

# 高透过率强伽马射线屏蔽玻璃的制备及其性能

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**摘 要:** 为了研发具有高透过率和强伽马射线屏蔽性能的新型玻璃材料, 以  $\text{SiO}_2\text{-PbO-M}_2\text{O}$  ( $\text{M}$  为碱金属元素) 体系的铅硅酸盐玻璃为基质, 设计并制备了几种不同  $\text{PbO}$  含量的伽马射线屏蔽铅玻璃。对屏蔽玻璃的伽马射线屏蔽性能进行了理论模拟与实验测试, 通过密度测试、膨胀系数测定仪、Fourier 红外光谱、Raman 光谱和分光光度计对样品进行了表征, 并探讨了氧化物组分( $\text{PbO}$ 、 $\text{K}_2\text{O}$  和  $\text{Na}_2\text{O}$ )对屏蔽玻璃结构和性能的影响机理。测试结果表明:  $\text{PbO}$  含量为 50% (质量分数) 的屏蔽玻璃对  $^{60}\text{Co}$  伽马射线的屏蔽率可达到 50%, 且在 400~800 nm 波长范围内线性透过率可达到 85% 以上。此外, 该屏蔽玻璃还具有良好的化学稳定性和热稳定性。本工作可以为开发用于核工业、医学诊断和原子科学研究等领域的高性能屏蔽玻璃材料提供有益的参考和指导。

**关键词:** 透过率; 伽马射线; 辐射屏蔽; 玻璃

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## 1 Introduction

With the rapid development of nuclear science and technology, gamma radiation is widely used in medical diagnosis, non-destructive element analysis, non-destructive evaluation of metal pipeline welds, disinfection treatment, and other medical, scientific, and industrial fields<sup>[1-5]</sup>. However, as a type of high-energy electromagnetic radiation, gamma rays are likely to cause radiation harm and environmental pollution, potentially leading to the mutation or even death of living tissues if exposed to highly penetrating gamma radiation for extended periods without effective protection. To ensure the reliable and safe utilization of gamma radiation in various areas, it is essential to develop materials with robust gamma shielding performance<sup>[6-7]</sup>.

Concrete has been widely used for radiation shielding due to its low cost and compatibility with architectural design. However, the protective effect of ordinary concrete is limited. Research findings indicate that long-term exposure to nuclear radiation can cause concrete to crack, leading to water penetration and a reduction in density and structural strength<sup>[8-10]</sup>. The composition of concrete also changes significantly,

which introduces uncertainty into design process<sup>[11-13]</sup>. Moreover, once concrete is cast and formed, it is challenging to observe its internal radiation sources, greatly limiting its application scenarios.

Glass, as a typical window material, has attracted significant attention from researchers due to its unique chemical and physical advantages<sup>[14]</sup>. The preparation process for glass is relatively convenient, and a wide variety of active elements, such as transition metals and non-metal elements, can be doped into glass. These dopants give rise to unique properties, such as specific color and fluorescence effects. Thus, the application scenarios for glass are expanded<sup>[15]</sup>. Among these, lead-based radiation shielding materials are widely used in ionizing radiation protection due to their reliable physical properties<sup>[16-17]</sup>. In the nuclear industry and high-energy physics laboratories, materials such as lead-impregnated rubber, lead glass, and lead-polyethylene-boron mixtures are used for temporary or permanent shielding. Lead-based glass doped with heavy metal oxide  $\text{PbO}$  has been widely used in radiation shielding for a long time due to its reliable light transmission properties, facilitating the observation and monitoring of radiation areas.

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In 2010, Culea *et al.*<sup>[18]</sup> investigated the relationship between the amount of CeO<sub>2</sub> and structure and physical properties of CeO<sub>2</sub>–GeO<sub>2</sub>–PbO glass and glass ceramics. In 2012, Singh *et al.*<sup>[19]</sup> incorporated ZnO and CeO<sub>2</sub> simultaneously into Al<sub>2</sub>O<sub>3</sub>–PbO–B<sub>2</sub>O<sub>3</sub> glass and investigated its structure and optical performances. In 2014, Li *et al.*<sup>[20]</sup> prepared a type of plexiglass material containing Pb and Sm functional particles, and its transmission rate could reach more than 80%. However, the shielding rate for gamma ray with an energy of 167 keV is less than 30%. In 2018, Guo *et al.*<sup>[21]</sup> prepared a radiation-proof inorganic glass with a nominal composition of 26SiO<sub>2</sub>–50PbO–12In<sub>2</sub>O<sub>3</sub>–12Gd<sub>2</sub>O<sub>3</sub> by the molten pouring method. The glass exhibits a transmittance of more than 80% in the band above 500 nm and is highly sensitive to gamma rays and neutrons (especially intermediate and thermal neutrons), which shows reliable protection ability. In 2021, Singh *et al.*<sup>[22]</sup> found that the addition of TiO<sub>2</sub> could effectively improve the gamma rays and neutron shielding properties of CeO<sub>2</sub>–PbO–B<sub>2</sub>O<sub>3</sub> glass. However, little work related to the effect of PbO content on the transmittance and shielding properties of simple glass systems has been carried out.

