Theta-phase stabilization by rare-earth and alkali incorporation in sol-gel derived alumina

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Funding information
European Commission, Grant/Award Number: 739566; European Regional Development Fund, Grant/Award Number: 313011R453; European Research Council, Grant/Award Number: 681652; Chinese Scholarship Council, Grant/Award Number: 201506955051

Abstract
Bottom-up synthesis of alumina suspensions doped with trivalent (Eu3+) or monovalent (K+) ions is reported as a means to generate crystalline transition-phase alumina with increased thermal stability. Dynamic light scattering was used to track the stability of precursor sols, showing how the dissolved cations contribute to the stabilizing double layer and particle separation in the liquid phase. The incorporation of alkali or rare-earth dopants into the alumina structure further influences the thermal conversion and crystallization behavior. The Kissinger activation energy of the $\theta \rightarrow \alpha$ phase transition in $\text{Al}_2\text{O}_3$ indicates an inhibitory effect of Eu$^{3+}$ and K$^+$ on the formation of the stable $\alpha$ phase, also confirmed by X-ray diffraction. The intensity ratio of the $^7\text{F}_2/^7\text{F}_1$ characteristic photoemission bands of Eu$^{3+}$ was used to probe the local symmetry as a function of calcination temperature to further corroborate this observation.

KEYWORDS
alumina, europium, sol-gel, XRD

1 INTRODUCTION

Aluminum oxide is one of the most widely used technical ceramics,1,2 Besides the thermodynamically stable $\alpha$-$\text{Al}_2\text{O}_3$ phase (corundum, sapphire, ruby) with its high melting point of 2050°C, a variety of further crystalline polymorphs—the so-called transition phases3—exist at moderate temperatures of $T < 1100°C$, giving rise to a broad number of potential applications, for example, requiring variable amounts of defect density, meso-porosity or structural symmetry.4 For example, $\gamma$-$\text{Al}_2\text{O}_3$ is often utilized in industrial processes as catalyst substrate or catalyst on its own.5 Upon heating above 800–900°C, it undergoes a sequence of phase transitions which eventually lead to the formation of the stable $\alpha$-$\text{Al}_2\text{O}_3$, typically at temperatures around 1100–1200°C.6 Due to the stability of the $\alpha$-phase, bottom-up synthesis is required when aiming to produce the low-temperature phases.

Among other precipitation methods, sol-gel synthesis is a widely investigated route for this purpose.4,7–9 The primary features of sol-gel synthesis are the comparably low synthesis temperature, high achievable purity, high material homogeneity, and the possibility to deposit thin films at relatively
low cost and decent quality. In particular, this method provides easier access to long-term stable, water-based suspensions of ceramic material with nano- or micro-sized particles, which could be used in wet printing applications where such "ink" properties are of paramount importance. Recently, \(^{10,11}\) aluminum oxide (Al\(_2\)O\(_3\)) thin films have attracted interest due to their high transparency in the ultraviolet, visible and near-infrared range as well as their chemical and thermal stability. For example, their corrosion resistance in aggressive environments while maintaining optical transparency makes such films suitable for protective layers in environmental applications (e.g., adherent \(\gamma\)-Al\(_2\)O\(_3\) films with high visible light transmission were deposited on glass housings for fluorescent lamps). As a further advantage, doping in the wet stage is comparably straightforward; it offers a very wide range of dopant concentrations (often beyond what can be obtained in gas-phase synthesis) and homogeneous dopant incorporation into the solid material. Through the choice of precursors, dopants and synthesis conditions, the product’s structure, morphology, and physical properties (e.g., optical properties\(^{12}\)) can be tailored to meet certain application needs. The addition of cations\(^{13,14}\) with larger ionic radii (relative to Al\(^{3+}\)) was described to retard the phase transition to \(\alpha\)-Al\(_2\)O\(_3\), thereby increasing the temperature range at which metastable phases can be utilized.\(^{12}\) For example, the phase-transition temperature of \(\gamma\)- to \(\alpha\)-Al\(_2\)O\(_3\) increases when doping with monovalent cations, depending linearly on the ionic radius of the added cation.\(^{13}\) Beyond alkali ions, doping with polyvalent species such as cerium ions can affect the occurrence of Al\(_2\)O\(_3\) polymorphs.\(^{15}\) Addition of Ce\(^{3+}\) and Ce\(^{4+}\) to \(\gamma\)-Al\(_2\)O\(_3\) was demonstrated to retard the phase transformation to \(\alpha\)-Al\(_2\)O\(_3\) and stabilize the \(\gamma\)-Al\(_2\)O\(_3\) phase. The resulting thermal stability of the transition phases could be advantageous, e.g., for functionalized alumina coatings on glasses, where particular polymorphs are favored.

