The Synthesis of Single Tetragonal Phase Zirconia by Sol-Gel Route

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Abstract— *Zirconia with tetragonal phase is a widely used functional material to toughen ceramics. At room temperature zirconia usually presents in the less stable form of monoclinic phase. In this paper, room temperature single tetragonal phase zirconia stabilized by yttria was successfully synthesized by a sol-gel route at a relative low temperature (≤1000oC). The calcination mechanism of zirconia was determined by thermogravimetric analysis and differential scanning calorimetry, which indicated that phase formation of zirconia started above 600oC. X-ray diffraction patterns showed stabilized with 3mol % yttria was insufficient to obtain fully single tetragonal phase zirconia. As the content of the stabilizer increased, single tetragonal phase zirconia was obtained as observed by Raman spectrum and X-ray diffraction. With 4mol% yttria content, zirconia remains stable with the desired tetragonal phase at room temperature.*

Keywords— ***Zirconia, tetragonal phase, sol-gel, phase characterization.***

Highlights

(1) nYSZ (n=3, 3.5, and 4) were synthesized by Pechini sol-gel route successfully.
(2) The phase status of 3YSZ, 3.5YSZ, and 4YSZ was investigated.
(3) The 4YSZ with the pure tetragonal phase at room temperature was obtained.

I. INTRODUCTION

Zirconia (ZrO_2) is a widely used ceramic material with high melting point, high strength, and good wear and erosion resistance. ZrO_2 exhibits three crystallographic phases: monoclinic (*m*), tetragonal (*t*), and cubic (*c*). At room temperature, zirconia usually keeps monoclinic phase. Phase transformation of ZrO_2 occurs during heating or cooling processes, with the following transformation equation (1) [1, 2]:

$$\mathit{monoclinic}\ \underset{950℃}{\overset{1000℃\text{-}1170℃}{\rightleftarrows}}\ \mathit{tetragonal}\ \overset{2370℃}{\rightleftarrows}\ \mathit{cubic}\ \overset{2680℃}{\rightleftarrows}\ \text{liquid} \qquad (1)$$

There are two types tetragonal phase of ZrO_2, transformable and non-transformable (metastable tetragonal phase). The non-transformable tetragonal phase ZrO_2 is remarkable resistance and does not undergo the phase transformation to monoclinic phase. It is usually used for thermal barrier coatings due to the good thermomechanical properties [3, 4]. Transformable tetragonal phase ZrO_2 is usually called toughened ceramic. It can be obtained at room temperature by doping with a suitable content stabilizer. The most common stabilizer is Y_2O_3. Martensitic phase transformation *t* to *m* occurs once the stress status within materials changes. This phase transformation has great technological importance. It can absorb the energy of crack propagation, thus restraining it, which is the basis for the transformation toughening of ceramic components. A large amount of surface and interfacial energy is introduced when decreasing the crystallite size to the nanoscale, hence the free energy of phase transformation is different from the micron scale. Therefore, those unstable phases of ZrO_2 can exist in the stable or metastable state at room temperature. Nowadays, low fracture toughness is one of the serious drawbacks of new ceramics, especially for thermal barrier coatings [5-8]. So it is necessary to explore toughening methods for these kinds of ceramics. However, although stabilised or partially stabilised zirconia with yttria (YSZ) has been widely studied by other researchers, either synthesized by solid state reaction, or wet chemical methods such as via sol-gel method, there is lack of studies on using Pechini sol-gel method, which using citric acid as complexing agent and ethylene glycol as surfactant, particularly for the transformable tetragonal phase ZrO_2. The traditional sol-gel method cannot be widely used due to the rare and expensive organometallic precursor and metal alkoxides. By using Pechini sol-gel method, metal salts can be used as precursor that much cheaper than those materials. Furthermore, despite ZrO2 stabilized with different contents of Y_2O_3 has already been studied, there is no study on the phase status of Y_2O_3 with a narrow range content as reported in this paper 3, 3.5, and 4mol%. Within this range, single tetragonal phase ZrO_2 can be synthesized under 1000^{o}C. Moreover, single tetragonal phase ZrO_2 is difficult to be synthesized. They normally synthesized by sol-gel method that consists of both monoclinic and tetragonal phases, plus a little cubic phase. Therefore, In this paper, single transformable tetragonal phase ZrO_2 has been synthesized successfully using Pechini sol-gel method. The calcination mechanism, phase characterization, and Raman shifts were studied.

II. MATERIALS AND METHODS

ZrO_2 cannot keep single tetragonal phase at room temperature, so stabilizers were used to obtain tetragonal phase ZrO_2. The most common and widely used stabilizer is Y_2O_3, so in this paper, zirconia stabilized by yttria with a certain ratio [3YSZ, (3mol% Y_2O_3 stabilized ZrO_2), 3.5YSZ, and 4YSZ] were synthesized.

