

Immobilization of simulated $An4+$ in radioactive sludge using waste electronic sealing glass via microwave sintering: Mechanism and performance

Yong Liu

Shenzhen University

Peilin Shi

Shenzhen University

Zhengxin Wu

Shenzhen University

Xingwang Dai

Shenzhen University

Yuzhen Mai

Shenzhen University

Hongyu Tao

Shenzhen University

Chengyan Yan

University of South China

Gaiyuan Chen

Shenzhen University

Jiawei Li

lijiawei949966360@163.com

Shenzhen University

Research Article

Keywords: Radioactive Sludge, Microwave Sintering, High-Zinc Borosilicate Glass, Simulated radionuclides

Posted Date: September 30th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11058285/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Immobilization of simulated An^{4+} in radioactive sludge using waste electronic sealing glass via microwave sintering: Mechanism and performance

Yong Liu ^a, Peilin Shi ^a, Zhengxin Wu ^a, Xingwang Dai ^a, YuZhen Mai ^a, Hongyu Tao ^a, ChengYan Yan ^b, Gaiyuan Chen ^{a**}, Jiawei Li ^{a*}

^a College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen, 518060, PR China

^b School of Resource Environment and Safety Engineering, University of South China, Hengyang, Hunan, 421001, PR China

* Corresponding author: Tel: +86 187 1165 1211
E-mail address: lijiawei@szu.edu.cn; lijiawei949966360@163.com;

** Co-Corresponding author: Tel: +86 182 4130 0695
E-mail address: chen808099@163.com

Abstract

A high-zinc borosilicate glass recycled from waste electronic sealing glass is used to immobilize a radioactive-sludge simulant containing CeO_2 as a surrogate for tetravalent actinides. Samples are microwave-sintered at 1100, 1200, and 1300 °C and assessed in terms of phase evolution, microstructure, chemical durability, density, and porosity. The optimal CeO_2 contents for vitrification are approximately 5, 9, and 14 wt.%, respectively. Below these limits, Ce remains dispersed as mixed Ce(III) and Ce(IV), whereas at higher loadings, Ce-rich regions develop and crystalline CeO_2 forms. Increasing CeO_2 loading depolymerizes the glass network. Ce leach rates remain between 10^{-4} and 10^{-6} g m⁻² d⁻¹ and decrease with time, while porosity is lowest near the solubility limits. These results identify suitable loading and sintering conditions for the rapid microwave immobilization of radioactive sludge using industrial waste glass.

Keywords

Radioactive Sludge; Microwave Sintering; High-Zinc Borosilicate Glass; Simulated radionuclides

1 Introduction

With the continued development of nuclear energy technology, the long term safe disposal of highly radioactive waste has become an important scientific and engineering issue for the sustainable development of the nuclear industry. Such waste usually contains actinides, fission products, and various nonradioactive components, with complex compositions and broad compositional variation. For glass waste forms, an ideal treatment route should not only increase waste loading, but also ensure that the waste form maintains good structural integrity and chemical durability during storage and disposal. Gin et al. carried out an international collaborative study on the long term behavior of high level nuclear waste glass and pointed out that the long term performance of nuclear waste glass is closely related to glass composition, structure, and reaction processes [1]. Jantzen et al. studied durable glasses designed for long service periods and suggested that rational glass composition design is beneficial for the effective immobilization of nuclear waste over extended time scales [2]. Deshkar et al. investigated alkali aluminoborosilicate glasses and found that compositional changes affect crystallization behavior and chemical durability, indicating that waste loading should not be evaluated separately from glass structure and performance [3]. Sheng et al. conducted vitrification experiments on liquid waste from nuclear power plants, and their results showed that liquid waste can be converted into waste forms suitable for storage and disposal through vitrification [4]. Fabian et al. studied the structure of multicomponent borosilicate glasses using high Q neutron diffraction and reverse Monte Carlo modeling, and found that different components alter the atomic arrangement and local structure of the glass [5]. Sahu et al. used molecular dynamics simulations to investigate simplified sodium borosilicate glasses and concluded that compositional variation affects glass structure and dynamic behavior [6]. Bauer et al. studied the structure of hydrous sodium borosilicate glasses and found that water related components change the glass network environment and local structural features [7]. Fabian et al. further investigated uranium loaded borosilicate glasses, and their results showed that uranium can enter the glass system and interact with the surrounding oxygen coordination environment [8]. Motokawa et al. examined the nanoscopic structure of borosilicate glasses containing additives for nuclear waste vitrification and pointed out that complex additives modify the internal structural distribution of the glass [9]. These studies indicate that the performance of glass waste forms is not determined by waste loading alone, but is jointly governed by glass composition, network structure, element distribution, and processing conditions.

CeO₂ is commonly used as a surrogate for tetravalent actinides in sludge related immobilization studies. Cerium can exist as both Ce³⁺ and Ce⁴⁺, and therefore the behavior of Ce in glass cannot be explained only by its total content. Zhu et al. investigated the structural features, crystallization kinetics, and leaching resistance of CeO₂ doped borosilicate glasses, and found that CeO₂ affects borate structure, the fraction of nonbridging

oxygen, crystallization behavior, and leaching resistance [10]. Fu et al. studied the influence of CeO₂ on the structure and properties of borosilicate glass from a perspective beyond the refining process, and showed that increasing CeO₂ content raises melt viscosity and depolymerizes the glass network [11]. Yu et al. prepared multiple alkaline earth borosilicate glasses containing 3 to 20 wt.% CeO₂ and analyzed the Ce³⁺/Ce⁴⁺ ratio, crystallization behavior, and chemical stability. They concluded that the accommodation range of CeO₂ is related to glass structure, Ce valence, and chemical durability [12]. Kamat et al. studied the partitioning and clustering mechanisms of rare earth cations in alkali aluminoborosilicate glasses and found that rare earth ions such as Nd³⁺ gradually transform from isolated species to clusters with increasing content, followed by nanoscale separation [13]. Quintas et al. investigated the effects of compositional variation on charge compensation of AlO₄ and BO₄ units and crystallization tendency in rare earth rich aluminoborosilicate glasses, and pointed out that alkali and alkaline earth ions can modify glass structural units and crystallization behavior [14]. Quintas et al. also studied the effects of alkali and alkaline earth cations on the local environment of Nd and found that different cation compositions change the local coordination environment of Nd [15]. Kidari et al. investigated the solubility of La and Nd in simplified high level waste glasses and found that La and Nd form apatite phases after exceeding their accommodation range in the glass, resulting in depolymerization of the glass network [16]. These results suggest that the behavior of CeO₂ in the waste electronic sealing glass and sludge simulant system should be assessed by considering addition amount, sintering temperature, Ce valence, glass structure, crystal formation, and leaching resistance together.

The reaction of glass waste forms in aqueous solution is closely related to their long term performance. Neeway et al. developed an ion exchange interdiffusion model and indicated that this model can be used to understand element migration during the long term behavior of nuclear waste glass [17]. Bunker studied the molecular mechanisms of silicate glass corrosion and suggested that glass composition, solution interaction, and surface reaction layer formation jointly affect the corrosion process of glass [18]. Weber et al. investigated radiation effects in crystalline ceramic materials used for the immobilization of high level nuclear waste and plutonium, and pointed out that radiation can alter the structure of immobilization materials and affect their service performance [19]. Mohd Fadzil et al. studied glasses for immobilizing rare earth oxide waste and found that liquidus temperature and chemical durability limit waste loading [20]. Lu et al. used high energy X ray diffraction and molecular dynamics simulations to investigate the structure of ISG borosilicate nuclear waste glasses, and found that short range and medium range structures change with composition [21]. Subedi and Tutchton used first principles calculations to study the atomic structure of uranium incorporated sodium borosilicate glasses and pointed out that the local coordination environment of uranium is affected by the surrounding glass network [22]. Xue et al. used a self propagating synthesized zirconolite rich matrix for the rapid disposal of simulated Ce bearing radioactive soil waste, and their results showed that Ce surrogate

nuclides can be immobilized through selected phases [23]. Chen et al. rapidly synthesized $\text{Gd}_2\text{Zr}_{2-x}\text{Ce}_x\text{O}_7$ waste forms by spark plasma sintering and investigated their chemical durability, suggesting that phase composition plays an important role in surrogate nuclide immobilization [24]. Han et al. used continuous microwave sintering for the rapid solidification of simulated radioactive contaminated soil and found that temperature and doping level affect solidification performance [25]. Chen et al. used microwave sintering to immobilize simulated An^{4+} in radioactive sludge and analyzed its mechanism and performance. Their results showed that microwave sintering can promote sludge simulant immobilization and affect the final performance of the waste form [26].

Based on the above studies, a sludge simulant was prepared in this work according to the measured sludge composition and mixed with waste electronic sealing glass. The mixtures were microwave sintered at 1100, 1200, and 1300 °C with different CeO_2 additions, and additional samples were prepared at intervals of 1 wt.% near the apparent threshold. X ray diffraction, Fourier transform infrared spectroscopy, X ray photoelectron spectroscopy, scanning electron microscopy with energy dispersive spectroscopy, high resolution transmission electron microscopy, selected area electron diffraction, leaching tests, bulk density measurement, and apparent porosity measurement were used to analyze the phase composition, structure, valence state, microstructure, and physicochemical properties of the samples. This study aims to clarify the CeO_2 addition boundary at different sintering temperatures and to reveal the effects of temperature and CeO_2 content on structural evolution, Ce distribution, Ce valence, leaching resistance, and densification of the glass waste forms.

2 Experimental

2.1 Preparation

The sludge simulant was designed from the measured composition of settled sludge collected from the bottom of an intermediate- and high-level radioactive-sludge storage tank in China. The original sludge was used only for compositional analysis and not as an experimental feedstock. Major constituents were measured by inductively coupled plasma mass spectrometry, inductively coupled plasma optical emission spectrometry, and ion chromatography. Na, Al, and Fe were the dominant elements, with smaller amounts of Ca, Si, and other constituents. Analytical-grade reagents were used to reproduce the measured composition, as listed in Table 1. The reagents were weighed in the required proportions and dispersed in anhydrous ethanol at a liquid-to-solid ratio of 1.5:1. After mechanical stirring for 24 h, the slurry was dried at 105 ± 2 °C for 24 h and mixed in an ultrasonic resonance mixer at 60 Hz for 30 min. The resulting powder was sealed, protected from light, and kept dry.

The industrial waste-glass powder was prepared from discarded electronic sealing-glass fragments. This high-zinc borosilicate glass supplied B_2O_3 , SiO_2 , ZnO , and the other glass-forming components. The fragments were wet-ball-milled in ultrapure water for 4 h, dried at 105 ± 2 °C for 48 h, and passed through a 200-mesh sieve. X-ray fluorescence spectroscopy and inductively coupled plasma optical emission spectrometry were used to determine the composition shown in Table 2. This pretreatment reduced particle-size variation and improved mixing without changing the original glass composition.

