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Preparation and thermodynamic equilibrium analysis of neodymium disilicate *via* sol-precipitation and sintering

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Neodymium disilicate powders were synthesized *via* a sol-precipitation method with different precipitants (i.e., ammonia, ammonium bicarbonate and urea) and subsequent sintering. The samples were characterized by X-ray diffraction. In addition, a theoretical relationship between neodymium ion concentrations in different precipitation equilibrium solutions was also investigated and analyzed based on thermodynamic equilibrium calculation. The results show that the precipitant type has an impact on the phase compositions of the precursors and the sintered products. In the synthesis, neodymium ions can be completely precipitated as amorphous neodymium hydroxide with ammonia as a precipitate at pH 8~9. For ammonium bicarbonate as a precipitate, the precursor type is related to both carbon concentration and pH value. The excessive hydroxide forms neodymium hydroxycarbonate in a heated urea solution. The possible formation mechanism of silicon sol in the presence of different precipitants was discussed.

Keywords: Precipitant, Precursor, Neodymium disilicate, Thermodynamis.

Introduction

Inorganic pigments are widely used in the field of ceramic decoration [1-3]. As is known, the coloring ions of ceramic pigments are from mainly transition metal elements. However, some ceramic pigments contain a certain amount of heavy metal elements, which are strictly controlled due to the corresponding environmental protection issues [4-7]. Due to special structure and low toxicity, rare-earth ions are also widely used as colorants in ceramic pigments [8, 9]. In addition, some functional ceramic pigments are reported, such as effect pigments [10, 11], luminescent pigments [12, 13], phosphorescent pigments [14, 15] and near-infrared reflective pigments [16-19]. Moreover, recent work [20, 21] revealed that neodymium disilicate (i.e., $Nd_2Si_2O_7$) powder can be applied as a functional ceramic pigment with allochroic effect under various illuminants. $Nd_2Si_2O_7$ powder has a violet red color under an incandescent lamp, while presents a blue color under a fluorescent lamp. The mechanism of color change under different illuminations was discussed in detail in a previous work [22].

Solid-state reaction and sol-gel methods are the main preparation routes for $Nd_2Si_2O_7$ pigment [20-22]. However, solid-state reaction usually requires harsh reaction conditions, such as high temperatures and/or long treatment time [23, 24]. Although sol-gel method can achieve a low-temperature preparation, it needs long-reaction time and precursors with severe agglomeration during drying, leading to the formation of a poor dispersibility of the resultant powder. In a previous study [25], $Nd_2Si_2O_7$ powder was synthesized *via* a sol-precipitation method with different precipitants. This sol-precipitation method is a relatively simple way for the synthesis of $Nd_2Si_2O_7$ pigment. However, different precipitants have a greater impact on the phase composition of the precursor and the final product. The relevant reasonable explanations on the precipitation process of the precursor powder with different precipitants are not reported so far.

As is well known, thermodynamic equilibrium analysis is an effective method for describing the precipitation process of ceramic materials. Many studies [26-28] reported that the thermodynamic equilibrium calculation could establish the equilibrium diagram to provide a theoretical guide for the precipitation reaction. Li et al. [29] investigated the precipitation process of silicate species in $(NH_4)_2WO_4$-$(NH_4)_2CO_3$-NH_3-H_2O system by thermodynamic analysis. Their experimemtal results consisted with the theoretical calculation.

In this paper, neodymium disilicate powders were synthesized *via* a sol-precipitation method with different precipitants (i.e., ammonia, ammonium bicarbonate and urea) and subsequent sintering. The phase compositions of the precursors and the sintered products with different precipitants were discussed. In addition, the thermodynamic equilibrium parameters of precursors in different precipitation equilibrium solutions were also

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calculated and discussed based on the thermodynamic data and mass conservation.

