Chemical durability of $\text{Gd}_2\text{Zr}_2\text{O}_7$ transparent ceramics under different pH conditions

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Abstract

To study the influence of acidic and alkaline environments on the leaching behavior of $\text{Gd}_2\text{Zr}_2\text{O}_7$ immobilization matrix in deep geological landfills, and to directly reflect the change of leaching behavior on its appearance, the chemical durability of $\text{Gd}_2\text{Zr}_2\text{O}_7$ transparent ceramics was investigated in different pH environments in this study. The leaching results demonstrate that the normalized leaching rates in acidic environments are higher than those in alkaline and neutral environments. The transmittance of the leached transparent ceramics in the visible range decreases slightly at $\text{pH} \leq 9.0$, and the macroscopic color of all samples fades after leaching. The leaching behavior leads to lattice contraction and increment of surface roughness, but it exhibits no significant effect on the surface elemental distribution. In conclusion, $\text{Gd}_2\text{Zr}_2\text{O}_7$ transparent ceramics show excellent chemical durability in a weak alkaline environment, and the leaching behavior causes the discoloration of $\text{Gd}_2\text{Zr}_2\text{O}_7$ transparent ceramics.

1. Introduction

As non-renewable energy sources are increasingly being exploited and depleted, clean and efficient nuclear energy is now an important option. A certain amount of spent fuel and radioactive nuclear wastes will inevitably be generated in the process of developing and utilizing nuclear technology. The safe handling and disposal of radioactive wastes, especially high-level radioactive wastes (HLWs) with long half-life, are one of the key points for the sustainable development of the nuclear industry [1, 2]. Many studies on the disposal of HLWs have been conducted as far back as the last century. Ringwood et al. were inspired by natural reactors and came up with the idea of synthetic rock (SYNROC) immobilization [3]. It has been proved that pyrochlore with the general formula $\text{A}_2\text{B}_2\text{O}_7$ is a promising matrix for actinide wastes immobilization after years of research [4–7]. Trivalent actinides, such as Am can be immobilized in its A site, while tetravalent actinides (such as Pu) can be immobilized in its B site [8, 9].

Among the family of pyrochlore, the preparation process and immobilization properties of $\text{Gd}_2\text{Zr}_2\text{O}_7$ (GZO) ceramics have been extensively studied due to their excellent chemical durability, physical stability, thermal stability, radiation resistance, et al [10–16]. In the group of them, chemical durability is an important factor to evaluate the safety of waste form when it contacts with aqueous solutions in deep geological landfills. Table 1 lists the normalized release rates (LR_i) of each element for evaluating the chemical durability of GZO by various research teams in recent years, mainly using Materials Characterization Center-1 (MCC-1) and the standard Product Consistency Test (PCT) leaching experiments [17–24]. From the statistical results, it can be concluded that both powder and bulk leaching experiments demonstrate excellent chemical durability for GZO samples with different grain sizes [17–22]. However, it is noteworthy that the above study only investigates the chemical durability of GZO ceramics in deionized water. The real geological environment is extremely complex, and both acidic and alkaline environments can affect the leaching behavior of the immobilization matrix. To the knowledge of the literature research, the chemical durability of monazite $\text{Ce}_{0.5}\text{Pr}_{0.5}\text{PO}_4$ ceramics at different pH has been studied [25, 26]. Therefore, the study of the chemical durability of GZO ceramics at different pH values is extremely valuable.

Table 1
The normalized release rates of several Gd/Zr in the literature.

Experimental model	Sample status	Leaching conditions	Ceramic grain size	$LR_i (\text{g} \cdot \text{m}^{-2} \cdot \text{d}^{-1})$		reference
				Gd	Zr	
MCC-1	bulk	90°C, deionized water	78 nm	$10^{-2}-10^{-3}$	$10^{-4}-10^{-6}$	[17]
MCC-1	bulk	Not specified	~ 400 nm	$10^{-3}-10^{-5}$	$10^{-4}-10^{-6}$	[18]
	bulk		~ 800 nm	$10^{-3}-10^{-5}$	$10^{-4}-10^{-6}$	
MCC-1	bulk	70°C, deionized water	1–2μm	-	$10^{-5}-10^{-7}$	[19]
MCC-1	bulk	40/70°C, deionized water	~ 5 μm	$10^{-3}-10^{-5}$	$10^{-4}-10^{-7}$	[20]
PCT	powder	70°C, deionized water	~ 5 μm	$10^{-4}-10^{-5}$	$10^{-5}-10^{-7}$	[21]
PCT	powder	90°C, deionized water	> 5 μm	1.87×10^{-7}	2.64×10^{-7}	[22]