In this study, we report on the bottom-up synthesis of stable europium-doped alumina suspensions for generating monoclinic \(\theta\)-Al\(_2\)O\(_3\) with enhanced thermal stability. The influence of Eu\(^{3+}\) and K\(^+\) doping, respectively, on phase transitions and polymorph stabilization is explored. Furthermore, photoluminescence of Eu\(^{3+}\) is used as a probe for the structural symmetry of crystalline precipitates.

2 | EXPERIMENTAL PROCEDURES

2.1 | Sol-gel synthesis

Alumina sols were synthesized from precursor solutions consisting of aluminum isopropoxide (98%, MKBH8764V, Aldrich) and deionized water with nitric acid (65%, Merck) as catalyst, comparable to the procedure of Yoldas\(^{16,17}\) and Liu.\(^{18}\) Potassium nitrate, KNO\(_3\) (99.9%, Jenapharm) and europium nitrate pentahydrate, Eu(NO\(_3\))\(_3\)-5H\(_2\)O (99.9%, MKBK1103V, Aldrich) were used as dopants. A typical synthesis procedure involved initial hydrolysis of the precursor under vigorous stirring of aluminum isopropoxide with excess water at 80°C for 45 min in a flask equipped with a reflux condenser. Potassium and europium dopants and nitric acid were added to the solution before allowing the mixture to react under stirring for 24 h at 90°C. The resulting molar ratios were Al(i-Pro)\(_3\):H\(_2\)O:HNO\(_3\) = 1:249:0.25 with 0.01 mol Eu\(^{3+}\) or K\(^+\), respectively. Powders were formed from solution by drying at 90°C for 48 h and subsequent calcination in air for various times at temperatures ranging from 500 to 1300°C in a standard laboratory furnace. An overview of this procedure is presented in Figure 1.

2.2 | Characterization

The pH of the solutions was measured using a pH meter (HANNA HI2020) after calibration with standard buffer solutions at pH 4.01, 7.01, and 10.01 under standard laboratory conditions.
conditions. Aging behavior of the sols was characterized by determining time-series of the particle size distribution via dynamic light scattering (DLS, ZetaSizer Nano ZS, Malvern UK) with a 632.8 nm laser.

Non-calcined powders, that is, those only dried at 90°C for 48 h but without further heat treatment, were analyzed via differential scanning calorimetry (Netzsch DSC 404F3 Pegasus) coupled with thermogravimetric analysis. Measurements were performed up to 1500°C in air at varying heating rates from 5 to 20 K/min.

Calcined powders were characterized post-mortem via X-ray diffraction analysis (MiniFlex 600, Rigaku) with Cu-Kα radiation over a diffraction angle range (2θ) of 10°–90° at a scanning speed of 1°/min.

The photoluminescence behavior of europium-doped powders was evaluated using a high-resolution spectrofluorometer FluoroLog-3 (Horiba Jobin Yvon GmbH) equipped with double monochromators in the excitation and emission channels. A Xe lamp (450 W) was used as excitation source for the static measurements. The excitation spectra were collected in the spectral range of 350–550 nm detecting the emission at 612 nm. The emission spectra were collected in the range of 450–750 nm.

3 | RESULTS AND DISCUSSION

3.1 | Sol stability

The pH values of K⁺- and Eu³⁺-doped and undoped sols with different aging times (1–10 days) ranged from 3.9 to 4.1, suggesting that the aging time does not affect sol conditions significantly.

