Structural evolution and synthesis mechanism of ytterbium disilicate powders prepared by cocurrent chemical coprecipitation method

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Abstract

Ytterbium disilicate powders were synthesized by cocurrent chemical coprecipitation method. The influence of Si/Yb molar ratio and calcination temperature on compositions and structures of $\text{Yb}_2\text{Si}_2\text{O}_7$ products were investigated. The formation mechanism and thermal behavior of precursor as well as the phase evolution of $\text{Yb}_2\text{Si}_2\text{O}_7$ were also discussed in depth. Results show that pure $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ powders with nanoscale size can be obtained from the precursor with Si/Yb molar ratio of 1.1 after being calcinated at temperatures above 1200 °C. The $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor is an amorphous polymer cross-linked with $[\text{Si-O-Yb}]$ -chain segments which are formed through Yb atoms embedding in the $[\text{Si-O-Si}]$ -network. After a continuous dihydroxylation and structural ordering, the amorphous precursor transformed to $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$ crystals by atomic rearrangement. Elevated calcination temperature can induce to the coordination structures and environment evolutions of structural units and then converted to stable (Si_2O_7) groups and (YbO_6) polyhedrons, which results in the formation of $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$.

1. Introduction

SiC ceramic matrix composites (CMCs) have been regarded as new generation hot section materials applied in gas turbine engines due to their excellent high-temperature capability, which can provide critical support for leading the revolutionize development of advanced vehicle technologies. However, SiC CMCs exhibit lower durability in high-velocity combustion resulting from the rapid surface recession in oxidizing and water vapor environment [1, 2]. As a result, environmental barrier coatings (EBCs) emerged as the times require for protecting SiC CMCs substrate materials against corrosive media [3–7].

With the development of EBCs system and corresponding iteration of advanced materials, rare earth silicates have been focused on the new generation EBCs materials due to their excellent environment resistance [4, 7–11]. Among them, ytterbium disilicate ($\text{Yb}_2\text{Si}_2\text{O}_7$) and ytterbium monosilicate (Yb_2SiO_5) are demonstrated as promising candidate materials for EBCs based on their superior high-temperature phase stability, excellent chemical and mechanical compatibility with SiC, lower oxygen permeability and so on [9, 12–16]. Especially, the $\text{Yb}_2\text{Si}_2\text{O}_7$ has a much closer coefficient of thermal expansion (CTE, $3.7\text{--}4.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) than that of Yb_2SiO_5 ($6.5\text{--}7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) to SiC-CMCs substrate (ca. $4.5\text{--}5.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) [17], which is benefit to improve the bond strength between EBCs and substrate, as well as retard the thermal stress in EBC coating during thermal cycling. In addition, $\text{Yb}_2\text{Si}_2\text{O}_7$ has better thermochemically compatible with thermally grown SiO_2 than that of Yb_2SiO_5 , which is highly competitive in ensuring system stability of EBC coating. Furthermore, the $\text{Yb}_2\text{Si}_2\text{O}_7$ materials also exhibit excellent corrosion resistance of water vapor and $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (CMAS). B.T. Richards et al. [18] prepared a bi-layer $\text{Yb}_2\text{Si}_2\text{O}_7/\text{Si}$ EBC coating on SiC substrates through an optimal design of CTE matching, which exhibited excellent steam-cycling durability at 1316 °C in a flowing 90% $\text{H}_2\text{O}/10\%\text{O}_2$ environment. Zhong et al. [19] developed a tri-layer $\text{Yb}_2\text{SiO}_5/\text{Yb}_2\text{Si}_2\text{O}_7/\text{Si}$ EBC coating on SiC CMCs by atmospheric plasma spray technique. After 40–50 thermal cycles between room temperature and 1350 °C, the $\text{Yb}_2\text{Si}_2\text{O}_7$ layer still

maintained better structural integrity resulting from their outstanding thermal shock resistance. Zhao et al. [20] investigated the CMAS resistance of $\text{Yb}_2\text{Si}_2\text{O}_7$ and Yb_2SiO_5 coatings. Results indicated that the $\text{Yb}_2\text{Si}_2\text{O}_7$ coating shows better CMAS corrosion resistance than that of Yb_2SiO_5 coating at 1300 °C, which is attributed to the reductive diffusion transport capacity of molten salt compositions. Stolzeburg et al. [21] studied the interaction of $\text{Yb}_2\text{Si}_2\text{O}_7$ and Yb_2SiO_5 materials with CMAS engine deposits at 1300 °C. After 96 hours exposure, no discernable reaction can be observed between $\text{Yb}_2\text{Si}_2\text{O}_7$ and CMAS, thus the $\text{Yb}_2\text{Si}_2\text{O}_7$ material displayed superior chemical stability in CMAS corrosion environment. Comprehensive analysis shows that $\text{Yb}_2\text{Si}_2\text{O}_7$ materials exhibit great potential applying in EBCs system.