Generally, its crystal and microscopic structure are characterized to study the influence of leaching experiments on its structure when studying the chemical durability of the immobilization matrix. If the degree of damage to the immobilization matrix can be reflected through intuitive changes (such as macroscopic shape, appearance color, et al.), which is an important value in actual immobilization applications. Therefore, GZO transparent ceramics with a certain light transmittance can be used for chemical durability research to achieve this goal. For the time being, GZO transparent ceramics have been successfully produced by researchers. Qi et al. have used SPS sintering technology to prepare GZO transparent ceramics with a maximum in-line transmittance of 70% at a wavelength of 2000 nm [27]. Li et al. have been produced GZO transparent ceramics with a maximum in-line transmittance of 77.3% at 1300 nm by vacuum sintering [28]. The GZO transparent ceramics were prepared by vacuum sintering technique, the specific preparation process can be referred to in the previous study. In this work, the chemical durability of GZO transparent ceramics under different pH conditions was investigated [28]. The chemical durability was evaluated by the MCC-1 method at solution environments of pH = 3.0, 5.0, 7.0, 9.0, 11.0. After completing the 42-day leaching experiment, the normalized release rates were measured to investigate the effect of pH on its chemical durability. The optical properties and crystal structure changes of the samples before and after leaching were characterized by solid ultraviolet absorption spectrophotometer, grazing incident X-ray diffraction, Raman spectroscopy, atomic force microscopy and scanning electron microscopy.

2. Experimental Sections

2.1 Fabrication of GZO transparent ceramics

GZO nanopowders were prepared by the combustion method. $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Aladdin), $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (99.9%, Aladdin), and glycine ($\geq 99\%$, Aladdin) were weighed at stoichiometric amounts and dissolved in deionized water. The appropriate amount of ammonia was slowly added to this solution until the pH value was adjusted to 4.0 and then heated in a water bath until it became a gel state. The gel was transferred to a muffle furnace and heated up to 300 °C for

30 min. The gel burned rapidly and formed a precursor powder when the temperature reached the ignition point of glycine. The precursor powder was calcined at 1200 °C for 2 h, and then ball-milled with deionized water for 24 h. The GZO powder was obtained after drying. The powder was dry pressed into disks and cold isostatically pressed at 200 MPa for 3 min. The disks were pre-sintered at 1400 °C for 3 h, then vacuum sintered at 1825 °C for 6 h, and the sintered samples were annealed at 1500 °C for 5 h finally. The preparation process was the same as described previously [26].

2.2 Leaching experiments

The parameters and conditions corresponding to each leaching experiment are listed in Table 2. Six GZO transparent ceramics were taken (numbered 0-5) for grinding and polishing with sample number 0 as a blank comparison. Then, samples numbered 1-5 were cut into regular rectangular blocks with dimensions of 7.7 × 7.8 × 0.9 mm, 7.7 × 7.8 × 0.9 mm, 7.7 × 8.1 × 1.0 mm, 7.7 × 8.7 × 0.9 mm and 7.8 × 7.8 × 0.9 mm, respectively. The samples were sonicated in deionized water repeatedly and dried to constant weight at 100 °C. The treated GZO transparent ceramics of No. 1-5 were suspended in the center of a PTFE vessel containing 80 ml liquid. The pH values of the liquids in the PTFE vessels of No. 1-5 were adjusted to 3.0, 5.0, 7.0, 9.0 and 11.0. The acidic conditions were configured with the nitric acid solution, neutral condition with deionized water, and alkaline conditions were adjusted with sodium hydroxide solution. Finally, all the above PTFE containers were transferred to a 90 °C oven for 1, 3, 7, 14, 21, 28, 35 and 42 days.

Table 2

Parameters of leaching experiment.