In this paper, three types of transparent silicate glass with different PbO contents were prepared using a high-temperature melting forming method. The density, expansion coefficient, FTIR, Raman analysis, and transmittance of the glass were characterized. The gamma-ray protection abilities of the three types of glass were investigated through experimental and theoretical methods. The chemical and thermal stability of the glass were also characterized. Additionally, the influence mechanism of the structural and performance differences among the three types of glass is analyzed and discussed.

## 2 Experimental

### 2.1 Sample preparation

Analytical pure quartz sand (SiO<sub>2</sub>, purity 99.5%, in mass fraction, the same below), Shihu Stone Powder Factory of Donghai County), lead monoxide (PbO, purity 99.0%, Hubei KewoDe Chemical Co., Ltd.), potassium nitrate (KNO<sub>3</sub>, purity 99.0%, Tianjin Jinyao Xiangcheng Technology Co., Ltd.), and sodium nitrate (NaNO<sub>3</sub>, purity 99.0%, Tianjin Jinyao Xiangcheng Technology Co., Ltd.) were selected as raw materials for the preparation of three types of gamma-ray shielding glass materials using the high-temperature melting method. Considering the volatility of the raw materials, the quantity of lead monoxide was slightly excessive by 1% (in mass fraction) to ensure that the actual composition content of the lead silicate glass closely matched the designed composition content. An appropriate quantity of raw materials was thoroughly mixed and added in batches to a 3 L quartz crucible under an air atmosphere at 1 200 °C. The materials were then melted for approximately 14 h

at 1 250 °C. The uniform melt was quickly poured into a preheated 150 mm×150 mm×50 mm stainless steel mold at 750 °C. Finally, the quenched glasses were annealed at 450 °C for 12 h and allowed to cool naturally to room temperature. These three different types of glasses are named S1, S2, and S3, as shown in Table 1. Finally, the quenched glasses were annealed at 450 °C for 12 h and cooled naturally to room temperature. These three different types of glasses are named S1, S2, S3, as shown in Table 1.

**Table 1 Composition of the glass sample**

| Sample No. | w/%              |     |                  |                   |
|------------|------------------|-----|------------------|-------------------|
|            | SiO <sub>2</sub> | PbO | K <sub>2</sub> O | Na <sub>2</sub> O |
| S1         | 52               | 33  | 8                | 7                 |
| S2         | 41               | 50  | 5                | 4                 |
| S3         | 31               | 66  | 3                | 0                 |

w is mass fraction.

### 2.2 Characterization

The density of the three glass samples was measured based on Archimedes' principle. Three samples, each measuring 10 mm×10 mm×5 mm, were first cut from the original glass. Each side was finely ground and slightly chamfered. These samples were then accurately weighed and immersed in deionized water for density measurement. The density of the glass samples was obtained by averaging the results of three measurements.

The thermal expansion coefficient of the glass samples was measured using a Netzsch DIL 402 expansion coefficient tester. The sample size was  $\phi$ 6 mm×50 mm. The two ends were parallel, with a heating rate of 5 °C/min.

The infrared spectra were measured using a PerkinElmer Spectrum 100 FTIR Spectrometer, in attenuated total reflectance-Fourier transform infrared (ATR-FTIR) mode. The glass sample size was 20 mm×20 mm×10 mm, and the scanning range was 400–4 000 cm<sup>-1</sup>.

The Raman spectra were measured using a HORIBA LabRAM HR800 high-resolution Raman spectrometer. The laser wavelength was 532 nm, and the acquisition range was 300–1 500 cm<sup>-1</sup>. The size of the glass sample was 20 mm × 20 mm × 10 mm, and the two major surfaces were polished.

The transmittance of the glass samples was measured by a Shimadzu UV/VIS/NIR spectrophotometer. The wavelength range was 350–900 nm.

The gamma-ray shielding test was carried out at China Academy of Engineering Physics. The sample size was 150 mm×150 mm×50 mm. <sup>60</sup>Co was used as the radioactive source, and a NaI detector was used to measure the background radiation in the experimental space. The count *n* of the two gamma-ray omnipotent peaks of 1.173 MeV and 1.332 MeV after the rays passed through the shielding material, and the count *n*<sub>0</sub> without

the sample, were recorded. The software was used to analyze and process the data, remove the background, and calculate the net count of the two gamma-ray omnipotent peaks of  $^{60}\text{Co}$  as the omnipotent peak count. The gamma shielding rate  $I$  of the material was calculated by:

$$I = \frac{n_0 - n}{n_0} \times 100\% \quad (1)$$

The chemical stability test was carried out at Chengdu Guangming Glass Co., LTD. The acid stability and moisture stability of the glass samples were tested according to GB/T 7962.14—2010 and GB/T 7962.15—2010, respectively.

