In the present study, transparent Y₂O₃ ceramics were successfully fabricated via colloidal processing, employing polyethyleneimine (PEI) as an effective dispersant. The effect of PEI on nanosized Y₂O₃ suspensions was characterized by zeta-potential, adsorption behavior, rheological properties, and sedimentation test. The addition of PEI shifted the IEP of the Y₂O₃ powder towards a more alkaline pH range, and the adsorption of PEI on the Y₂O₃ surfaces gradually increased with the amount of PEI until reaching the saturation adsorption at 1.5 w%. The PEI amount at 1.5 w% was superior for the preparation of Y₂O₃ suspension as a result of a lower viscosity or sedimentation behavior. The viscosity of the suspension depended on the solids loading, increasing with the amount of powder. The optimal rheological behavior was achieved with 29 w% Y₂O₃ in the suspension, enabling the centrifugal slip casting of complex-shaped green bodies with a packing density of 43%. Including an additional CIP treatment boosted the packing density of the green compacts, achieving above 50%. Vacuum sintering the compacts at 1700 °C for 5 h yielded high-density ceramics exhibiting an in-line transmittance of approximately 73 % at a wave-length of 1100 nm.

Keywords: Y₂O₃, suspension, rheological behavior, transparent ceramics

During the consolidation process, it is widely acknowledged that colloidal processing offers advantages in facilitating the production of large-sized and complex-shaped green compacts, exhibiting a homogeneous microstructure and the desired green density, whereas traditional dry uniaxial pressing methods often pose challenges in achieving such characteristics. The critical technology of colloidal processing is to achieve a stable ceramic suspension with a high solids loading, low viscosity, and good dispersibility. This is crucial for both enhancing the ease of handling and attaining a final product with high reliability. In both aqueous and non-aqueous nanopowder suspensions, the presence of a high surface area and a reduced separation distance among the nanoparticles gives rise to attractive interactions, thereby causing rapid settling and aggregation of the suspensions. Therefore, to get well-dispersed and stable nanopowder suspensions, the major stabilization...
Mechanisms, including electrostatic, steric, or electrosteric stabilization mechanisms should be introduced in ceramic colloidal processing to offset the van der Waals attraction. This often necessitates the addition of suitable dispersants that are adsorbed from solution onto the particle surfaces to control the interparticle forces, inhibit aggregation, and achieve stability. Mouzon et al. found that electrosteric stabilization in the presence of polyelectrolyte A40 was effective for obtaining well-dispersed Y₂O₃ suspensions. The optimal concentration of A40 was determined to be 1.0 w/%, yielding the lowest viscosity of the suspension. Sun prepared a stable suspension with 81 w/% solids loading, using water-soluble copolymer (0.2 w/% Ib104 plus 0.3 w/% Ib600) as both a dispersing and gelling agent. The transmittance measured at 1100 nm of the resultant Y₂O₃ ceramics was found to be 80.9 %. More recently, a novel aqueous colloidal processing route has been explored to improve the stability and dispersion of Y₂O₃ suspensions through the combined use of a ZrO₂ coating agent and polyelectrolyte dispersant. However, the use of the coating agent necessitates a higher sintering temperature or pressure-assisted sintering during the sintering process in order to densify the final products. Over the past few decades, a series of anionic polymers has often been utilized to effectively improve the stability of Y₂O₃ suspensions. However, fewer investigations of the preparation of Y₂O₃ aqueous suspension by adding cationic dispersants have been reported, and those available were not systematic.