No.	pH of Solution	Sample's size (W × L × H)	Volume of Solution	Experimental temperature
0	-	-	-	-
1	3	7.7 × 7.8 × 0.9 mm	80 ml	90°C
2	5	7.7 × 7.8 × 0.9 mm	80 ml	90°C
3	7	7.7 × 8.1 × 1.0 mm	80 ml	90°C
4	9	7.7 × 8.7 × 0.9 mm	80 ml	90°C
5	11	7.8 × 7.8 × 0.9 mm	80 ml	90°C

2.3 Characterizations

The leaching concentrations (C_i) of Gd and Zr were measured in the leachate under different pH conditions by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7700 ×). The normalized element rates LR_i ($\text{g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) are calculated according to the following formula:

$$LR_i = \frac{C_i \cdot V_i}{f_i \cdot S_A \cdot t} \quad (1)$$

where the five variables in the equation represent the concentration of the element i in the leached solutions after the leaching experiment (C_i , g/ L), the quality percentage of the element i in the specimen (f_i , wt%), the surface area of the specimen (S_A , m^2), the volume of the leached solutions (V_i , L) and the duration time (t , d) [23,24,29]. Linear transmission spectra before and after leaching were measured in the 200-2500 nm wavelength range by solid ultraviolet absorption

spectrophotometer (SolidSpec-3700, Shimadzu, Japan). The changes in the crystal structure of GZO ceramics were analyzed by grazing incidence X-ray diffraction (GIXRD; Bruker; D8 Advance) with Cu K α radiation ($\lambda_1=1.54056$ Å, $\lambda_2=1.54439$ Å and $\lambda_{ave.}=1.54248$ Å). The Raman spectra were obtained using a Raman spectrometer (Raman; InVia, Renishaw, Britain) with an excitation wavelength of 785 nm. Surface morphology and root-mean-square (RMS) surface roughness of the samples were analyzed using atomic force microscopy (AFM; Seiko SPA-300HV, Japan) in tapping mode. The micro-morphology of the GZO ceramics was observed using field-emission scanning electron microscopy (FESEM; SU8020, Hitachi, Japan), and their elemental distribution was analyzed using an energy-dispersive X-ray spectrometer (EDX) attached to the FESEM device.

3. Results And Discussion

3.1 Aqueous durability analysis

Figure 1(a) and (b) show LR_i ($i = \text{Gd, Zr}$) values at different pH (pH = 3.0, 5.0, 7.0, 9.0 and 11.0), and Table 3 lists the 42-day normalized release rates for GZO transparent ceramics. The LR_i values gradually decrease with increasing leaching time in different leaching environments. The higher LR_i values during the initial phase of leaching may be related to preferential leaching of species from defective regions, such as surfaces, grain boundaries, etc. [30]. LR_{Gd} and LR_{Zr} fluctuate slightly between 14 and 35 days in the leachate at pH = 7.0, 9.0 and 11.0. Slight fluctuations in LR_i values are normal for short-term leaching tests (42 days). The leaching rates gradually reach their upper limitation with increasing time, which results in fluctuating of leaching rates [31]. In the acidic environment, the standardized release rates of Gd and Zr are higher in the leachate at pH = 3.0 than the counterpart of pH = 5.0. At pH = 3.0 and 5.0, the LR_{Gd} on the 42nd day is $6.64 \times 10^{-5} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ and $1.91 \times 10^{-5} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, and the LR_{Zr} are $2.78 \times 10^{-5} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ and $5.06 \times 10^{-6} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, respectively. In the alkaline environment, the $LR_{Gd/Zr}$ is higher at pH = 11.0 than pH = 9.0. At pH 9.0 and 11.0, the LR_{Gd} on the 42nd day is $2.95 \times 10^{-7} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ and $1.50 \times 10^{-6} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, and the LR_{Zr} are $2.91 \times 10^{-7} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ and $3.08 \times 10^{-6} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, respectively. The LR_i values under neutral conditions are intermediate between acidic and basic conditions. The LR_{Gd} and LR_{Zr} on the 42nd day are $1.62 \times 10^{-6} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ and $2.50 \times 10^{-6} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$.

