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ORIGINAL PAPER: FUNDAMENTALS OF SOL-GEL AND HYBRID MATERIALS PROCESSING

Fabrication of CeO_2–Nd_2O_3 microspheres by internal gelation process using $M(OH)_m$ and $[MCit{\cdot}xH_2O]$ ($M{=}Ce^{3+}$, Ce^{4+}, and Nd^{3+}) as precursors

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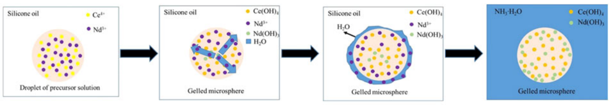
Abstract

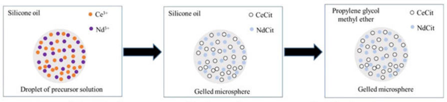
CeO_2–Nd_2O_3 microspheres were successfully prepared by internal gelation process using $M(OH)_m$ and $[MCit{\cdot}xH_2O]$ ($M = Ce^{3+}$, Ce^{4+}, and Nd^{3+}, Cit is $(C_6O_7H_5)^{3-}$) as precursors. The effects of $Nd(NO_3)_3$ content on the stability of precursor solution and on the microstructure of the sintered microspheres were investigated. The gelled microspheres and sintered composite microspheres were characterized by Fourier transform-infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), and X-ray fluorescence (XRF) spectroscopy. The distribution of Nd^{3+} in the microspheres was also investigated by line scanning of SEM. The results indicated that the citrate salt in the gelled microspheres was $[MCit{\cdot}xH_2O]$ ($M = Ce^{3+}$ and Nd^{3+}). Compared with composite microspheres prepared with $M(OH)_m$ ($M = Ce^{4+}$ and Nd^{3+}) as a precursor, the mass fraction of Nd_2O_3 in composite microspheres prepared with $[MCit{\cdot}xH_2O]$ as a precursor highly coincided with the theoretical value. There was no concentration gradient in the microspheres and the distribution of Nd^{3+} was homogeneous. Phase composition of the composite microspheres was $Ce_{0.75-x}Nd_{0.25+x}O_{1.85}$ and CeO_2.

Graphical Abstract

The gelation process of microspheres prepared with hydroxide.



The gelation process of microspheres prepared with hydroxide



The gelation process of microspheres prepared with citrate

Highlights

- CeO_2–Nd_2O_3 microspheres were prepared by internal gelation process with $M(OH)_m$ and $[MCit{\cdot}xH_2O]$ as precursors.
- The mass fraction of Nd_2O_3 in composite microspheres prepared with $[MCit{\cdot}xH_2O]$ highly coincides with the theoretical value.
- No concentration gradient existed in the microspheres and the distribution of Nd^{3+} was homogeneous.

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Keywords Internal gelation process · CeO_2–Nd_2O_3 microspheres · Cerium hydroxide · Neodymium hydroxide · Citrate salts

1 Introduction

The subcritical accelerator-driven system is considered as an effective method for transmutation of Pu, minor actinides (MAs), and long-lived fission products (LLFPs), which have high radioactivity and lasting radiotoxicity [1–4]. For avoiding the formation of new transuranium actinides due to the neutron capture by ^{238}U and achieving the maximum transmutation efficiency, inert matrix fuels (IMF) with a ceramic matrix, such as Mo, MgO, ZrO_2, and ZrN [4–6] are advantageous [5, 7]. Due to structural stability under irradiation, inertia of neutrons, similar sintering behavior, and thermal properties of PuO_2 and CeO_2 can also be used as an inert matrix material [1, 8–10].

Pellet and sphere-pac are two types of IMF. Compared with pellet fuels, sphere-pac fuels have some advantages as the following: the dustless fabrication with sol–gel or gel-casting methods, swelling can be reduced or eliminated by storing gas in the gap or releasing out the gas through the particle boundary [11]. Sphere-pac IMF can be prepared by infiltration of porous ceramic microspheres with MA nitrate solution [7] and co-sol–gel process with nitrate solution containing MA and metal ion to prepare the inert matrix [12]. But the nonuniform porosity of the porous ceramic microspheres, or diffusion process during the thermal treatment, may lead to inhomogeneity of the MA distribution in the microspheres prepared by infiltration technique [12, 13].

As an advanced method that directly converts droplet of precursor solution into microspheres, internal gelation process has been widely used to prepare nuclear fuel and IMF [14–18]. Preparation of CeO_2 microspheres has also been investigated by internal gelation, with cerium hydroxide as the precursor [10, 19–22], and no other precursor was used to prepare CeO_2 microspheres. Cerium citrate, as another kind of precursor, which was used to prepare CeO_2 powder by sol–gel process [23, 24], can also possibly be used to prepare CeO_2 microspheres. Citrate salts were often used to prepare lanthanide oxide [25, 26], and could be used to prepare composite microspheres containing MAs and LLFPs, because lanthanides and trivalent actinides have similar chemical properties.