Experimental

The main ingredients include neodymium nitrate tetraethyl orthosilicate (TEOS, $C_8H_{20}O_4Si$, 98 wt.%, Guangzhou Chemical Reagent Factory, China) and hexahydrate ($Nd(NO_3)_3 \cdot 6H_2O$, 99.5 wt.%, Ganzhou Ruihua Rare-earth Co. Ltd., China). Ammonia (NH_4OH, 25 wt.%), ammonium bicarbonate (NH_4HCO_3, analytical grade) and urea (($NH_2)_2CO$, 99.0 wt.%) as precipitants were purchased from Tianjin Fuchen Chemical Reagent Factory, China. Polyethylene glycol (PEG-10000, analytical grade) was used as a surfactant. Absolute ethanol (C_2H_5OH, 99.7%) and deionized water were obtained from Guangzhou Qianghui Bose Instrument Co. Ltd., China.

$Nd(NO_3)_3 \cdot 6H_2O$ and TEOS with a molar ratio of 1:1 were dissolved in 400 ml alcohol-water solution. 2.5 g PEG-10000 was firstly added into the mixture solution above, and then the mixture was added in dropwise into the precipitant solution (2 mol/L NH_4OH or NH_4HCO_3) to keep the solution pH values 8-9 under vigorous stirring at room temperature. After 12 h, the resultant suspension was filtered and washed for three times with deionized water, and dried at 60 °C for 24 h. For ($NH_2)_2CO$ as a precipitant, the concentration ratio of ($NH_2)_2CO$ and the total metal ions was 15:1. The mixture solution was heated to 95 °C and kept at this temperature for 6 h. The precipitate was filtered, washed and dried by using the same procedure above. The dried precipitates were ground in an agate mortar and calcined at 1,200 °C for 5 h, respectively.

The phase compositions of the precursor and sintered product were determined by a model PW-1710 X-ray diffractometer (XRD, Philips Co. Ltd., The Netherlands), using Cu $K\alpha$ radiation.

Results and Discussion

Fig. 1 shows the XRD patterns of the synthesized samples with different precipitants. The precursor obtained with NH_4OH is amorphous $Nd(OH)_3$ phase (JCPDS No. 83-2035). When the sintering temperature reaches 1,200 °C, the tetragonal $Nd_2Si_2O_7$ (JCPDS No. 22-1177) is the main crystalline phase for the sample synthesized with NH_4OH (see Fig. 1(a)). For the precursor obtained with NH_4HCO_3, there are some obvious diffraction peaks in the XRD pattern, which coincides with a unknown phase of $Nd_2(CO_3)_3 \cdot xH_2O$. In some previous studies [30, 31], the precursor obtained with ($NH_4)_2CO_3$ as a precipitant could be $Nd_2(CO_3)_3 \cdot$ 2.5H_2O, $Nd_2(CO_3)_3 \cdot 4H_2O$ or $Nd_2(CO_3)_3 \cdot 8H_2O$. After the precursor produced with NH_4HCO_3 is sintered at 1,200 °C, the main crystalline phases are $Nd_4Si_3O_{12}$ (JCPDS No. 42-0171), Nd_2SiO_5 (JCPDS No. 40-0284)
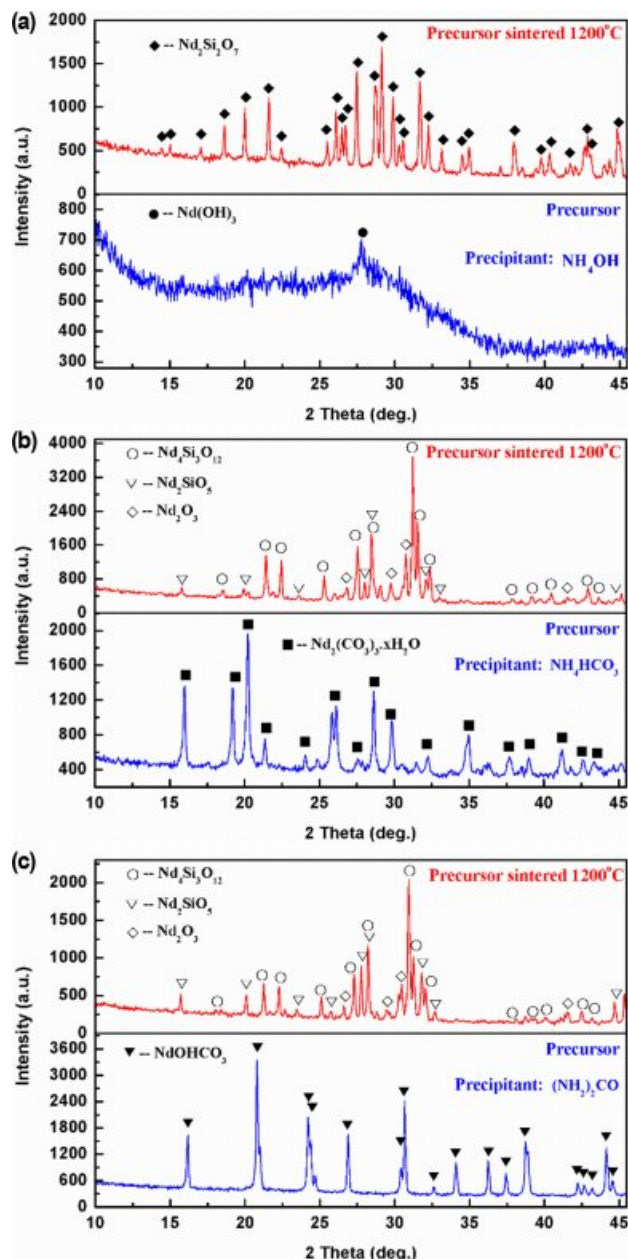