Up to date, EBCs system are generally built by thermal spraying technical, which are strongly dependent on the processing of coating and the quality of raw materials. For rare earth silicates, the chemical compositions and crystal structures have a significantly influence on their mechanical and corrosion resistance [17, 22–25]. Rare earth silicates powders are mainly synthesized by solid-state reaction [19, 26–30], hydrothermal syntheses [31], sol-gel [32–36] and chemical coprecipitation methods [37]. For solid-state reaction method, rare earth silicates powders were synthesized through direct reaction between rare earth oxide and silicon oxide at relatively higher calcination temperature, however, the obtained powders usually have micron-scale and exhibit agglomeration to some extent. In addition, impurity phases will mingle in the final powder products resulting from inadequate reaction and insufficient mixing of raw materials, which leads to uniform composition of the rare earth silicates materials. Hydrothermal synthesis method was also conducted to synthesize rare earth silicates in current research. However, higher specific surface area of the ultrafine powders (20–30 nm) brings great difficulties to the preparation of coating. Besides inherent impurities are difficult to eliminate through the optimization of synthesis process, which limits its further development. Comparatively, sol-gel and chemical coprecipitation methods are effective approaches to prepared moderate particle size, uniform composition and high purity rare earth silicates by controlling the stoichiometric molar ratio of starting materials. Up to date, the relative synthesis mechanism of rare earth silicates by sol-gel method have not been clarified yet. In our previous studies, a novel cocurrent chemical coprecipitation method have been developed to synthesize Yb_2SiO_5 [38] and dysprosia-stabilized zirconia (DySZ) powders [39], which has advantages of low cost, composition controllable, easy access to high purity and homogeneous powder materials.

According to the ionic and synthesis temperature [22, 23, 40–44], rare earth disilicates ($\text{RE}_2\text{Si}_2\text{O}_7$) have seven different crystal types, which were denoted by capital letters A, B, C, D, E, F, and G in the original work of Felsche et al. [22, 23, 42]. However, only three crystal types of $\text{Yb}_2\text{Si}_2\text{O}_7$ can be identified by X-ray diffraction, $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$ has triclinic structure with space groups $P\bar{1}$ or $P1$, meanwhile $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ and $\gamma\text{-Yb}_2\text{Si}_2\text{O}_7$ present monoclinic structure with space groups $C2/m$, and P_{21}/c , respectively. In addition, $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ have been confirmed to be only stable phase in high temperature, which are endow with high expectations to satisfy the application requirements of EBC coating in extremely deteriorated environment of gas turbine engines.

In our present work, $\text{Yb}_2\text{Si}_2\text{O}_7$ powders were synthesized via a cocurrent chemical coprecipitation method for the first time. The influence of Si/Yb molar ratio in starting materials and calcination temperature on phase composition and crystal structure of $\text{Yb}_2\text{Si}_2\text{O}_7$ were investigated. The structural evolution as well as synthesis mechanism of $\text{Yb}_2\text{Si}_2\text{O}_7$ were also delineated in detail.

2. Experiments

2.1. Raw materials

In current study, reagent-grade ytterbium oxide (Yb_2O_3 , purity $\geq 99.99\%$), hydrochloric acid (HCl , $\approx 36\%$ wt. %), tetraethyl orthosilicate (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\approx 28\%$ wt. % silicon oxide) and ammonia water ($\text{NH}_3\cdot\text{H}_2\text{O}$, $\approx 25\%$ wt. % in water) were used as main raw materials. Ethanol ($\text{C}_2\text{H}_5\text{OH}$, $\approx 96\%$ wt. %, Analytical purity) and deionized water were used as auxiliary materials.

2.2. Synthesis of $\text{Yb}_2\text{Si}_2\text{O}_7$ powders

The $\text{Yb}_2\text{Si}_2\text{O}_7$ powders were synthesized by a cocurrent chemical coprecipitation method which has been developed in our previous work [38]. Different from traditional chemical coprecipitation method, the liquid reaction system of precursor formation can maintain a stable pH environment based on the well-designed reaction mother liquor and controllable current speed of precipitant, which can promote the precipitation product formed more evenly.

In the first instance, Yb^{3+} containing solution was prepared through the chemical reaction of Yb_2O_3 powders with boiled hydrochloric acid solution. Meanwhile, TEOS hydrolysate was prepared by mixing TEOS, ethyl alcohol and deionized water with volume ratio of 1:4:2. Subsequently, the two solutions were mixed and stirred, forming a homogeneous metal-ion solution. In addition, the precipitant was prepared by diluting the ammonia with isovolumetric deionized water. After that, the metal-ion solution and precipitant were respectively injected into a stirred ammonia solution which has a pH value of 9–10. The pH value of the reaction environment was controlled by adjusting the injection rate of precipitant. After the injection, the obtained precipitation solution was stirred for 30 min and then aged for 24 h. Then, the remaining Cl^- and NH_4^+ were removed sequentially with deionized water and ethanol to prepare a wet $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor. Finally, the precursor powders was obtained after drying at $110\text{ }^\circ\text{C}$ for 12 h, and then calcined for 10 h in ambient atmosphere with a temperature range of $400\text{--}1400\text{ }^\circ\text{C}$. Based on the phase diagram of the $\text{Yb}_2\text{O}_3\text{--SiO}_2$ system [12, 42], the $\text{Yb}_2\text{Si}_2\text{O}_7$ precursors were synthesized with different Si/Yb molar ratios (9:10, 10:10 and 11:10), which are noted as Y_1 , Y_2 and Y_3 respectively. The associated $\text{Yb}_2\text{Si}_2\text{O}_7$ materials calcined at various temperatures are labeled in form of Y_{n-c} , in which $n = 1, 2$ or 3 , c is the calcination temperature.

2.3. Characterization

The crystallographic phases of the calcined powders were identified by an X-ray diffractometer (XRD, D8 advanced, Bruker AXS, Germany, Cu K α radiation, $\lambda = 0.15406$ nm) in a range of $2\theta = 5\text{--}85^\circ$. Thermal behavior of the precursor was analyzed by a thermal analyzer (STA 449C, Netzsch, Germany). Thermogravimetric (TG) and differential scanning calorimetry (DSC) curves were obtained through heating the precursor in air with $10^\circ\text{C}/\text{min}$ from room temperature to 1200°C . The morphology and crystal structure of the as-prepared $\text{Yb}_2\text{Si}_2\text{O}_7$ powders were analyzed by transmission electron microscopy (TEM, Tecnai G2 F20, FEI CO., USA). The phase composition and structural evolution from precursor to final product were studied by Fourier transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet iS50, USA) with wave number in range of $400\text{--}4000\text{ cm}^{-1}$.