The aim of this work is to prepare homogeneous CeO_2–Nd_2O_3 microspheres with $M(OH)_m$ and citrate salts as precursors by co-sol–gel process. Neodymium ion Nd^{3+} was used as a surrogate for the trivalent actinides. Due to that the typical IMF contain 5–30 wt% of MA; CeO_2–Nd_2O_3 microspheres with varying amounts of Nd_2O_3 (5–30 wt%) were prepared. Neodymium ion Nd^{3+} distribution in the microspheres was investigated.

2 Experimental section

2.1 Preparation of CeO_2–Nd_2O_3 microspheres with $M(OH)_m$ ($M=Ce^{4+}$ and Nd^{3+}) as a precursor

CeO_2–Nd_2O_3 microspheres were synthesized with $M(OH)_m$ as the precursor, based on a literature procedure [22]. It was a typical sol–gel process for the preparation of oxide microspheres. Specifically, ammonia (25% concentration, Beijing Chemical Works, China) was dissolved in the 1.6 M $Ce(NH_4)_2(NO_3)_6$ (99% purity, Sinopharm Chemical Reagent Co., Ltd., China) solution, and the pH of the solution could be changed by varying the molar ratio of $NH_3{\cdot}H_2O/Ce(NH_4)_2(NO_3)_6$. Quantitative $Nd(NO_3)_3{\cdot}6H_2O$ (99% purity, Shanghai Macklin Biochemical Co., Ltd, China) was dissolved into Ce^{4+}-containing solution to prepare the microspheres with different mass fractions of Nd_2O_3. Hexamethylenetetramine (HMTA) (99% purity, Sinopharm Chemical Reagent Co., Ltd., China) and urea (99% purity, Sinopharm Chemical Reagent Co., Ltd., China) were dissolved into deionized water to prepare the solution consisting of 3.2 M HMTA and 3.2 M urea. Precursor solution was prepared by mixing the Nd-containing solution and solution containing 3.2 M HMTA and 3.2 M urea with equal volume, then the precursor solution was cooled to 4 °C for at least 30 min to diminish the hydrolysis of HMTA. The precursor solution was dropped into 90 °C silicon oil. The droplets could maintain spherical shape due to their surface tension. On heating by the hot silicon oil, the spherical droplets solidified within a few seconds by the decomposition of HMTA. The gelled microspheres were aged for at least 30 min. Then, the microspheres were washed with trichloroethylene (TCE) (99% purity, Sinopharm Chemical Reagent Co., Ltd., China) to remove the silicone oil on the surface of the gelled microspheres. A concentration of 0.5 M ammonia was used to remove the NH_4NO_3 and uncreated urea, etc. Then, the gelled microspheres were treated with hydrothermal treatment to decompose the urea resin generated during the internal gelation process. The spheres were washed with distilled water to remove the organic compound and then washed with propylene glycol methyl ether (99% purity, Sinopharm Chemical Reagent Co., Ltd., China) to remove water in the microspheres. Then, the washed microspheres were dried at 60 °C for at least 12 h, and sintered at 1400 °C for 2 h.

2.2 Preparation of CeO_2–Nd_2O_3 microspheres with citrate salts as precursors

$Ce(NO_3)_3·6H_2O$ (99.5% purity, Sinopharm Chemical Reagent Co., Ltd., China), and anhydrous citric acid (H_3Cit) (99.5% purity, Sinopharm Chemical Reagent Co., Ltd., China) were dissolved into deionized water to prepare a solution consisting of 2 M cerium nitrate and 2 M citric acid. Quantitative $Nd(NO_3)_3·6H_2O$ (99% purity, Shanghai Macklin Biochemical Co., Ltd., China) was dissolved into Ce^{3+}-containing solution to prepare the microspheres with different mass fractions of Nd_2O_3. HMTA and urea were dissolved into deionized water to prepare the solution consisting of 3.0 M HMTA and 3.0 M urea, hereafter noted as H–U solution. Both solutions were cooled to 4 °C for at least 30 min. Under magnetic stirring, the Nd^{3+}-containing solution and the H–U solution was mixed with equal volume, then the acrylic acid (AA) (Sinopharm Chemical Reagent Co., Ltd., China) was added into the solution, and the molar ratio of AA/HMTA was unity. Then, 0.4 wt% *N*,*N*′-methylenebisacrylamide (97% purity, Sinopharm Chemical Reagent Co., Ltd., China) and 0.2 wt% ammonium persulfate (99% purity, Sinopharm Chemical Reagent Co., Ltd., China) were also added into the precursor solution. The final solution was stirred, until a clear solution was obtained, and then cooled to 4 °C for at least 10 min to diminish the hydrolysis of HMTA and restrain the polymerization of AA.

