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Research Article

Effect of CeO_2/Ag_2O on Etching Ratio and Crystallization Shrinkage of Photosensitive Glass-Ceramics

Bin Hu[1,2], Querui Hu[2,3], Baoping Yuan[2], Tianlai Yu[2], Xiaopu Chen[2], Dahong Mo[2], Xuejian Su[2], Bin Lin[1*]

[1]School of Materials and Energy, School of Mechanical and Electrical Engineering, University of Electronic Science and Technology of China, Chengdu 611731, China
[2]CDGM Glass CO., Ltd., Chengdu 610100, People's Republic of China
[3]Instiitute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 611731, China
E-mail: bin@uestc.edu.cn

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Abstract: Based on Li_2O-Al_2O_3-SiO_2 system, photosensitive glass-ceramics with different CeO_2/Ag_2O ratios were prepared using the melting method. To improve the yield of through-hole processing in photosensitive glass-ceramics and the service life of Micro Electro Mechanical systems (MEMS), the effect of CeO_2 content on the transmittance of various samples before and after UV exposure was examined. Additionally, the effect of CeO_2/Ag_2O ratio on the crystallization shrinkage and etching performance of photosensitive microcrystalline glass was studied both before and after heat treatment. The research results indicate that the optimal CeO_2/Ag_2O ratio in the photosensitive microcrystalline glass component is approximately 0.03%/0.12%, and the transmittance of the basic glass sample is about 50.8% (@ 310 nm, 1mm thickness). The crystallization shrinkage rates before and after glass exposure are 0.08% and 0.26%, respectively. The highest etching ratio is about 18:1.

***Keywords*:** photosensitive glass-ceramic; transmittance; crystallization shrinkage rate; etching ratio

1. Introduction

The nucleating agent in the Li_2O-Al_2O_3-SiO_2 photosensitive microcrystalline glass composition obtains energy after being illuminated at a certain wavelength, and accumulates into submicroscopic nuclei [1]. After heat treatment, the nuclei can induce the formation of lithium metasilicate crystals (Li_2SiO_3). Because of its different tolerance to HF acid compared with transparent glass substrates, Li_2SiO_3 crystals are more soluble in acidic solutions than glass matrix materials [2]. By controlling UV exposure and heat treatment regimes, pre-designed microstructures can be obtained on photosensitive glass-ceramics materials, resulting in a series of physical and chemical performance changes such as resistance to HF acid [3]. Glass through-hole (TGV) technology, as a new high density interconnection technology, is a key technology for the preparation of glass transfer plate in MEMS [4, 5]. In the existing technology, the researches on photosensitive glass-ceramics are mainly focused on reducing the dielectric constant and dielectric loss of the materials [6, 7]. However, in TGV processing and application of photosensitive glass-ceramics, high crystallization shrinkage and low etching ratio may lead to excessive warping, strength reduction and micro-cracks of TGV transfer plates, and lead to virtual welding, delamination and fracture of various integrated devices. In this paper, the effects of photosensitive glass components on crystallization

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shrinkage and etching ratio of glass were studied in detail in order to obtain lower crystallization shrinkage and higher etching ratio.

2. Experiment

Table 1 shows the composition of the studied photosensitive glass-ceramics. Analytically pure SiO_2, $Al(OH)_3$, Li_2CO_3, KNO_3, $NaNO_3$, ZnO, CeO_2, $AgNO_3$ and Sb_2O_3 are used as raw materials. The raw materials were mixed evenly and added to a platinum crucible. The platinum crucible was kept at 1500 ℃ for 10 h, and then the clarified and homogenized glass liquid was poured into a preheated cast iron mold. The mold was placed in a muffle furnace preheated to 450 ℃ for 4 h and then the glass was cooled in the furnace.

Table 1. Composition of photosensitive glass-ceramics

No.	SiO_2	Li_2O	Al_2O_3	K_2O	Na_2O	ZnO	CeO_2	Ag_2O	Sb_2O_3
CA1	78.5	9	5	4	2	1	0	0.12	0.4
CA2	78.5	9	5	4	2	1	0.03	0.12	0.4
CA3	78.5	9	5	4	2	1	0.06	0.12	0.4
CA4	78.5	9	5	4	2	1	0.09	0.12	0.4
CA5	78.5	9	5	4	2	1	0.09	0.24	0.4

The molded glass was processed into Φ 38×1 mm glass sheet and polished. There were two selected samples. One was irradiated under GGU500 UV light (power: 500 W, optic power density: 1.8 mW/cm^2, radiation wavelength: 313 nm, exposure time: 30 min) and the other was unexposed basic glass. Then the heat treatment was performed at 500 ℃/2 h + 580 ℃/1 h. Finally, the acid etching was performed with 5% hydrofluoric acid solution. Ultraviolet-visible-near-infrared spectrophotometer (U-4100, Hitachi) was used to measure the transmittance of the samples in the range of 250–1000 nm.