Polyethyleneimine (PEI) has been employed as a cationic dispersant to enhance the stability of ceramic powder suspensions such as ZrO₂, Y-TZP, SiC, and Si₃N₄. In a neutral or acidic environment, the positively charged PEI could adsorb on ceramic particle surfaces, resulting in an electrosteric effect that hinders the flocculation of the ceramic suspension. Xu et al. reported that PEI was used as a dispersant to improve the dispersion properties of Y₂O₃ powders (average particle size of 200 nm) in ethanol. Adding 1.5 w/% PEI, a Y₂O₃ alcoholic suspension with a solids loading of 20.8 g/% and a viscosity of less than 0.1 Pa·s at a shear rate of 10 s⁻¹ was obtained. In this work, PEI was selected as a dispersant for aqueous Y₂O₃ suspensions. The colloidal properties of Y₂O₃ suspensions with regard to PEI amount are extensively elucidated. In addition, the effect of ceramic solids loading on the rheological properties of the PEI-based suspensions was also explored. Subsequently, the optimal conditions for Y₂O₃ suspensions were determined and used to produce cylindrical green compacts by centrifugal slip casting. Then the vacuum sintering was carried out to fabricate the Y₂O₃ ceramics. Finally, optical transmission of the resultant sintered samples was examined.

2 EXPERIMENTAL PART

2.1. Raw materials

In the present study, commercially available, high-purity Y₂O₃ (99.99%) was utilized. This powder has a specific surface area of 8.17 m²/g measured through N₂ adsorption (Model TriStar II 3020, Micrometritics Instrument Corp., Norcross, GA). The morphology of the as-received powder, measured by scanning electron microscopy (SEM), is illustrated in Figure 1, revealing that the primary particle size was approximately 96 nm. Before preparing the suspension, the powder underwent pretreatment. Polyethyleneimine (PEI) (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), with an average molecular weight of 10,000 was taken as the dispersant.

2.2 Preparation process

A series of Y₂O₃ suspensions at a solids loading of 5 g/%, containing increasing amounts of dispersant (expressed as the total mass of Y₂O₃ powder), were prepared. In a typical procedure, the dispersant was dissolved in distilled water in a polyethylene jar containing zirconia balls. Then Y₂O₃ powder was gradually added to the mixture. The resultant suspensions were ball-milled for 6 h in a planetary mill.

Various suspensions at the optimal dispersant amount with a solids loading ranging from 10 g/% to 31 g/% for different ball-milling times were prepared following the same procedure.

Y₂O₃ green bodies were fabricated by a centrifugal slip-casting method. Selected, concentrated Y₂O₃ suspensions were poured into the molds and left for consolidation using a laboratory centrifuge at constant speed of 3000 min⁻¹ for 40 min. After 24 h at room temperature, the green bodies were extracted from the mold, and further oven dried at 80 °C for over 12 h. Then, the green bodies were pre-sintered at 1000 °C for 4 h in a muffle furnace to remove the organic additives, and subsequently sintered at 1700 °C for 5 h in a vacuum of
The samples were cut into fractured slices, and subsequence field-emission scanning electron microscope (FE-SEM) microstructure of the green bodies was observed using a distilled water as the immersion medium. The red spectrophotometer (Model Lambda 750S, Perkin red spectrophotometer (Model Lambda 750S, Perkin Elmer, CT, USA). In this measurement, 5 w/% Y2O3 suspension was employed and the pH was adjusted using 1 mol/L HCl and 1 mol/L KOH aqueous solution.

To study the adsorption behavior of the PEI, Y2O3 suspensions with 5 w/% solids loading were utilized. The as-received suspensions were centrifuged at 3000 min⁻¹ for 40 min, the supernatants were poured out and the sediments were dried in the oven at 100 °C for 5 h. Afterwards, the adsorbed amount of PEI was determined using a DTA/TG analyzer (Model SETSYS Evolution-16, Setaram, Lyons, France) by measuring the weight loss of the dried powders during heating in a flowing oxygen atmosphere.

Rheological behavior mainly focuses on the viscosity curve of Y2O3 suspensions that were evaluated using a cone-plate viscometer (Brookfield DV-II+Pro, Brookfield Engineering Laboratories, USA) at room temperature.

The stability of the Y2O3 suspension was easily characterized by sedimentation tests, which offer an approximation of colloidal stability. The suspensions were kept in glass graduated cylinders for more than 60 h and the volume of the sedimentation as a percentage of the total suspension volume (Normalized volume) was measured as a function of settling time.