3. Results And Discussion

3.1 Phase composition of the synthesized products

$\text{Yb}_2\text{Si}_2\text{O}_7$ precursors with different Si/Yb molar ratios were calcined at a temperature range from 900°C to 1400°C , the corresponding XRD patterns are shown in Fig. 1. It can be seen that no crystallization peak can be detected in the XRD patterns of obtained products calcined at 900°C , indicating that the calcined products still maintain amorphous state. After calcination at 1000°C , obvious crystallization behavior can be observed from the XRD patterns. However, the calcined products exhibit different phase compositions with each other. With the Si/Yb molar ratio of precursors less than or equal to the standard stoichiometry of $\text{Yb}_2\text{Si}_2\text{O}_7$, the calcined products (Y_{1-1000} and Y_{2-1000}) are composed of unsteady $\text{X1-Yb}_2\text{SiO}_5$ (JCPDS Card No.52-1187) and $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$ (JCPDS Card No.301439). Meanwhile, $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$ and $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ (JCPDS Card No. 25-1345) coexist in the calcined product (Y_{3-1000}) which was transformed from the precursor with Si/Yb molar ratio higher than the standard stoichiometry of $\text{Yb}_2\text{Si}_2\text{O}_7$. Correlation analysis confirmed that the synthesis temperatures of $\text{X1-Yb}_2\text{SiO}_5$, $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$ and $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ are between 900°C and 1000°C . In addition, low-temperature phase $\text{X1-Yb}_2\text{SiO}_5$ has been identified with synthesis temperature lower than 950°C in our previous research [38]. With the calcination temperature elevated to 1100°C , significant compositional change of the Y_{1-1100} and Y_{2-1100} can be observed in the XRD patterns. It can be seen from Fig. 1a that, the Y_{1-1100} is composed of $\text{X2-Yb}_2\text{SiO}_5$ (JCPDS Card No.40-0386), $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ and trace of $\text{X1-Yb}_2\text{SiO}_5$, and the characteristic diffraction peaks of $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$ disappeared. In addition, only $\text{X2-Yb}_2\text{SiO}_5$ and $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ can be identified in Y_{2-1100} (Fig. 1b). Compared with that calcined at 1000°C , $\text{X2-Yb}_2\text{SiO}_5$ and $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ were formed in the Y_{1-1100} and Y_{2-1100} . Differently, the Y_{3-1100} has the same phase compositions as Y_{3-1000} , in which the peak intensity of $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ increased significantly, as shown in Fig. 1c. Therefore, it can be inferred that the phase transformations from $\text{X1-Yb}_2\text{SiO}_5$ to $\text{X2-Yb}_2\text{SiO}_5$ and from $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$ to $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ occurred during the calcination process within $1000^\circ\text{C}\text{--}1100^\circ\text{C}$. As the calcination temperature comes to 1200°C , the $\text{X1-Yb}_2\text{SiO}_5$ and $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$ transformed into $\text{X2-Yb}_2\text{SiO}_5$ and $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ completely in the Y_{1-1200} and Y_{3-1200} , respectively. Further raising the calcination temperatures to 1300°C and 1400°C , the calcined products exhibit the constant phase composition as that after calcined at 1200°C , exhibiting

excellent phase stability. Somewhat differently, the calcined products $Y_{1-1200/1300/1400}$ and $Y_{2-1200/1300/1400}$ are composed of $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ and $X2\text{-Yb}_2\text{SiO}_5$, while the calcined products $Y_{3-1200/1300/1400}$ consist of pure $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ phase. There is no doubt that complex structural and phase evolutions occurred in $\text{Yb}_2\text{Si}_2\text{O}_7$ products between 900 ~ 1200 °C in our present work. The calcination temperature plays a major role in determining the phase composition and structure of $\text{Yb}_2\text{Si}_2\text{O}_7$ products, and thermally stable components can be obtained in $\text{Yb}_2\text{Si}_2\text{O}_7$ powders with the calcination temperature above 1200 °C.

The effect of Si/Yb molar ratio on phase composition of as-synthesized $\text{Yb}_2\text{Si}_2\text{O}_7$ powders were summarized and illustrated in Fig. 2a. It can be seen that both phase composition and crystal structure of the calcined products were strongly affected by the molar ratio of Si/Yb. With the molar ratio of 0.9 and 1.0, Yb_2SiO_5 impurities always exist in the final products, which cannot be eliminated by the elevated calcination temperature. In addition, the ending temperature for stable component are 1200 °C and 1100 °C, respectively, indicating that the increased molar ratio of Si/Yb promoted the transformation from X1 to $X2\text{-Yb}_2\text{SiO}_5$, which has been confirmed in our previous work [38]. As the Si/Yb molar ratio increased to be 1.1, $\text{Yb}_2\text{Si}_2\text{O}_7$ powders were synthesized without impurities in the temperature range of 1000 °C~1400 °C. It is worth noticed that the ending temperature for obtaining thermally stable $\text{Yb}_2\text{Si}_2\text{O}_7$ powders is 1200 °C, which is higher than that prepared with Si/Yb molar ratio of 1.0. The phase transformation from α to $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ might be inhibited by the increased Si/Yb molar ratio. In a word, the final calcination temperature as well as the Si/Yb molar ratio of starting materials have significantly influence on the components and crystal structures of $\text{Yb}_2\text{Si}_2\text{O}_7$ powders. In our present work, desired $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ powders were successfully synthesized through the optimization of calcination temperature and Si/Yb molar ratio. Figure 2b shows the XRD pattern of $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ powders prepared at 1200 °C. It can be seen that the as-prepared $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ powders exhibit favorable crystallinity and are free of impurities.