2.2 Experimental procedure

CeO_2 was added to the simulated sludge as a non-radioactive actinide surrogate. Waste glass made up 60 wt.% of each batch, while the simulated sludge and CeO_2 together accounted for the remaining 40 wt.%. Each batch weighed 6.000 g. Sample codes identify both sintering temperature and CeO_2 loading, as shown in Table 3. For example, 1100°C-Ce5 contains 5 wt.% CeO_2 in the combined sludge- CeO_2 fraction and was sintered at 1100 °C. Each powder batch was mixed and ground thoroughly with anhydrous ethanol, dried, and transferred to a 10 mL alumina crucible. Samples were microwave sintered in air in a multifunction microwave muffle furnace. The temperature was raised to 1000 °C at 20 °C min⁻¹ and then to the target temperature at 10 °C min⁻¹. After a 50 min hold, the samples were cooled naturally in the furnace.

Previous work showed that 60 wt.% borosilicate glass promotes vitrification of simulated radioactive sludge [26]. Dehydration, dehydroxylation, and carbonate decomposition in the sludge-glass mixture occur mainly below 1000 °C. Sintering temperatures of 1100, 1200, and 1300 °C were therefore selected to compare their effects on glass formation, viscous-flow densification, and CeO_2 precipitation. The principal series contained 5, 10, 15, or 20 wt.% CeO_2 . Additional samples were prepared at 1 wt.% intervals near each apparent solubility threshold so that the limit was not inferred solely from the wider 5 wt.% spacing.

2.3 Characterization

Powder phases were analyzed with a Bruker D8 Venture X-ray diffractometer using Cu K α radiation with a wavelength of $\lambda = 1.5406$ Å. Continuous scans were collected over $2\theta = 5^\circ$ to 90° at 5° min^{-1} . XRD data were fitted by the Rietveld method, and the net areas of the selected peaks were calculated with Jade. For samples containing crystalline CeO_2 , the pattern with the strongest CeO_2 reflections was used as the reference, and the amorphization fraction was calculated from Eq. (11) [27].

$$f_A = 1 - \frac{\sum_{i=1}^n \frac{A_i^{\text{sintered}}}{A_i^0}}{n} \quad (1)$$

In Eq. (1), f_A is the amorphization fraction, A_i^0 is the net area of the i th CeO_2 reflection in the reference sample, A_i^{sintered} is the net area of the corresponding reflection in another sintered sample, and n is the number of reflections included in the calculation. The CeO_2 reflections at approximately 28.5° , 33.1° , 47.5° , 56.4° , and 59.1° were used.

Glass-network structure was examined with a Thermo Fisher Scientific Nicolet is50 Fourier transform infrared spectrometer. Elemental chemical states were analyzed with a Thermo Fisher Scientific K-Alpha X-ray photoelectron spectrometer using Al $K\alpha$ radiation at 1486.6 eV and an operating voltage of 12 kV. Samples were ultrasonically cleaned in ethanol and vacuum dried before measurement. High-resolution Ce 3d spectra were acquired at a pass energy of 50 eV, and binding energies were calibrated to the C 1s peak at 284.8 eV. The Ce 3d spectra were deconvoluted with Gaussian-Lorentzian functions to compare the relative Ce^{3+} and Ce^{4+} contents.

Microstructure was examined by scanning electron microscopy and transmission electron microscopy using a Quanta 400 FEG and a Talos F200, respectively. Elemental distributions were measured by energy-dispersive X-ray spectroscopy. Bulk density ρ_b and apparent porosity π_t were measured at room temperature with a Dahometer DE-200T and calculated from Eqs. (22) and (33), respectively [25].

$$\rho_b = \frac{m_1}{m_2 - m_3} \times \rho_w \quad (2)$$

In Eq. (2), m_1 is the dry sample mass, m_2 is the water-saturated sample mass, m_3 is the apparent mass of the saturated sample suspended in water, and ρ_w is the density of the saturating liquid at the measurement temperature.

$$\pi_t = \frac{m_2 - m_1}{m_2 - m_3} \times 100\% \quad (3)$$

Apparent porosity was calculated from the differences among the dry, saturated, and suspended masses. The mass terms are defined as in Eq. (33).

Chemical durability was evaluated with a modified accelerated leaching protocol based on ASTM C1285 Test Method B. The purpose was to compare representative waste forms under intensified hydrothermal conditions. Samples were ground to 75 to 150 μm , and their specific surface areas were measured by nitrogen

adsorption. Deionized water at pH 7 was used as the leachant at 105 °C, with a powder-to-solution mass ratio of 10:1. Polytetrafluoroethylene liners were soaked in anhydrous ethanol for 10 min, ultrasonically cleaned in deionized water for 20 min, and dried at 105 °C. Leachates were sampled after 3, 7, 14, 21, 28, and 35 d, and the removed volume was replaced with an equal volume of deionized water. Elemental concentrations were measured by atomic absorption spectroscopy, and normalized leach rates were calculated from Eq. (44) [24, 28–30].

$$RL_i = \frac{C_i V}{SA \cdot f_i \cdot t} \quad (4)$$

In Eq. (4), RL_i is the normalized leach rate of element i in $\text{g m}^{-2} \text{d}^{-1}$, C_i is its concentration in the leachate in g m^{-3} , V is the leachate volume in m^3 , SA is the powder surface area, f_i is the mass fraction of element i in the waste form, and t is the leaching time. The experimental SA/V ratio was approximately 2000 m^{-1} .

3 Results and discussion

3.1 Phase-evolution

XRD patterns were collected from all samples to determine their phase assemblages. The patterns obtained after sintering for 50 min at 1100, 1200, and 1300 °C are shown in Fig. 1(a₁-c₁). Every sample exhibited a broad amorphous halo over $2\theta = 20^\circ$ to 40° . As the CeO_2 content increased, reflections appeared near 28.5° , 33.1° , 47.5° , 56.4° , and 59.1° , consistent with fluorite-type CeO_2 . At 1100 and 1200 °C, these reflections were already visible at 10 wt.% CeO_2 . At 1300 °C, distinct CeO_2 reflections did not appear until the loading reached 15 wt.%. CeO_2 precipitation therefore depended on both loading and sintering temperature. No other well-defined Ce-bearing crystalline phase was detected. Once the glass could no longer accommodate all of the added Ce, the excess appeared mainly as CeO_2 rather than as a complex Ce silicate or borate. To locate the apparent CeO_2 solubility boundary more precisely, compositions near the first detectable CeO_2 reflection were prepared at 1 wt.% intervals in addition to the initial 5 wt.% series. The refined patterns are shown in Fig. 1(a₂-c₂). Based on the absence or presence of a separate CeO_2 phase by conventional XRD, the apparent CeO_2 solubility limits were approximately 5, 9, and 14 wt.% at 1100, 1200, and 1300 °C, respectively. The boundary shifted to higher loading as temperature increased. Ce accommodation in this glass was therefore governed not only by the initial composition but also by melt formation, diffusion, and structural rearrangement during sintering. At higher temperature, lower melt viscosity and faster mass transport can promote dissolution of the starting CeO_2 particles and redistribution of Ce through the glass, delaying the appearance of a separate crystalline phase. Earlier studies also report temperature-dependent dissolution of Ce in simulated nuclear-waste

glasses and precipitation of CeO₂ once the glass solubility limit is exceeded. The present temperature trend is consistent with that melting and crystallization behavior.

Figure 1(a₃-c₃) compares the amorphization fractions of samples that contained crystalline CeO₂. The 1100°C-Ce20 sample, which had the strongest CeO₂ reflections, served as the reference. At a given CeO₂ loading, the amorphization fraction generally increased with sintering temperature; all analyzed samples sintered at 1300 °C had values above 0.5. At a fixed temperature, the fraction generally decreased as CeO₂ loading increased. These trends agree with both the diffraction patterns and the identified solubility boundaries. Higher temperature promoted CeO₂ dissolution and redistribution into the glass and reduced the proportion retained as long-range-ordered CeO₂. Further increases in loading eventually exhausted the structural capacity of the glass. The added Ce could then no longer enter the amorphous phase uniformly, and the amount of residual or reprecipitated CeO₂ increased.

The phase evolution can thus be described as a continuous progression. Below the apparent solubility limit, XRD detected no separate CeO₂ phase, indicating that Ce was predominantly dispersed in the amorphous matrix. The glass approached saturation as the loading neared the boundary. Further CeO₂ addition produced a crystalline CeO₂ phase whose intensity increased with loading. The shift in the XRD-defined boundary from about 5 wt.% at 1100 °C to about 14 wt.% at 1300 °C shows that higher sintering temperatures substantially increased Ce accommodation under the conditions used here.

3.2 FT-IR analysis

After the apparent CeO₂ solubility boundary had been identified at each temperature, FT-IR spectroscopy was used to examine local changes in the glass network. The spectra in Fig. 2(a₁-a₃) have similar overall profiles at 1100, 1200, and 1300 °C. All contain the broad absorption bands typical of borosilicate glass, indicating that neither CeO₂ loading nor sintering temperature changed the basic type of glass network.

The bands at approximately 3400 and 1600 cm⁻¹ remained at nearly constant positions and showed no systematic dependence on CeO₂ loading or sintering temperature. They are therefore assigned mainly to adsorbed water and surface hydroxyl groups rather than to Ce-induced changes in the bulk glass network. The band near 1450 cm⁻¹ is associated primarily with asymmetric B-O stretching in three-coordinate [BO₃] units, although asymmetric C-O stretching from a small amount of CO₃²⁻ may overlap this region [33]. Boron occurs as both trigonal [BO₃] and tetrahedral [BO₄] units in borosilicate glass. Asynchronous stretching of B-O bonds in planar [BO₃] units produces a marked dipole change and absorption across roughly 1200 to 1500 cm⁻¹. The sludge simulant contained Na₂CO₃ and CaCO₃, but the samples were sintered at 1100 to 1300 °C. Absorption in

this region cannot therefore be assigned directly to residual starting carbonates; minor carbonate signals may instead reflect surface recarbonation during cooling, grinding, or storage. Because the $[\text{BO}_3]$ and CO_3^{2-} bands overlap, the intensity near 1450 cm^{-1} cannot provide a rigorous measure of $[\text{BO}_3]$ content. It is used here only as supporting evidence for borate units, while changes in the BO_3/BO_4 population are interpreted together with the other bands and the overall network response. The broad principal band from 800 to 1300 cm^{-1} arises mainly from Si-O stretching in $[\text{SiO}_4]$ tetrahedra and includes contributions from Si-O-Si bridges, Si-O non-bridging oxygen, and different Q^n environments [32, 34–35]. The continuous distribution of local Si-O environments in an amorphous glass causes these modes to overlap into a broad band. Absorption from 700 to 800 cm^{-1} is assigned mainly to symmetric stretching of Si-O-Si linkages. Its presence in every sample confirms that the silicate framework remained an important part of the glass after sintering. The 450 to 550 cm^{-1} region contains low-frequency bending modes of Si-O-Si and the $[\text{SiO}_4]$ framework and may also include local Ce-O vibrations. Because the Ce-O and silicate modes overlap, this band cannot distinguish Ce coordinated within the glass from Ce in precipitated CeO_2 . The analysis therefore focuses on the relative components of the 800 to 1300 cm^{-1} band and is interpreted together with XRD, XPS, and HRTEM/SAED results [32].