The solution cooled to 4 °C was dropped into silicon oil of 90 °C with a syringe to form gel microspheres. The spheres were aged for 2 h after all of the gelled spheres settled at the bottom of the column to make sure that the urea resin could be modified thoroughly. The gelled spheres were washed successively by using TCE to remove the silicon oil on the surface of the gelled microspheres and propylene glycol methyl ether to remove the TCE. Compared with that in the "Preparation of CeO_2–Nd_2O_3 microspheres with $M(OH)_m$ ($M=Ce^{4+}$ and Nd^{3+}) as a precursor" section, the present washing treatment produced less waste liquid, and fewer steps were needed. The washed spheres were dried for at least 6 h in an oven at 60 °C. Finally, the spheres were sintered in atmospheres at 1400 °C for 2 h.

2.3 Characterization

A digital pH meter was used to measure the pH of the precursor solution before it was dropped into the hot silicon oil. An LVDV-1 digital rotation viscometer was used to measure the viscosity, and the rotation speed of the rotator was 6 rpm. The infrared spectra of the samples were recorded by VERTEX 70 (Burker, Germany). The phase identification of sintered microspheres was done by using D/max-2500 X-ray diffraction (Rigaku, Japan). A Hitachi S-5500 scanning electron microscope (Hitachi, Japan) was used to observe the microstructure of the microspheres and homogeneity of the neodymium element in microspheres. An XRF spectrometer (Thermo Fisher, China) was used to measure the mass fraction of CeO_2 and Nd_2O_3 in the microspheres.

3 Results and discussion

3.1 Characterization of sol precursor containing citrate salts

As previous investigation indicated, the Ce^{4+} and Nd^{3+} of the precursor solution would exist in the forms of $Ce(OH)_4$ and $Nd(OH)_3$ in the gelled microspheres prepared by internal gelation process [27, 28]. The citrate salts have two existing forms, namely $[MCit·xH_2O]$ and $[M_2(HCit)_3·2H_2O]$, where $M=Ce^{3+}$ and Nd^{3+}, Cit stands for $(C_6O_7H_5)^{3-}$ and HCit for $(C_6O_7H_6)^{2-}$ [23]. The states of citrate salts in the gelled microspheres were characterized by Fourier-transform infrared (FT-IR) spectroscopy and is shown in Fig. 1. Figure 1 displays a typical infrared spectrum of citrate salts, whose characteristic bands are at 1577 cm^{-1} and 1384 cm^{-1} [24]. The characteristic bands of HMTA, urea, nitrate, and citric acid disappear, which indicate that HMTA, citric acid,and urea were hydrolyzed completely. The difference of the infrared spectra between $[MCit·xH_2O]$ and $[M_2(HCit)_3·2H_2O]$ is whether there are four bands in the region 1380–1460 cm^{-1}. The citrate salt with four bands in its infrared spectra in the region is $[M_2(HCit)_3·2H_2O]$ [23].

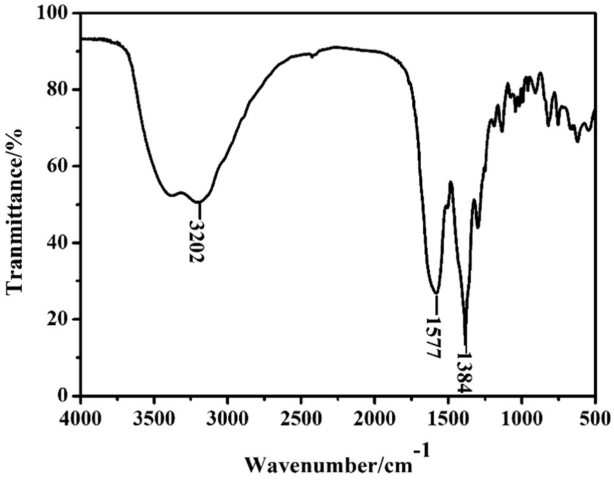

Fig. 1 Infrared spectrum of gelled microspheres prepared by citrate salts

It can be concluded that citrate salt in the gelled microspheres was [MCit·xH_2O].