The thermal stability test method is as follows: Six samples of each of the three types of annealed samples, measuring 10 mm×10 mm×4 mm, were taken. Grinding and polishing treatment were carried out first. Then, the three types of samples were placed in the annealing furnace with a heating temperature of 120 °C and an annealing time of 60 min. After the heat treatment, the samples were immersed in ice water for at least ten seconds and then annealed at a temperature 10 °C higher than the previous one after being wiped with alcohol. The thermal stability  $\Delta T$  of each sample is calculated using the following equation:

$$\Delta T = \frac{\Delta T_1 N_1 + \Delta T_2 N_2 + \Delta T_3 N_3 + \cdots + \Delta T_i N_i}{N_1 + N_2 + N_3 + \cdots + N_i} \quad (2)$$

where  $\Delta T_1, \Delta T_2, \Delta T_3, \dots, \Delta T_i$  indicates the temperature difference between furnace temperature and water at each measurement, and  $N_1, N_2, N_3, \dots, N_i$  is the number of sample fractures per measurement.

### 3 Results and discussion

#### 3.1 Density

The protective capability of glass materials against high-energy rays primarily depends on their ability to absorb radiation. This ability is closely linked to the mass absorption coefficient, density, and energy of the rays interacting with the glass components. It is widely recognized that silicate glasses containing heavy metal elements such as lead, bismuth, and barium offer superior radiation shielding properties. Consequently, these glasses tend to have a higher density<sup>[23–24]</sup>. Figure 1 illustrates the relationship between the density and the lead content in the glass. As shown, the density of the glass increases with the rising content of lead. When the PbO content reaches 66%, the density of the sample climbs to 4.78 g/cm<sup>3</sup>. This increase in density results from substituting SiO<sub>2</sub>, K<sub>2</sub>O, and Na<sub>2</sub>O with PbO, which has a molecular weight of 223.2 g/mol compared to 60.08 g/mol for SiO<sub>2</sub>, 94.20 g/mol for K<sub>2</sub>O, and 61.98 g/mol for Na<sub>2</sub>O. Additionally, Pb has a larger ionic radius (2.02 Å) compared to Si (1.95 Å), K (1.95 Å), and Na (1.95 Å) within the glass matrix. Therefore, the glass

structure becomes more compact as Pb substitutes for Si, K, and Na<sup>[25]</sup>. Although increasing the density enhances the glass's shielding performance, it may also significantly alter its optical properties, thermal properties, and chemical stability due to the increased content of heavy metals. Furthermore, the production of high-transmittance glass becomes more challenging.

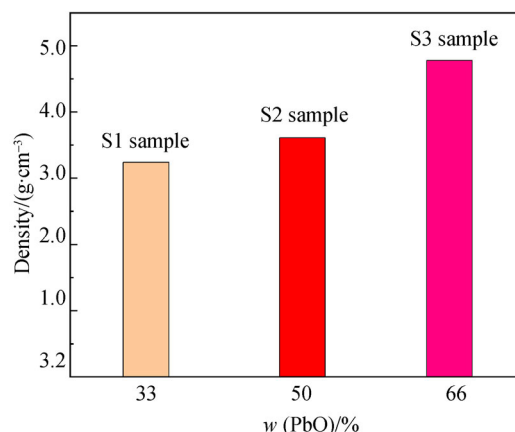


Fig. 1 Glass density of glass with different PbO content

#### 3.2 Coefficient of expansion

The coefficient of thermal expansion of glass varies among different types, primarily influenced by their composition and manufacturing process. This coefficient must be carefully considered during the glass preparation process, especially when the glass is to be combined with other materials or used under extreme temperature conditions. A high coefficient of thermal expansion can lead to stress accumulation and potential cracking. Table 2 displays the thermal expansion coefficient, glass transition temperature ( $T_g$ ), and expansion softening temperature ( $T_f$ ) of the three prepared glass samples.

Table 2 Coefficients of thermal expansion ( $\alpha$ ), glass transition temperature and expansion softening temperature of three glass samples

| Sample No. | $\alpha \times 10^7 / ^\circ\text{C}$ | $T_g / ^\circ\text{C}$ | $T_f / ^\circ\text{C}$ |
|------------|---------------------------------------|------------------------|------------------------|
| S1         | 103.6                                 | 431.4                  | 498.1                  |
| S2         | 92.8                                  | 434.3                  | 497.5                  |
| S3         | 89.2                                  | 425.3                  | 468.2                  |

As shown in Table 2, the thermal expansion coefficient of the glass samples decreases from  $103.6 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$  to  $89.2 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ , and the values of  $T_g$  and  $T_f$ . In the glasses studied, a low concentration of PbO ( $x=0.33$ ) serves as an external oxide in the network, forming  $[\text{PbO}_6]$  structural units with six coordination numbers acting as modifiers that disrupt the network. Conversely, at higher concentrations of PbO ( $x=0.50$  and  $x=0.66$ ), it functions as a glass-forming agent, contributing to  $[\text{PbO}_4]$  structural units with four coordination numbers that integrate into the network. With sufficient free oxygen,  $[\text{PbO}_6]$  units transform into  $[\text{PbO}_4]$  units, which connect with  $[\text{SiO}_4]$  tetrahedra to

form a new network structure that helps mend the disrupted network<sup>[26–28]</sup>. Thus, the presence of  $[\text{PbO}_4]$  units in the glass can reduce the thermal expansion coefficient to some extent. Additionally, the inclusion of low-melting-point PbO enhances its fluxing effect. Moreover, the addition of alkali metal oxides  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  in both S1 and S2 samples, which serve as external oxides in the glass network, allows alkali metal ions to move and diffuse easily within the glass, reducing its viscosity at high temperatures and facilitating melting. While these oxides are effective fluxes, they also contribute to an increase in the thermal expansion coefficient. Therefore, the changes in the thermal properties of the three glass samples result from the combined effects of PbO,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$ .