The principal band from 800 to 1300 cm^{-1} was deconvoluted as shown in Fig. 2(b₁-b₁₂). In the Q^n notation commonly used for silicate glasses, n is the number of bridging oxygen atoms attached to a $[\text{SiO}_4]$ tetrahedron. The fitted components were assigned to Q^0 orthosilicate $[\text{SiO}_4]^{4-}$ units at approximately 820 to 850 cm^{-1} , Q^1 pyrosilicate $[\text{Si}_2\text{O}_7]^{6-}$ units at approximately 900 to 950 cm^{-1} , Q^2 chain-silicate $[\text{Si}_3\text{O}_9]^{6-}$ units at approximately 950 to 1000 cm^{-1} , Q^3 sheet-silicate $[\text{Si}_4\text{O}_{11}]^{6-}$ units at approximately 1050 to 1100 cm^{-1} , and Q^4 three-dimensional SiO_2 network units near 1200 cm^{-1} . Higher- Q^n fractions provide a relative measure of silicate network connectivity, although fitted positions and intensities also depend on glass composition and local structure. Figure 2(c) shows that Q^2 and Q^4 were the most abundant components in most samples, accounting for about 26 to 33% and 27 to 33%, respectively. Q^3 accounted for about 14 to 18%, Q^1 for 14 to 23%, and Q^0 for only 5 to 6%. The network therefore contained both moderately and highly polymerized units rather than a single dominant Q^n species. The consistently small Q^0 fraction also indicates that added CeO_2 mainly redistributed the Q^n populations instead of converting the network extensively into isolated $[\text{SiO}_4]$ units.

At all three temperatures, the combined fraction of the more highly polymerized Q^3 and Q^4 units generally decreased with increasing CeO_2 . At $1100\text{ }^\circ\text{C}$, $\text{Q}^3 + \text{Q}^4$ fell from about 50% in Ce5 to approximately 47, 46, and 41% in Ce10, Ce15, and Ce20, respectively. The corresponding sequence at $1200\text{ }^\circ\text{C}$ was about 51, 47, 47, and 43%, and that at $1300\text{ }^\circ\text{C}$ was 51, 48, 47, and 47%. The change in Q^4 was especially clear: its fraction decreased from 33% in Ce5 to 27, 28, and 30% in Ce20 at 1100 , 1200 , and $1300\text{ }^\circ\text{C}$, respectively. At high Ce loadings, Q^1 increased markedly at 1100 and $1200\text{ }^\circ\text{C}$, reaching 23 and 22% in Ce20 compared with 14 and 16% in Ce5. The fitted spectra therefore indicate a redistribution from higher- to lower- Q^n units as CeO_2

loading increased, consistent with lower network polymerization and more non-bridging oxygen. Similar depolymerization has been reported for CeO₂-doped borosilicate glasses [10, 11].

Sintering temperature moderated the Ce-induced network change, particularly at high Ce loading. For Ce5, the combined Q³ + Q⁴ fraction was approximately 50, 51, and 51% at 1100, 1200, and 1300 °C, respectively. For Ce20, it increased from 41% at 1100 °C to 43% at 1200 °C and 47% at 1300 °C. The Q¹ fraction in Ce20 likewise decreased from 23% at 1100 °C and 22% at 1200 °C to 17% at 1300 °C. Raising the temperature within the range studied did not further depolymerize the silicate network. Instead, more Q³ and Q⁴ units were retained at high CeO₂ loading. This trend parallels the rise in the XRD-defined apparent solubility limit from about 5 wt.% at 1100 °C to 9 wt.% at 1200 °C and 14 wt.% at 1300 °C: the higher-temperature samples retained greater network connectivity at larger Ce loadings. This agreement is a correlation between structural measurements. FT-IR alone cannot locate Ce within the network or determine its valence, so the mechanism must also be assessed from XPS and microscopy.

Increasing CeO₂ loading therefore decreased the fraction of highly polymerized silicate units, while higher sintering temperatures moderated this structural change at high CeO₂ contents. The Ce 3d XPS results provide further insight into the charge compensation of Ce within the borate network and the distinct structural roles of Ce(III) and Ce(IV).

3.3 Chemical-state analysis

XPS was used to determine the Ce valence states in the Ce5 to Ce20 waste forms sintered in air at the three temperatures. The results are shown in Fig. 3. Ce and the principal glass-matrix elements were detected in every survey spectrum in Fig. 3(a₁-c₁). The high-resolution Ce 3d spectra were deconvoluted with Gaussian-Lorentzian functions, as shown in Fig. 3(a₂-c₃). Spin-orbit coupling and final-state effects give the Ce 3d region a complex multiplet structure, so valence cannot be assigned from a single peak. A conventional ten-peak model was used. The Ce(III) components were assigned to u₀ at approximately 900.2 eV, v₀ at 881.8 eV, u' at 903.8 eV, and v' at 885.9 eV. The Ce(IV) components were assigned to u at approximately 901.9 eV, u'' at 905.7 eV, u''' at 917.6 eV, v at 893.8 eV, v'' at 887.2 eV, and v''' at 898.8 eV. The corresponding fitted areas were used to calculate the relative amounts of Ce(III) and Ce(IV). Both states were present in every sample, showing that some Ce(IV) introduced as CeO₂ was reduced to Ce(III) during sintering. Mixed Ce(III)/Ce(IV) populations are commonly observed in Ce-doped borosilicate glasses and have also been resolved by Ce 3d fitting [12].

At a fixed sintering temperature, the Ce³⁺/Ce⁴⁺ ratio did not vary monotonically with CeO₂ loading. Instead, it broadly tracked the XRD-defined solubility boundary. The ratio was generally higher when the CeO₂

content was at or below the apparent limit and decreased as loading rose beyond it, indicating a larger relative Ce(IV) fraction. XRD placed the apparent limits at about 5, 9, and 14 wt.% at 1100, 1200, and 1300 °C. Below these values, Ce was mainly dispersed in the glass as mixed Ce(III) and Ce(IV). Above them, the added Ce could no longer be incorporated uniformly, and a separate CeO₂ phase appeared. Because Ce in CeO₂ is predominantly Ce(IV), this precipitation is consistent with the lower Ce³⁺/Ce⁴⁺ ratio measured by XPS. XPS probes a finite near-surface depth and therefore integrates the signals from several local Ce environments. The data show that CeO₂ precipitation coincided with an increase in the relative Ce(IV) content, but they do not establish that every additional Ce(IV) ion belonged to a CeO₂ crystal. SEM-EDS and HRTEM/SAED were used to resolve that distribution. Temperature also affected Ce valence. At a fixed loading, the relative Ce(III) content generally increased as the temperature rose from 1100 to 1200 and 1300 °C. The highest Ce³⁺/Ce⁴⁺ ratio, 1.668, occurred in 1300°C-Ce10. All samples were sintered in air, indicating that external atmosphere alone did not determine the final valence. The high-temperature Ce-O redox equilibrium and the local structure of the glass melt also contributed. The temperature-induced increase in the apparent CeO₂ solubility limit occurred together with the overall rise in Ce(III). Because Ce³⁺ and Ce⁴⁺ differ in charge and local coordination requirements, this change may affect their interaction with oxygen and the surrounding glass-network units. Redistribution of Qⁿ units in the 800 to 1300 cm⁻¹ FT-IR band confirms that the silicate network changed at the same time. The present measurements do not establish a direct causal relationship. They instead indicate coupled adjustment of Ce valence, Ce incorporation, and network structure during high-temperature sintering.

High-resolution O 1s spectra were also fitted with Gaussian-Lorentzian components to examine how CeO₂ affected oxygen coordination in the glass, as shown in Fig. 3(a4-c5). The spectra were resolved into O_{M-O}, O_{NBO}, O_{BO}, and O_{HBE} contributions together with a Na_{KLL} Auger component that overlaps the high-binding-energy side of O 1s. O_{BO} is associated mainly with bridging Si-O-Si, Si-O-B, and B-O-B environments, whereas lower-binding-energy O_{NBO} is assigned mainly to non-bridging Si-O-M or B-O-M groups, where M is Na, Ce, or another modifying cation. After subtraction of the Na_{KLL} contribution near 536 eV, O_{HBE} at about 533.05 eV includes contributions from surface hydroxyl groups, adsorbed water, and carbonate. Components at 532.05 to 532.26 eV and 531.08 to 531.54 eV were assigned to O_{BO} and O_{NBO}, respectively, and the 530.00 to 530.76 eV component was assigned to mixed metal-oxygen environments, O_{M-O} [31]. Because bridging oxygen generally lies at higher binding energy than non-bridging oxygen, their relative areas provide a measure of network polymerization. At 1100 °C, BO/NBO decreased from 1.11 to 1.04 as the CeO₂ content rose from 5 to 10 wt.%. It decreased from 1.10 to 0.99 at 1200 °C. The values for 1300°C-Ce10 and 1300°C-Ce15 were 1.07 and 0.92, respectively. The overall decline with CeO₂ loading indicates conversion of some bridging-oxygen environments into non-bridging ones and a reduction in network polymerization. Coordination of Ce with network oxygen may give Ce an increasingly modifying role, reconstructing Si-O-Si, Si-O-B, or B-O-B

linkages into less polymerized Si/B-O-Ce environments. The O 1s results therefore agree with the FT-IR evidence that Ce is accommodated more uniformly at low loading and progressively modifies and depolymerizes the network as its concentration increases.

Together, the XRD, FT-IR, and XPS data show that the state of Ce depended on loading, temperature, and the capacity of the glass matrix. At low CeO₂ loading, Ce was dispersed mainly in the glass as mixed Ce(III) and Ce(IV). Near and above the apparent solubility limit, the Ce³⁺/Ce⁴⁺ ratio decreased and crystalline CeO₂ appeared. Higher temperature increased the apparent solubility limit, generally increased the relative Ce(III) content, and altered the Qⁿ distribution. Ce incorporation, valence change, and network reorganization were therefore coupled during sintering. The SEM-EDS and HRTEM/SAED results below test this interpretation by locating Ce within the glass and crystalline regions.