Archimedes’ immersion method was applied to determine the densities of the obtained green bodies. The relative density was determined by calculating the ratio of the actual density to the theoretical density of Y2O3, using distilled water as the immersion medium. The microstructure of the green bodies was observed using a field-emission scanning electron microscope (FE-SEM). The samples were cut into fractured slices, and subsequently coated with gold to enhance their conductivity before being examined. Subsequently, polished pellets with a thickness of 1.2 mm, which were cut from the sintered specimens, were employed to measure the optical transmittance using an ultraviolet/visible/near-infrared spectrophotometer (Model Lambda 750S, Perkin Elmer, CT, USA).

3 RESULTS AND DISCUSSION
3.1 Optimization of PEI amount

As previously mentioned, achieving effective colloidal processing and maximizing uniformity in the green bodies depends on the ability to produce a suspension that is not only well-dispersed, but also possesses a relatively high solids loading.26 This objective was realized through the addition of the PEI dispersant to a water-based solution, effectively stabilizing the suspension. The optimization of the operational parameters was identified through a sequence of analyses and assessments.

Zeta-Potential Analysis Figure 2 illustrates the relationship between the zeta-potential value and the amount of PEI for individual fresh dilute suspensions of Y2O3. For Y2O3 powder without PEI, increasing the pH value from 6.2 to a significantly basic range, the surface charges of the particles experienced a notable shift, transitioning from a positive charge to a negative charge. This shift was a clear sign of an isoelectric point (IEP) of approximately 9.7, where the suspension was in its least stable state in terms of particle agglomeration. With the increasing of the pH, a steep increase is observed in the absolute value of the zeta potential. In the case of Y2O3 containing 0.5 w/% PEI, the values of the zeta potential changed to positive across the pH range < 10.9, indicating PEI successfully adsorbed on the surface of Y2O3 particles. This phenomenon can be attributed to the fact of polyethyleneimine (PEI) being a cationic polyelectrolyte. When acid was introduced to a suspension containing PEI, it reacted with the basic –NH– groups in PEI, leading to their neutralization and the formation of a positively charged polymer structure (–NH+–). Consequently, these positively charged groups exhibited a strong affinity for adsorption onto negatively charged Y2O3 surfaces through electrostatic interactions, causing a shift in the IEP towards a more alkaline range. Then, at a higher PEI amount of 1.5 w/%, the IEP moved to a pH of 11 due to the absorption of PEI on the Y2O3 particles. With the further increasing amount of PEI, there was no notable alteration in the zeta-potential, indicating a state of saturation adsorption. Additionally, both within the selected amount range of PEI and across the entire pH range, the absolute value of the potential remained below 30 mV, indicating a lack of sufficient electrostatic repulsion to disperse the powder particles.

![Figure 2: Zeta-potential of Y2O3 particles in the absence and presence of various amounts of PEI](image-url)
Adsorption of PEI onto Y2O3 particles

Figure 3 presents the variation in the adsorption amount of PEI on the surface of Y2O3 powder particles as a function of the initial PEI addition. As evident from Figure 3, the adsorption of PEI on the surface of Y2O3 particles gradually rose with an increase in PEI amount from 0.1 w/% to 1.5 w/%. Afterwards, a saturation adsorption amount of 0.5 mg/m² was observed. The adsorption amount was kept almost constant as the PEI amount exceeded 1.5 w/%, revealing that PEI on the surface of Y2O3 particles had reached its adsorption limit, in agreement with the results of the zeta-potential measurement.