### 3.3 FTIR spectra

FTIR analysis was used to study the vibrations in the three prepared lead silicate glasses, as shown in Fig. 2. Fig. 2 compares the FTIR spectra obtained for the three silicate glasses. The slight peak around  $3600\text{ cm}^{-1}$  is due to O–H stretching vibrations. This weak vibration indicates that the glass samples are not hygroscopic.<sup>[28–29]</sup> The sharp peak around  $540\text{ cm}^{-1}$  is due to the symmetric metal vibrations like Pb/Si–O bonding. The strong peak at  $1200\text{ cm}^{-1}$  is due to the antisymmetric stretching vibration of Si–O–Si. Around  $905\text{ cm}^{-1}$  in the S2 and S3 samples, a weak peak appears, which is attributed to either non-bridging of Si–O bands or Pb–O–Pb asymmetric stretching vibrations.<sup>[30–32]</sup> The weak peak at about  $810\text{ cm}^{-1}$  is attributed to stretching vibrational modes of Si–O–Si links of the  $[\text{SiO}_4]$  tetrahedra<sup>[33]</sup>. With the increase in PbO content in the glass, the strong peak at  $1200\text{ cm}^{-1}$  shifts to lower wave numbers, due to the transformation of added PbO into  $[\text{PbO}_4]$  units with a coordination number of 4 in the network under the condition of sufficient free oxygen. These  $[\text{PbO}_4]$  units participate in the formation of silicate networks, which corresponds to the appearance of weak peaks at  $905\text{ cm}^{-1}$  and the weakening of peak intensity at  $810\text{ cm}^{-1}$ <sup>[34–36]</sup>.

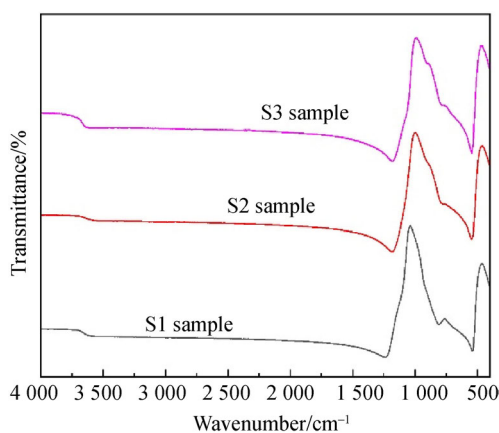


Fig. 2 FTIR spectra of glasses with different PbO content

### 3.4 Raman analysis

Fig. 3 shows the Raman spectra used to study the

vibration type of the functional groups in the three prepared lead silicate glass samples. In the spectra, a distinct silicate peak appears between  $900\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$ , which corresponds to Si–O–Si antisymmetric stretching vibrations. The positions around the  $850$ ,  $910$ ,  $970\text{ cm}^{-1}$  and  $1060\text{ cm}^{-1}$  represent silicon-oxygen tetrahedral structural units ( $Q^0$ ,  $Q^1$ ,  $Q^2$ , and  $Q^3$ ) with 0, 1, 2, and 3 bridge oxygens, respectively<sup>[37–39]</sup>. As seen from the figure, with the increase in PbO content, the  $Q^2$  and  $Q^3$  structural unit peaks in the silica network structure become weaker, and the  $Q^0$  and  $Q^1$  structural unit peaks increase, indicating that the silicate network structure is depolymerizing. Simultaneously, the vibration peaks at  $480\text{ cm}^{-1}$  and  $780\text{ cm}^{-1}$  are obviously enhanced, and these peaks correspond to the characteristic vibration of Pb–Si–O, indicating an increase in the degree of participation of the  $[\text{PbO}_4]$  units in the formation of the silicate network<sup>[36, 40–42]</sup>. This conclusion complements and agrees with the results of FTIR.

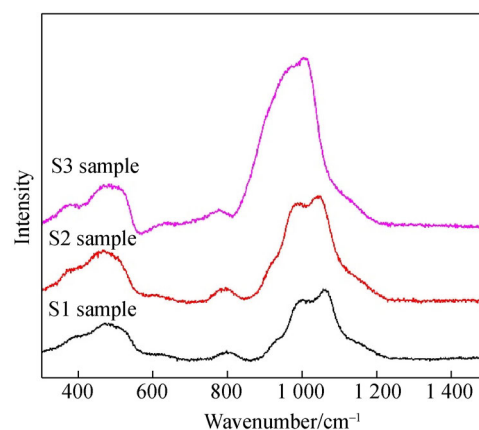


Fig. 3 Raman spectra of glasses with different PbO content

### 3.5 Ion packing density

Makishima and Mackenzie propose that the ion packing density ( $V_t$ ) of multicomponent glasses can be calculated using the additive formula<sup>[43]</sup>:

$$V_t = \rho \frac{\sum V_i N_i}{\sum M_i N_i} \quad (3)$$

where  $\rho$  indicates the density of the glass,  $N_i$  is the oxide content (in mole fraction),  $M_i$  is the relative molecular mass, and  $V_i$  is a coefficient derived from the ionic radius. Table 3 shows the  $V_i$  values of  $\text{SiO}_2$ , PbO,  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$ . The calculated ion packing density values of the S1, S2 and S3 samples are shown in Fig. 4. The ion packing density is defined as the ratio of the minimum theoretical volume occupied by the ions to the corresponding effective volume of the glass, indicating the tightness of the atomic packing inside the glass<sup>[44]</sup>. It can be seen from Fig. 4 that with the increase of PbO content, the ion packing density of the glass sample gradually increases, which shows that the compressible free volume per unit volume of the glass sample becomes smaller. PbO with high concentration ( $x = 0.50$  and  $x =$