Dynamic light scattering was used to obtain further data on the size of sol constituents and, thereby, the stability of the sol towards particle precipitation and agglomeration over time. For reference, a typical aggregate size distribution determined from DLS is shown in Figure 2A (here, the representation of size distribution by intensity gives more weight to large particles, as bigger particles contribute more strongly to the scattered intensity; such data, although related, is not directly reflecting the amounts of certain particle size fractions). The “Z-average” size is generally taken to represent the particle size distribution by DLS and is expected to capture size changes with sufficient sensitivity. The Z-average values of the sol constituents are shown in Figure 2B, over a timeframe of up to 3 weeks, starting right after preparation (day 1). Apparently, for all sols there is a minor instability in the first 7 days after preparation, shown by the decreasing average size over that time frame. However, for aging times exceeding 7 days, the Z-average approaches a constant value. The unstable regime at the early stage of aging was also reported for silica sols. It is understood as a transient effect resulting from the temporary formation and subsequent separation of larger, stable structures. After aging for 7 days, the Z-average hydrodynamic diameters remained relatively constant throughout the experimental period, which means that the colloids are well shielded against collision and in turn do not aggregate further to create larger clusters.

Although the three different sols showed comparable trends, the actual Z-average values seem to be affected by the choice of dopant: The presence of K⁺ lead to increased Z-average values compared to the undoped solutions, while addition of Eu³⁺ had the opposite effect. This can be explained by the structure of the nucleated boehmite particle and its local environment in solution: with a point of zero charge at pH ~8.5 and an isoelectric point at pH ~9,22 dispersed particles of Al(OH)₃ in aqueous solution at pH ~4 (as for all sols investigated here), are expected to carry positive surface charges, leading to an adsorbed double layer of the nitrate anions around the solid species, schematically presented in Figure 3.

The boehmite colloid can be described as [(AlOOH)ₘ nH⁺,aq · (n − x)NO₃⁻]X⁻ xNO₃⁻, which is composed of a (doped) core of (AlOOH)ₘ, a close layer of nH⁺,aq · (n − x)NO₃⁻, and a diffusion layer of xNO₃⁻, where m corresponds to the number of ALOOH in the core, n is the number of H⁺,aq adsorbed on the core (n < m), and (n − x) represents the number of NO₃⁻ ions in the close and diffusion layer, respectively (Figure 3A). Given the uncertainty as to whether the aqueous hydrogen ion (H⁺,aq) is actually H⁺, H₃O⁺, [H₂O−H−OH₂]⁺ (Zundel configuration)

![Figure 2](image-url) Dynamic light scattering of alumina sols. (A) DLS size distribution by scattering intensity of the undoped alumina sol on the 14th day, form which the z-average is determined by way of example. (B) Development of the z-average values of the three investigated sols as a function of aging time.
or [O(H–OH)2]3+ (Eigen configuration), this ion is referred to here as the “hydrogen ion,” H+aq. As approximation of the effective size of such an ion, we use the radius of a water molecule, \( r_W = 1.38 \, \text{Å} \).\(^{25} \) After doping europium nitrate into the sol, some Eu\(^{3+} \) replace H+aq on the particle surface. Eu\(^{3+} \) has an ionic radius of \( \sim 0.95 \, \text{Å} \); therefore, it occupies less space around the core at a three times higher positive charge. As a result, the density of NO\(_3^-\) in the close layer increases with Eu\(^{3+} \) doping. At the same time, the layer becomes thinner. This effect even spreads to the diffusion layer, thus, the double layer is compressed, creating a more compact arrangement (Figure 3B). Therefore, the mean Z-average diameter of the Eu\(^{3+} \)-doped colloids is smaller than that of the undoped material. Further confirmation for this assumption is obtained when considering the electric field strength \( F = Z/r^2 \) (where \( Z \) is the ionic charge and \( r \) is the ionic radius).\(^{26,27} \) Trivalent and tetravalent ions (including the rare earths) typically possess high field strength, \( F \geq 1.5 \, \text{Å}^{-2} \).\(^{27} \) This generates a smaller and more closely bound surrounding, which in turn reduces the particle sizes within the sol.

Having the same electric charge as H+aq (radius of 1.38 Å), the K+ ion has a comparable radius of 1.37 Å. However, considering that alkali metals could be easily hydrated, the hydrated radius of K+ increases to 2.16 Å,\(^{28} \) resulting in an increase of the mean Z-average diameter for the K+-doped micelle. While the sols contain similar amounts of nitrates through addition of nitric acid, the dissolved cations K+ and Eu\(^{3+} \) change the double layer and the conditions around the dispersed particles in different manners: Both dopants are expected to partially replace H+aq in the immediate vicinity of the dispersed AlOOH. However, K+ has a lower field strength (\( F < 0.4 \, \text{Å}^{-2} \)),\(^{27,29} \) which leads to a more loosely bound inner layer of charge balancing nitrates, and therefore a larger micelle.