Suspension Rheological Properties

Dispersants play a role in improving the rheological and dispersion stability of suspensions, both of which are very dosage-sensitive. Figure 4 depicts the variations in the viscosity of the Y2O3 suspensions with varying PEI amounts in the range from 0 w/% to 2.5 w/%, at the shear rate of 1.32–264 s⁻¹. All Y2O3 suspensions exhibited clear shear thinning behavior, indicative of a non-Newtonian rheological behavior. As is obvious in Figure 4a, the inclusion of PEI dispersant notably enhanced the stability of the Y2O3 suspension, exhibiting a rapid reduction in viscosity as the increased PEI amount in the range of not exceeding 1.5 w/%, as a result of the absorption of PEI on the surfaces of powder particles. Upon regulating the PEI amount from 0 w/% to 1.5 w/%, the viscosity of Y2O3 suspensions presented a substantial transformation, shifting from 134.7 mPa·s to 2.7 mPa·s at a shear rate of 13.2 s⁻¹, as seen in Figure 4b. Then, at higher PEI contents of up to 2.0 w/% and 2.5 w/%, a minor increase in the viscosity of the suspension was detected. This observation was explained by the mutual cross-linking effect of the PEI after reaching adsorption saturation on the powder surfaces, which subsequently led to a deterioration in the stability of the suspension. The suspension containing 1.5 w/% PEI exhibited the lowest viscosity value, which is indicative of a superior suspension stability, enabling easy particle movement.

Sedimentation test

A sedimentation plot versus the time of Y2O3 suspensions with various PEI amounts is presented in Figure 5. It is observed from Figure 5 that the suspension in the absence of PEI settled rapidly within 30 min. After 120 min, the normalized volume of the suspensions at
tained a value of 0.94. Further extending the settling time, it was noted that the sedimentation volume of the suspension remained unchanged, indicating the occurrence of severe flocculation. \( \text{Y}_2\text{O}_3 \) nanoparticles with a high surface energy easily gave rise to severe agglomeration among the particles. This agglomeration, in turn, triggered flocculation within the suspension, ultimately leading to the complete loss of fluidity among the particles in the suspension. In the case of containing PEI, the starting settling time of the slurry was delayed, and settling was observed to be much slower, due to the PEI adsorbed on the \( \text{Y}_2\text{O}_3 \) powder. PEI is a highly branched macromolecule with a general chemical formula of \([-\text{CH}_2-\text{CH}_2-\text{NH}-]_n\). The partially ionized or non-ionized PEI could adsorb onto the negatively charged surface and thus provide an electrosteric or steric stabilization for ceramic suspensions. It was reported that the degree of PEI dissociation (\( \alpha \)) exhibits an increasing trend as the pH decreases, and partially dissociated PEI with \( \alpha = 0.1 \) at pH = 10 can be obtained. 24 The pH of the suspension without pH adjustment was approximately 9.4, at which \( \alpha \) value of partially dissociated PEI was \( \approx 0.1 \). In all cases of suspensions with PEI, the low absolute potential indicated that positively charged polymer groups adsorbed onto the surface of powder could not provide sufficient electrostatic repulsive force to prevent the aggregation of particles. As seen from the results of the zeta-potential measurement in Figure 2. Moreover, lower viscosity and sedimentation of suspensions with PEI were achieved, revealing that the stabilization of suspensions may be dominated by incorporation of electrosteric and steric effects developed from the ionized and unionized PEI. The higher sedimentation can be explained in view of the lack of enough electrostatic or steric forces to overcome the Van der Waals attraction force for PEI amounts less than 1.0 w%, due to incomplete coverage of the \( \text{Y}_2\text{O}_3 \) particle surfaces. However, after a certain amount of 1.5 w%, the settling volume increased again due to excessive PEI molecules in solution. A mass of free polymers in solution entangled with each other, thus causing depletion flocculation. 22 The optimum PEI amount that can be added to a \( \text{Y}_2\text{O}_3 \) suspension to achieve suspension stability was found to be 1.5 w%, which possessed the lowest viscosity and small sedimentation.