0.66) is used as a glass-forming agent, and the  $[\text{PbO}_4]$  structural units form a good connection structure with the silicon oxide tetrahedron, which plays a role in repairing the glass network. This conclusion is consistent with the results of FTIR.

**Table 3**  $V_i$  of each oxide in the glass component

| $V_i/(\text{kJ}\cdot\text{cm}^{-3})$ |              |                      |                       |
|--------------------------------------|--------------|----------------------|-----------------------|
| $\text{SiO}_2$                       | $\text{PbO}$ | $\text{K}_2\text{O}$ | $\text{Na}_2\text{O}$ |
| 14.0                                 | 11.7         | 18.8                 | 11.2                  |

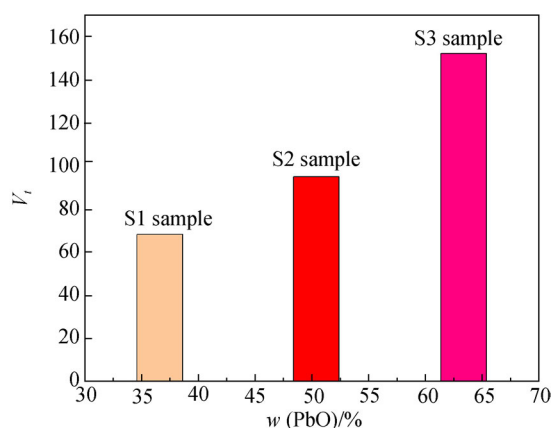


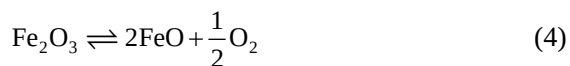
Fig. 4 Ion packing density of glass with different PbO content

### 3.6 Transmittance

The anti-radiation glass also needs to exhibit high transmittance in the visible light range to ensure the convenience of observation and use. Figure 5 shows the transmittance spectra of the three kinds of glass in the wavelength range of 350–900 nm. It can be seen from the figure that with the increase in PbO content in the glass composition, the absorption cutoff shifts toward longer wavelengths, and there is a significant decline in the transmittance of the S3 sample. The transmittance of the S2 sample is almost the same as that of the S1 sample. In the wavelength range of 400–800 nm, the linear transmittance of the S1 and S2 samples can reach more than 85%.

The increase in PbO content and the decrease in alkali metal oxide content in the glass lead to an increase in the number of non-bridging oxygen, which reduces the energy required for the energy gap transition due to the increase in the number of electrons in the oxygen-rich ion environment. Therefore, the increase in the number of non-bridging oxygen is the cause of the red shift of the absorption cutoff of the wavelength<sup>[23, 30]</sup>.

The existence of iron or its compounds in the glass greatly increases the light absorption rate, resulting in glass coloring, which is the main factor causing the decrease in glass transmittance.  $\text{Fe}_2\text{O}_3$  and  $\text{FeO}$  in the glass exist in the following equilibrium<sup>[25]</sup>:



From the equilibrium equation, the equilibrium shifts to the left as the oxygen content increases. The free

oxygen that can be provided increases when the alkali metal content is too high, which promotes Fe to generate  $\text{Fe}_3\text{O}_4$  in the glass structure and causes coloring, thereby greatly reducing the transmittance. Therefore, to improve the glass transmittance, it is necessary not only to use raw materials with low iron content and crucibles with low iron content and corrosion resistance but also to reduce the content of free oxygen. It is necessary to reduce the content of alkali metals, especially the content of  $\text{Na}_2\text{O}$ , because  $\text{Na}_2\text{O}$ , as an oxide outside, acts as a network breaker and can provide free oxygen for the glass. In addition, based on the mixed alkali effect, a small amount of  $\text{K}_2\text{O}$  can be introduced to replace part of  $\text{Na}_2\text{O}$  to improve the transmittance<sup>[26–28]</sup>. Therefore, the permeability of the glass can be improved by strictly controlling the iron content of the introduced raw materials and making full use of the double alkali effect of the glass.

From the above analysis, it is illustrated that although the PbO content of the S1 sample is lower than that of the S2 sample, the transmittance of the S2 sample is basically equivalent to that of the S1 sample due to the excessive  $\text{K}_2\text{O}$  content. The transmittance of the S3 sample is significantly lower than that of the S1 and S2 samples due to the higher content of PbO and the addition of a single alkali metal.