3.2 Preparation of composite microspheres with 30 wt% Nd_2O_3

Since the typical IMF contain 30 wt% of MA, composite microspheres with 30 wt% Nd_2O_3 prepared with the $M(OH)_m$ (M=Ce^{4+} and Nd^{3+}) were compared with microspheres prepared with the [MCit·xH_2O] (M=Ce^{3+} and Nd^{3+}). Microspheres were prepared with the $M(OH)_m$ that the $NH_3{\cdot}H_2O/Ce^{4+}$ molar ratio was 1 and [MCit·xH_2O] as precursors. In order to investigate the difference of the preparation of CeO_2–Nd_2O_3 between $M(OH)_m$ and [MCit·xH_2O] microspheres, mass fractions of Nd_2O_3 in the sintered microspheres were determined by the XRF spectrometer, as shown in Table 1. As can be seen from Table 1, Δm was the difference of the determined value and theoretical value; the determined value of Nd_2O_3 in the sintered microspheres prepared by $M(OH)_m$ was different from the theoretical value with the difference of −9.52 wt%, which indicates that a large amount of Nd^{3+} was lost in the aging and washing processes. Figure 2 is the distribution of Nd^{3+} in a crosssection of the sintered microspheres prepared using $M(OH)_m$ and [MCit·xH_2O] as precursors. It was recorded with the line scanning of SEM. As can be seen from Fig. 2a, an obvious concentration gradient existed in the microspheres, and the concentration of Nd^{3+} at the edge of the microspheres was higher than that in the center. This was presumably attributed to the large difference of the solubility product constant Ksp between $Ce(OH)_4$ (2×10^{-48}) and $Nd(OH)_3$ (Ksp = 3.2×10^{-22}). The results indicated that the transformation of Ce^{4+} into $Ce(OH)_4$ and Nd^{3+} to $Nd(OH)_3$ did not occur simultaneously. Transformation of Ce^{4+} into $Ce(OH)_4$ started much earlier than that of Nd^{3+} into $Nd(OH)_3$. During the aging process in the gelled microspheres, water was produced and released out of the microspheres. The neodymium ion Nd^{3+} that had not been transformed into $Nd(OH)_3$ can be dissolved in the water. When the water was carried out of the microspheres, the Nd^{3+} ions dissolved in the water were also carried out of the microspheres, which led to the loss of Nd^{3+} in the gelled microspheres. When the gelled microspheres were washed with 0.5 M $NH_3{\cdot}H_2O$, whose pH was 11.47, Nd^{3+} could be transformed into $Nd(OH)_3$ completely. The gelation process of the microspheres prepared with $M(OH)_m$ as a precursor is schematically demonstrated in Fig. 3.

However, there was almost no loss of Nd^{3+} in the microspheres prepared by [MCit·xH_2O], as shown in Table 1. As can be seen in Fig. 2b, no concentration gradient existed in the microspheres, and the distribution of Nd^{3+} was homogeneous, because of the small difference of formation constants between [CeCit·xH_2O] with the lgK of 9.85 and [NdCit·xH_2O] with the lgK of 9.70. The gelation process of microspheres prepared with [MCit·xH_2O] as a precursor is schematically demonstrated in Fig. 4.

Since the pH has an important effect on the gel formation, the effect of $NH_3{\cdot}H_2O/Ce^{4+}$ molar ratio on the composite microspheres should also be investigated. Table 2 shows the effect of $NH_3{\cdot}H_2O/Ce^{4+}$ molar ratio on the

Table 1 Mass fraction of Nd_2O_3 in the sintered microspheres determined by X-ray fluorescence spectrometer

Precursor	Theoretical value (wt%)	Determined value (wt%)	Δm (wt%)
$M(OH)_m$ ($NH_3{\cdot}H_2O/Ce^{4+}$ (molar ratio) = 1)	30	20.48	−9.52
[MCit·xH_2O]	30	30.10	+0.10

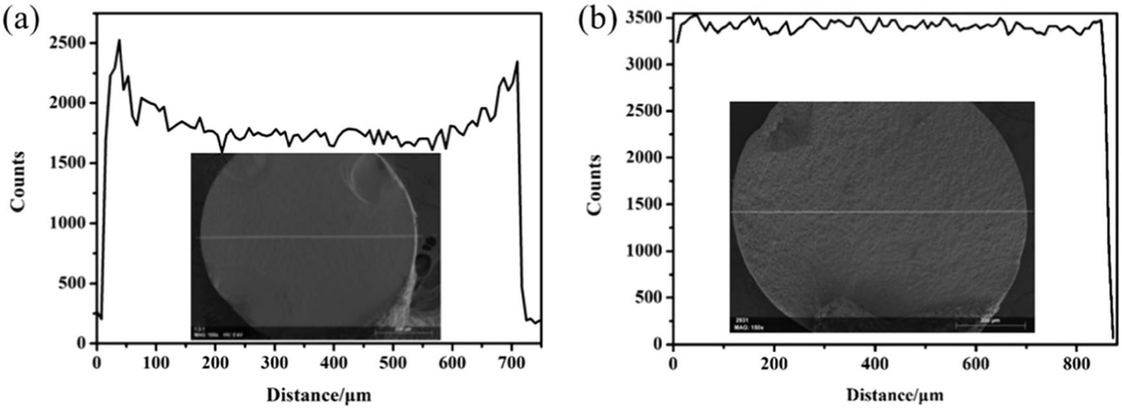

Fig. 2 The distribution of Nd^{3+} in a cross section of the sintered microspheres prepared by $M(OH)_m$ **a** and [MCit·xH_2O] as precursors **b**