3.2 Microstructure of the $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ powders

The morphology and structural characteristics of $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ powders were analyzed by TEM. Figure 3 shows the morphology and microstructure of the $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ powders after calcination at 1200 °C. It can be seen that the $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ powders exhibit irregular shape and have a particle size of about 70 ~ 100 nm (Fig. 3a). In addition, there is obvious agglomeration between $\text{Yb}_2\text{Si}_2\text{O}_7$ particles probably attributing to its high activity, which is different from that of Yb_2SiO_5 powders [31, 35, 38]. Figure 3b illustrates the high-resolution image and corresponding electron diffraction pattern of $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ powders. A set of arranged lattice fringes are discriminated clearly in the HRTEM image, demonstrating that the $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ powders were synthesized with high crystallinity. In addition, the measured interplanar spacing in Fig. 3b is 3.195 Å, which corresponds to the (021) crystal plane of $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$. The SAED (selected area electron diffraction) pattern of $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ is present in top right corner of Fig. 3b, which can be indexed as [01-2] zone axis of $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ with monoclinic symmetry and $C2/m$ space group [42].

3.3 Formation mechanism of $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor

In this study, $\text{Yb}_2\text{Si}_2\text{O}_7$ powders were synthesized by cocurrent chemical coprecipitation method whose mechanism is quite different from that of traditional ones. Therefore, fundamental studies on the structural characteristics and formation mechanism of the $\text{Yb}_2\text{Si}_2\text{O}_7$ precursors were conducted to understand the synthesis process as well as to realize the controllable preparation of $\text{Yb}_2\text{Si}_2\text{O}_7$ powders.

For the purpose of comparison, the precursors of ytterbium oxide (Yb_2O_3) and silicon oxide (SiO_2) were synthesized through the precipitation reaction of YbCl_3 , ethyl orthosilicate with ammonia, respectively, via the same cocurrent coprecipitation method. Figure 4 shows the FTIR spectra of Yb_2O_3 , SiO_2 and $\text{Yb}_2\text{Si}_2\text{O}_7$ precursors. It can be seen that the characteristic absorption peaks of the $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor are significantly different from the other two precursors, resulting from its special chain segment structure. In the FTIR spectra of the Yb_2O_3 , SiO_2 and $\text{Yb}_2\text{Si}_2\text{O}_7$ precursors, the strong and broad absorption peak located at around 3380 cm^{-1} can be assigned to the O-H stretching modes of hydroxyl originated from residual water, ethanol molecules as well as intrinsic hydroxyl groups in precursors [45, 46]. The deformation vibration of H_2O is also observed at 1622 cm^{-1} and 1634 cm^{-1} , which can be attributed to the structural and residual water. In addition, the peaks at 1515 cm^{-1} and 1394 cm^{-1} for Yb_2O_3 precursor as well as 1538 cm^{-1} and 1404 cm^{-1} for $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor were identified to the bending vibration of $-\text{CH}_3/\text{CH}_2$ and stretching vibration of C-O in alkoxy groups of ethanol molecules [47], which has been confirmed in the synthesis process of ytterbium silicate powders [38]. The absence of relevant characteristic peaks in SiO_2 precursor can be benefited to the trace of ethanol residue, which is also certificated by the weaker integral strength of peak at 3382 cm^{-1} . Moreover, the insufficient dealkylation reaction of TEOS in hydrolysis process can also result in the existence of alkyl groups.

It is obviously that the structural differences among the Yb_2O_3 , SiO_2 and $\text{Yb}_2\text{Si}_2\text{O}_7$ precursors were reflected in characteristic absorption peaks ranged from 400 to 1100 cm^{-1} . In the FTIR spectrum of Yb_2O_3 precursor, the absorption peaks located at 667 cm^{-1} and 426 cm^{-1} corresponded to bending vibration of Yb-OH bond and the stretching vibration of Yb-O bonds [46], respectively, none of other vibration mode can be detected. Comparatively, the SiO_2 precursor presents complex chain segment structure.

Researches [45, 48–55] have shown that the cross-linked polymer with spatial-opened skeleton structure will be formed through the hydrolysis and polycondensation of TEOS, in which the $-\text{[Si-O-Si]}-$ network was surrounded by coordinated hydroxyl. In our present work, the SiO_2 precursor was synthesized in a strong alkali environment. Accelerated polycondensation can promote the connection of colloidal particles, resulting in the formation of large-scaled network structure. In the FTIR spectrum of SiO_2 precursor, the 1085 cm^{-1} peak have been proven to be associated with the transverse optical (TO) mode of Si-O-Si asymmetric bond stretching vibration [45, 49]. Meanwhile, the 799 cm^{-1} and 464 cm^{-1} peaks were assigned to symmetric stretching and bending vibration of network Si-O-Si bonds [49, 50, 56], respectively. Moreover, the stretching vibration mode of typical Si-OH bonds reflect in the corresponding

peak at 959 cm^{-1} [49]. During the synthetic process of $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor, Yb^{3+} and TEOS were coprecipitated in ammonia solution. It is worth noticed that the FTIR spectrum exhibits the same characteristics in spectral lines as that of SiO_2 precursor, which indicates that approximated cross-linked polymer with spatial-opened skeleton structure may be formed in the $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor. In our previous work, Yb_2SiO_5 precursor was synthesized with the same method. It is certain that the binding energies of both Si-OH and Yb-OH bonds were influenced with each other, which confirmed the structural difference in chain segments between Yb_2SiO_5 and SiO_2 precursor. Therefore, the obvious offset of characteristic absorption peaks in FTIR spectrum of $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor can also confirm the formation of $-\text{[Si-O-Yb]}-$ network. Similar as the SiO_2 precursor, the 989 cm^{-1} peak can be identified as TO mode of Si-O-Yb asymmetric bond stretching vibration, as well as the 920 cm^{-1} and 472 cm^{-1} peaks correspond to the stretching vibration of Si-OH bonds and bending vibrations of Si-O-Yb bonds, respectively. Moreover, the 688 cm^{-1} peak is assigned to bending vibrations of Yb-OH bond. In the FTIR spectrum of $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor, the Si-O-Si symmetric stretching disappeared significantly, which is also due to the formation of $-\text{[Si-O-Yb]}-$ network.