### 3.2 Thermal analysis

STA data shown in Figure 4 (on dried powders) reveal that the major fraction of the overall mass loss which results from sol calcination occurs in the temperature range up until \( \sim 500^\circ\text{C} \) and reaches about \( \sim 40\% \). This is in agreement with the expected loss of adsorbed water (\( T < 200^\circ\text{C} \)), the decomposition of nitrate groups, and loss of H\(_2\)O from boehmite AlO(OH) (\( T \sim 300–500^\circ\text{C} \)). Above 500°C, the weight signal stabilizes at a plateau, indicating that calcination is complete: alumina coatings deposited on conventional soda-lime-silicate glasses could be fully calcined below the glass transition temperatures of the substrate. Upon further heating, no remarkable enthalpic effects are detected up until \( T \sim 1100^\circ\text{C} \).

The broad event between 600 and 1100°C represents a variety of phase transitions of the commonly known metastable phases of Al\(_2\)O\(_3\).\(^{30,31} \) Typically, an exothermic peak in the range of 1100°C is associated with the phase transition of metastable θ-Al\(_2\)O\(_3\) to the thermodynamically stable α-phase. For temperatures beyond this transition temperature, further transitions are usually not observed. The position of the latter phase transition generally shifts to higher temperatures for the doped samples, regardless of the applied heating rate \( \alpha \).

Table 1 summarizes the phase transition peak temperatures \( (T_{pt}) \) derived from DSC for a variety of heating rates.

The apparent phase transition energy \( E_{pt} \) of the \( \theta \rightarrow \alpha \)-Al\(_2\)O\(_3\) transition was estimated using the Kissinger equation\(^{32} \):

\[
\ln \left( \frac{T_{pt}^2}{\alpha} \right) = \frac{E_{pt}}{RT_{pt}} + \ln \left( \frac{E_{pt}}{R} \right) - \ln (\nu),
\]

where \( T_{pt} \) represents the phase transition peak temperature when heated at a heating rate of \( \alpha \). \( R \) and \( \nu \) indicate the gas constant and the frequency factor, respectively. To determine the
Effective phase transition energy, datasets were plotted according to Equation (1) (Figure 4B). From the slope of the linear fit, the corresponding phase transition energy of the samples was calculated to $E_{pt} = 399.3$ kJ/mol (pure Al$_2$O$_3$), 490.6 kJ/mol (K$^+$-doped Al$_2$O$_3$) and 630.4 kJ/mol (Eu$^{3+}$-doped Al$_2$O$_3$). $E_{pt}$ represents an effective energy barrier which is to be overcome during transformation of the metastable Al$_2$O$_3$ into the stable phase, but also depends on experimental conditions. The relative increase of this energy barrier is taken as evidence for the inhibitory effect of Eu$^{3+}$ and K$^+$ on the $\theta \rightarrow \alpha$ alumina phase transition, similar to observations by Zhu.33,34

3.3 | Crystallization behavior

Based on the DSC results, various calcination temperatures were considered for dried alumina powders and subsequent investigation of the crystal phases formed. XRD results are summarized in Figure 5 for different temperatures and calcination times. Independent of the potassium and europium doping, the primary crystal phase in the dried powders is boehmite AlO(OH) (ICDD 01-074-1895), suggesting that the aluminum oxy hydroxide which is expected to form in the wet chemical synthesis does not undergo further reaction upon drying. In particular, solvent evaporation seems to facilitate cluster aggregation instead of crystal growth, which is indicated by the comparably broad peaks in the diffraction patterns. This points to an almost complete reaction of the precursors, with only minor amounts of unreacted species in sol, and is in agreement with the mostly stable particles sizes observed during aging (Figure 2B).

Upon heating at 500°C, all three powders show a transformation from boehmite to $\gamma$-Al$_2$O$_3$ (ICDD 00-010-0425). This transformation is accompanied by a dehydroxylation,4,6 which explains the mass loss detected in the TG data (Figure 4A).