3.4 Microstructure and morphology

Samples Ce5 and Ce15 sintered at 1100, 1200, and 1300 °C were selected for SEM, EDS elemental mapping, HRTEM, SAED, and local EDS analysis to examine Ce distribution and test the XRD-defined solubility boundaries. The results are compiled in Fig. 4. Panels (a₁-f₁) show the SEM images; (a₂-f₇) show maps of Si, Al, Ca, Ce, Na, and O; (a₈-f₈) show HRTEM images; (g, h, i, k, and l) show EDS spectra from the red-circled regions in the corresponding TEM images; and (j) shows the SAED pattern from the selected region in 1200°C-Ce5. The apparent CeO₂ solubility limits at 1100, 1200, and 1300 °C were about 5, 9, and 14 wt.%, respectively. Ce5 was at or below the boundary at every temperature, whereas Ce15 exceeded it in all three cases. Comparing the two loadings therefore reveals the transition from uniform Ce dispersion to local enrichment and crystallization.

The SEM images and elemental maps show relatively continuous matrices for Ce5 at all three temperatures, with no large Ce-rich agglomerates. Si, Al, Ca, O, and Na were distributed continuously across the observed regions, and the diffuse Ce signal indicates relatively uniform incorporation in the glass. This agrees with the absence of a distinct CeO₂ phase by XRD. Although Ce5 was close to the approximately 5 wt.% boundary at 1100 °C, most Ce remained accommodated by the glass at the scale examined. At 1200 and 1300 °C, Ce5 lay well below the corresponding limits and was again distributed uniformly. Ce15 showed a different morphology. Particles, bands, or blocks with distinct boundaries were present at all three temperatures, and the Ce maps concentrated in these regions while the surrounding matrix contained less Ce. Si was depleted at the Ce-rich particles and remained concentrated in the surrounding glass. O, Ca, Al, and Na were more diffuse and did not show the same degree of enrichment. Once the CeO₂ loading exceeded the capacity of the glass, part of the Ce therefore segregated into compositionally distinct regions. This transition from uniform dispersion to

local enrichment is consistent with clustering and phase separation of rare-earth cations after their solubility limit in borosilicate glass is reached.

HRTEM and SAED resolved the corresponding local structures. Ce5 was dominated by short-range disorder, and the selected regions showed irregular contrast and diffuse diffraction characteristic of an amorphous glass. Local EDS detected O, Ca, Si, Al, Na, and Ce together, supporting the conclusion that Ce at low loading was dispersed within the multicomponent glass. In Ce15, periodic lattice fringes appeared within Ce-rich regions, indicating a crystalline phase with long-range order. For 1200°C-Ce15, the selected-area pattern contained sharp, regularly arranged spots. The representative spots were indexed to the $(\bar{1}\ \bar{3}1)$, $(\bar{3}\ \bar{3}\ \bar{1})$, $(\bar{2}0\bar{2})$, and $(\bar{1}3\bar{3})$ planes, all consistent with the zone law for the $[\bar{3}2\bar{3}]$ zone axis. Angles of approximately 40.46° and 49.54° between adjacent diffraction vectors agreed with the geometry expected for cubic fluorite CeO₂. The indexed pattern confirms crystalline CeO₂ in the Ce-rich region and provides local structural evidence for the CeO₂ detected by XRD. The lattice fringes and SAED pattern also show that the Ce-rich features in the SEM and EDS maps were not merely compositional fluctuations. Periodic fringes were likewise observed locally in 1100°C-Ce15 and 1300°C-Ce15, consistent with those samples exceeding their respective XRD-defined CeO₂ solubility limits. Local EDS of the Ce-rich regions in the 1100 and 1300 °C Ce15 samples gave Ce mass fractions of 77.24 and 79.46 *wt.%* and atomic fractions of 31.0% and 31.3%, respectively. The matrix elements Si and Al were depleted, and the Ce/O mass and atomic ratios were broadly consistent with CeO₂, further identifying these particles as a CeO₂-rich phase.

At the microscopic scale, Ce immobilization proceeded from glass incorporation to supersaturation and crystallization. Within the apparent solubility range, Ce was distributed comparatively uniformly, with no marked enrichment by SEM-EDS and predominantly amorphous contrast by HRTEM and SAED. Once the CeO₂ loading exceeded the boundary, the glass approached saturation, excess Ce accumulated locally, and crystals with a defined CeO₂ lattice formed.

The microscopy results, together with XRD, FT-IR, and XPS, show that CeO₂ loading controlled the local distribution of Ce, while sintering temperature adjusted both the accommodation limit and the formation of Ce-rich crystals. Ce5 retained a largely homogeneous amorphous structure. Ce15 contained Ce-rich regions and CeO₂ crystals at all three temperatures, in agreement with the apparent limits of about 5, 9, and 14 *wt.%* at 1100, 1200, and 1300 °C. Crystals at high loading were confined to local regions within a much larger amorphous matrix. The waste forms therefore remained glass-dominated rather than becoming fully crystalline. Within the solubility range, the glass accommodated Ce uniformly; above it, local CeO₂ crystallization relieved the supersaturation. The microscopy supplies direct evidence for the progression inferred from the long-range-order information provided by XRD.

3.5 Chemical durability

Figure 5 presents the PCT leach results for glass waste forms prepared at different temperatures and CeO₂ loadings. Panels (a), (b), and (c) show the normalized leach rates of Na, Al, and Si, while (d₁), (d₂), and (d₃) show the Ce rates for samples sintered at 1100, 1200, and 1300 °C, respectively. Na, Al, and Si, which are major constituents of the glass matrix, generally leached faster than Ce. The normalized Ce rate remained mainly between 10⁻⁴ and 10⁻⁶ g m⁻² d⁻¹ and declined overall with time, indicating effective chemical retention of Ce by the waste forms.

For every sample, the normalized rates of Na, Al, and Si fell sharply between days 3 and 7. Na showed the highest initial release at day 3 and then decreased rapidly; Al and Si followed the same pattern. Readily soluble surface constituents and more reactive surface regions were consumed early, while hydration and the initial alteration layer increasingly restricted transport into the solution. All three rates rose to varying degrees between days 7 and 14. Their simultaneous rebound suggests a response of the glass matrix rather than isolated release of one element. Continued penetration of the leachant can hydrolyze Si-O-Si and Si-O-Al linkages and expose fresh reaction fronts, allowing renewed release of Na, Al, and Si around day 14.

The Ce response varied with its incorporation state. At 1100 °C in Fig. 5(d₁), Ce10, which exceeded the apparent solubility limit, had a substantially higher normalized Ce rate on day 3 than Ce5 and showed a pronounced secondary increase by day 14. Related behavior occurred at 1200 and 1300 °C in Fig. 5(d₂) and (d₃). Samples above the apparent solubility limit generally released more Ce at early times and responded sooner, whereas Ce release from samples below the limit was delayed.

This difference is consistent with the location of Ce in the waste forms. Below the apparent solubility limit, most Ce was distributed within the continuous glass network and coordinated by the surrounding silicate and aluminate units. Early leaching affected mainly the outer surface, before the reaction front reached much of the Ce-bearing interior. The glass network therefore shielded Ce and kept its normalized release rate low. With time, water penetrated more deeply and hydrolyzed the network, eventually exposing Ce that had been retained farther from the surface. This produced the delayed Ce response.

Above the apparent solubility limit, part of the excess Ce segregated into CeO₂ crystals or other Ce-rich regions at the surface, near the surface, or along interfaces between the glass and the precipitated phase. These regions were accessible earlier as the reaction advanced inward. Hydration and hydrolysis of the adjacent glass could therefore release Ce sooner, accounting for the larger and earlier response in the supersaturated samples. In samples below the limit, Ce became widely exposed only after the corrosion front had penetrated and disrupted more of the surrounding glass.

After day 14, the normalized Na, Al, and Si rates in Fig. 5(a-c) declined again. Ce in Fig. 5(d₁-d₃) followed the same overall trend and gradually stabilized. Changes became smaller after day 21, and the rates remained low from days 28 to 35. Continued reaction likely produced a more stable hydrated layer, a Si-rich alteration layer, or other secondary products that restricted inward transport of the leachant and outward transport of dissolved species. Ce leached much more slowly than the main glass-matrix elements throughout the test and remained at low rates at long times. Keeping the CeO₂ loading within the apparent solubility range reduced the proportion of readily accessible Ce near the surface and gave more stable Ce retention under these conditions.

3.6 Bulk density and apparent porosity

Figure 6 shows the bulk density and apparent porosity at each temperature and CeO₂ loading. Density generally increased with CeO₂ content at all three temperatures because Ce is heavier than the other principal elements in the simulated sludge and glass and because CeO₂ addition altered densification. At 1100 °C, density rose from 2.622 g cm⁻³ at 5 wt.% to 2.680 g cm⁻³ at 20 wt.%. At 1200 °C, it increased from 2.630 to 2.711 g cm⁻³. Both series showed a clear plateau between 5 and 10 wt.%. At 1300 °C, density increased continuously from 2.700 to 2.756 g cm⁻³ and remained higher than in the lower-temperature series, consistent with more effective densification. Apparent porosity changed non-monotonically. It was lowest at 5 wt.% for samples sintered at 1100 and 1200 °C and then increased with loading. At 1300 °C, porosity decreased from 0.26% at 5 wt.% to 0.24% at 10 wt.% before rising rapidly to 0.55% at 20 wt.%.

The porosity minimum at each temperature occurred near the corresponding apparent CeO₂ solubility range. Below this range, the higher Ce³⁺/Ce⁴⁺ ratio and progressive incorporation of Ce were associated with lower porosity. Once the loading exceeded the apparent limit, the relative Ce(IV) content increased, Ce exerted a stronger modifying effect on the network, and excess CeO₂ precipitated at or near the glass surface. These changes coincided with increasing porosity. All three series showed substantially higher porosity at 20 wt.%, indicating that excessive CeO₂ loading impaired densification. The measurements establish this correlation but do not by themselves prove that the Ce valence change directly caused the porosity response.