Fig. 1. XRD patterns of prepared samples with different precipitants, (a) NH_4OH, (b) NH_4HCO_3 and (c) ($NH_2)_2CO$.

and Nd_2O_3 (JCPDS No. 43-1023) (see Fig. 1(b)). The XRD pattern for the precursor obtained with ($NH_2)_2CO$ is in agreement with that for $NdOHCO_3$ (JCPDS No. 27-1296). The main crystalline phases of the precipitate sintered at 1,200 °C are also $Nd_4Si_3O_{12}$, Nd_2SiO_5 and Nd_2O_3 (see Fig. 1(c)). After sintering, the phase compositions of the precursors prepared with different precipitants are inconsistent, indicating a poor element (i.e., Si and Nd) homogeneity of the precursors. In order to explain the result above, the reaction processes of the systems with different precipitants should be further analyzed based on thermodynamic equilibrium calculation.

For the prepared precursors, the neodymium element

is precipitated as different precipitates. Two variables such as temperature and pressure are usually constants for the precipitation process in the solution. Therefore, in this study, the diagram of the precipitated ion concentration and pH value at different precipitation equilibrium solutions are drawn for further discussion.

In the system of Nd^{3+}-NH_4OH-H_2O (NH_4OH as a precipitant), the relevant reactions are shown in Table 1. Based on the principle of mass balance, the mathematical model of $\lg[Nd]_T$ vs pH value can be deduced, where $[Nd]_T$ is the total concentration of Nd in equilibrium solution. The concentration is used instead of the activity for the calculation. The total concentration of Nd can be obtained by

$$[Nd]_T = [Nd^{3+}]_h + [Nd(OH)^{2+}]_h \qquad (1)$$

where $[Nd^{3+}]_h$ and $[Nd(OH)^{2+}]_h$ are the concentration of Nd^{3+} and $Nd(OH)^{2+}$, respectively. The mathematical relationships of $[Nd^{3+}]_h$ and $[Nd(OH)^{2+}]_h$ can be expressed as follows:

$$[Nd(OH)^{2+}]_h = [Nd^{3+}]_h \cdot [OH^-] \cdot 10^{5.50} \qquad (2)$$

$$[Nd^{3+}]_h = [OH^-]^{-3} \cdot 10^{-21.49} \qquad (3)$$

where $[OH^-]$ is the concentration of OH^- in the equilibrium solution. According to Eqs. (2) and (3), Eq. (1) can be re-written as

