Effect of CeO$_2$ on the Structure of Silicate Glass Cured Body

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Abstract. In this paper, samples of $x$CeO$_2$·(100-$x$) (SiO$_2$·Al$_2$O$_3$·CaO) ($x$: 0~15) glass solidified body was prepared by a high temperature melting method. The structural characteristics and thermal stability of CeO$_2$ silicate glass-cured bodies were characterized by means of density porosity test, XRD, Raman, DSC and SEM. The results show that the addition of CeO$_2$ does not change the basic structure of the glass, which is located in the pores of the silicate glass grid and plays a network modification role. When the added amount is less than 5% wt, homogeneous glass is easily formed. CeO$_2$ is uniformly distributed in the glass body, and no enrichment occurs. When the added amount is more than 8% wt, CeO$_2$ easily crystallizes during cooling.

1. Introduction
Soil is an important part of human living environment and the basis of human society. With the development of society and the nuclear industry, the radioactive contamination of soil has aroused widespread concern around the world. At present, the treatment methods for radioactively contaminated soil include physical restoration, chemical restoration and biological restoration. However, these methods cannot be used to solve the problem of radioactive pollution caused by a nuclear accident. On-site glass curing technology is considered to be an ideal treatment method for nuclear contaminated soil, and it is also one of the frontier and hot issues in the field of nuclear waste disposal.

Because element Ce is close to the radionuclide Pu in its chemical properties, ionic radius, and electronegativity, Ce is often used to simulate the behavior of radionuclide Pu when studying the solidified body of high-level radioactive waste. The composition and structural characteristics of the material determine its performance. Therefore, understanding the structural stars of CeO$_2$ in silicate glass can provide a reference for silicate glass or glass-ceramic curing CeO$_2$. In this paper, different proportions of tracer nuclides CeO$_2$ were added to the surrounding soil of a radioactively contaminated area. The solidified body was obtained by high-temperature melting and cold quenching. The structure and performance of the solidified body were observed.

2. Experiment
2.1. Sample Preparation
The soil around the nuclear test site was selected as the solidified substrate, and Ce$^{4+}$ was used as the simulated radioactive contaminated soil to simulate the Pu$^{4+}$ radionuclide as the research object. The formula calculation is performed by analysing the pure chemical reagent CeO$_2$ and the surrounding soil. The CeO$_2$ impurity ratio is shown in Table 1. According to the requirements for preparing about 50g of glass, weigh the corresponding raw materials, fully grind and mix them, and then put them into
the corundum crucibles. Put the 6 crucibles containing the raw materials into the high-temperature resistance furnace and raise the temperature to 1350°C at a rate of 10°C min. After holding for 1 hour, the crucible was taken out and cooled in the air to obtain a sample of the solidified body. The samples were marked with Ce-0 and Ce-15. Agate mortar was used to grind some samples into powder for subsequent analysis and testing.

| sample | CeO₂ | Sand soil |
|--------|------|-----------|
| Ce0    | 0    | 100       |
| Ce1    | 1    | 99        |
| Ce3    | 3    | 97        |
| Ce5    | 5    | 95        |
| Ce8    | 8    | 92        |
| Ce15   | 15   | 85        |

2.2. Characterization method
The X-ray diffraction analyzer (D8 advance, Germany) was used to observe the phase and crystallization of the sample, powder method, copper target, with scanning angle 2q: 5 ~ 70°. The Raman spectrum of the sample was collected using an Invia laser Raman spectrometer (Renishaw, UK). The wavelength of the light source was 514.5 nm, and the spectral range was 200 ~ 1600cm⁻¹. A Spectrum One Fourier Transform Infrared Spectrometer (PE Company, USA) was used to test the infrared spectrum of the sample, and the tablet method was used to collect the spectrum: 400-4000cm⁻¹. Differential scanning calorimetric analysis was performed on glass samples using SDT Q600 thermal analyzer (TA, USA). Test conditions: room temperature ~1000°C with 20°C/min and nitrogen protection. The scanning electron microscope (qutan 250 EFI, USA) was used to observe the Ce distribution in the samples.

3. Result and discussion
3.1. XRD analysis
With the increase of CeO₂ content, the sample gradually changed from transparent glassy solids to dark green opaque solids, of which sample of Ce-0 is coolness and transparent, samples of Ce-1, Ce-3, and Ce-5 are transparent glassy solids that deepen in green in order, samples of Ce-8 and Ce-15 are dark green Opaque solid. Figure 1 shows an XRD pattern of a sample of a cured glass. It can be seen from the figure that when CeO₂ is not added (Fig. 1 Ce-0), there is no diffraction peak in the XRD pattern of the sample, and it is a silicate glass at this time. After CeO₂ was added, the structure of the sample was changed from the XRD pattern. In the solidified body whose CeO₂ amount is 1 to 6 wt.%, the existence of crystals could not be detected, and the sample had an amorphous structure. When the content of CeO₂ reached 8 wt.%, the diffraction peak of CeO₂ appeared in the XRD pattern, which further increased the content of CeO₂, the intensity of the diffraction peak increased, and no other diffraction peak appeared. This indicates that CeO₂ in the batch cannot be dissolved in the solidified body, or has reacted with the calcium phosphate glass substrate to form monazite. XRD analysis shows that under the experimental conditions, CeO₂ can form a homogeneous glass with the calcium phosphate glass matrix. When the content of CeO₂ is greater than 8 wt.%, a characteristic peak of CeO₂ appears, indicating that the solid solubility of the soil has been exceeded, and a homogeneous glass body can no longer be formed.
3.2. Density test and apparent porosity test