For treatment temperatures up to 800°C, $\gamma$-Al$_2$O$_3$ is the only detected crystal phase in all powders. Upon further heating to 900°C, while $\gamma$-Al$_2$O$_3$ remains the primary crystal phase, minor traces of the tetragonal $\delta$-Al$_2$O$_3$ (ICDD 00-016-0394) are observed in all samples. In addition, monoclinic $\theta$-Al$_2$O$_3$ (ICDD 01-010-0414) appeared in the undoped and in the K$^+$-doped alumina (but not in the powders containing Eu$^{3+}$). However, treatment at 1000°C facilitates the transformation towards $\theta$-Al$_2$O$_3$ also for the europium-doped alumina. At this temperature, first signals of the thermodynamically stable $\alpha$-phase are also detected in all sols. However, while the $\alpha$-phase is found in the undoped alumina already following comparably short treatment times of 1 h, significantly longer treatment times are required in the doped powders for this phase to appear (Figure 5B,D,F). This opens a window for the fabrication of pure $\theta$-Al$_2$O$_3$. The dopants impede structural re-configuration within the Al$_2$O$_3$ particles even at low dopant concentration, which is an indicator for homogeneous dopant distribution.

For powders treated at temperatures between 1100 and 1300°C, all diffraction patterns show primarily signals of $\alpha$-Al$_2$O$_3$, except for the europium-doped powders at temperatures...
FIGURE 5  XRD results on doped alumina powders. X-ray diffraction pattern of undoped (A, B), K⁺-doped (C, D) and Eu³⁺-doped (E, F) samples for varying temperatures with 16 h treatment time (A, C, E) and for various treatment times at 1000°C (B, D, F)
$T < 1150°C$. In this sample, the metastable $\theta$-$\text{Al}_2\text{O}_3$ remains the primary crystal phase, with minor amounts of $\alpha$-$\text{Al}_2\text{O}_3$. The metastable $\theta$-$\text{Al}_2\text{O}_3$ is still observed for even higher treatment temperatures; full transformation to corundum is not observed before reaching a temperature of 1300°C. This is in stark contrast to the undoped alumina powder, where pure $\alpha$-$\text{Al}_2\text{O}_3$ is already detected for $T \approx 1100°C$. The potassium-doped alumina resembles the transformation behavior of pure $\text{Al}_2\text{O}_3$ powders, as at temperatures of $T > 1100°C$, no $\theta$-$\text{Al}_2\text{O}_3$ was detected. For treatment temperatures of $T > 1200°C$, the occurrence of $K_{1.5}\text{Al}_{11}\text{O}_{17.25}$ (ICDD 00-039-0050) and $\text{EuAlO}_3$ (ICDD 00-030-0012), respectively, was observed in the doped powders. In $K^+$-doped powders treated at 1300°C, traces of aluminum oxide ($\text{Al}_{5.667}\text{O}_4$, ICDD 01-080-1385) were detected and decreased peak intensities of $K_{1.5}\text{Al}_{11}\text{O}_{17.25}$ were seen.

### 3.4 | Eu$^{3+}$ photoluminescence

The excitation spectra of selected Eu$^{3+}$-doped alumina samples are presented in Figure 6A. Six transitions are detected, i.e., $^7F_0 \rightarrow ^5D_4$ (~361 nm), $^5G_4$ (~378 nm), $^5L_6$ (~393 nm), $^5D_3$ (~413 nm), $^5D_2$ (~463 nm) and $^5D_1$ (~530 nm). All of these are f-f transitions, of which $^7F_0 \rightarrow ^5L_6$ is the most intense. Powders calcined at 90°C show a pronounced

**FIGURE 6** Fluorescence spectra of Eu$^{3+}$-doped alumina. (A) Excitation spectra (monitoring 612 nm photoemission) of selected Eu$^{3+}$-doped sol-gel derived alumina calcined at different temperatures for 16 h. The 90°C sample was annealed for 48 h. (B) Normalized emission spectra of selected Eu$^{3+}$-doped sol-gel derived alumina calcined at different temperatures for 16 h. The 90°C sample was annealed for 48 h. The transitions are assigned following Binnemans$^{36}$
splitting of the $^5G_4$ and the $^5D_1$ transitions. With increasing temperature, this splitting gets weaker and eventually vanishes at 1200°C. The $^5D_2 \rightarrow ^7F_0$ electric dipole transition is hypersensitive, that is, the oscillation strength changes with changes of the surrounding crystal field. The samples treated up to 1150°C show similar spectral profiles. However, the change in intensity ratios of the transition assigned to $^5D_2$ in powders heated at 1200 and 1300°C indicates a severe alteration of the chemical environment around the Eu$^{3+}$ ion. This corresponds with the transformation region of $\theta$-Al$_2$O$_3$ to $\alpha$-Al$_2$O$_3$ seen by DSC and XRD (see Figures 4A and 5E), and the subsequent formation of minor amounts of EuAlO$_3$.