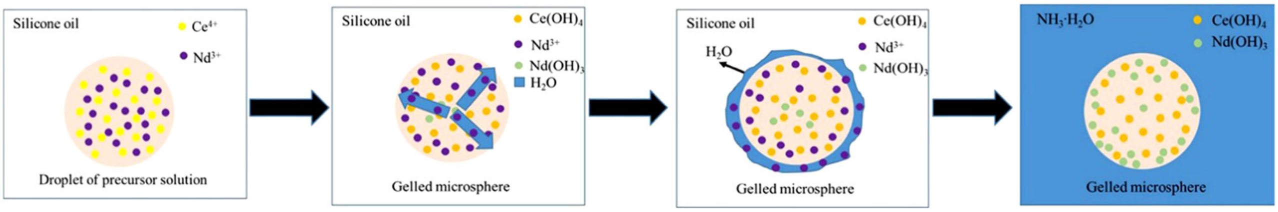

Fig. 3 The gelation process of microspheres prepared with cerium hydroxide and neodymium hydroxide

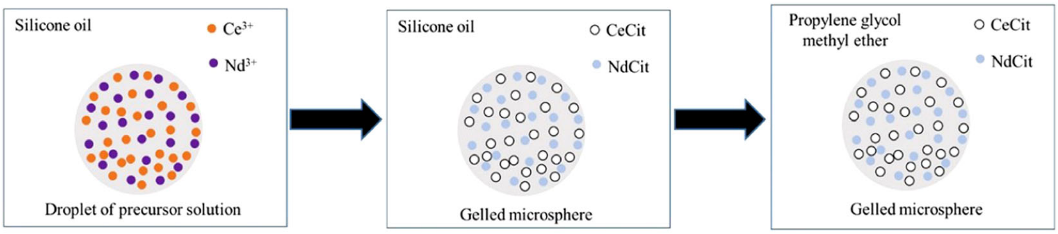

Fig. 4 The gelation process of microspheres prepared with citrate salts

Table 2 Mass fraction of Nd_2O_3 in the sintered microspheres prepared with $M(OH)_m$ with different $NH_3 \cdot H_2O/Ce^{4+}$ molar ratios

$NH_3 \cdot H_2O/Ce^{4+}$ molar ratio	Theoretical value (wt%)	Determined value (wt%)	Δm (wt%)
2	30	20.95	−9.05
2.5	30	21.83	−8.17
3	30	23.27	−6.73
3.5	30	26.85	−3.15

composite microspheres prepared with cerium hydroxide as the precursor, with the $NH_3 \cdot H_2O/Ce^{4+}$ molar ratio varying from 2 to 3.5. With the increasing of the $NH_3 \cdot H_2O/Ce^{4+}$ molar ratio, the mass fraction of Nd_2O_3 in the sintered microspheres became higher with the differences varying from −9.05 to −3.15 wt%. It indicates that more Nd^{3+} was retained during the aging and washing processes.

Although the $NH_3 \cdot H_2O/Ce^{4+}$ molar ratio varied to 3.5, significant differences between the determined value and the theoretical value of Nd_2O_3 in the sintered microspheres prepared with $M(OH)_m$ as the precursor still existed, as shown in Table 2. The sharp increase of the viscosity of the precursor solution is considered to be an onset of the gelation. As can be seen from Fig. 5, the onset earlier with the $NH_3 \cdot H_2O/Ce^{4+}$ molar ratio went from 1 to 3.5. The increase in the $NH_3 \cdot H_2O/Ce^{4+}$ molar ratio led to the increase in the mass fraction of Nd_2O_3 in the sintered microspheres, but the stability of the precursor solution got worse. The stabilization time of the sol had been shortened to 20 min, when the $NH_3 \cdot H_2O/Ce^{4+}$ molar ratio was 3.5. The results indicate that the more ammonia was added to the solution, the more effectively hydrolysis processes were eliminated and the faster hydroxide was formed.