Figure 5 is the schematic diagram showing the formation mechanism of the $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor. It is undoubtedly that the $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor gone through a series of complicated chemical reactions and structural evolution during the synthesis process. Firstly, the solution containing positive trivalent Yb ions was obtained through the reaction between Yb_2O_3 and hot hydrochloric acid. The solution has strong acidity due to the slightly excessive acid. Meanwhile, the hydrolysis reaction of TEOS was activated by the nucleophilic attack of water molecules on the Si atom when blending with alcohol and water [57]. Subsequently, the hydrolysis process was accelerated by the strong acid environment resulting from the mingle with Yb^{3+} solution. As a results, a lot of monosilicic acids were produced in the cation solution, which is also attributed to the inhibition in polymerization by acidic environment. Therefore, coprecipitation of Yb^{3+} and monosilicic acids was realized by the continuous injection of cation solution into a large volume solution rich in ammonia. During the coprecipitation, the polymerization of monosilicic acids became the dominated process. Researches [51, 58, 59] have shown that silicon oxygen ions will be generated through the dehydrogenation of monosilicic acids, then a nucleophilic attack to Si-OH groups of surrounding monosilicic acids occurred, and finally $-\text{[Si-O-Si]}-$ network formed inevitably resulting from oxygen dimerization reaction. However, the reaction system of $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor is totally different from that of SiO_2 due to the existence of Yb^{3+} , in which the nucleophilic reaction was inhibited. Instead, the electronegative silicon oxygen ions were absorbed by Yb^{3+} as ligands, which induced the formation of ion clusters with Yb^{3+} as core. In the subsequent polycondensation process, the Yb may be embedded as bridging atoms in the $-\text{[Si-O-Si]}-$ network, which resulted in the formation of $-\text{[Si-O-Yb]}-$ network. Different from the SiO_2 precursor, both Si and Yb act as crosslinked atom in $-\text{[Si-O-Yb]}-$ chain links. So, it can be concluded that the $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor were synthesized in the form of cross-linked polymers with bimetallic crosslinking points in $-\text{[Si-O-Yb]}-$ chain segments.

3.4 Thermal behavior of the $\text{Yb}_2\text{Si}_2\text{O}_7$ precursors

The TG-DSC analysis was applied to investigate the thermal behavior of the $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor, and the corresponding curves are shown in Fig. 6. A continuous weight loss can be detected with the increased temperature, and the ceramic yield is about 83.6%. The weight loss can be attributed to the evaporation of adsorbed water and ethanol as well as the removal of bound water and constituent groups in $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor. Based on the mass lost rate, the TG-DSC curves can be divided into four sections (Fig. 6). In section A, the precursor undergone a rapid weightlessness of 13.2% below 300 °C. Within this section, a broad endothermic peak can be observed in the DSC curve, which is attributed to the evaporation of adsorbed water, ethanol as well as to the removal of the bound water. With the temperature increasing from 300 to 500 °C (section B), the weight loss of precursor is about 2.7%. The appearance of exothermic peak can be corresponded to the decomposition of trace organic groups. In section C, the residual carbon was burn out in 500 ~ 800 °C with a minimal loss of weight (ca.1%). In section D, no obvious weight loss can be detected. However, a sharp exothermic peak at 1065°C was clearly observed in the DSC curve, which indicates the crystallization of $\text{Yb}_2\text{Si}_2\text{O}_7$.

Figure 7 shows the FTIR spectra of $\text{Yb}_2\text{Si}_2\text{O}_7$ precursors after calcination at 400 °C~ 900 °C. The $\text{Yb}_2\text{Si}_2\text{O}_7$ precursors present similar characteristic spectra before and after calcination, indicating a high similarity in structure and composition. After calcination at 400 ~ 900 °C, the precursors exist stably in the form of amorphous phase, which is consistent with the fact shown in Fig. 2. In the FTIR spectra, the characteristic absorption peaks located at about 3380 cm^{-1} are mainly associated with the O-H stretching modes of hydroxyl groups in the calcined precursors. The adsorbed water and ethanol molecules as well as the bound water have been removed in calcination process. In addition, the integral strength of 3380 cm^{-1} peaks [49] tends to weaken with the increased temperature, suggesting that the dihydroxylation is in continuous progress during the calcination process in the temperature range of 400 ~ 900 °C. Similarly, the intensities of the characteristic peaks shown in the blue dotted box display a downward tendency except for the peak at 1634 cm^{-1} . Due to the exposure to atmosphere, trace of water will be absorbed on the surface of tested powders with high specific surface area, which is responsible to the constant visible of the peaks at 1634 cm^{-1} [45] and 3380 cm^{-1} . Meanwhile, the other peaks at 1538 cm^{-1} and 1404 cm^{-1} can be attributed to the gradual dealkylation [48]. Previous analysis has shown that the 989 cm^{-1} and 472 cm^{-1} peaks represent the stretching and bending vibrations of Si-O-Yb bonds [45], concurrently the 920 cm^{-1} [48] and 688 cm^{-1} [45] peaks can be assigned to the bending vibrations of Si-OH and Yb-OH bonds in $\text{Yb}_2\text{Si}_2\text{O}_7$ precursors. However, the related characteristic peaks exhibit a significant shift although the calcined precursors remain amorphous. It is visible that the peak position for stretching vibration of Si-O-Yb bonds has shifted from 989 cm^{-1} to 973 cm^{-1} , and those for bending vibration of Si-O-Yb bonds have a deviation to about 500 cm^{-1} . Meanwhile, there are also slight shifts in peak positions for the bending vibrations of Si-OH and Yb-OH bonds. It is worth noting that the intensities of peaks around 970 cm^{-1} and 500 cm^{-1} become stronger with the increased temperature, while that of the peak at around 700 cm^{-1} displayed a decreased trend, which indicated that the polarity of Si-O bond and the symmetry of Si-O-Yb bond are strengthened. Therefore, it can be inferred combining with the TG-DSC analysis that -Si-O-Yb- structure consisted of Yb, Si and O atoms only was formed by the removal of hydroxyl and continuous