Table 3 42-day normalized release rates values for GZO transparent ceramics.

No.	pH of Solution	Sample's size (W × L × H)	Volume of Solution	Experimental temperature
0	-	-	-	-
1	3	7.7 × 7.8 × 0.9 mm	80 ml	90°C
2	5	7.7 × 7.8 × 0.9 mm	80 ml	90°C
3	7	7.7 × 8.1 × 1.0 mm	80 ml	90°C
4	9	7.7 × 8.7 × 0.9 mm	80 ml	90°C
5	11	7.8 × 7.8 × 0.9 mm	80 ml	90°C

Overall, the GZO transparent ceramics exhibit high leaching rates under acidic conditions. The leaching rate is lower in the alkaline environment and is lowest in the weak alkaline environment (pH = 9.0). The reason may be related to the dissolution mechanism of the GZO transparent ceramics. In acidic conditions, H⁺ in the leaching solution with the hydrolysis products Gd(OH)₃ and Zr(OH)₄, which accelerates the hydrolysis reaction and results in leachate with high concentrations of Gd and Zr. Whereas in alkaline conditions, OH⁻ reacts rapidly with the sample and finally reaches the

saturation point in the leaching solution. This results in a higher content of Gd and Zr in the leachate at pH = 11 than at pH = 9, but both are lower than in the acidic environment [32].

3.2 Optical properties of ceramics

The transmission spectra of all GZO transparent ceramics in the wavelength range of 0-2500 nm before and after leaching are shown in Fig. 2. Overall, it can be concluded that there is no significant change in the transmittance of GZO transparent ceramics after leaching. There is a slight decrease when $\text{pH} \leq 7$ for the maximum transmittance is located in the infrared region, which remains essentially unchanged in the alkaline environment. Furthermore, the transmittances of GZO transparent ceramics display a decrease in the visible region when $\text{pH} \leq 9$. The reason for the variation in transmittance findings is due to the leaching experiments conducted at different pH levels, where the leaching solution corroded the surface of the ceramics, resulting in the change of transmittance. Figure 2(f) presents the macroscopic appearance of GZO ceramics before and after leaching. The letters below the samples can be clearly seen before and after leaching. Besides, all the ceramics before leaching have a faint orange color, which can be attributed to the absorption of Gd^{3+} ions or inherent defects in the samples [28]. In the case of the samples after leaching, this orange color fades due to partial leaching of Gd^{3+} . Of course, it is also possible that some optical properties have changed due to the corrosion of the sample surface by the leaching solution. This phenomenon indicates that the leaching experiments indeed cause changes in the transmittance of the GZO transparent ceramics and their macroscopic colors.

3.3 Crystal structure analysis

The samples before and after leaching were characterized by GIXRD to study the effect of leaching experiment on the crystal structure. The grazing incidence angle $\gamma = 1.0^\circ$ was used and the corresponding detection depth is 360 nm [33]. The GIXRD characterization results in Fig. 3(a) present that the GZO ceramics before and after leaching are in pyrochlore structure (PDF No. 80-0469). In general, the leaching experiments do not result in changes in the phase structure. The diffraction intensity of the ceramics after the leaching experiment is reduced to different degrees, which is more pronounced in acidic conditions than alkaline and neutral conditions. Compared with other leaching environments, the crystal structure of GZO ceramics is destroyed to a greater extent under acidic conditions, which is in line with the leaching results. Figure 3(b) shows an enlarged pattern of GIXRD between $2\theta = 28^\circ$ and 36° . The XRD patterns of all the samples display a shift towards higher 2θ values after leaching, which indicates that the leaching experiments caused lattice contraction.

In order to further compare the damage degree at different pH environments, the GIXRD data with $\gamma = 1.0^\circ$ was fitted and analyzed. The lattice parameters of the samples before and after leaching are listed in Table 4. At the same time, the line graphs of the interplanar spacing, unit cell volume and lattice contraction rates of different samples are plotted in Fig. 4. It can be seen from Fig. 4(a) that the interplanar spacing (d) decreases more significantly under acidic conditions over other pH conditions. On the whole, the interplanar spacing change at pH = 9.0 is the lowest one. The corresponding cell volume change can be seen in Fig. 4(b) with the smallest change at pH = 9.0 and its lattice contraction rate of 0.06%. When pH = 3.0, the lattice contraction rate exhibits the highest value of 0.77%. All in all, the change in lattice contraction caused by leaching is small. Based on the above results, the chemical durability of GZO ceramics under alkaline conditions is better than that under acidic conditions.