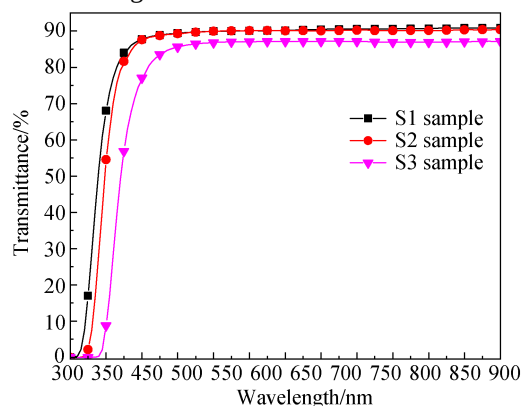


Fig. 5 Transmittance spectra of glasses with different PbO content

### 3.7 Gamma ray shielding properties

Silicate-based heavy metal oxide glass is an important transparent shielding material in radiation engineering; therefore, it is necessary to investigate its radiation shielding properties for making them suitable for use in nuclear reactor glass windows and other applications requiring light transmission radiation shielding.

The gamma rays could collide with the orbital electrons of atoms when passing through the glass, resulting in the photoelectric effect, the Compton effect, and the formation of electron pairs. Because these effects are exacerbated by the increase in the specific gravity and mass of the irradiated substance, the general protective glass should contain heavy metal oxides such as  $\text{PbO}$  and  $\text{Bi}_2\text{O}_3$ . Lead is a substance with a higher atomic number in nature and exhibits a relatively strong

ability to block gamma rays. Bismuth should not be doped into glass in large quantities because of its corrosive and toxic effects on both furnace refractories and single crucible precious metals. In addition, some substances also have good blocking ability for gamma rays, but some of them are very rare on Earth and relatively expensive (such as gold with an atomic number of 79), and some substances themselves also exhibit certain radioactivity (such as polonium and other metal elements with an atomic number greater than 83), which will do harm to human beings. Therefore, it is more reasonable to use lead to block gamma rays. The mass absorption coefficient  $\omega$  ( $\text{cm}^2/\text{g}$ ) can be used to compare the absorption ability of substances to radiation, and its value can be calculated by the Lambert–Beer law. The mass absorption coefficient ( $\omega$ ,  $\text{cm}^2/\text{g}$ ) can be used to compare the absorption ability of substances to radiation. This parameter can be calculated using the Lambert–Beer law<sup>[27, 29]</sup>:

$$\omega = -\ln\left(\frac{I}{I_0}\right)/(\rho d) \quad (5)$$

where  $I_0$  and  $I$  represent the incident and transmitted photon intensities, respectively,  $\rho$  is the density of the glass, and  $d$  is the thickness of the glass. Silicate glass is composed of various oxides, and its mass absorption coefficient can be calculated using a simple additive formula. Therefore, the mass absorption coefficient of the whole glass ( $\omega_G$ ) can be calculated from the content of different oxides in the glass:

$$\omega_G = \sum P_i \omega_i \quad (6)$$

where  $P_i$  is the mass fraction of the oxide and  $\omega_i$  is the mass absorption coefficient of the oxide. Table 4 shows the mass absorption coefficients of  $\text{SiO}_2$ ,  $\text{PbO}$ ,  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  for gamma rays with different energies.

**Table 4 Mass absorption coefficients of oxides for gamma rays of different energies**

| Oxide                 | Mass absorption coefficient |         |         |
|-----------------------|-----------------------------|---------|---------|
|                       | 0.5 MeV                     | 1.0 MeV | 2.0 MeV |
| $\text{SiO}_2$        | 0.087                       | 0.064   | 0.045   |
| $\text{PbO}$          | 0.151                       | 0.070   | 0.046   |
| $\text{K}_2\text{O}$  | 0.087                       | 0.063   | 0.044   |
| $\text{Na}_2\text{O}$ | 0.086                       | 0.062   | 0.043   |

The shielding rates of S1, S2 and S3 samples with 50 mm thickness to gamma rays of different energies are shown in Table 5.

**Table 5 Calculated values of gamma shielding properties of three kinds of glass samples**

| Sample No. | Density/( $\text{g}\cdot\text{cm}^{-3}$ ) | Shielding rate for different energies $\gamma$ rays/% |         |         |
|------------|-------------------------------------------|-------------------------------------------------------|---------|---------|
|            |                                           | 0.5 MeV                                               | 1.0 MeV | 2.0 MeV |
| S1         | 3.24                                      | 82.63                                                 | 65.54   | 51.85   |
| S2         | 3.61                                      | 88.22                                                 | 69.91   | 55.72   |
| S3         | 4.78                                      | 95.44                                                 | 80.28   | 66.40   |

As is illustrated in Table 5, with the increase in  $\text{PbO}$  content in the glass composition, the shielding rate of the samples against gamma rays gradually increases. For the S1, S2, and S3 samples, their measured shielding rates against  $^{60}\text{Co}$  gamma rays with an energy of 1.2 MeV are 41%, 50%, and 63%, respectively. The calculated results are somewhat different from the test results, which indicates that the actual shielding performance of glass is not merely the result of the simple addition of various components. It may also be affected by the actual composition content of the glass, the melting process, and the uniformity within the glass matrix. Among them, the S3 sample has a higher shielding performance for gamma rays. However, due to the high lead content, the glass is yellow and the linear transmittance in the wavelength range of 400–800 nm is significantly lower than that of the other two types of glass. Therefore, it is not suitable for use in environments with certain requirements for light transmittance. In contrast, the S2 sample is the same color as the S1 sample; both are colorless and transparent. Moreover, the transmittance of the S2 sample can still reach a high level while ensuring reliable shielding performance.