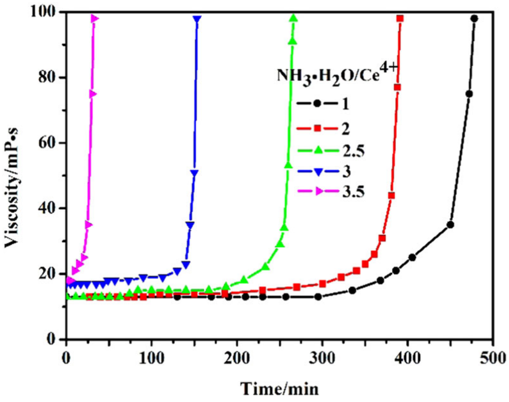

Fig. 5 The variation in the viscosity of the precursor solutions with different $NH_3 \cdot H_2O/Ce^{4+}$ molar ratios

3.3 Preparation of CeO_2–Nd_2O_3 microspheres with citrate salts as precursor

As discussed in the "Preparation of composite microspheres with 30 wt% Nd_2O_3" section, the determined mass fraction of Nd_2O_3 in composite microspheres prepared by $[MCit \cdot xH_2O]$ highly coincides with the theoretical value. Different quantities of $Nd(NO_3)_3 \cdot 6H_2O$ were added into the precursor solution to study whether the addition of Nd^{3+} affect the stability of precursor solution and the performance of CeO_2–Nd_2O_3 microspheres.

Figure 6 shows the variation in pH (*a*) and viscosity (*b*) of the precursor solutions, with different contents of Nd^{3+}. As shown in Fig. 6a, with the increase of Nd^{3+} in the precursor solution, the initial and ultimate pH of the precursor solution became slightly lower. As shown in Fig. 6b, the onset of gelation became slightly lower with the increase of Nd^{3+}. The results indicate that the stability of precursor solutions did not change much with the increase of Nd^{3+}.

Mass fractions of Nd_2O_3 in the sintered microspheres prepared by [MCit·xH_2O], with different contents of Nd^{3+}, were measured by XRF spectrometry and the results are presented in Table 3. Very small differences existed between the determined value and the theoretical value, indicating that the determined mass fraction of Nd_2O_3 in composite microspheres highly coincides with the theoretical value. The results demonstrate that the addition of Nd^{3+} did not affect the gelation process of [MCit·xH_2O] in the microspheres.

Figure 7 is the surface of the sintered microspheres with different mass fractions of Nd_2O_3. Figure 7 indicates that the microspheres have good sphericity. Figure 8 is the cross section of the sintered microspheres with different mass fractions of Nd_2O_3. The cross sections are porous, and are composed of irregularly shaped particles, which is a feature present in the preparation of all lanthanide oxides [24]. All results indicate that the addition of Nd^{3+} did not affect the microstructure of microspheres.

Figure 9 is the Nd^{3+} distribution in cross section of the sintered microspheres with different mass fraction of Nd_2O_3. Figure 9 indicates that, a small undulation exists in the distribution of Nd^{3+} in the microspheres, which was mainly caused by topographical variation of the cross sections of the sintered microspheres. Without this undulation,

Table 3 Mass fraction of Nd_2O_3 in the sintered microspheres prepared by citrate salts with different contents of Nd^{3+}

Theoretical value (wt%)	Determined value (wt%)	Δm (wt%)
5	4.59	−0.41
10	9.38	−0.62
15	14.99	−0.01
20	20.26	+0.26
25	25.21	+0.21
30	30.10	+0.10

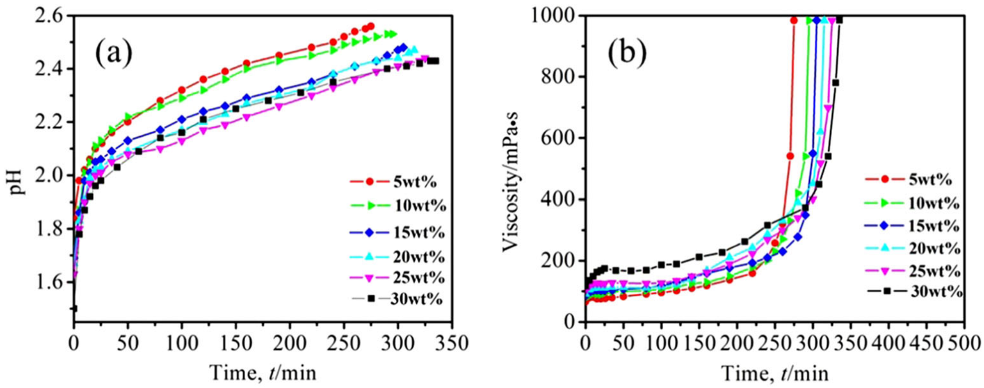

Fig. 6 The variation in pH **a** and viscosity **b** of the precursor solutions with different contents of Nd^{3+}