The emission spectra recorded for 393 nm excitation are presented in Figure 6B. Five distinct transitions from the $^5D_0$ excited state can be distinguished: $^7F_0$ (~589 nm), $^7F_1$ (~592 nm), $^7F_2$ (~616 nm), $^7F_3$ (~653 nm), and $^7F_4$ (694 nm). The most intense band is from $^7F_2$. Emission band splitting is enhanced with increasing treatments temperature, following the transition from the hydroxide to the crystalline alumina phases (Figure 6B, 1300°C).

The hypersensitive induced electric dipole $^5D_0 \rightarrow ^7F_2$ transition enables probing of local symmetry, for example, when its intensity is compared to the insensitive magnetic dipole transition of $^5D_0 \rightarrow ^7F_1$ (e.g., Ref. [35]): the ratio of the transition intensities $R = I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)$ can be used as an indicator for the asymmetry of Eu$^{3+}$ coordination sites, whereby $^5D_0 \rightarrow ^7F_2$ is forbidden for centrosymmetric sites (Laporte’s rule). With stronger site distortion, the relative intensity of the $^5D_0 \rightarrow ^7F_2$ transition increases over that of $^5D_0 \rightarrow ^7F_1$, see Figure 7. Starting from a value of ~2.85 for dried powders, $R$ increases up to ~4.35 for alumina calcined at 1100°C. This reflects the decrease in symmetry while transiting through the metastable phases, with the highest $R$ corresponding to the monoclinic $\theta$-phase. When increasing the calcination temperature to beyond 1100°C, $R$ decreases again, indicating that the Eu$^{3+}$ ion is located in an environment with higher local symmetry, which is consistent with expectation from the formation of higher symmetry $\alpha$-Al$_2$O$_3$ and EuAlO$_3$.

4 | CONCLUSION

A bottom-up sol-gel synthesis route for Eu$^{3+}$ and K$^+$-doped $\theta$-Al$_2$O$_3$ from stable boehmite sols is reported. Varying thermal treatment conditions provided mixtures of metastable crystalline phases like $\gamma$-Al$_2$O$_3$, $\delta$-Al$_2$O$_3$, $\theta$-Al$_2$O$_3$ and the thermodynamically stable $\alpha$-Al$_2$O$_3$. The addition of 0.01 mol% KNO$_3$ or Eu(NO$_3$)$_3$·5H$_2$O to the sol formulation had an impeding effect on the phase transitions, in particular, shifting the peak crystallization temperature of $\alpha$-Al$_2$O$_3$ by up to ~100 K and opening-up a process window for $\theta$-Al$_2$O$_3$. Eu$^{3+}$ photoluminescence enables further tracking of the variations which occur in structural symmetry while passing through the different Al$_2$O$_3$ polymorphs.

ACKNOWLEDGMENTS

This project was conducted as part of the training activities at the Centre for Functional and Surface Functionalized Glass (FUNGGLASS), supported by the European Commission (GA 739566) and co-funded by the European Regional Development Fund (CEGLASS, GA 313011R453). Partial funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (grant 681652) is gratefully acknowledged. PT was supported by the Chinese Scholarship Council (GA 201506955051). We thank our colleague U. S. Schubert for generous access to the dynamic light scattering device. Assistance in fluorescence spectroscopy and X-ray diffraction measurements by Mr. Christian Zeidler and Ms. Nadja Greiner-Mai from the Otto-Schott-Institute of Materials Research, Friedrich Schiller University Jena is gratefully acknowledged.

AUTHOR CONTRIBUTIONS

PT and LM prepared the samples and performed the experiments with support from MZ and RS. PT, LM, RS, and LW conducted data analysis and wrote the manuscript.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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