

The Correlation of Optical Transmittance with Structural Evolution in Fluorozirconate Glass (ZLANI) Thin Films as a Function of Thermal Annealing

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ZLANI is a fluorozirconate glass consisting of Zr, La, Al, Na, In and F and is being developed for use as the matrix in multilayer optical nanocomposites containing BaCl₂ and rare earth elements, in order to create designer fluorochlorozirconate (FCZ) ZBLAN-based glass-ceramics with potential applications including up- and down-convertors in photovoltaics [1]. To better control the optical property of the ZLANI glass matrix, in this work we explored the effect of heat treatment on the composition, structure and optical property of ZLANI thin films and developed a better understanding about how these three properties are correlated.

The ZLANI thin films were deposited by pulsed laser deposition (PLD) and annealed at different temperatures. Changes to the composition and structure were studied by transmission electron microscopy (TEM). Careful analysis of the electron diffraction patterns was carried out to determine changes to the atomic bonding and to follow the crystallization process. The individual broad peaks in the radial profile obtained by azimuthal averaging within a sector of each amorphous ring were assumed to be Gaussians and the radial profile was assumed to be the sum of Gaussians. The radial profile curve was fitted using a custom-written code to allow the corresponding real-space values for the diffraction ring positions and widths to be determined.

EDX analysis results of the ZLANI thin films showed that the composition was unchanged by annealing, but a clear structural evolution of the ZLANI glass was observed. Figure 1 shows HREM images and diffraction patterns for ZLANI thin films both as-deposited and after annealing at different temperatures, together with a plot of the positions and widths of the broad diffraction rings for the first three amorphous film conditions. Changes in crystallinity and diffraction ring position and width can be seen. Changes to the optical transmittance as a function of annealing are shown in Figure 2 and the changes can be explained by the structural evolution. The initial increase in transmittance for the 100°C annealed ZLANI thin film is ascribed to structural relaxation in the amorphous state and the reduction of defects, including color centers. After the 200°C anneal the transmittance decreases as a result of the heterogeneous formation of crystalline nuclei (outlined in yellow in Fig. 1c) and changes in the local bonding (a decrease in the Zr-Zr distance and a change in the Na coordination number from 7 to 6 or 8). Finally, the shape of the transmittance curve changes after the 300°C anneal due to wider-scale crystallization of the ZLANI film: the major crystal phases were determined to be Zr₂F₈(H₂O)₆ and ZrO₂ [2].

References:

- [1] R.L. Leonard et al., *J. Non-Cryst. Solids*, **366** (2013), p. 1.
 [2] This research was supported by the National Science Foundation under Collaborative grants #DMR 1600783 and #DMR 1600837. The authors acknowledge Adam Evans, The University of Tennessee Space Institute, for synthesizing ZLANI target glass, and Frank Barrows, Northwestern University, for help with part of the code used in the curve fitting method. Use of the Center for Nanoscale Materials, an Office of Science user facility, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

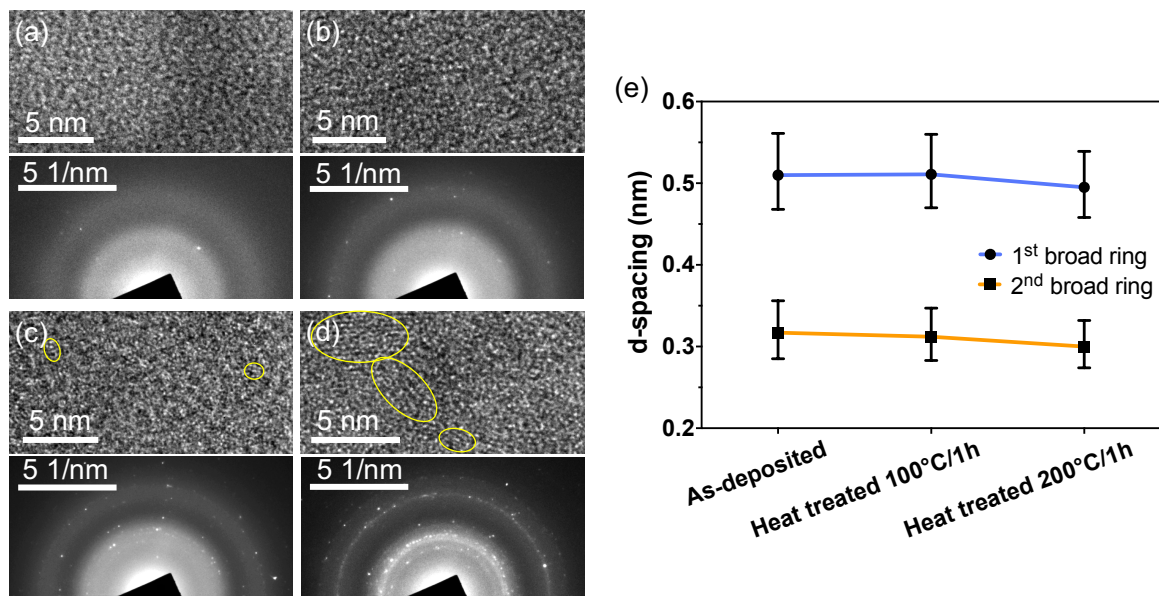


Figure 1. HREM images and electron diffraction patterns for the ZLANI thin films: (a) as-deposited, and after heat treatment for 1 hour at (b) 100°C, (c) 200°C and (d) 300°C. The atom clusters in (c) and small crystals in (d) are outlined in yellow. (e) Plot of the positions and widths of the 1st and 2nd broad diffraction rings for the as-deposited, 100°C and 200°C annealed ZLANI thin films.

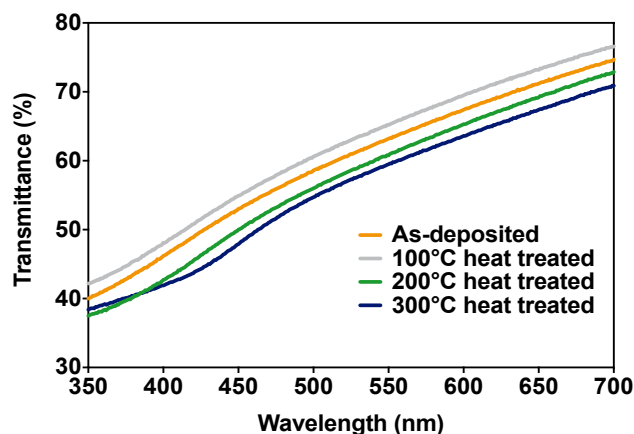


Figure 2. Transmittance of ZLANI films in as-deposited state and after heat treatment for 1 hour at 100°C, 200°C and 300°C.