$$\lg[Nd]_T = 20.51 - 3pH + \lg(1 + 10^{pH-8.50}) \qquad (4)$$

The diagram of $\lg[Nd]_T$ vs pH can be proposed according to Eq. (4), as shown in Fig. 2. Clearly, in the whole pH value range, the concentration of Nd in the equilibrium solution sharply decreases with the increase of pH value, which is attributed to the formation of $Nd(OH)_3$ (see Fig. 1(a)). Moreover, a high pH value of equilibrium solution is beneficial for the precipitation of Nd ions. When the pH value is 8~9, the concentration of Nd ions is the range of 10^{-3}~10^{-6} mol/L. In this experiment, the pH value of the equilibrium solution is 8.72 before the precursor is filtered, which can be defined as an almost complete precipitation. Zhu et al. [33] found that $Nd(OH)_3$ nanoparticles with different morphologies can be synthesized using a microemulsion-precipitation method with NH_4OH as a precipitant in the presence of cetyltrimethyl ammonium bromide.

Table 1. Equilibrium formulas and constants of Nd^{3+}-NH_4OH-H_2O system (25 °C)

Number	Formula	$\lg K$	Ref.
1	$NH_4^+ = H^+ + NH_3$	-9.25	[27]
2	$H_2O = H^+ + OH^-$	-14.00	[29]
3	$Nd(OH)_3 = Nd^{3+} + 3OH^-$	-21.49	[32]
4	$Nd(OH)^{2+} = Nd^{3+} + OH^-$	-5.50	[32]

Arunachalam et al. [34] also reported that a facile chemical precipitation method was used to prepare $Nd(OH)_3$ nanopowder at an ambient temperature without the addition of any surfactants.

In the system of Nd^{3+}-NH_4HCO_3-H_2O (NH_4HCO_3 as a precipitant), the hydrolysis equation of NH_4HCO_3 can be expressed by

$$NH_4HCO_3 + H_2O \rightarrow H_2CO_3 + NH_4OH \qquad (5)$$

The other relevant reactions are listed in Table 2. Based on the principle of mass balance, the mathematical model of $\lg[Nd]_T$ vs pH value is deduced, where $[Nd]_T$ is the total concentration of Nd ions in the equilibrium solution. The concentration is used instead of the activity for the calculation. The total concentration of Nd ions can be expressed by

$$[Nd]_T = [Nd^{3+}]_c + [Nd(OH)^{2+}]_c \qquad (6)$$

where $[Nd^{3+}]_c$ and $[Nd(OH)^{2+}]_c$ are the concentration of Nd^{3+} and $Nd(OH)^{2+}$, respectively. The mathematical relationships of $[Nd^{3+}]_c$ and $[Nd(OH)^{2+}]_c$ can be obtained as follows:

$$[Nd(OH)^{2+}]_c = [Nd^{3+}]_c \cdot [OH^-] \cdot 10^{5.50} \qquad (7)$$

$$[Nd^{3+}]_c = [CO_3^{2-}]^{-3/2} \cdot 10^{-16.49} \qquad (8)$$

where $[OH^-]$ and $[CO_3^{2-}]$ are the concentrations of OH^- and CO_3^{2-} in the equilibrium solution, respectively. According to the mass balance of the system, the concentrations of OH^- and CO_3^{2-} can be established by

$$[C]_T = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] \qquad (9)$$

where $[C]_T$ is the total concentration of C in the
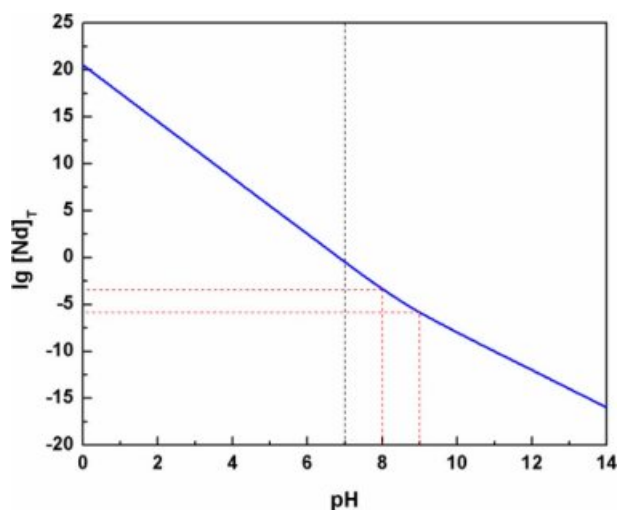
Fig. 2. The $\lg[Nd]_T$ vs pH value diagram of Nd^{3+}-NH_4OH-H_2O system.