ordering. The removal of hydroxyl and the continuous ordering and are the dominant factors in resulting to the change of peak position and peak intensity in FTIR spectra of the calcined precursors. For comparison, the FTIR spectra of Yb_2O_3 and SiO_2 are also provided in Fig. 7. It is obvious that no characteristic peaks of both Yb_2O_3 and SiO_2 can be observed in the FTIR spectra of the calcined precursors, which further confirmed that the structure form of $[\text{Si-O-Yb}]$ - network was relatively stable below 900 °C.

3.5 Phase transformation and synthesis mechanism of $\text{Yb}_2\text{Si}_2\text{O}_7$ powders

The various phase compositions of $\text{Yb}_2\text{Si}_2\text{O}_7$ powders obtained at different calcination temperature confirmed that a phase transformation from $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$ to $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ occurred with the elevated temperatures. Figure 8 displays the crystal structure diagrams of $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$ and $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$. As shown in Fig. 8a and 8c, the α -polymorph $\text{Yb}_2\text{Si}_2\text{O}_7$ includes 22 independent constituent atoms which build isolated $(\text{Si}_3\text{O}_{10})$ chain-like groups, (SiO_4) tetrahedra, (YbO_6) and (YbO_8) polyhedral structural units [22, 40, 42]. Among them, the $(\text{Si}_3\text{O}_{10})$ groups are constituted by three (SiO_4) tetrahedrons with two Si-O-Si bridges, and the adjacent bridges exhibit a significant difference in bond angles. In addition, isolated (SiO_4) tetrahedrons possess high distortion in length and angle of Si-O bonds compared with that of ideal tetrahedrons. In the (YbO_6) and (YbO_8) polyhedral structural units, the Yb atoms were coordinated separately by six and eight oxygens which belong to the $(\text{Si}_3\text{O}_{10})$ groups or (SiO_4) tetrahedrons. It is distinctly different that only (Si_2O_7) groups and (YbO_6) polyhedral structural units exist in the monoclinic $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ crystals [43, 44, 60], as shown in Fig. 8b and 8d. The (Si_2O_7) groups can be considered as a structure with two (SiO_4) tetrahedrons connected through a Si-O-Si bridge with 180° bond angle. In this group, the (SiO_4) tetrahedrons show low degree of distortion. Except for the bridging oxygen, the others can be coordinated with adjacent Yb to form (YbO_6) polyhedral structural units. In despite of the fact that the $\text{Yb}_2\text{Si}_2\text{O}_7$ can exist steadily as α -polymorph in room temperature, it is still a metastable phase in terms of thermal stability [44]. Enough heat input from nearby surroundings can induce the phase transformation towards $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$, in which a twisted structure was transformed into an ideal stretched one due to the energy optimization.

Figure 9 shows the FTIR spectra of $\text{Yb}_2\text{Si}_2\text{O}_7$ precursors after calcination at 1000 °C~ 1200 °C. It was clearly observed that the calcined products exhibit a completely different characteristic peak compared with that after calcination at 900 °C. As we known that the powder products both calcined at 1000 °C and 1100 °C are composed of $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$ and $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$, thus the characteristic absorption peaks of α and $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ are all present in the related FTIR spectra. Meanwhile, the typical FTIR spectrum of $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ was obtained from the pure-phase powder product after calcination at 1200 °C. Therefore, it can be concluded that the peaks located at 1096 cm^{-1} , 980 cm^{-1} , 908 cm^{-1} , 849 cm^{-1} , 565 cm^{-1} , 537 cm^{-1} , 499 cm^{-1} and 472 cm^{-1} are all belong to $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$, which have also been confirmed in the related research works [32]. In the FTIR spectrum, the peaks at 1096 cm^{-1} and 849 cm^{-1} are ascribed to

the stretching vibration of silicon atoms against bridging and non-bridging oxygen atoms in (Si_2O_7) groups [45, 61], respectively. While the 980 cm^{-1} and 908 cm^{-1} peaks [32, 62] correspond to the stretching modes of ytterbium atoms against oxygen atoms in Yb-O-Yb chains normal and subparallel to Si-O-Si chain, respectively. In addition, the 565 cm^{-1} and 537 cm^{-1} peaks can be assigned to the stretching and bending vibrations of Yb-O bonds in (YbO_6), and the peaks at 499 cm^{-1} and 472 cm^{-1} [62, 63] are all associated with the bending vibration of various categories of Si-O bonds. Consequently, it is logical that these peaks located at 1129 cm^{-1} , 1042 cm^{-1} , 1000 cm^{-1} , 946 cm^{-1} , 881 cm^{-1} , 722 cm^{-1} , 693 cm^{-1} , 557 cm^{-1} , 514 cm^{-1} and 429 cm^{-1} could be identified to the characteristic absorption peaks of $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$, the complexity of spectrum can be attributed to the diverse structural units as shown in Fig. 8c.