4 Conclusions

High-zinc borosilicate glass derived from waste electronic sealing glass was used to immobilize a radioactive-sludge simulant containing CeO₂ as a surrogate for tetravalent actinides. The microwave-sintered waste forms had XRD-defined apparent CeO₂ solubility limits of about 5, 9, and 14 wt.% at 1100, 1200, and

1300 °C, respectively. Within these ranges, Ce was distributed mainly in the glass and occurred as mixed Ce(III) and Ce(IV). Above the boundary, Ce became locally enriched and crystalline CeO₂ precipitated. Increasing CeO₂ loading reduced the fraction of highly polymerized Qⁿ units and increased non-bridging oxygen, while higher sintering temperature partly limited this depolymerization at high loading. SEM-EDS, HRTEM, and SAED directly confirmed the transition from uniform incorporation to local enrichment and crystallization. The normalized Ce leach rate remained mainly between 10⁻⁴ and 10⁻⁶ g m⁻² d⁻¹ and decreased with leaching time. Samples within the apparent solubility range retained Ce more consistently. Density generally increased with CeO₂ loading and sintering temperature, whereas the lowest porosity occurred near the corresponding solubility range. Excess CeO₂ precipitation increased porosity and hindered densification. Sintering temperature and CeO₂ loading must therefore be matched to balance Ce accommodation, network connectivity, chemical durability, and densification. These findings support the use of industrial waste glass for microwave immobilization of radioactive sludge containing tetravalent actinides.

Radiation resistance was not examined in this study. Gamma irradiation has been reported to promote the conversion of Ce³⁺ to Ce⁴⁺ in CeO₂–PbO–B₂O₃ glasses [36]. The evolution of Ce valence, glass-network structure, and precipitated phases under different radiation types and cumulative doses remains unresolved. Future work should compare phase assemblage, network structure, defect formation, and microstructure before and after irradiation to assess long-term structural stability.

Author contributions

Yong Liu: Supervision, Project administration. **Peilin Shi:** Conceptualization, Methodology, Investigation, Writing-original draft, Writing-review & editing. **Zhengxin Wu:** Data analysis. **Xingwang Dai:** Resources, Visualization. **Yuzhen Mai:** Resources. **Hongyu Tao:** Writing-review & editing. **Chengyan Yan:** Formal analysis. **Gaiyuan Chen:** Project administration, Funding acquisition. **Jiawei Li:** Supervision, Data analysis.

Declaration of Competing Interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work. There is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of the manuscript entitled. The Natural Science Foundation of Hunan Province Basic Research Project for Young Students (2026JJ90187).

Acknowledgments

The authors sincere thanks that the National Natural Science Foundation of China (No. 42277458), the Project in the Field of Equipment Advance Research (No.80927015101), Shenzhen Science and Technology Program (ZDSYS20230626091501002), LingChuang Research Project of China National Nuclear Corporation (No. CNNC-LCKY-202258), LingChuang Research Project of China National Nuclear Corporation (No.CNNC-LCKY-2022064), Shenzhen Challenge-Based Project (JBGS2024-431-003).

Data Availability Statement

In accordance with the data policy of the target journal, it is hereby stated that data is shared for the sample data involved in this work.

References

1. Gin S, Abdelouas A, Criscenti LJ, Ebert WL, Ferrand K, Geisler T, Harrison MT, Inagaki Y, Mitsui S, Mueller KT, Marra JC, Pantano CG, Pierce EM, Ryan JV, Schofield JM, Steefel CI, Vienna JD (2013) An international initiative on long-term behavior of high-level nuclear waste glass. *Mater Today* 16(6):243–248.
<https://doi.org/10.1016/j.mattod.2013.06.008>
2. Jantzen CM, Brown KG, Pickett JB (2010) Durable glass for thousands of years. *Int J Appl Glass Sci* 1(1):38–52.
<https://doi.org/10.1111/j.2041-1294.2010.00007.x>
3. Deshkar A, Parruzot B, Youngman RE, Gulbiten O, Vienna JD, Goel A (2022) Compositional dependence of crystallization and chemical durability in alkali aluminoborosilicate glasses. *J Non-Cryst Solids* 598:121694.
<https://doi.org/10.1016/j.jnoncrysol.2022.121694>
4. Sheng J, Choi K, Song MJ (2001) Vitrification of liquid waste from nuclear power plants. *J Nucl Mater* 297(1–2):13–20.
[https://doi.org/10.1016/S0022-3115\(01\)00598-0](https://doi.org/10.1016/S0022-3115(01)00598-0)
5. Fabian M, Sváb E, Proffen T, Veress E (2008) Structure study of multi-component borosilicate glasses from high-Q neutron diffraction measurement and RMC modeling. *J Non-Cryst Solids* 354(12–13):3296–3301.
<https://doi.org/10.1016/j.jnoncrysol.2008.01.024>
6. Sahu P, Ali SM, Shenoy KT, Mohan S, Arvind A, Sugilal G, Kaushik CP (2021) Molecular dynamics simulations of simplified sodium borosilicate glasses: the effect of composition on structure and dynamics. *Phys Chem Chem Phys* 23:15917–15929.
<https://doi.org/10.1039/D1CP00207D>
7. Bauer U, Behrens H, Reinsch S, Morin EI, Stebbins JF (2017) Structural investigation of hydrous sodium borosilicate glasses. *J Non-Cryst Solids* 473:1–9.
<https://doi.org/10.1016/j.jnoncrysol.2017.03.023>
8. Fabian M, Sváb E, Zimmermann MV (2013) Structure study of new uranium loaded borosilicate glasses. *J Non-Cryst Solids* 376:88–94.
<https://doi.org/10.1016/j.jnoncrysol.2013.09.004>
9. Motokawa R, Kaneko K, Oba Y, Nagai T, Okamoto Y, Kobayashi T, Kumada T, Heller WT (2022) Nanoscopic structure of borosilicate glass with additives for nuclear waste vitrification. *J Non-Cryst Solids* 576:121352.

- <https://doi.org/10.1016/j.jnoncrysol.2021.121352>
10. Zhu HZ, Wang F, Liao Q, Liu D, Zhu Y (2019) Structure features, crystallization kinetics and water resistance of borosilicate glasses doped with CeO₂. *J Non-Cryst Solids* 518:57–65.
<https://doi.org/10.1016/j.jnoncrysol.2019.04.044>
11. Fu J, Zhao J, Li S, Zhang H, Shi S, Zhang J, Liu S (2024) Influence of CeO₂ on the structure and properties of borosilicate glass: an investigation from the perspective besides the refining process. *J Non-Cryst Solids* 623:122690.
<https://doi.org/10.1016/j.jnoncrysol.2023.122690>
12. Yu H, Xin R, Zhang X, Liu H, Zheng K, Zhao J, Zhan L, Xu C, Wan W, Zhu Y, Huo J (2021) Crystallization behavior, quantitation of Ce³⁺/Ce⁴⁺ and chemical stability analysis of multiple alkaline earths borosilicate glasses for immobilizing simulated tetravalent actinides. *J Non-Cryst Solids* 558:120642.
<https://doi.org/10.1016/j.jnoncrysol.2021.120642>
13. Kamat H, Wang F, Barnsley K, Hanna JV, Tyryshkin AM, Goel A (2021) Insight into the partitioning and clustering mechanism of rare-earth cations in alkali aluminoborosilicate glasses. *Chem Mater* 33(15):5881–5893.
<https://doi.org/10.1021/acs.chemmater.1c01352>
14. Quintas A, Caurant D, Majérus O, Charpentier T, Dussossoy JL (2009) Effect of compositional variations on charge compensation of AlO₄ and BO₄ entities and on crystallization tendency of a rare-earth-rich aluminoborosilicate glass. *Mater Res Bull* 44(12):2305–2312.
<https://doi.org/10.1016/j.materresbull.2009.05.009>
15. Quintas A, Majérus O, Lenoir M, Caurant D, Klementiev K, Webb A (2008) Effect of alkali and alkaline-earth cations on the neodymium environment in a rare-earth rich aluminoborosilicate glass. *J Non-Cryst Solids* 354(2–9):98–104.
<https://doi.org/10.1016/j.jnoncrysol.2007.06.077>
16. Kidari A, Dussossoy JL, Brackx E, Caurant D, Magnin M, Bardez-Giboire I (2012) Lanthanum and neodymium solubility in simplified SiO₂-B₂O₃-Na₂O-Al₂O₃-CaO high level waste glass. *J Am Ceram Soc* 95(10):3198–3205.
<https://doi.org/10.1111/j.1551-2916.2012.05273.x>
17. Neeway JJ, Kerisit SN, Liu J, Zhang JD, Zhu ZH, Riley BJ, Ryan JV (2016) Ion-exchange interdiffusion model with potential application to long-term nuclear waste glass performance. *J Phys Chem C* 120(17):9374–9384.
<https://doi.org/10.1021/acs.jpcc.6b03681>
18. Bunker BC (1994) Molecular mechanisms for corrosion of silica and silicate glasses. *J Non-Cryst Solids* 179:300–308.

- [https://doi.org/10.1016/0022-3093\(94\)90708-0](https://doi.org/10.1016/0022-3093(94)90708-0)
19. Weber WJ, Ewing RC, Catlow CRA, Diaz de la Rubia T, Hobbs LW, Kinoshita C, Matzke H, Motta AT, Nastasi M, Salje EKH, Vance ER, Zinkle SJ (1998) Radiation effects in crystalline ceramics for the immobilization of high-level nuclear waste and plutonium. *J Mater Res* 13:1434–1484.
<https://doi.org/10.1557/JMR.1998.0205>
20. Mohd Fadzil S, Hirma PR, Schweiger MJ, Riley BJ (2015) Liquidus temperature and chemical durability of selected glasses to immobilize rare earth oxides waste. *J Nucl Mater* 465:657–663.
<https://doi.org/10.1016/j.jnucmat.2015.06.050>
21. Lu X, Ren M, Deng L, Benmore CJ, Du J (2019) Structural features of ISG borosilicate nuclear waste glasses revealed from high-energy X-ray diffraction and molecular dynamics simulations. *J Nucl Mater* 515:16–26.
<https://doi.org/10.1016/j.jnucmat.2018.12.041>
22. Subedi KN, Tutchton RM (2024) Atomic structure of uranium-incorporated sodium borosilicate glasses: an ab initio study. *Phys Rev B* 110:104204.
<https://doi.org/10.1103/PhysRevB.110.104204>
23. Xue JL, Zhang KB, He ZS, Zhao WW, Li WW, Xie DY, Zhang HB (2018) Rapid disposal of simulated Ce-bearing radioactive soil waste using self-propagating synthesized zirconolite-rich waste matrices. *Ceram Int* 44(12):14534–14540.
<https://doi.org/10.1016/j.ceramint.2018.05.070>
24. Chen SZ, Liu XD, Shu XY, Yang JX, Wang L, Zhang KB, Wang XQ, Zhang HB, Lu XR (2018) Rapid synthesis and chemical durability of $\text{Gd}_2\text{Zr}_{2-x}\text{Ce}_x\text{O}_7$ via SPS for nuclear waste forms. *Ceram Int* 44(16):20306–20310.
<https://doi.org/10.1016/j.ceramint.2018.08.018>
25. Han W, Wu D, Xuan J, Wei G, Wang J, Luo F, Xie Y, Lu X (2022) Rapid solidification of simulated radioactive contaminated soil by continuous microwave sintering: effects of temperature and doping level. *J Environ Manag* 324:116342.
<https://doi.org/10.1016/j.jenvman.2022.116342>
26. Chen GY, Li JW, Chen M, Xie YP, Zhang TJ, Yang Y, Zhou T, Huang K, Mai YZ, Shi KY, Liu Y (2024) Immobilization of simulated An^{4+} in radioactive sludge via microwave sintering: mechanistic and performance. *J Nucl Mater* 597:155148.
<https://doi.org/10.1016/j.jnucmat.2024.155148>
27. Chen M, Li JW, Xie YP, Shi KY, Zhu AL, Chen GY, Li XY, Liu Y (2022) A novel $\text{Sr}_2\text{Nd}_6(\text{SiO}_4)_6\text{O}_2$ glass-ceramics for rapid immobilization of FP and An^{3+} co-doped uranium tailings by microwave sintering: mechanism and performance. *J Nucl Mater* 563:153640.