Table 4
Interplanar spacing d (Å) and Cell parameters of before and after leaching Gd₂Zr₂O₇ ceramics.

Element	pH	Leaching time (days)							
		1d	3d	7d	14d	21d	28d	35d	42d
Gd	3	8.82×10^{-3}	1.83×10^{-3}	4.78×10^{-4}	1.96×10^{-4}	9.06×10^{-5}	5.72×10^{-5}	6.25×10^{-5}	6.64×10^{-5}
	5	4.18×10^{-4}	1.10×10^{-4}	3.86×10^{-4}	6.67×10^{-5}	2.61×10^{-5}	2.46×10^{-5}	2.24×10^{-5}	1.91×10^{-5}
	7	1.43×10^{-4}	8.01×10^{-6}	6.03×10^{-6}	1.26×10^{-5}	2.45×10^{-6}	9.56×10^{-6}	7.95×10^{-6}	1.12×10^{-6}
	9	9.87×10^{-5}	2.52×10^{-6}	1.69×10^{-6}	1.39×10^{-6}	2.52×10^{-6}	3.16×10^{-6}	4.32×10^{-7}	2.95×10^{-7}
	11	5.20×10^{-5}	1.17×10^{-5}	1.88×10^{-5}	4.38×10^{-6}	2.70×10^{-6}	3.73×10^{-6}	1.63×10^{-6}	1.50×10^{-6}
Zr	3	5.24×10^{-3}	2.82×10^{-4}	2.78×10^{-4}	1.71×10^{-4}	1.14×10^{-4}	9.09×10^{-5}	5.99×10^{-5}	2.78×10^{-5}
	5	2.32×10^{-4}	8.74×10^{-5}	3.74×10^{-5}	1.66×10^{-5}	7.84×10^{-5}	8.83×10^{-5}	5.72×10^{-5}	5.06×10^{-6}
	7	1.69×10^{-5}	7.75×10^{-6}	1.91×10^{-6}	1.22×10^{-6}	1.44×10^{-6}	1.08×10^{-6}	2.86×10^{-6}	2.50×10^{-6}
	9	7.54×10^{-5}	2.04×10^{-6}	1.85×10^{-6}	1.50×10^{-6}	1.43×10^{-6}	1.06×10^{-6}	1.05×10^{-6}	2.91×10^{-7}
	11	3.46×10^{-4}	4.83×10^{-5}	2.48×10^{-5}	6.51×10^{-6}	8.68×10^{-6}	1.92×10^{-6}	5.82×10^{-6}	3.08×10^{-6}

Raman spectroscopy can be used to detect metal-oxygen vibration modes and local structural changes of the samples before and after leaching, which can be cross-validated with the GIXRD results. The Raman spectra of the samples before and after leaching are shown in Fig. 5, which exhibit five Raman activity modes of the pyrochlore structure [34]. The results are in line with the conclusion that leaching does not lead to structural changes. Among these Raman activity modes, A_{1g} corresponds to the O-Zr-O bending vibration, E_g corresponds to the Zr-O bending vibration, and F_{2g} corresponds to the Zr-O and Gd-O stretching vibration [35]. It can be seen from the Raman spectra that the GZO ceramics do not present significant changes after leaching at different pH levels. There is no obvious decrease in intensity like the GIXRD diffraction peaks, and only a slight weakening of the Raman characteristic peaks exists. This is because the characterization depth of Raman is at the micron level, whereas the depth of GIXRD detection is at the submicron level. Thus, the Raman spectra do not exhibit an obvious change. This result also explains that the leaching experiments at different pH levels cause damage to the crystal structure of GZO ceramics in the sub-micron range.