equilibrium solution. Moreover, $[CO_3^{2-}]$, $[HCO_3^-]$ and $[H_2CO_3]$ are the concentrations of CO_3^{2-}, HCO_3^- and H_2CO_3, respectively. The mathematical relationships of $[HCO_3^-]$ and $[H_2CO_3]$ can be obtained as follows:

$$[HCO_3^-] = [CO_3^{2-}] \cdot 10^{10.33-pH} \tag{10}$$

$$[H_2CO_3] = [HCO_3^-] \cdot 10^{6.35-pH} \tag{11}$$

Based on Eqs. (10) and (11), Eq. (9) can be rearranged by

$$[CO_3^{2-}] = \frac{[C]_T}{1 + 10^{10.33-pH} + 10^{16.68-2pH}} \tag{12}$$

According to Eqs. (7), (8) and (12), Eq. (6) can be deduced as

$$\lg[Nd]_T = -16.49 + \frac{3}{2} \cdot \lg(1 + 10^{10.33-pH} + 10^{16.68-2pH})$$
$$+ \lg(1 + 10^{pH-8.50}) - \frac{3}{2} \cdot \lg[C]_T \tag{13}$$

For the given values of $[C]_T$ at a certain pH value, the diagram of $\lg[Nd]_T$ *vs* pH value can be obtained from Eq. (13) by a computer software named Origin 8.0.

The $\lg[Nd]_T$ *vs* pH value diagram of the Nd^{3+}-NH_4HCO_3-H_2O system with different total carbon concentrations at equilibrium is shown in Fig. 3. Clearly, the patterns of the $\lg[Nd]_T$ *vs* pH curves with different total carbon concentrations are similar. The concentration of Nd ions sharply decreases with the increase of pH value in the range of 7~10, which is attributed to the formation of $Nd_2(CO_3)_3$. A further increase of pH value results in the increase of Nd ion concentration due to the partial dissolution of $Nd_2(CO_3)_3$. In fact, precipitates with a low solubility are preferentially precipitated in the equilibration solution [29]. That is, the lower position of the curve is beneficial to the formation of the precipitate in the $\lg[Nd]_T$ *vs* pH value diagram. According to the theoretical calculation, the precipitate may be $Nd_2(CO_3)_3$ or $Nd(OH)_3$, when NH_4HCO_3 is used as a precipitant. When the $[C]_T$ value is 10^{-6} mol/L, the precipitate is $Nd_2(CO_3)_3$ in the pH value range of 7.0~8.3. The precipitate is $Nd(OH)_3$ in

the pH value range of 8.3~14.0. Moreover, the pH value range of $Nd_2(CO_3)_3$ presence becomes greater with the increase of $[C]_T$ value. In this experiment, the $[C]_T$ value exceeds 0.01 mol/L. The precipitate is thus $Nd_2(CO_3)_3$ for the equilibrium solution in the pH value range of 8~9. Due to the special structure of Nd element, neodymium carbonate generally exists as hydrated carbonates. Liu et al. [36] found that neodymium carbonate with an orthorhombic system was synthesized using NH_4HCO_3 as a precipitant, which contained a certain amount of water. Zhu et al. [37] reported that $Nd_2(CO_3)_3 \cdot 8H_2O$ with various morphologics and sizes was synthesized using a microemulsion-assisted solvothermal method in the presence of Na_2CO_3. In addition, there also can be formed poorly-ordered nanoparticulate precursors, as termed amorphous amorphous neodymium carbonate [38].