- <https://doi.org/10.1016/j.jnucmat.2022.153640>
28. Seaborg GT (1993) Overview of the actinide and lanthanide (the f) elements. *Radiochim Acta* 61(3–4):115–122.
- <https://doi.org/10.1524/ract.1993.61.34.115>
29. Li FP, Liu LS, Yang ZM, Li S (2021) Physical and mechanical properties and micro characteristics of fly ash-based geopolymer paste incorporated with waste granulated blast furnace slag (GBFS) and functionalized multi-walled carbon nanotubes (MWCNTs). *J Hazard Mater* 401:123339.
- <https://doi.org/10.1016/j.jhazmat.2020.123339>
30. Corkhill CL, Cassingham NJ, Heath PG, Hyatt NC (2013) Dissolution of UK high-level waste glass under simulated hyperalkaline conditions of a colocated geological disposal facility. *Int J Appl Glass Sci* 4(4):341–356.
- <https://doi.org/10.1111/ijag.12042>
31. Tan P, Shu X, Wen M, Li L, Lu Y, Lu X, Chen S, Dong F (2022) Characteristics of cerium doped aluminosilicate glass as simulated radioactive waste forms: effect on structures and properties. *Prog Nucl Energy* 150:104299.
- <https://doi.org/10.1016/j.pnucene.2022.104299>
32. Liu H, Kaya H, Lin YT, Ogrinc A, Kim SH (2022) Vibrational spectroscopy analysis of silica and silicate glass networks. *J Am Ceram Soc* 105(4):2355–2384.
- <https://doi.org/10.1111/jace.18206>
33. Brooker RA, Kohn SC, Holloway JR, McMillan PF (2001) Structural controls on the solubility of CO₂ in silicate melts: Part II: IR characteristics of carbonate groups in silicate glasses. *Chem Geol* 174(1–3):241–254.
- [https://doi.org/10.1016/S0009-2541\(00\)00318-1](https://doi.org/10.1016/S0009-2541(00)00318-1)
34. Kucharczyk S, Sitarz M, Zajac M, Deja J (2018) The effect of CaO/SiO₂ molar ratio of CaO-Al₂O₃-SiO₂ glasses on their structure and reactivity in alkali activated system. *Spectrochim Acta A Mol Biomol Spectrosc* 194:163–171.
- <https://doi.org/10.1016/j.saa.2018.01.018>
35. Huang LJ, Shu XY, Tan P, Xuan JT, Wen MF, Lu YX, Liu TH, Ding CC, Chen JM, Dong FQ, Li XA, Lu XR (2023) Role of radioactive waste on microstructure evolution and performance in natural aluminosilicate system. *J Radioanal Nucl Chem* 332(7):2653–2666.
- <https://doi.org/10.1007/s10967-023-08938-w>
36. Singh GP, Kaur P, Kaur S, Kaur R, Singh DP (2013) Conversion of Ce³⁺ to Ce⁴⁺ ions after gamma ray irradiation on CeO₂-PbO-B₂O₃ glasses. *Phys B Condens Matter* 408:115–118.
- <https://doi.org/10.1016/j.physb.2012.09.005>

623 **Table 1** Radioactive-sludge metal concentrations in wet sludge and composition of the sludge simulant

Element	Content (mg kg ⁻¹)	Chemical ingredients	Content	
			wt. %	mol. %
Ca	1.64×10^3	CaCO ₃	3.772	2.588
Mg	1.94×10^1	Mg(OH) ₂	0.030	0.05
Na	1.94×10^4	Na ₂ CO ₃	42.031	53.249
Al	1.09×10^4	Al(OH) ₃	29.017	25.486
Fe	5.28×10^3	Fe ₂ O ₃	13.903	5.952
Si	5.33×10^3	SiO ₂	10.500	12.017
Cr	2.81×10^2	Cr ₂ O ₃	0.378	0.347
Ni	2.77×10^2	NiO	0.359	0.301
Mo	1.22×10^1	MoO ₃	0.008	0.008

624

625 **Table 2** Oxide composition of waste electronic sealing-glass powder

Chemical ingredients	Content wt. %	Chemical ingredients	Content wt. %	Chemical ingredients	Content wt. %
SiO ₂	46.49	Na ₂ O	7.60	CaO	7.07
MgO	0.80	Al ₂ O ₃	4.30	K ₂ O	2.12
B ₂ O ₃	14.95	BaO	0.33	ZnO	15.87
Others	0.47				

626

627 **Table 3** Sample compositions, designations, and sintering temperatures

Sample	Additive amount of raw materials (g)			Sintering temperature
	Simulation of radioactive sludge (g)		BSG (g)	
	Radioactive sludge base materials (g)	CeO ₂ (g)		
1100°C-Ce5	2.28	0.12	3.6	1100°C 1200°C 1300°C
1100°C-Ce10	2.16	0.24	3.6	
1100°C-Ce15	2.04	0.36	3.6	
1100°C-Ce20	1.92	0.48	3.6	
1200°C-Ce5	2.28	0.12	3.6	
1200°C-Ce10	2.16	0.24	3.6	
1200°C-Ce15	2.04	0.36	3.6	
1200°C-Ce20	1.92	0.48	3.6	
1300°C-Ce5	2.28	0.12	3.6	
1300°C-Ce10	2.16	0.24	3.6	
1300°C-Ce15	2.04	0.36	3.6	
1300°C-Ce20	1.92	0.48	3.6	

628

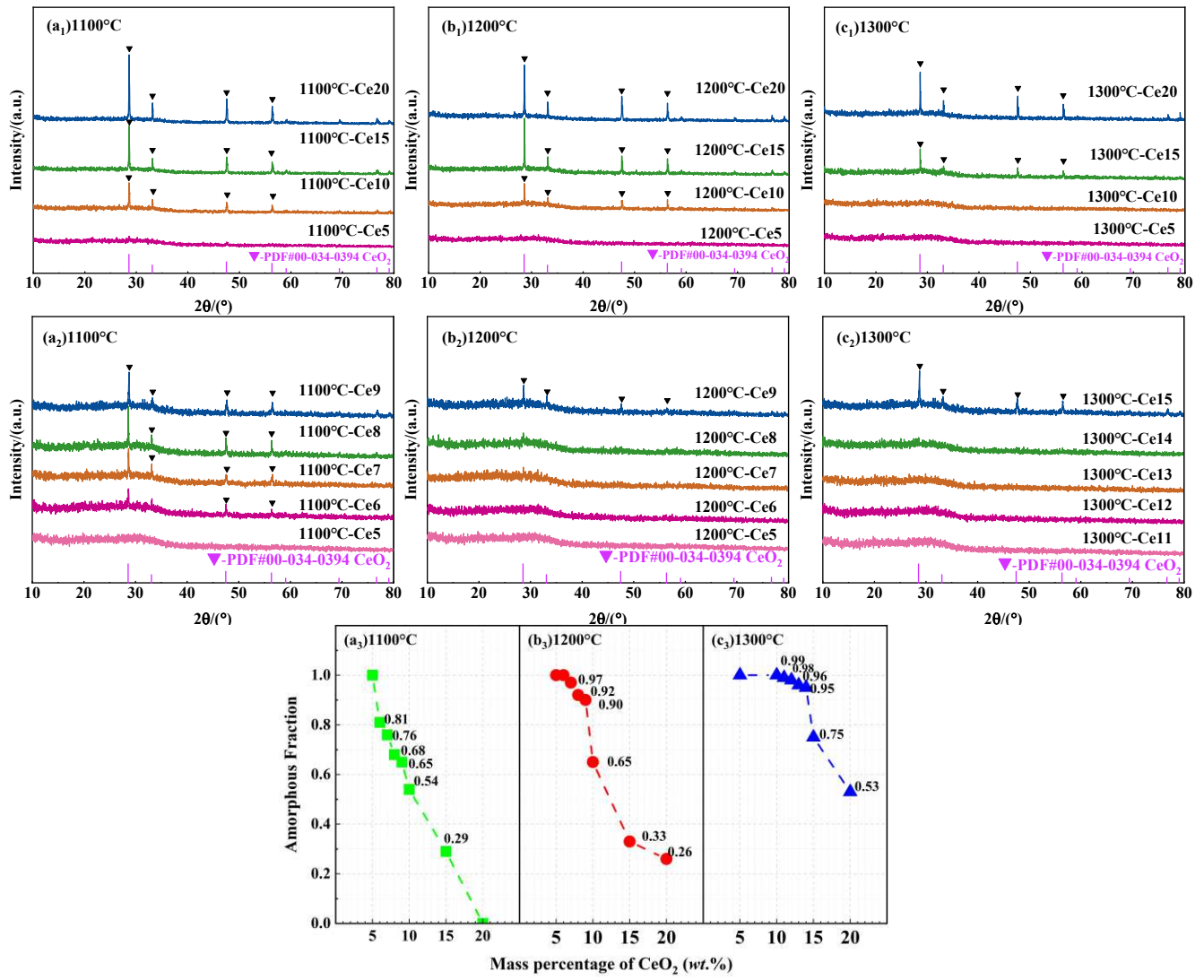


Fig. 1 Phase composition and amorphization of waste forms at different CeO₂ loadings and sintering temperatures: (a₁-c₁) XRD patterns for samples containing 5 to 20 wt.% CeO₂; (a₂-c₂) XRD patterns for the refined composition series; (a₃-c₃) amorphization fractions of samples containing crystalline CeO₂