3.4 Analysis of micro-morphology and elemental distribution

AFM was used to study the effect of leaching experiments on the surface morphology of GZO transparent ceramics. The three-dimensional surface morphology (scanning size of 10×10 μm²) of the samples before and after leaching is shown

in Fig. 6. A few scratches formed by sanding and polishing can be observed in the figure for the samples before leaching. There are also little small amounts of sharp tapered bumps in the nanometer range. From the AFM results of the leached samples, it can be concluded that the sharp tapered bumps are smoothed and passivated after the leaching experiment regardless of the pH conditions. This phenomenon is due to the hydrolysis reaction of the samples in the solution. At $\text{pH} \leq 7.0$, the scratches formed by polishing are still clearly observed after leaching and are not significantly different from those before leaching. In alkaline environments, especially at $\text{pH} = 11.0$, the scratches become indistinct. The depressions of the scratches may be filled with hydrolysis products from the samples, making the scratches unobtrusively observable. From its overall microscopic appearance, it is more likely that the surface is covered with a film of hydrolysis products. The root-mean-square roughness (RMS) values before and after sample leaching are listed in Fig. 6 and Fig. 7 displays the changing trend of RMS. Because of the hydrolysis products partially covering the ceramic surface, the RMS increases for all samples after leaching, but they are still in the nanometer range. The percentage of increase is most significant with RMS values as high as 46.06 nm, especially at $\text{pH} = 11.0$. In conclusion, the AFM characterization results also verify that GZO ceramics are indeed subjected to corrosion on their surfaces during the leaching experiments.

SEM-EDX characterization results of GZO ceramics before and after leaching are shown in Fig. 8 at different pH values. Figure 8(a) shows the morphology and elemental distribution of the original samples, and Fig. 8(b)-(f) correspond to $\text{pH} = 3.0-11.0$. The surface morphology of the sample before leaching shows a flat surface with some bumps and dips due to polishing during the pre-treatment. The samples retain these bumps and dips and have not been subjected to more pronounced corrosion after leaching. For the elemental distribution statistics, all the Gd, Zr, and O elements are uniformly distributed after leaching. There is no significant elemental aggregation and dispersion are observed, indicating that no new phase is produced in the leached sample, which is in consistent with the GIXRD results. This is also due to the better hydrothermal stability of GZO ceramics and their low leaching rates, which do not have a significant effect on the elemental distribution.

4. Conclusions

In this study, the GZO transparent ceramics prepared by a two-step method were subjected to leaching experiments at different pH values to study their chemical stability. In general, all the samples present excellent chemical durability under different pH values. From their normalized leaching rates results, GZO transparent ceramic shows the highest leaching rate at $\text{pH} = 3.0$, while the lowest LR_i values are obtained at $\text{pH} = 9.0$. The leached transparent ceramics show a slight decrease of in-line transmittance, and its macroscopic color also fades. The crystal structure of the leached samples exhibits a slight lattice contraction in the nanometer depth range with a maximum contraction rate of 0.77% at $\text{pH} = 3.0$. The microstructural analysis reveals that the hydrolysis products elevate the surface roughness, but do not significantly affect the distribution of their elements. The above experimental results indicate that leaching causes changes in the appearance of GZO transparent ceramics and it demonstrates excellent chemical durability in a weak alkaline environment, which has theoretical guiding significance for its use as an immobilization matrix.

Declarations

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Figures

Figure 1

The 42-day normalized release rates (LR_i) of (a) Gd and (b) Zr.

Figure 2

Transmission spectra after 42 days of immersion in (a)-(e) pH=3, 5, 7, 9 and 11 solutions, (f) digital photographs of ceramics before and after leaching.

Figure 3

GIXRD patterns of GZO transparent ceramics after and before leaching (a) with $\gamma = 1.0^\circ$, magnification mode (b) at $2\theta = 28^\circ - 36^\circ$.

Figure 4

(a) The variation of the partial interplanar spacing after leaching, (b) cell volume and lattice shrinkage before and after leaching.

Figure 5

Raman spectra of GZO transparent ceramics before and after leaching.

Figure 6

AFM (10×10 μm²) images of the sample surface before and after leaching in different pH environments.

Figure 7

The changing trend of root-mean-square roughness (RMS) values corresponding to AFM characterization.

Figure 8

SEM-EDX images of GZO transparent ceramics before and after leaching. (a) original sample, (b) - (f) pH = 3-11.