Unfortunately, there are few reports on the FTIR study of $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$. Research showed that the FTIR characteristic peaks at $1000\text{--}1100\text{ cm}^{-1}$ are mainly from the stretching vibrations of Si-O bonds in Si-O-Si chains for rare earth disilicates [61]. As for $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$, (Si_3O_{10}) chain-like groups are the unique structural unit containing Si-O-Si chain. Thus, the 1042 cm^{-1} and 1000 cm^{-1} peaks should be associated with the stretching vibrations of Si atoms against O atoms in Si-O-Si chains, and the double-peak distribution may be attributed to the difference in bond length and bond angle of various types of Si-O-Si chains in (Si_3O_{10}) groups. In addition, it has been confirmed that the bending vibrations of bridging oxygen bond in Si-O-Si usually give expression to the peaks in the range of $600\text{--}800\text{ cm}^{-1}$ [61, 62], which can provide a tenable inference that the 722 cm^{-1} and 693 cm^{-1} peaks can also trace to the (Si_3O_{10}) groups and correspond to Si-O-Si with difference bond angles. In particular, there is no relative characteristic peak can be detected in the FTIR spectrum of $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$, which is resulted from the D_{3d} symmetrical structure of (Si_2O_7) groups (180° bond angle in Si-O-Si) [61]. Wen et al. [35] investigated the FTIR spectrum of Yb_2SiO_5 and have affirmed the ascription of 930 cm^{-1} and 870 cm^{-1} to asymmetric and symmetric stretching vibrations of Si-O bonds for isolated (SiO_4) tetrahedrons. As the similar structural units in $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$, the corresponding vibration modes of that should be identified to the peaks located at 946 cm^{-1} and 881 cm^{-1} . In which, the 946 cm^{-1} peak may be associated with the asymmetric stretching vibrations of Si-O bonds and the 881 cm^{-1} peak should be assigned to the symmetric stretching vibrations of Si-O bonds in highly distorted (SiO_4) tetrahedrons. Moreover, correlativity researches [34, 44, 61, 62] have shown that the FTIR characteristic peaks located at $500\text{--}600\text{ cm}^{-1}$ and $400\text{--}500\text{ cm}^{-1}$ are usually originated from the stretching vibrations of Yb-O bonds and bending vibrations of Si-O bonds, respectively. So, it can be inferred that the 557 cm^{-1} and 514 cm^{-1} peaks should be assigned to the Yb-O stretching vibrations in (YbO_6) and (YbO_8) groups. Meanwhile, the 429 cm^{-1} peak corresponds to the low-frequency bending vibrations of Si-O bonds from isolated (SiO_4) tetrahedrons or (Si_3O_{10}) groups. Echoed with that the 1129 cm^{-1} peak can be assigned to the high-frequency bending vibrations of the Si-O bonds [34].

Based on the infrared spectrum shown in Fig. 9, it can be seen clearly that the characteristic peaks of $\alpha\text{-Yb}_2\text{Si}_2\text{O}_7$ disappeared gradually with the elevated calcination temperature, a phase transformation from

α to β - $\text{Yb}_2\text{Si}_2\text{O}_7$ happened exactly during the calcination process above 1000 °C. As mentioned earlier, the structural units of β - $\text{Yb}_2\text{Si}_2\text{O}_7$ are composed of (Si_2O_7) groups and (YbO_6) polyhedrons which is completely different from that of α - $\text{Yb}_2\text{Si}_2\text{O}_7$. Therefore, it can be deduced that both of (SiO_4) tetrahedrons and $(\text{Si}_3\text{O}_{10})$ groups experienced structural changes to form (Si_2O_7) groups, as well as (YbO_8) to (YbO_6) polyhedrons. During the process of phase transformation, the external energy plays a role in inducing the breaking of Si-O bonds in (SiO_4) tetrahedrons and $(\text{Si}_3\text{O}_{10})$ groups and then promoted the formation of stable (Si_2O_7) groups, which is responsible to the disappearance of (SiO_4) tetrahedrons and $(\text{Si}_3\text{O}_{10})$ groups characteristic peaks for stretching vibrations in the FTIR spectrum of $\text{Yb}_2\text{Si}_2\text{O}_7$ calcined at 1200 °C. In addition, the characteristic peaks of bending vibration modes were also affected by the structural evolution of (Si_xO_y) groups, including the vanishing of 1129 cm^{-1} and the shift of 429 cm^{-1} peak. It is worth mentioning that the Si-O stretching vibration of Si-O-Si chains in $(\text{Si}_3\text{O}_{10})$ groups disappeared in the FTIR spectrum of $\text{Yb}_2\text{Si}_2\text{O}_7$ calcined at 1100 °C, while the bending vibration of the corresponding Si-O bond are greatly weakened. In addition, the peak of the symmetrical stretching vibration of the (SiO_4) tetrahedron exhibits a significant shape change. It illustrated that the polarity of bridging oxygen bond in Si-O-Si chains decreased and then the bridging oxygen bond broke as well as the peak shape change of the highly distorted (SiO_4) tetrahedron shows an improvement in the symmetry of the isolated (SiO_4) tetrahedron. Therefore, it can be reasonably inferred that $(\text{Si}_3\text{O}_{10})$ groups were divided into (SiO_4) units through the fracture of Si-O-Si and then formed (Si_2O_7) groups of β - $\text{Yb}_2\text{Si}_2\text{O}_7$. As a kind of units owned by both α and β - $\text{Yb}_2\text{Si}_2\text{O}_7$, the characteristic peaks of (YbO_6) polyhedrons can be regarded as located at 565 cm^{-1} , 557 cm^{-1} and 537 cm^{-1} , thus the deviation of 565 cm^{-1} and 557 cm^{-1} peaks as well as the decrease in peak intensity of 537 cm^{-1} peaks can be attributed to the changed structural parameters and coordination environments of (YbO_6) polyhedrons. Similarly, the 514 cm^{-1} peak is regarded as the characteristic vibration modes of Yb-O bonds in (YbO_8) polyhedrons according to the obvious absence in β - $\text{Yb}_2\text{Si}_2\text{O}_7$ resulted from the structural transformation from (YbO_8) to (YbO_6) polyhedrons. Overall, the metastable α - $\text{Yb}_2\text{Si}_2\text{O}_7$ converted to a stable β - $\text{Yb}_2\text{Si}_2\text{O}_7$ through a reconstructive progress.