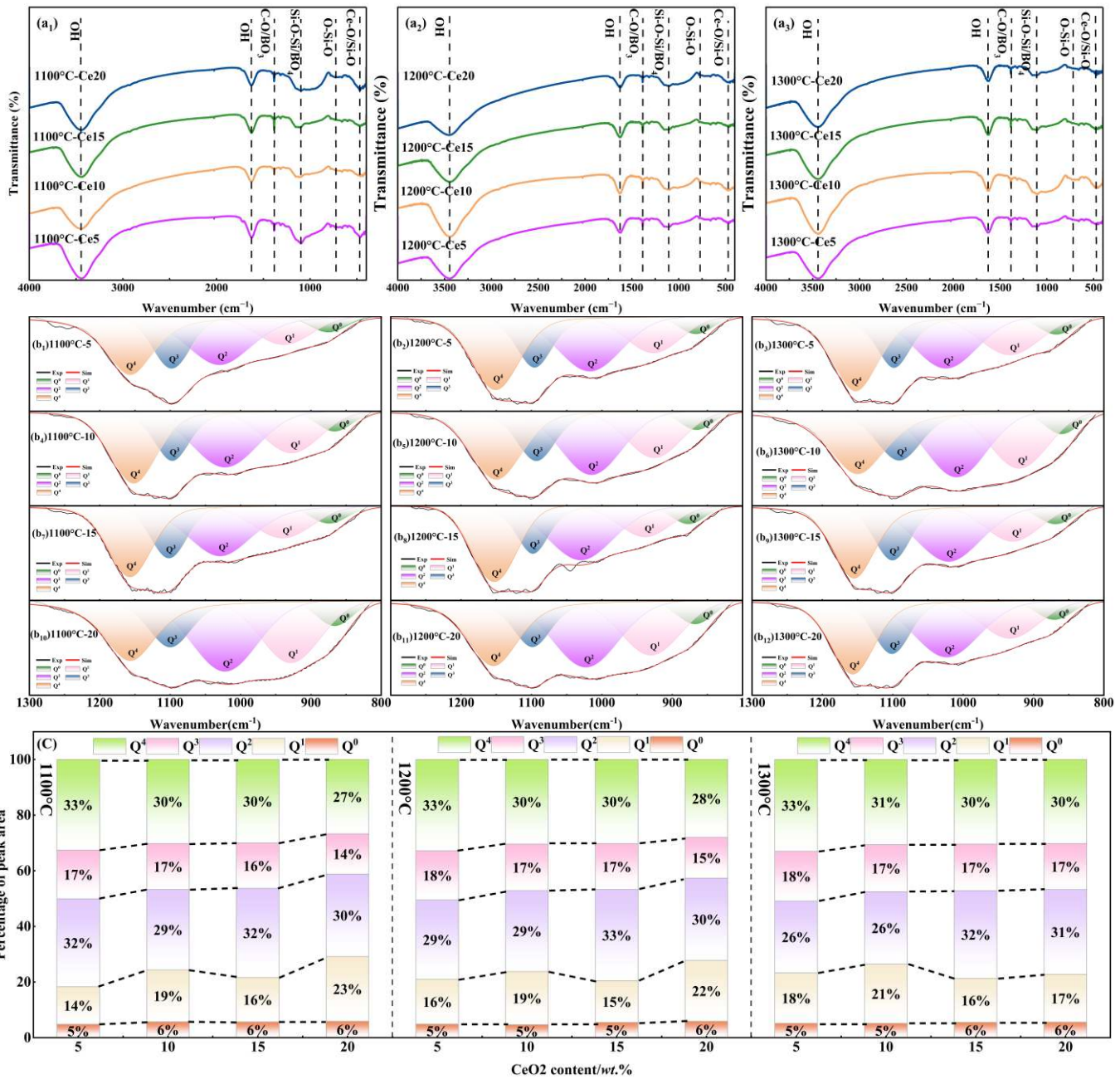


Fig. 2 FT-IR analysis of waste forms at different CeO₂ loadings and sintering temperatures: (a₁-a₃) spectra at 1100, 1200, and 1300 °C; (b₁-b₁₂) deconvolution of Qⁿ units in the 800 to 1300 cm^{-1} band; (c) relative peak areas of the Qⁿ units

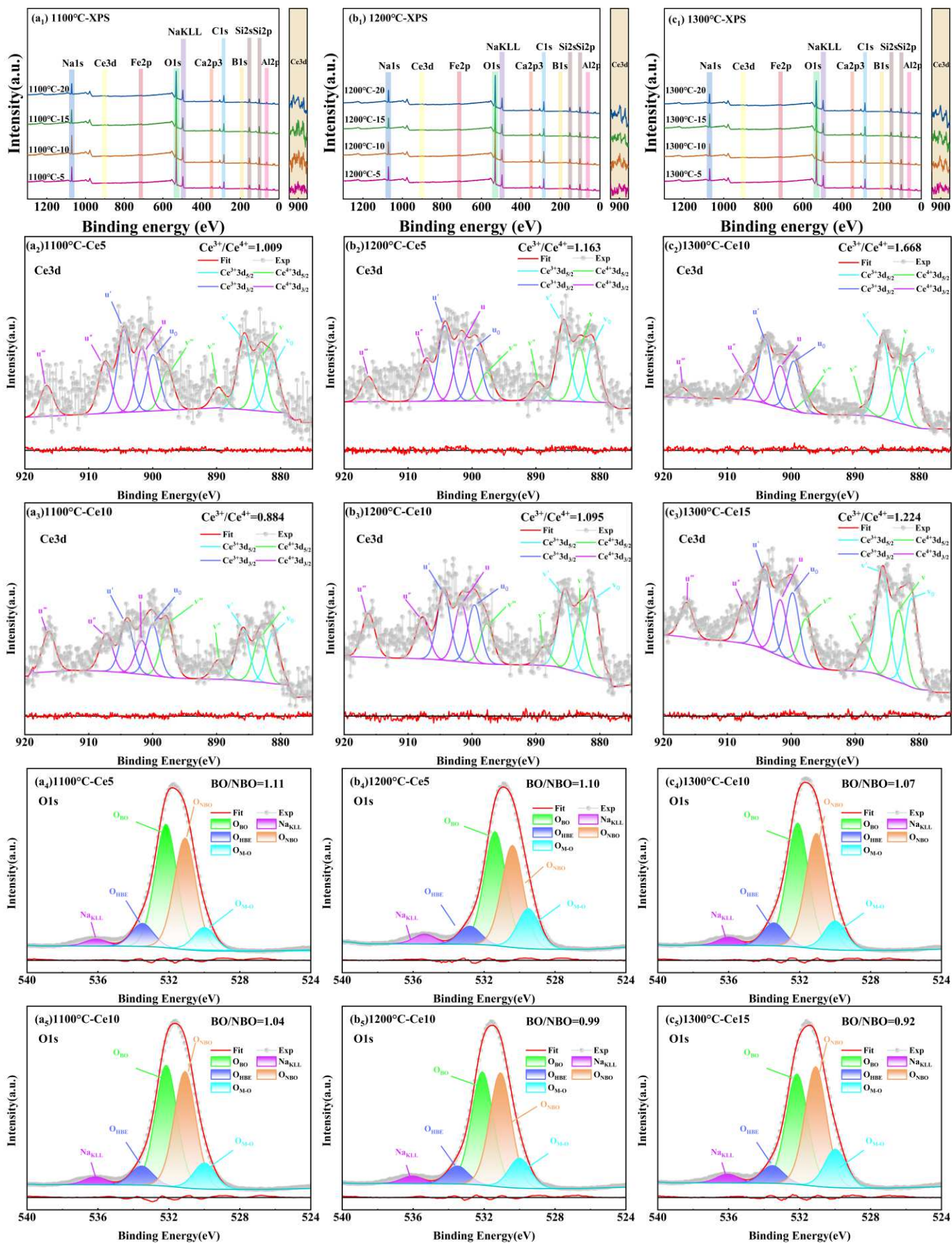
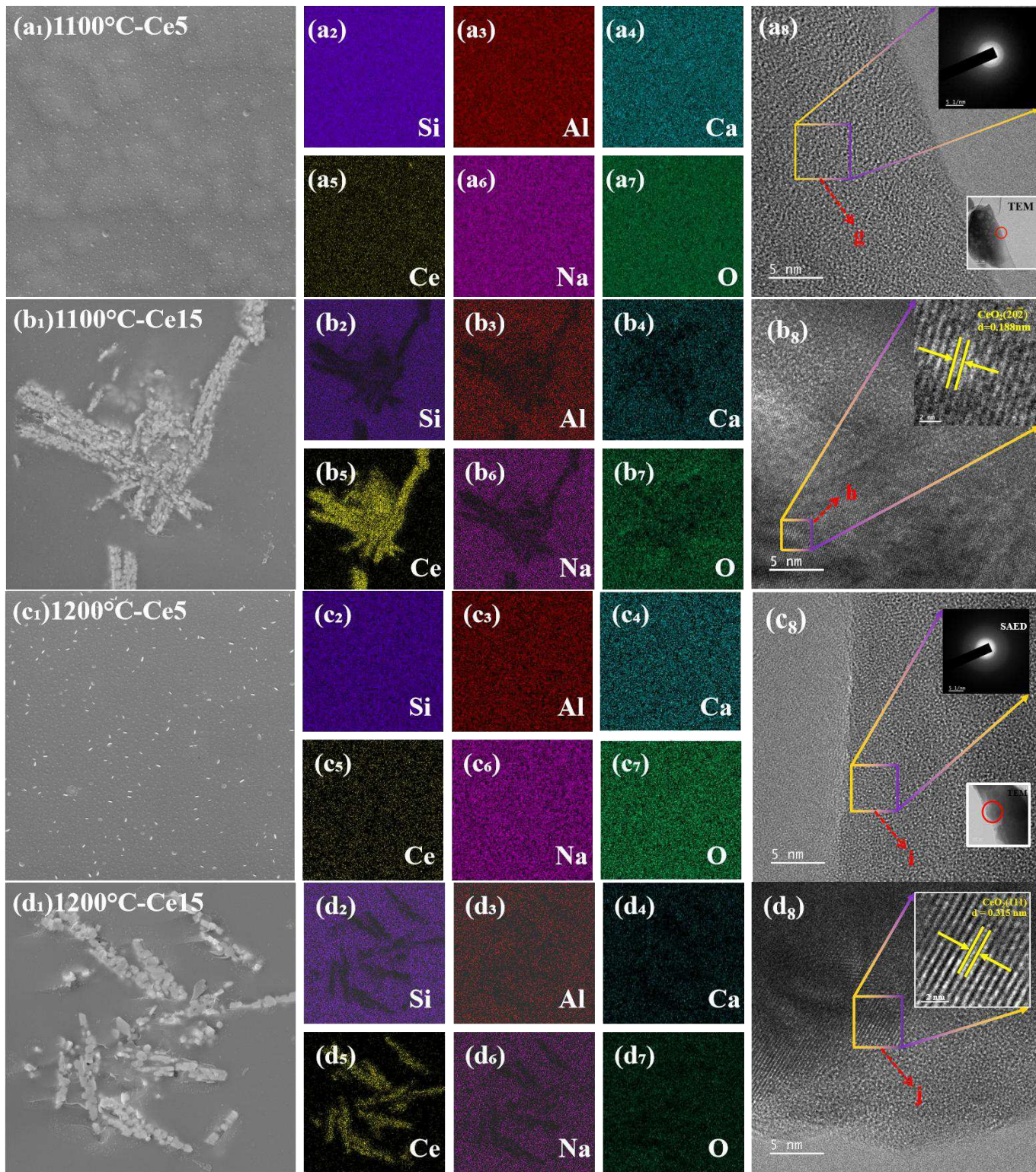