In the system of Nd^{3+}-$CO(NH_2)_2$-H_2O ($CO(NH_2)_2$ as a precipitant), the hydrolysis of $CO(NH_2)_2$ can be expressed as follows:

$$CO(NH_2)_2 + 3H_2O \xrightarrow{heat} CO_2 + 2NH_4OH \tag{14}$$
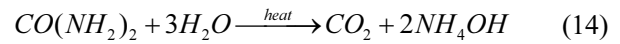
The hydrolysate is similar to that of Eq. (5). However, the hydrolysis process of $CO(NH_2)_2$ requires auxiliary heating. In this experiment, the hydrolysis temperature is kept at 95 °C. At this temperature, the relevant equilibrium constants are difficult to obtain. According to the XRD result in Fig. 1(c), the precipitate obtained in the presence of $(NH_2)_2CO$ is neodymium hydroxycarbonate (i.e., $NdOHCO_3$). The main reactions for the formation of $NdOHCO_3$ can be expressed as follows:
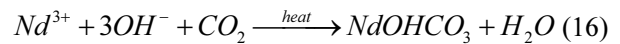
$$NH_4OH \rightarrow NH_4^+ + OH^- \tag{15}$$

$$Nd^{3+} + 3OH^- + CO_2 \xrightarrow{heat} NdOHCO_3 + H_2O \tag{16}$$

Table 2. Equilibrium formulas and constants of Nd^{3+}-NH_4HCO_3-H_2O system (25 °C).

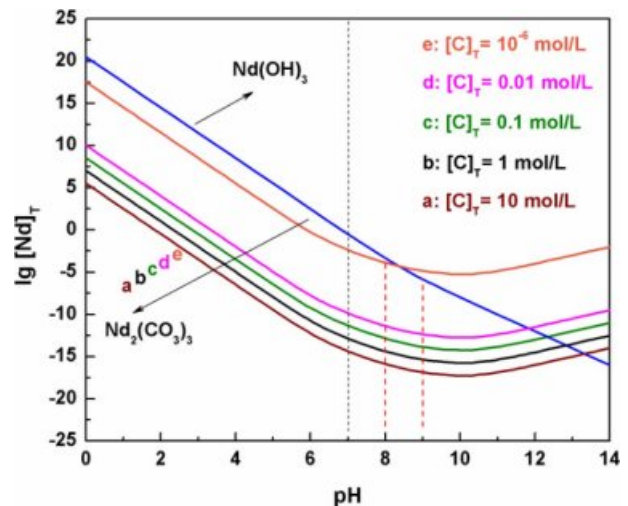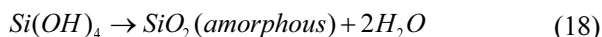| Number	Formula	lg K	Ref.
1	$NH_4^+ = H^+ + NH_3$	-9.25	[27]
2	$H_2O = H^+ + OH^-$	-14.00	[29]
3	$Nd(OH)_3 = Nd^{3+} + 3OH^-$	-21.49	[32]
4	$Nd(OH)^{2+} = Nd^{3+} + OH^-$	-5.50	[32]
5	$H_2CO_3 = H^+ + HCO_3^-$	-6.35	[29]
6	$HCO_3^- = CO_3^{2-} + H^+$	-10.33	[29]
7	$Nd_2(CO_3)_3 = 2Nd^{3+} + 3CO_3^{2-}$	-32.97	[35]

Fig. 3. The $\lg[Nd]_T$ *vs* pH value diagram of Nd^{3+}- NH_4HCO_3-H_2O system with different total carbon concentrations at equilibrium.

From Table 2 (see No. 3 and No.7), the equilibrium constant of $Nd_2(CO_3)_3$ is smaller than that of $Nd(OH)_3$, indicating that $Nd_2(CO_3)_3$ is preferentially precipitated. However, in the hydrolysis solution of $(NH_2)_2CO$, hydroxide concentration is much higher than that of carbon dioxide. The excessive hydroxide may thus cause the formation of $NdOHCO_3$ in the heated equilibrium solution. In fact, a ultrafine $NdOHCO_3$ powder was also synthesized using $(NH_2)_2CO$ as a precipitant by a hydrothermal method [39]. Some studies showed reaction temperature and pressure both have important effects on the formation of $NdOHCO_3$. Tahara et al. [40] synthesized hexagonal and orthorhombic $Nd(CO_3)OH$ *via* a hydrothermal reaction at 220 ºC and different pressures. Dentric $NdOHCO_3$ nanostructures were prepared using a facile hydrothermal approach [41].