3. Results and discussions

3.1 *Transmittance*

A two-step heat treatment process of 500 ℃/2 h + 580 ℃/1 h was adopted to carry out crystallization heat treatment for all samples, i.e., UV exposed and unexposed glass samples were simultaneously crystallized. As a comparison, the apparent morphology image of glass samples is shown in Figure 1. After crystallization, the exposed glasses become opaque, indicating that a large number of crystals are precipitated in the glass, as shown in Figure (g)–(j). In this work, the wavelength range we have chosen is between 250 and 400 nm.

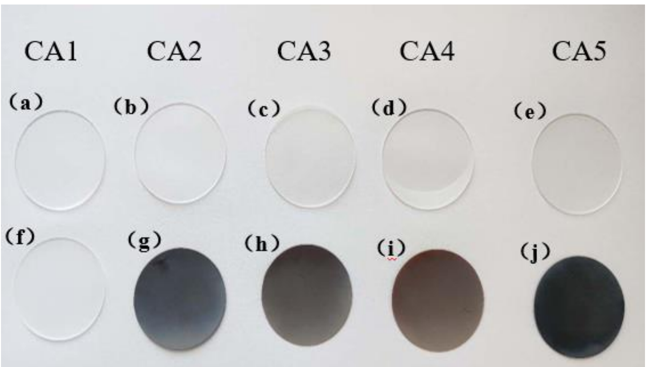

Figure 1. Comparison of the apparent morphology image of CA1-CA5 samples after crystallization, where (a)–(e) are unexposed samples, (f)–(j) are exposed samples

As can be seen from Figure 2, the transmittance curves of all glasses remain consistent after 350 nm. However, there is an absorption peak near 310 nm, which is mainly caused by the absorption of Ce^{3+}. Ultraviolet light can excite electrons in an outer d orbital of Ce^{3+} to a high energy state. In a solid glass network, the photo-generated electrons have to overcome a large barrier if they want to return back to their outer d orbital positions. These electrons are going to be swimming around Ce^{4+}, which is equivalent to an electron being captured by Ce^{4+} [8, 9].

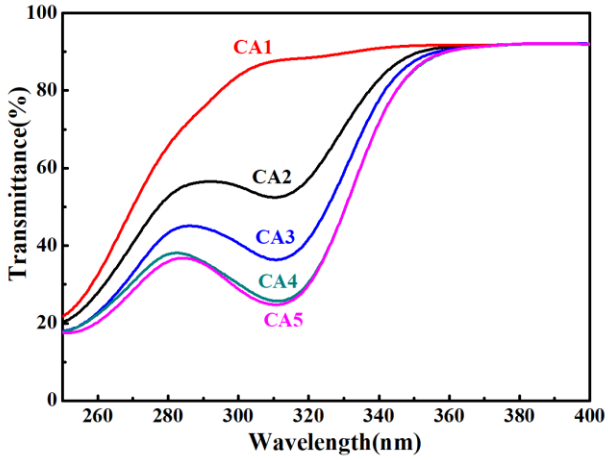

Figure 2. Transmittance of basic glass samples CA1-CA5

As an activator, the main function of CeO_2 is that after absorbing photons in the ultraviolet region, free electrons are released due to oxidation. These free electrons will be combined with the photosensitive metals in the glass during the subsequent heat treatment process to enhance the activity of the photosensitive glass, resulting in the enhancement of photosensitive property for the glass. When the content of CeO_2 was 0, 0.03%, 0.06% and 0.09%, the transmissibility of 310 nm was 88.1%, 50.8%, 34.5% and 24.2%, respectively (Figure 2: CA1-CA4). The transmittance of CA1 sample without CeO_2 is the highest. As CeO_2 content increases, the transmittance absorption peak at the 310 nm wavelength decreases, indicating that the increase of CeO_2 will cause the glass transmittance to be weakened in the ultraviolet region. In addition, as a photosensitive metal oxide, Ag_2O exists in glass in the form of ions and is easy to be reduced in matrix glass. Compared with the transmittance of CA4 and CA5 (Figure 2), it can be seen that the transmittance at 310 nm wavelength decreases slightly when the content of Ag_2O is twice as much.