Figure 10 shows the synthesis mechanism diagram of $\text{Yb}_2\text{Si}_2\text{O}_7$ powders. There have two clear periods during the entire synthetic process of β - $\text{Yb}_2\text{Si}_2\text{O}_7$ powders. In the period of precursor synthesis, a cross-linked polymer with Yb and Si as crosslinking atoms in $[\text{Si-O-Yb}]$ - chain segment was obtained through the embedding of Yb atoms in $[\text{Si-O-Si}]$ - network during the polycondensation process of monosilicic acids, which give the credit to the coprecipitation of Yb ions and monosilicic acids. Subsequently, the amorphous precursor experienced a structural conversion towards to α - $\text{Yb}_2\text{Si}_2\text{O}_7$ through the removal of hydroxyl of $[\text{Si-O-Yb}]$ - network and the continuous ordering of $[\text{Si-O-Yb}]$ - structure in calcination process, in which the $[\text{Si-O-Yb}]$ - structure was broken and restructured gradually, and then resulted in the formation of $(\text{Si}_3\text{O}_{10})$ groups, (SiO_4) tetrahedra, (YbO_6) and (YbO_8) polyhedral structural units. According to the effects of calcination parameters on phase composition of $\text{Yb}_2\text{Si}_2\text{O}_7$ powders, as shown in Fig. 2a, it can be asserted that both increased temperature and extended time had a significant function in realizing the

phase transformation from α to β -Yb₂Si₂O₇. During the transformation process, β -Yb₂Si₂O₇ with near-standard polyhedral structure generated accompanied by the evolution of structure and coordination environment for the structural units of α -Yb₂Si₂O₇ to (Si₂O₇) groups and (YbO₆) polyhedrons.

4. Conclusions

In this work, pure β -Yb₂Si₂O₇ powders with nanoscale size were successfully synthesized by cocurrent chemical coprecipitation method through optimizing the Si/Yb molar ratio and calcination temperature. With the Si/Yb molar ratio of precursor less than or equal to the standard stoichiometry of Yb₂Si₂O₇, Yb₂SiO₅ impurity forms in the powder products. In addition, elevated calcination temperature is beneficial to synthesis the desirable β -Yb₂Si₂O₇ powders. During the coprecipitation process, silicon oxygen ions can be absorbed around Yb³⁺ and acted as ligands to form ion clusters with Yb³⁺ core. Meanwhile, Yb is embedded in the -[Si-O-Si]- network in form of bridging atoms during the subsequent polycondensation process, leading to the formation of crosslinked polymer consisting of -[Si-O-Yb]- chain segments. The thermal behavior of the Yb₂Si₂O₇ precursor is a process of continuous hydroxyl removal and structural ordering of amorphous -[Si-O-Yb]- network. As a metastable phase, α -Yb₂Si₂O₇ will transformed to β -Yb₂Si₂O₇ with near-standard polyhedral structure resulting from the structural and coordination evolutions of constituent units under increased calcination temperature.

Declarations

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Figures

Figure 1

XRD patterns of the as-synthesized powders after calcination at various temperatures: (a) Y1-c; (b) Y2-c; (c) Y3-c

Figure 2

Phase compositions of the as-synthesized $\text{Yb}_2\text{Si}_2\text{O}_7$ powders as a function of Si/Yb molar ratio at various calcination temperature and XRD pattern of $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ powders (a) Phase composition; (b) XRD pattern

Figure 3

Morphology and high-resolution TEM images of the $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ powders: (a) Morphology; (b) HRTEM image with SAED pattern

Figure 4

FTIR spectra of Yb₂O₃, SiO₂ and Yb₂Si₂O₇ precursors

Figure 5

Schematic diagram showing the formation mechanism of Yb₂Si₂O₇ precursor synthesized by cocurrent chemical coprecipitation

Figure 6

TG-DSC curves of the $\text{Yb}_2\text{Si}_2\text{O}_7$ precursor conducted in air atmosphere from room temperature to 1200 °C

Figure 7

FTIR spectra of Yb₂Si₂O₇ precursors after calcination at 400 °C~ 900 °C

Figure 8

Crystal structure diagrams of $\text{Yb}_2\text{Si}_2\text{O}_7$: (a) (c) α - $\text{Yb}_2\text{Si}_2\text{O}_7$; (b) (d) β - $\text{Yb}_2\text{Si}_2\text{O}_7$

Figure 9

FTIR spectra of $\text{Yb}_2\text{Si}_2\text{O}_7$ precursors after calcination at 1000 °C~ 1200 °C

Figure 10

Schematic diagram of the synthesis mechanism for $\text{Yb}_2\text{Si}_2\text{O}_7$