The density and porosity of the cured body are shown in Table 2. As can be seen from Table 2, the bulk density of the nine kinds of cured body obtained in this experiment is between 2.3 and 2.8 g/cm$^3$. In the natural combustion state, the cured product of SHS is loose and porous, with a significant porosity of 15.7%, and a bulk density between 2.40 and 2.75 g/cm$^3$. The bulk density and apparent porosity of the solidified body obtained in this experiment are obviously due to the combustion products in the natural state of SHS. This shows that the sand is completely melted, and the gas can escape from the solidified body in the molten state better, resulting in a higher density and a lower porosity of the solidified body after cooling.

| Sample | Apparent porosity /% | Density /(g·cm$^{-3}$) |
|--------|----------------------|------------------------|
| Ce0    | 1.2                  | 3.02                   |
| Ce1    | 1.1                  | 2.98                   |
| Ce3    | 1.3                  | 2.89                   |
| Ce5    | 0.9                  | 3.01                   |
| Ce8    | 1.0                  | 2.95                   |
| Ce15   | 1.1                  | 3.06                   |

3.3. Raman analysis

Figure 2 is the Raman spectrum of the glass cured body. Due to the structural disorder of the glass, the full width at half maximum of the Raman spectrum is large. It can be seen that when CeO$_2$ is not added, the glass samples show strong and broad Raman bands at 698 cm$^{-1}$ and 1153 cm$^{-1}$, and two weak peaks at 1018 cm$^{-1}$ and 1260 cm$^{-1}$. A wide Raman band appears between 280 cm$^{-1}$ and 350 cm$^{-1}$ (Figure 2, Ce-0). The Raman peaks 698 cm$^{-1}$ and 1018 cm$^{-1}$ belong to the symmetrical stretching mode of bridge oxygen (POP) and the antisymmetric stretching vibration as (POP) in the Q2 tetrahedron. 1153 cm$^{-1}$ and 1260 cm$^{-1}$ belong to the Q2 tetrahedron. The symmetric (PO$_2$) and antisymmetric stretching vibration (PO2) of the non-bridged oxygen group belong to the bending vibration mode of the phosphorus-oxygen polyhedron chain near 300 cm$^{-1}$. With the increase of the amount of CeO$_2$ added, the Raman peak of 1260 cm$^{-1}$ weakened, indicating that the P=O group in the system decreased. The 698 cm$^{-1}$ and 1153 cm$^{-1}$ bands gradually widened and weakened, indicating that the amount of bridge oxygen in the system decreased. This is because the addition of CeO$_2$ to introduce metal ions and excess oxygen ions will stop the spatial cross-linking of P-O-P, resulting in a reduction in the number of bridge oxygen bonds in the glass.
3.4. Scanning analysis

Scanning electron microscopy was used to further analyse the micro-morphology of the partially cured body, and the results are shown in the figure 3. It can be seen that the solidified body is relatively dense without obvious voids and cracks. The element scan was used to analyse the distribution of Ce element in the solidified body, and the results are shown in the figure. It can be seen that the Ce element was uniformly distributed in the solidified body, and no aggregation occurred.

3.5. Thermal stability analysis

Figure 4 shows the DSC curve of the cured product. It can be seen that the glass transition temperature of the cured product is around 585°C. The maximum crystallization temperature and melting temperature of Ce-0 are 691°C and 946°C, respectively. It can be seen from Figure 4 that with the addition of CeO₂, the glass transition temperature of the glass sample indicates that the glass matrix structure of the cured body is similar. The crystallization start temperature and maximum crystallization temperature of samples of Ce-1, Ce-3, Ce-5 are not obvious. However, the crystallization temperature of all containing CeO₂ solidified bodies gradually increases with the increase of CeO₂ content, and the melting temperature of the solid solution gradually decreases, indicating that the addition of CeO₂ can effectively reduce the melting temperature of glass.
4 Conclusions

1) The addition of CeO$_2$ did not change the structure of the solidified substrate. CeO$_2$ forms homogeneous glass with silicate. When the added amount exceeds 8 wt. %, CeO$_2$ is precipitated in the silicate glass cured body.

2) The silicon-oxygen tetrahedron in the glass cured body mainly exists in the structure of Q2 group, and belongs to silicate glass. CeO$_2$ is located in the interstices of the silicate glass network structure and acts as a network modifier.

3) Ce is uniformly distributed in the solidified body without agglomeration. The addition of CeO$_2$ improves the thermal stability of silicate glass.

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