The transmittance of each sample after UV exposure is shown in Figure 3. The transmittance below 350 nm significantly decreases, and the higher CeO_2 content is, the lower transmittance is. This indicates that more Ce^{3+} are converted into Ce^{4+} due to the absorption of photons, and more Ag atoms are precipitated. When the content of CeO_2 in the glass is too low, it is unable to provide sufficient electrons for Ag^+ reduction, and the content of crystals in the glass after crystallization will be reduced. When the content of CeO_2 is too high, the transmittance of 310 nm wavelength will be reduced, as well as the penetration depth of ultraviolet exposure will be reduced, which will lead to the reduction of through-hole depth. Therefore, the content of CeO_2 should be strictly controlled.

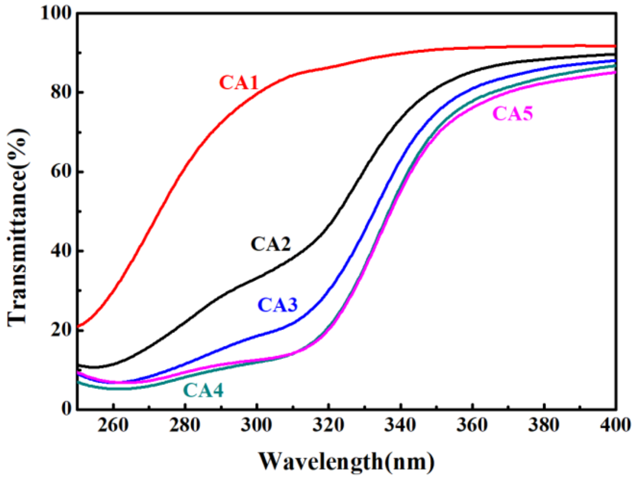

Figure 3. Transmittance of CA1-CA5 samples after exposure

3.2 *Crystallization shrinkage rate*

In the experiment, φ 38 × 1 mm circular samples were used to test the crystallization shrinkage rate. Under the condition of 500 ℃/2 h + 580 ℃/1 h heat treatment process, the average diameter of each sample before and after crystallization was measured, and the variations of each sample diameter were calculated, which is the crystallization shrinkage rate δ of photosensitive microcrystalline glass.

$$\delta = \frac{d_1 - d_2}{d_1} \tag{1}$$

In the formula, d_1 is the average diameter of the sample before crystallization and d_2 is the average diameter of the sample after crystallization.

Crystallization shrinkage rates δ_1 of unexposed samples are listed in Table 2. Due to the absence of crystal precipitation, the crystallization shrinkage rates remain at a lower level, with a variation range of 0.05%–0.13%. For the exposed samples, the crystallization shrinkage rate δ_2 is low (0.07%) when the glass composition does not contain CeO_2 (CA1). Under the same Ag_2O content (CA2-CA4), as the content of CeO_2 increases, the crystallization shrinkage rates of exposed samples gradually decreased from 0.26% to 0.18%. Moreover, When the content of Ag_2O increases (CA5), the crystallization shrinkage rate of the photosensitive glass-ceramics reaches its maximum value of 0.37%. The crystallization shrinkage rate of photosensitive glass samples is mainly optimized with the crystal content in the sample. The higher the crystal content is, the larger the crystallization shrinkage rate is.

Table 2. Crystallization shrinkage of CA1-CA5 samples before and after exposure

No.	δ_1（Before Exposure）	δ_2（After Exposure）
CA1	0.05%	0.07%
CA2	0.08%	0.26%
CA3	0.08%	0.23%
CA4	0.10%	0.18%
CA5	0.13%	0.37%

3.3 *Etching ratio*

The etching ratio *K* of photosensitive glass-ceramics is the ratio of the etching rate for the UV exposed crystalline part to the unexposed crystalline part of the glass [10]. After heat treatment at 500 ℃/2 h + 580 ℃/1 h and acid etching at 5% HF for 1 h, the weight of the glass samples before and after acid etching was weighed respectively. The weight loss rate of the glass samples was calculated according to Equation (3) and Equation (4), that is the etching loss rate Δ of glass.

$$K = \Delta_2/\Delta_1 \tag{2}$$

In the equation, Δ_2 is the etching loss rate of the exposed sample, Δ_1 is the etching loss rate of the unexposed sample.

$$\Delta_1 = (M_1 - m_1)/M_1 \tag{3}$$

$$\Delta_2 = (M_2 - m_2)/M_2 \tag{4}$$

Where, M_1 and M_2 are the weight of the samples before acid etching, m_1 and m_2 are the weight of the samples after acid etching.