For the prepared precursors, the silicon element is aggregated in the form of silicon sol, which is the result of hydrolysis and condensation of TEOS. The hydrolysis reaction of TEOS in abbreviated form can be given as

$$Si(OC_2H_5)_4 + 4H_2O \xrightarrow{catalyst} Si(OH)_4 + 4C_2H_5OH \tag{17}$$
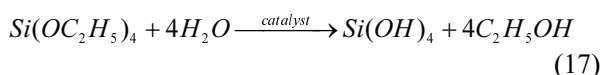
The condensation of silicon oxide can be expressed as

$$Si(OH)_4 \rightarrow SiO_2(amorphous) + 2H_2O \tag{18}$$

In the sol process of silicon alkoxide, generally, a homogeneous catalyst is used to facilitate the hydrolysis reaction since the reaction rate of hydrolysis is slow. Brinker et al. [42] proved that all the hydroxyl groups of $Si(OH)_4$ in hydrolysis reaction of TEOS are derived from water. Iler et al. [43] also proposed the mechanism for the basic hydrolysis of TEOS. The hydrolysis process of TEOS can be affected by some parameters like pH value, time and H_2O/Si molar ratio as well [44-46]. Noted that in general, the condensation reaction of silicon hydroxide is much faster than the hydrolysis reaction of silicon alkoxide.

In alkaline solution, the hydroxyl anions attack Si directly, leading to the abatement of Si-O bond and the acceleration of -OC_2H_5 group cleavage [43]. In this work, three reagents (i.e., NH_4OH, NH_4HCO_3 or $(NH_2)_2CO$) are selected as catalysts to promote the reaction of hydrolysis of TEOS, respectively. When a catalyst is NH_4OH, the hydroxide ions formed by the ionization of ammonia water can effectively attack Si, which is beneficial to the complete hydrolysis of TEOS. However, the other reagents (i.e., NH_4HCO_3 and $(NH_2)_2CO$) need to be hydrolyzed to form ammonia and then partially ionized, leading to the incomplete hydrolysis reaction. Therefore, there is a small amount of residual Nd_2O_3 that are not reacted due to the lack of silicon element, when NH_4HCO_3 or $(NH_2)_2CO$ is a catalyst.

Conclusions

Neodymium disilicate powders were prepared by a sol-precipitation method with different precipitants (i.e., ammonia, ammonium bicarbonate and urea) and subsequent sintering. The reaction processes of the systems with different precipitants were analyzed based on thermodynamic equilibrium calculation.

When NH_4OH was used as a precipitate, the precursor was amorphous $Nd(OH)_3$. The precursor obtained with NH_4HCO_3 was a unknown phase of $Nd_2(CO_3)_3 \cdot xH_2O$. $NdOHCO_3$ was the crystal phase of the precursor obtained in the presence of $(NH_2)_2CO$. In the system of Nd^{3+}-NH_4OH-H_2O, a high pH value for the equilibrium solution was beneficial for the precipitation of Nd ions. In the system of Nd^{3+}-NH_4HCO_3-H_2O, the precursor type was related to both carbon concentration and pH value. A low pH value was beneficial to $Nd_2(CO_3)_3$ formation, while a high pH value was beneficial to $Nd(OH)_3$ formation. In the system of Nd^{3+}-$CO(NH_2)_2$-H_2O, the excessive hydroxide could form $NdOHCO_3$ in the heated equilibrium solution. Only a precursor with NH_4OH could transform to a single $Nd_2Si_2O_7$ phase after it was sintered at 1,200 ºC for 5 h, which was due to the incomplete hydrolysis of TEOS in the presence of NH_4HCO_3 or $(NH_2)_2CO$.

Acknowledgements

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