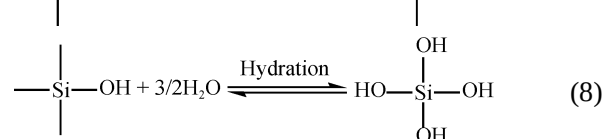
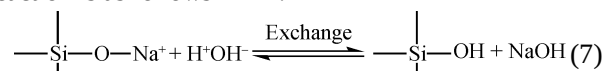
### 3.8 Chemical stability and thermal stability

The chemical stability of glass refers to the resistance of glass to the erosion of water, acid, alkali, salt, gas and other chemical reagent solutions. Table 6 shows the test results of chemical stability (acid resistance and moisture resistance) and thermal stability of the three kinds of glass. The smaller the value, the better the resistance to acid or moisture.

**Table 6 Test results of acid-resistant and moisture-resistant stability of three kinds of glass samples**

| Sample No. | Acid stability | Moisture stability | Thermal stability/ $^{\circ}\text{C}$ |
|------------|----------------|--------------------|---------------------------------------|
| S1         | 1              | 2                  | 133                                   |
| S2         | 1              | 2                  | 149                                   |
| S3         | 3              | 2                  | 151                                   |

The dissolution process of silicate glass in water is complex. The attack of water on glass begins with the ion exchange between  $\text{H}^+$  in water and  $\text{Na}^+$  in glass. The reaction is as follows<sup>[45–49]</sup>:



These three reactions are mutually causal and cyclic. The overall rate depends on equation (7) because it controls the rate of formation of  $\text{—Si—OH}$  and  $\text{NaOH}$ . Acids (except hydrofluoric acid) generally do not react

directly with glass, but they also play a role by water erosion of glass.

It can be seen from the reaction formula that the addition of external network oxides such as  $\text{Na}_2\text{O}$  will reduce the chemical stability of the glass. When the  $\text{SiO}_2$  content is too high, the solubility of the weak acid  $\text{Si}(\text{OH})_4$  is reduced due to the low pH of the acid. The equilibrium of equations (7) and (8) shifts to the left, thus reducing the erosion of the glass.

When lead glass is eroded by water, acid, and other media,  $[\text{Pb}-\text{OH}]$  groups are additionally formed and attach to its surface. Such groups increase with increasing  $\text{PbO}$  content in the glass composition and are readily soluble in acid and water. Therefore, the higher the  $\text{PbO}$  content in the glass, the worse the chemical stability. Under the combined action of several oxides, the moisture stability of the three samples is comparable. However, because the  $\text{SiO}_2$  content of S1 and S2 samples is higher than that of the S3 sample and the  $\text{PbO}$  content is lower than that of the S3 sample, the glass experiences less weight loss and better acid resistance under acidic environmental conditions.

In general, the thermal stability of glass is affected by its chemical stability and coefficient of expansion. Glass with good chemical stability does not easily react with acid or water and has certain inertness to most chemical substances, so it can maintain reliable stability in high-temperature environments; the value of the expansion coefficient is directly related to the composition of the glass and is generally inversely proportional to the thermal stability. It can be seen from Table 6 that the thermal stability of S3 glass is the best, while the thermal stability of S2 glass is not much different from that of S3 glass but exhibits better chemical stability. Therefore, it can be inferred that the influence of the glass expansion coefficient on thermal stability is much greater than its chemical stability. At the same time, it can be predicted that the S2 glass material has better environmental adaptability for actual production and application.

## 4 Conclusions

In summary, three kinds of colorless transparent silicate glasses with different  $\text{PbO}$  content were prepared using the high-temperature melting forming method. The differences in the structure and properties of the three glass samples result from the composition and content of their oxides ( $\text{SiO}_2$ ,  $\text{PbO}$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$ ). Among them, the linear transmittance of lead-based silicate glass with a  $\text{PbO}$  content of 50% can reach more than 85% in the wavelength range of 400–800 nm, and a 50% shielding rate of  $^{60}\text{Co}$  gamma rays can be exhibited for 50 mm thick glass. Therefore, this kind of glass, with reliable chemical stability and thermal stability, has great application potential in occasions with high transmittance requirements. Through the development of this study, we expect to provide new ideas and methods for the design

and preparation of silicate-based high-transmittance, intense gamma rays shielding glass and provide strong support for research in related fields. At the same time, in view of the shortcomings in the research work in this field, such as the poor resistance to gamma-ray irradiation of glass and the use of  $\text{PbO}$ , which does not meet the environmentally friendly shielding requirements of non-toxic and lead-free materials, researchers still need to explore in depth, so as to further provide an important material foundation and scientific theoretical support for the development and application of high-transmittance, intense gamma rays shielding material in China.