Table 3. Etching Ratio of CA1-CA5 Samples

No.	Δ_1	Δ_2	*K*

CA1	3.20%	3.26%	1:1
CA2	35.20%	2.15%	18:1
CA3	35.54%	2.30%	15:1
CA4	34.34%	2.50%	13:1
CA5	34.25%	2.41%	14:1

After acid etching, the etching rate of samples without CeO_2 is almost the same before and after exposure. Therefore, the etching ratio *K* is close to 1:1, as shown in Table 3. For the samples containing CeO_2, under the condition of the same Ag_2O content (CA2-CA4), when CeO_2 content is 0.03%, 0.06% and 0.09%, the etching ratio is 18:1, 15:1 and 13:1, respectively. With the increase of CeO_2 content, the etching ratio gradually decreases. This is because with the increase of CeO_2 content, the transmittance of the basic glass gradually decreases near 310 nm and the photon absorption efficiency of Ce^{3+} decreases during exposure, resulting in the decrease in crystal content in the photosensitive glass after crystallization. Under the condition of the same CeO_2 content, an appropriate increase of Ag_2O content can effectively promote the growth of crystal nuclei and limit the size of precipitated crystals. However, excessive Ag_2O content can easily lead to the decrease of the permeability of basic glass. At the same time, the unexposed part is prone to crystallization due to the high content of nucleating agent.

4. Conclusions

The Li_2O-Al_2O_3-SiO_2 photosensitive glass-ceramics were prepared by melting method. The effects of the photosensitizer/nucleator (CeO_2/Ag_2O) on the physical properties of the glass such as the transmittance, crystallization shrinkage and etching ratio were studied. The results show that by optimizing the content of photosensitizer and nucleating agent can reduce the crystallization shrinkage rate and improve the etching ratio of the glass. It can be applied to prepare MEMS, Integrate Passive Devices (IPD) and Radio Frequency (RF) devices, etc. Based on the above experiments, performance tests, analysis and discussions of the results, it is concluded that the optimal CeO_2/Ag_2O ratio in the photosensitive glass is about 0.03%/0.12%, the transmittance of the basic glass samples is about 50.8% (@310 nm, 1 mm thickness), and the crystallization shrinkage rate of the glass before and after exposure is 0.08% and 0.26%, respectively. The highest etching selection ratio is about 18:1.

Acknowledgments

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Conflict of interest

The authors declare no competing interests.

References

[1] Stookey S D. Photosensitive glass [J]. Industrial & Engineering Chemistry, 1949, 41 (4): 856-861.
[2] Zhao H, Zhang J, Chen H, et al. The effects of La_2O_3 doping on the photosensitivity, crystallization behavior and dielectric properties of Li_2O-Al_2O_3-SiO_2 photostructurable glass [J]. Ceramics International, 2018, 44 (17): 20821-20826.
[3] Voges M, Beversdorff M, Willert C, et al. Examination of the laser-induced variations in the chemical etch rate of a photosensitive glass ceramic [J]. Applied Physics A, 2007, 43 (2-3): 97.

[4] Takahashi S, Tatsukoshi K, Ono M, et al. Development of TGV Interposer for 3D IC [C]//International Symposium on Microelectronics. International Microelectronics Assembly and Packaging Society, 2013, 2013 (1): 000631-000634.
[5] Jin J K, Kwon S J. Fabrication and Performance Test of MEMS Catalytic Combustors Using Photosensitive Glass Wafer [J]. Transactions of the Korean Society of Mechanical Engineers A, 2009, 33 (3): 237-242.
[6] Berezhnoi A I, Ermakov Y M, Glushkov Y I, et al. Dielectric properties of lithium aluminosilicate photosensitive glass ceramics after various heat treatment and exposure processes [J]. Dokl. chem. technol, 1986.
[7] Zhang H, Zhu Y C, Cui Z, et al. Effect of Aluminum Content on Dielectric Properties of Photosensitive Glass-Ceramics [J]. Bulletin of the Chinese Ceramic Society, 2019.
[8] Kreibig U. Small silver particles in photosensitive glass: their nucleation and growth [J]. Applied physics, 1976, 10 (3): 255-264.
[9] Kim H J, Sang H L, Yon S J, et al. Effect of Sb_2O_3 on solarization of photosensitive glasses containing Ag and CeO_2 [J]. Korean Journal of Ceramic, 2001, 7: 58-62.
[10] D Hülsenberg, Bruntsch R. Glasses and glass-ceramics for application in micromechanics [J]. Journal of Non-Crystalline Solids, 1991, 129 (1-3): 199-205.