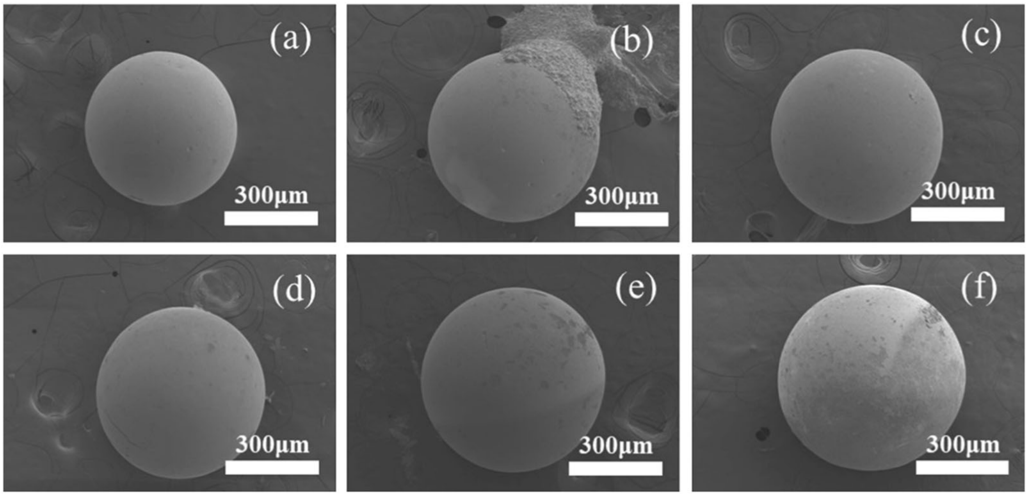

Fig. 7 The surface of the sintered microspheres with different mass fractions of Nd_2O_3: **a** 5 wt%; **b** 10 wt%; **c** 15 wt%; **d** 20 wt%; **e** 25 wt%; **f** 30 wt %

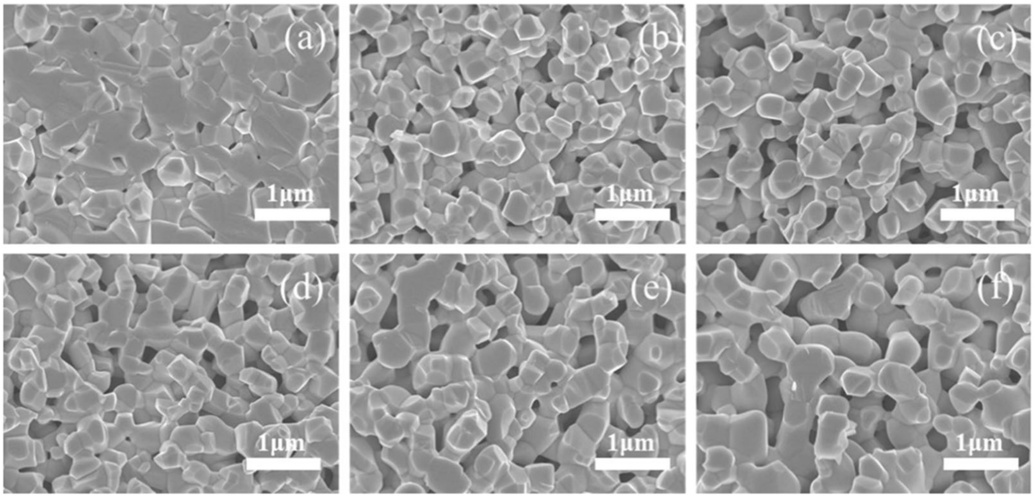

Fig. 8 The cross section of the sintered microspheres with different mass fractions of Nd_2O_3: **a** 5 wt%; **b** 10 wt%; **c** 15 wt%; **d** 20 wt%; **e** 25 wt%; **f** 30 wt%