Fig. 3 XPS analysis of waste forms at different CeO₂ loadings and sintering temperatures: (**a1-c1**) survey spectra; (**a2-c3**) Ce 3d spectra and peak deconvolution; (**a4-c5**) O 1s spectra and peak deconvolution



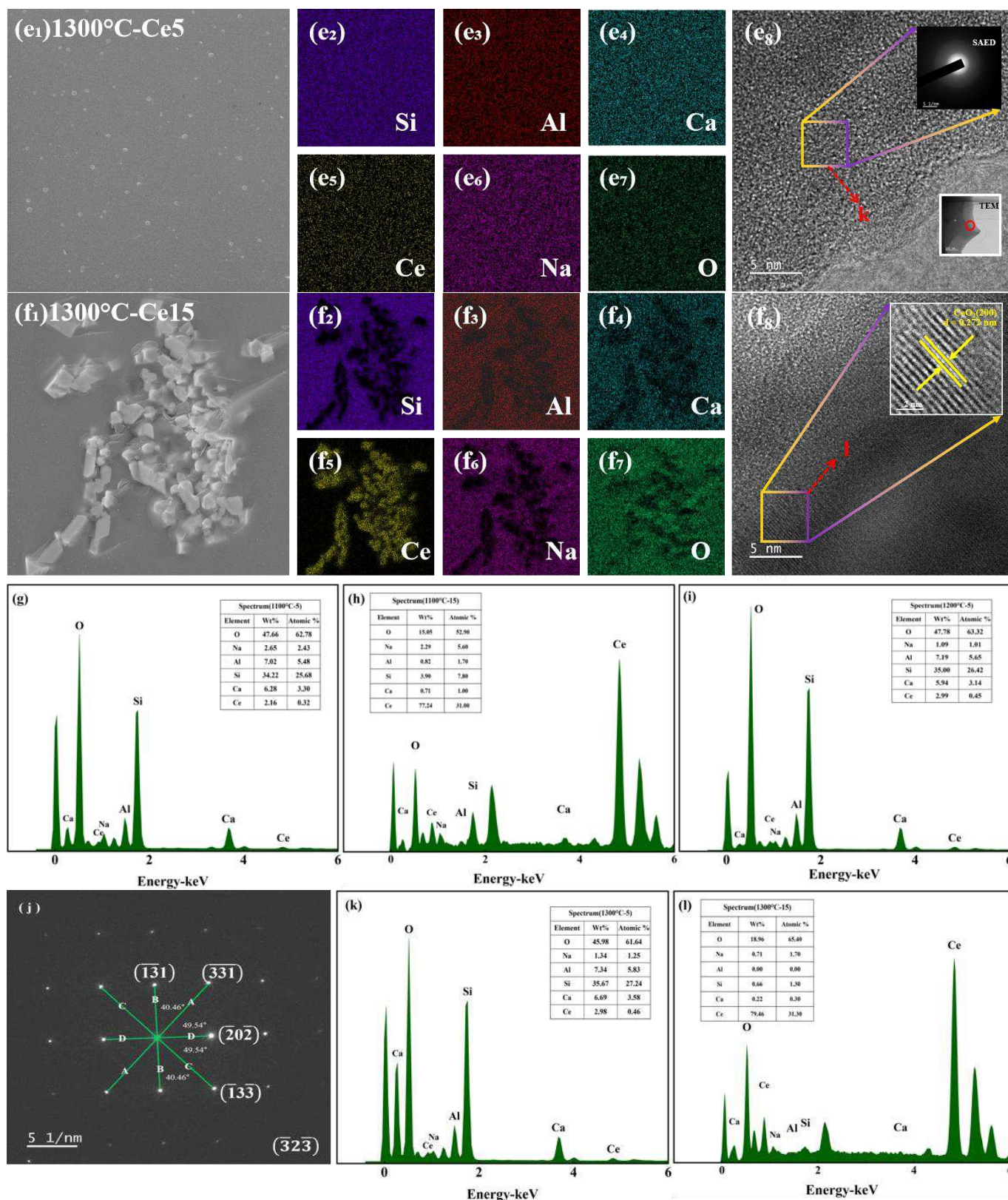


Fig. 4 Microstructure and elemental distribution of Ce5 and Ce15 waste forms: (**a₁-f₁**) SEM images; (**a₂-f₇**) Si, Al, Ca, Ce, Na, and O elemental maps; (**a₈-f₈**) HRTEM images; (**g, h, i, k, and l**) EDS spectra; (**j**) SAED pattern

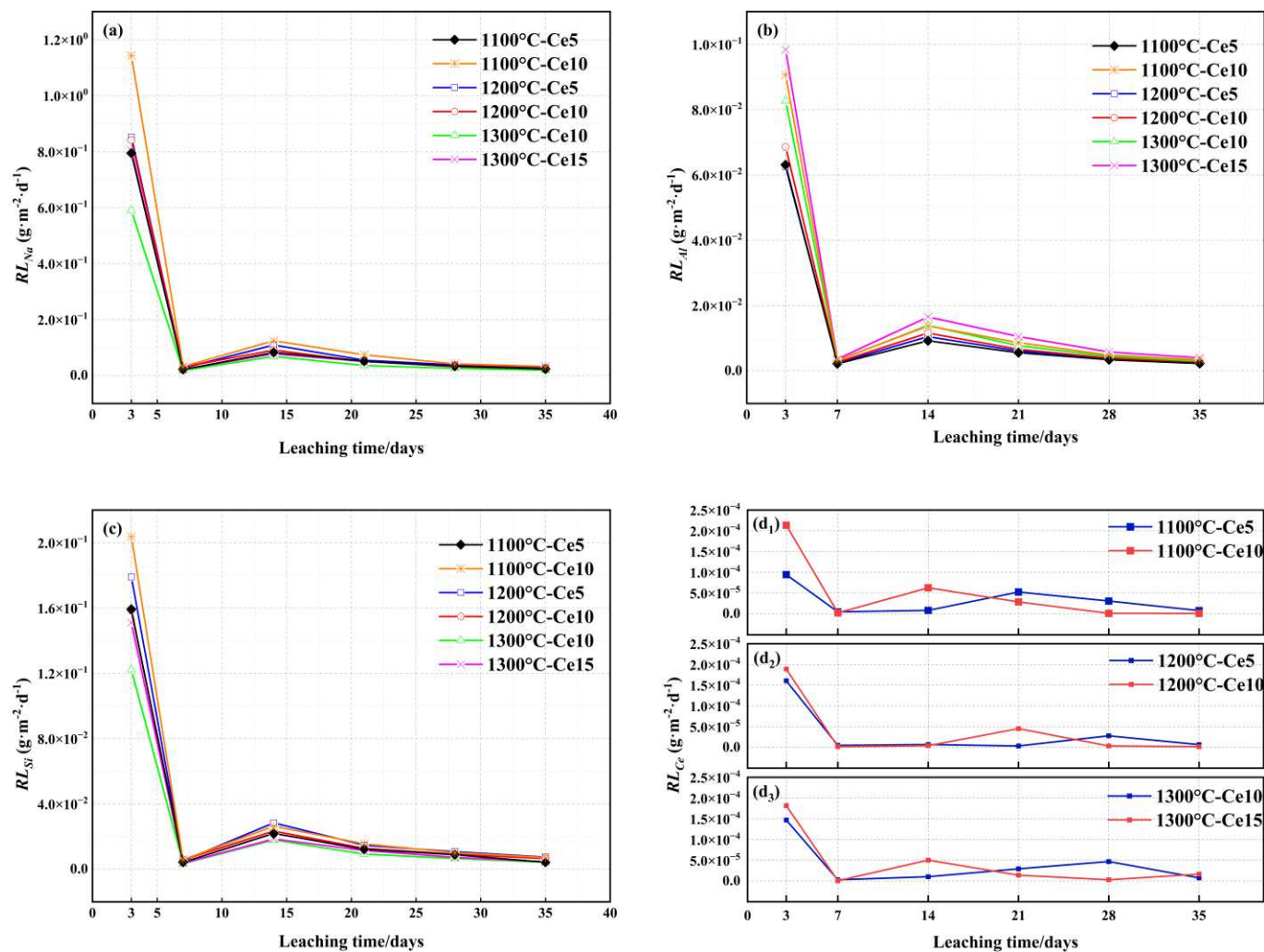


Fig. 5 Normalized leach rates of elements from glass waste forms prepared at different CeO_2 loadings and sintering temperatures: (a) Na; (b) Al; (c) Si; (d₁) Ce at 1100 °C; (d₂) Ce at 1200 °C; (d₃) Ce at 1300 °C

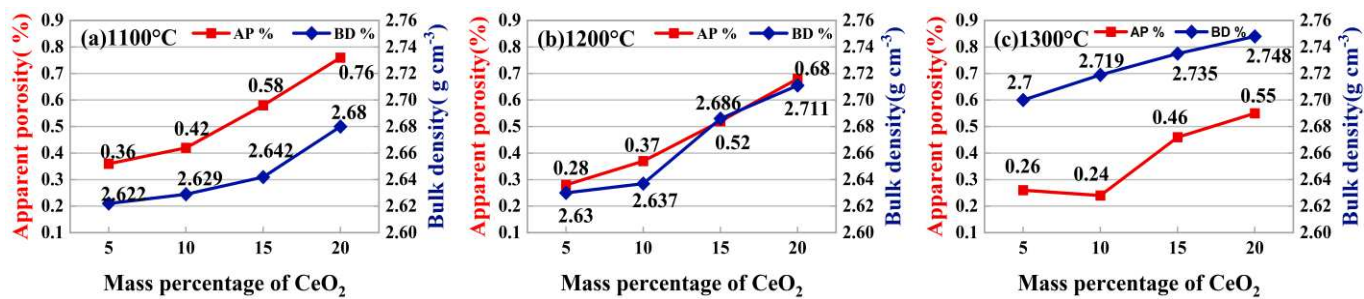


Fig. 6 Bulk density and apparent porosity of CeO₂-containing samples sintered at (a) 1100 °C, (b) 1200 °C, and (c) 1300 °C