**Optimization of dispersion time**

The viscosity presented in Figure 6 shows the efficiency of ball-milling time on the stability of suspensions containing 1.5 w% PEI, as a function of shear rate. It is evident that as the ball-milling time increased, the viscosity of the suspension decreased significantly. At a ball milling time of 1 h, the viscosity measured at a shear rate of 1.32 s\(^{-1}\) was 60.55 mPa·s. Moreover, upon reaching a ball-milling time of 6 h, the viscosity attained its minimal value of \( \approx 24 \) mPa·s at 1.32 s\(^{-1}\), which indicated the finest homogeneity in the \( \text{Y}_2\text{O}_3 \) system. Further extending the ball milling time to 8 h and 10 h resulted in a slight increase in viscosity to 25.90 mPa·s and 29.66 mPa·s, respectively. The purpose of ball milling is to achieve a uniformly dispersed suspension through the collisions between the milling balls and \( \text{Y}_2\text{O}_3 \) particles. In the initial stages of ball milling, specifically at 1 h and 2 h, the process focused on refining and homogenizing the powder particles. The application of external force through ball milling could enhance the penetration of the dispersing medium, resulting in its uniform dispersion among the \( \text{Y}_2\text{O}_3 \) particles. Additionally, this refined process effectively eliminated particle agglomeration and promoted the uniform adsorption of PEI onto the \( \text{Y}_2\text{O}_3 \) powder surfaces. Thus, increasing the ball-milling time could enhance the stability and fluidity of the \( \text{Y}_2\text{O}_3 \) suspensions, manifesting as a decrease in viscosity. However, the powder particles may become excessively ground and refined under prolonged mechanical impact of 8 h or 10 h, causing the higher specific surface area. These increases made the decrease in available volume of the dispersing medium within the system, narrowing the distance between the particles. Consequently, the Van der Waals attractive force increased and favored particle agglomeration, leading to an elevation in suspension viscosity and a subsequent decline in ball-milling efficiency. Furthermore, the higher specific surface area of the \( \text{Y}_2\text{O}_3 \) particles indicated that more of their surfaces were exposed into the liquid phase, causing the 1.5 w% PEI dosage to give inadequate coverage of the \( \text{Y}_2\text{O}_3 \) particle surfaces. Besides, a prolonged dispersion time can induce severe hydrolysis behavior of the nanosized \( \text{Y}_2\text{O}_3 \) powders and cause a significant amount of trivalent yttria cations and their hydroxo complexes in the suspension, strongly decreasing the stability of the suspension, shown by the following equations: 27

\[
\begin{align*}
\text{OH}^- + \text{H}_2\text{O} &= \text{Y} = \text{Y} - \text{OH} + \text{H}_2\text{O} \\
&= \text{Y} - \text{O}^- + \text{H}_3\text{O}^+ \\
\text{Y}^{3+} + 3\text{OH}^- &= \text{Y} (\text{OH})_3 \quad (s) \\
\text{Y}^{3+} + \text{OH}^- &= \text{Y} (\text{OH})^{2+}
\end{align*}
\]
Therefore, in this experiment, ball milling for 6 h was determined as the optimum dispersion condition.

Rheological study to optimize solids loadings of Y₂O₃ suspension

In colloidal processing, carefully controlling the appropriate solids loading of the suspension is crucial for achieving optimal particle packing in the green body, while also maintaining a suitable viscosity. Viscosity measurements were conducted at varying shear rates to investigate the impact of solids loading on the rheological behavior, as depicted in Figure 7. The solids loading of Y₂O₃ was varied from 15 wt% to 31 wt%. From Figure 7, it is observed that all the suspensions showed shear thinning behavior. Under the tested range of shear rates, the suspension containing 15 wt% solids loading exhibited lower viscosity than the other suspensions. This suspension exhibiting a remarkably low viscosity demonstrated exceptional fluidity, yet it was insufficiently viscous to form perfect green bodies. Therefore, it is advisable to elevate the solids loading to attain green bodies with a higher density. As Figure 7 shows, the viscosity of the suspension substantially boosted by increasing the solids loading. In all the cases, the viscosity of the suspension changed from 84.0 mPa·s to 1401.8 mPa·s at a shear rate of 1.32 s⁻¹. When the solids loading exceeded 31 wt%, it became too stiff to meet the testing-range requirements. This is attributed to the fact of higher hydrodynamic interaction resulting from the increasing number of particles as the solids loading increased. Additionally, by elevating the solids loading, the mean distance between the particles decreased, as a result, an intensified attractive force among them, leading to an increased viscosity. In the case of 29 wt%, the suspension exhibited a viscosity of less than 1000 mPa·s over a broad range of shear rates. This level of solids loading proved advantageous not only for achieving a high density of green bodies but also for casting.