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## Preparation and Properties of Glass with High Transmittance and Intense Gamma Ray Shielding

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### Extended Abstract

**Introduction** As a kind of high-energy electromagnetic radiation, gamma rays can lead to radiation effect and environmental pollution. To ensure the reliability and safety utilization of gamma radiations in different areas, materials with reliable gamma shielding performances should be developed. The existing efforts are to use glasses as alternative for the conventional radiation shielding materials. As a typical window material, glass itself has attracted wide attention due to its unique chemical and physical advantages. Among them, lead-based radiation shielding materials are widely used in the field of ionizing radiation protection due to their reliable physical properties. In the nuclear industry and high energy physics laboratories, different materials can be used for temporary or permanent shielding. The lead-based glass doped with heavy metal oxide PbO is widely used in the field of radiation shielding for a long time with reliable light transmission properties, which facilitates the observation and monitoring of radiation areas. In this paper, three kinds of transparent silicate glass with different PbO contents were prepared by a high-temperature melting forming method. The gamma-rays protection abilities of the three kinds of glass were investigated through experimental and thermal methods. The chemical and thermal stability of the glass were also analyzed. In addition, the influence mechanism of the structure and performance differences of the three kinds of glass was also discussed.

**Methods** Analytical pure quartz sand ( $\text{SiO}_2$ , purity 99.5%, in mass, the same below), lead monoxide (PbO, purity 99.0%), potassium nitrate ( $\text{KNO}_3$ , purity 99.0%) and sodium nitrate ( $\text{NaNO}_3$ , purity 99.0%) were selected as raw materials for preparation of three kinds of gamma-rays shielding glass materials by a high-temperature melting method. An appropriate amount of raw materials was thoroughly mixed and added to 3 L quartz crucible and heated in air at 1 200 °C. Then the raw materials were melted at 1 250 °C for 14 h. The uniform melt was quickly poured into the 150 mm×150 mm×50 mm stainless steel mold preheated at 750 °C. Finally, the quenched glasses were annealed at 450 °C for 12 h and cooled naturally to room temperature.

The density of the three glass samples was tested based on the Archimedes principle. The thermal expansion coefficient of glass samples was measured by a model Netzsch DIL 402 expansion coefficient tester. The infrared spectra were measured by a model Perkinelmer Spectrum 100 FTIR Spectrometer. The Raman spectra were tested by a model HORIBA LabRAM HR800 high-resolution Raman spectrometer. The gamma ray shielding test was completed in China Academy of Engineering Physics. The chemical stability test was completed in Chengdu Guangming Glass Co., LTD. The acid stability and moisture stability of the glass samples were tested according to the national standards GB/T 7962.14–2010 and GB/T 7962.15–2010, respectively. The thermal stability of the galss was also determined.

**Results and discussion** Glass structure becomes more compact with the exchange of Pb alternatives of Si, K and Na. Increasing the density of glass is conducive to improving its shielding performance, but this leads to significant changes in the optical properties, thermal properties and chemical stability of glass due to the increase of heavy metal content. The preparation of high transmittance glass is more difficult. The coefficient of thermal expansion of glass samples gradually decreases from  $103.6 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$  to  $89.2 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$ , and the values of  $T_g$  and  $T_f$  also decrease with the increase of mass fraction of PbO in glass components. The change of the thermal properties of the three glass samples is a result of the joint action of PbO,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ . The FTIR spectra show that the added PbO is transformed into  $[\text{PbO}_4]$  units with 4 coordination numbers into the network under the condition of sufficient free oxygen as PbO content in the glass increases. These  $[\text{PbO}_4]$  units participate in the formation of silicate networks. The Raman spectra indicate that the silicate network structure is de-polymerized as PbO content is increased, and the enhancement of the characteristic vibrational peaks corresponding to the Pb–Si–O indicates an increase in the degree of participation of the  $[\text{PbO}_4]$  units in the

formation of silicate network. The ion packing density of the glass sample gradually increases with the increase of PbO content, which shows that the compressible free volume per unit volume of the glass sample becomes smaller. PbO with a high concentration ( $x = 0.50$  and  $x = 0.66$ ) is used as a glass-forming agent, and the  $[\text{PbO}_4]$  structural units can form a connection structure with the silicon oxide tetrahedron, which plays a role in repairing the glass network.

The permeability of the glass can be improved *via* strictly controlling the iron content of the introduced raw materials and making full use of the double alkali effect of the glass. The actual shielding performance of glass is not a result of simple addition of various components. This can be affected by the actual composition content of the glass, melting process and endoplasmic uniformity. The influence of glass expansion coefficient on the thermal stability is much greater than that on its chemical stability.

**Conclusions** PbO with a high concentration ( $x = 0.50$  and  $x = 0.66$ ) was used as a glass-forming agent, and the  $[\text{PbO}_4]$  structural units could form a connection structure with the silicon oxide tetrahedron, playing a role in repairing the glass network. The measured shielding rate of  $^{60}\text{Co}$  gamma-ray could be 50% and the glass with 50% PbO content (in mass fraction) exhibited a linear transmission rate of more than 85% in the range of 400–800 nm. In addition, the reliable thermal and chemical stabilities were also reflected in the glass.

**Keywords** transmittance; gamma rays; radiation shielding; glass