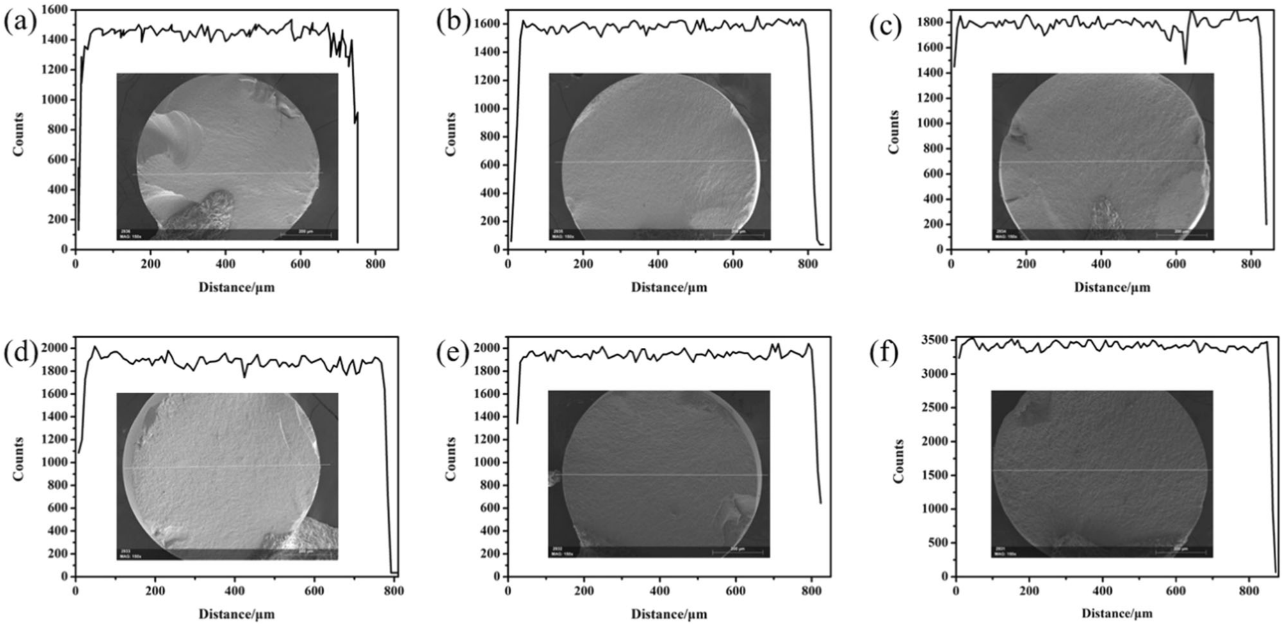

Fig. 9 The distribution of Nd^{3+} in a cross section of the sintered microspheres, with different mass fractions of Nd_2O_3: **a** 5 wt%; **b** 10 wt%; **c** 15 wt%; **d** 20 wt%; **e** 25 wt%; **f** 30 wt%

the distribution curves were basically a horizontal straight line. The results indicate that no concentration gradient existed in the microspheres, and the distribution of Nd^{3+} was homogeneous.

The crystalline structure of the sintered microspheres was determined using XRD. Figure 10 is the XRD patterns of sintered microspheres, with different mass fractions of Nd_2O_3. As we can see from Fig. 10a, all of the samples show diffraction peaks of $Ce_{0.75-x}Nd_{0.25+x}O_{1.85}$ solid solution (JCPDS Card No. 28-0266) and CeO_2 (JCPDS Card No. 81-0792). As shown in Fig. 10b, the deviation of the XRD peak toward the lower angle indicates that Ce^{4+} ions were progressively replaced by Nd^{3+} ions, leading to the expansion of the lattice parameter, in accordance with the Vegard's law. The results indicated that the phase of the composite microspheres was ceria-based solid solution, with the composition of $Ce_{0.75-x}Nd_{0.25+x}O_{1.85}$ and CeO_2.

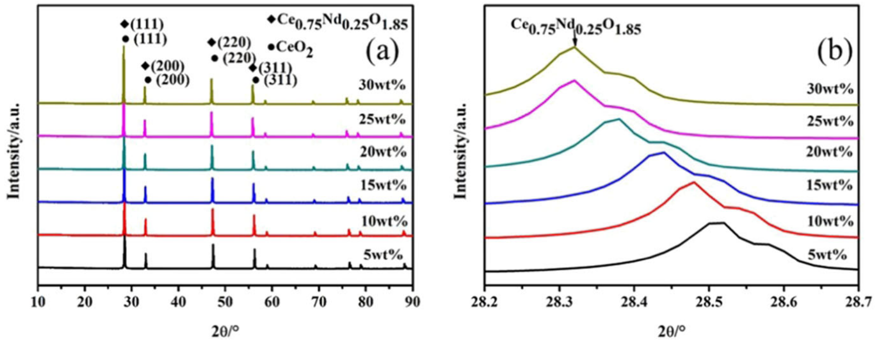

Fig. 10 The XRD patterns of sintered microspheres with different mass fractions of Nd_2O_3

4 Conclusions

CeO_2–Nd_2O_3 microspheres have been prepared by internal gelation process, with $M(OH)_m$ and $[MCit{\cdot}xH_2O]$ ($M{=}Ce^{3+}$, Ce^{4+}, and Nd^{3+}, Cit is $(C_6O_7H_5)^{3-}$) as precursors, respectively. The preparation process of composite microspheres with $M(OH)_m$ ($M{=}Ce^{4+}$ and Nd^{3+}) led to large losses of Nd^{3+}. However, there was no loss of Nd^{3+} in the preparation process of composite microspheres with $[MCit{\cdot}xH_2O]$ ($M{=}Ce^{3+}$ and Nd^{3+}) as a precursor. Compared with microspheres prepared with $M(OH)_m$, the mass fraction of Nd_2O_3 in composite microspheres prepared with $[MCit{\cdot}xH_2O]$ as precursor highly coincided with the theoretical value. The distribution of Nd^{3+} in the sintered composite microspheres was homogeneous. The CeO_2–Nd_2O_3 microspheres prepared with citrate salts as precursors were composed of $Ce_{0.75-x}Nd_{0.25+x}O_{1.85}$ and CeO_2.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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