Consolidation of Y₂O₃ suspensions and sintering of transparent ceramics

Consolidation of the green bodies using suspensions with various solids loading and 1.0 wt% PEI added was performed by centrifugal slip casting. Figure 8 demonstrates the influence of solids loading on the green relative density. As evident from Figure 8, the sample with a solids loading of 29 wt% exhibited the highest packing density of ≈43%. As the solids loading increased, the green relative density also increased. However, an exception was observed for the sample with 31 wt%, which exhibited a slightly lower density than the sample with 29 wt%. This deviation can be attributed to unsuitable rheological properties of the suspension, which aligned with the rheological behavior in Figure 7.

Figure 9 shows the fracture surfaces of Y₂O₃ green bodies with different solids loadings. There was a difference in the homogeneity among these samples. The green compacts for 15 wt% showed a poor dispersion of particles due to excessively low solids loading. At a 29 wt% solids loading, a more homogeneous and compact microstructure with small open pores can be observed. In sharp contrast, serious agglomeration and large pores were discovered in the green bodies of 31 wt% suspension, thereby decreasing their density and homogeneity. It is well known that green compacts exhibiting a narrow open pore size distribution and a uniform microstructure demonstrate superior sinterability, enabling facile densification at relatively lower sintering temperatures. According to the above analysis, the green bodies, which contained 1.5 wt% PEI and possessed a solids loading of 29 wt%, were selected for the fabrication of transparent ceramics. However, the packing density of 43% achieved was inadequate for subsequent pressureless sintering due to their porous structure. To further boost the packing density of the consolidated green bodies, an additional CIP treatment was utilized at a pressure of 200 MPa. The obtained green bodies demonstrated exceptional compressibility. Following the CIP treatment, the densities of the samples increased to over...
50%, indicating a significant improvement in their compaction properties.

Vacuum sintering was carried out on the consolidated green bodies. The relative density of the centrifugally cast ceramics was 99.9%. Figure 10 shows the optical transmission spectra of the mirror-polished Y$_2$O$_3$ ceramic specimen with a thickness of 1.2 mm. At the wavelengths of 1100 nm and 2000 nm, the in-line transparency approached 73% and 78%, respectively. The inset in Figure 10 is the corresponding image of the as-obtained ceramic specimen, exhibiting an approximate diameter of 9 mm and a length extending to 20 mm. Notably, the letters below the ceramic specimen were clearly visible, further emphasizing their remarkable optical transparency.

4 CONCLUSIONS

Transparent Y$_2$O$_3$ ceramics were prepared using a colloidal processing technique, employing nano-sized Y$_2$O$_3$ powders as the starting material. The effectiveness of the PEI in enhancing the colloidal stability of the aqueous Y$_2$O$_3$ suspension was investigated. The introduction of PEI shifted the IEP of Y$_2$O$_3$ powder towards a higher pH value. The adsorption of PEI on the Y$_2$O$_3$ surface increased with the amount of PEI and reached saturation adsorption at 1.5 w%. A well-dispersed Y$_2$O$_3$ suspension was obtained at an amount of 1.5 w%, at which the viscosity and sedimentation volume of the suspension decreased to a minimum value. By optimizing the ball-milling time, the stability of the suspension can be significantly improved. The viscosity of the suspension exhibited a dependence on solids loading, demonstrating an increase as the amount of powder boosted. A higher solids loading with suitable rheological behavior was achieved in the case of 29 w% of Y$_2$O$_3$ in the suspension, which for centrifugal slip casting led to complex-shaped green bodies with a packing density of 43%. By incorporating an additional CIP treatment, the packing density of the green compacts can be elevated beyond 50%. Subsequently, vacuum sintering at 1700 °C for 5 h resulted in high-density ceramics with an in-line transmittance of approximately 73% at 1100 nm.

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