges by creating non-bridging oxygen (NBO) atoms on the germanate tetrahedron results in the weakening/depolymerization of the germanate network. This effect is manifested by the shift of the main infrared band to lower frequency values (e.g. at 780 cm^{-1} for $x = 0.4$).

Figure 2 shows the infrared absorbance spectra of thin films deposited on stainless steel substrates at various oxygen pressures, in comparison with the corresponding spectrum of the target bulk glass ($x = 0.40$). The film deposited under the lowest oxygen pressure ($P(\text{O}_2) = 2\text{ Pa}$) exhibits its strongest band at 706 cm^{-1} , while the corresponding bulk material shows this feature around 780 cm^{-1} . Therefore, the thin film is likely to have a more depolymerized network structure (i.e. involving more non-bridging oxygen atoms) with respect

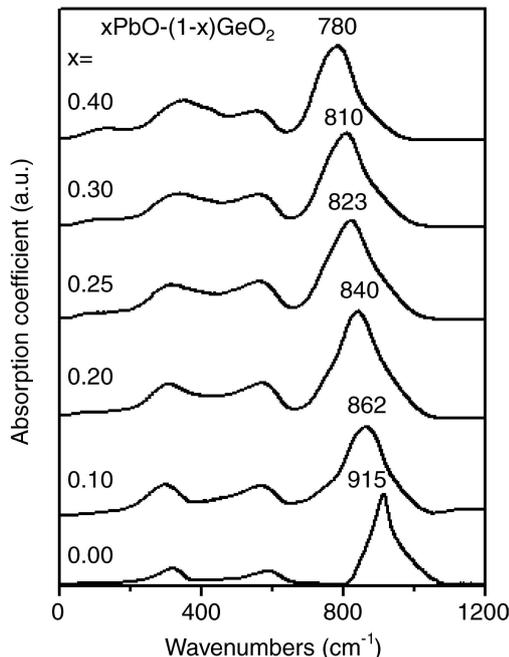


FIGURE 1 Absorption coefficient spectra of bulk glasses with composition $x\text{PbO}-(1-x)\text{GeO}_2$ ($0 \leq x \leq 0.4$)

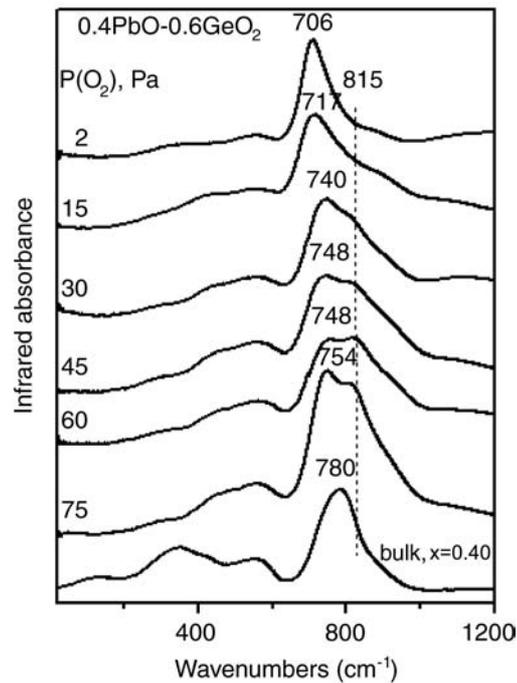


FIGURE 2 Infrared absorbance spectra of PLD films on stainless steel substrates prepared under different oxygen pressures. The spectrum of the bulk glass target, $0.4\text{PbO}-0.6\text{GeO}_2$, is shown for comparison

to the structure of the parent bulk glass. As the oxygen pressure increases the band upshifts in frequency, indicating that the excess oxygen atmosphere provided during the PLD procedure leads to formation of a more cross-linked germanate network structure. The film deposited at $P(\text{O}_2) = 75\text{ Pa}$ shows its main band near 750 cm^{-1} , approaching the frequency of the target bulk material. As shown in a previous infrared transmittance study by Canale et al. [7] on the same glass system, the composition $x = 0.60$ shows its strongest band at $\sim 725\text{ cm}^{-1}$. Comparison of this frequency value with the one in Fig. 2 for the film prepared in the lowest oxygen pressure suggests that this film should have an actual composition approaching $x = 0.67$ (pyrogermanate).

Figure 3 shows infrared absorbance spectra of thin films prepared from different target compositions ($x = 0.10, 0.25,$ and 0.40) under the same oxygen pressure (30 Pa). The main infrared band is measured at systematically lower frequencies as the PbO content of the target glass increases, and this is in accordance with the effect of the gradual depolymerization of the network due to creation of NBOs. Comparing with the spectra of bulk materials (Fig. 1) shows that film formation by PLD leads to a more depolymerized germanate network.

The thickness of the grown film structures was measured using a profilometer (KLA-Tencor Alpha Step 500IQ) and it was found to be in the range $1-2\text{ }\mu\text{m}$. When the oxygen pressure is increased while all other experimental parameters are kept constant, the deposition rate was found to exhibit a non-linear trend (i.e. for the $x = 0.40$ target and $P(\text{O}_2)$ ranging from 2 to 75 Pa the film thickness was found to increase from 1450 nm to 2200 nm , while for 60 Pa it was found to be $\sim 1700\text{ nm}$).

The background oxygen pressure also affects the dynamics of the ablation and plume-expansion procedure, leading

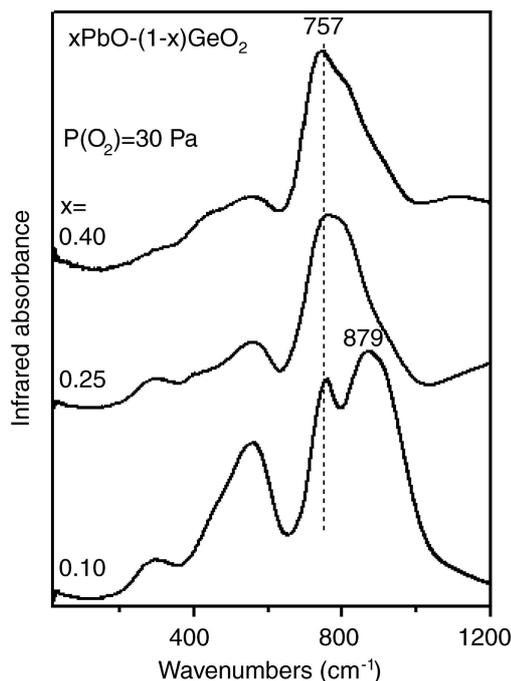


FIGURE 3 Infrared absorbance spectra of PLD films on stainless steel substrates developed from different target compositions $x\text{PbO}-(1-x)\text{GeO}_2$ ($x = 0.10, 0.25,$ and 0.40) under the same oxygen pressure, $P(\text{O}_2) = 30$ Pa

to variations of the optical properties of the films examined. The films deposited at higher oxygen pressures appear to have better transparency in the visible and also a better thickness uniformity, which can be attributed to alterations of the plasma-plume dynamics.

5 Conclusions

Lead-germanate glassy films have been obtained by pulsed laser deposition (PLD) from bulk glasses. The resulting structures were studied by infrared spectroscopy. It was found that PLD films on stainless steel substrates exhibit a more depolymerized glass network in comparison to the parent target glass compositions. Film preparation under elevated oxygen pressure was shown to result in increasing network polymerization and an improvement of optical and mechanical properties.

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