Single tetragonal phase ZrO_2 has been synthesized using the sol-gel method. The original materials are $ZrOCl_2 \cdot 8H_2O$ (98%, Sigma-Aldrich) and $Y(NO_3)_3 \cdot 6H_2O$ (99.8%, Sigma-Aldrich). According to the stoichiometric ratio, $ZrOCl_2 \cdot 8H_2O$ was firstly dissolved in a solvent (water), stirred until completely dissolved, $Y(NO_3)_3 \cdot H_2O$ added into the aqueous solution, and citric acid added as the complexing agent after $Y(NO_3)_3 \cdot H_2O$ was dissolved. The mixture was stirred until white precipitation was generated. Then, the pH value was adjusted by NH_4OH, which was slowly dripped into the solution until a transparent sol was obtained. The transparent sol was heated in an oven at 80°C to get xerogel, followed by a two-step calcination process: it was calcined at 350°C to remove the citric acid and at target temperature (600°C, 700°C, 800°C, 900°C, and 1200°C) to achieve crystallization. Fine YSZ powders were finally achieved via a 24-hour ball milling.

III. RESULTS AND DISCUSSIONS

3.1 Thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) analysis

The TGA-DSC curves of 3YSZ xerogel are shown in with a 5°C /min heating rate and a 100ml/min gas (nitrogen) rate. The blue line represents the DSC curve, with a small endothermic peak around 233°C, a small exothermic peak around 362°C, followed by an intense exothermic peak at 440°C, whilst at 556°C there is no obvious endothermic or exothermic peaks until 1200°C, but at 1300°C there is an endothermic peak in the DSC curve. According to the TGA curve (green line), the weight of the xerogel samples keep decreasing as the temperature increases until around 550°C, but the decreasing rate slows down in the range of 118°C to 190°C and then recovers at a higher decreasing rate until 550°C. There is no obvious weight loss after 550°C in the TGA curve.

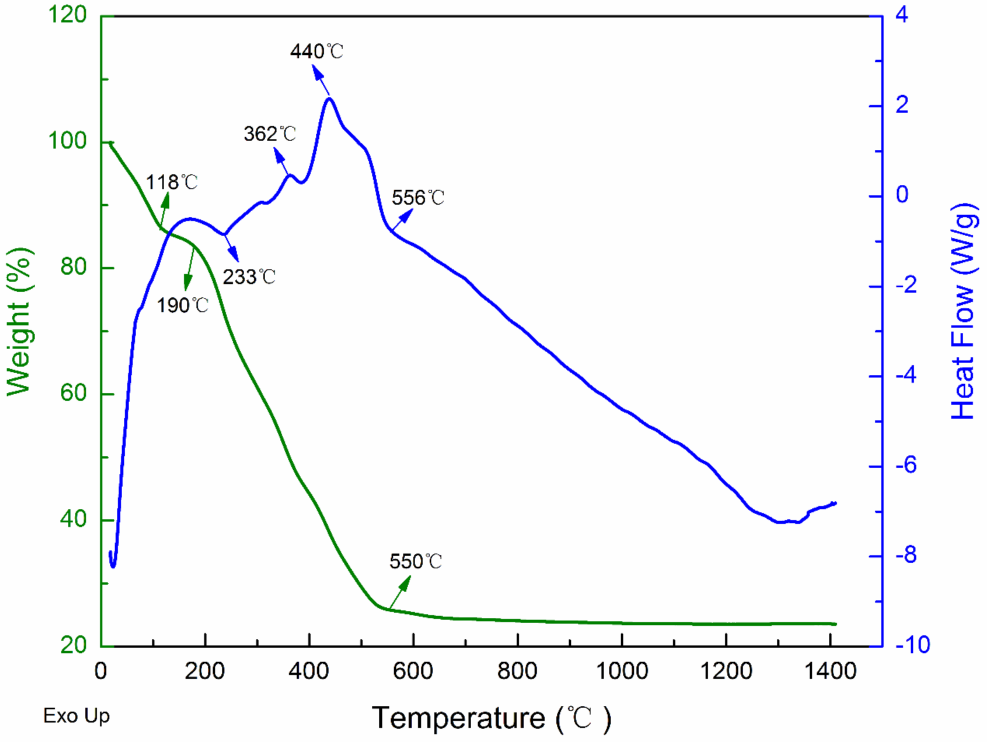

FIGURE 1 TGA-DSC CURVES OF 3YSZ XEROGEL

The small endothermic peaks in the DSC curve around 233°C are attributed to the volatilization of solvent (water) inside the closed hole in the xerogel and low molecular weight organics, which absorb a lot of heat during the volatilization process corresponding to the DSC curve. In the TGA curve, the decreasing weight rate shows a relatively slow rate in that temperature range. The DSC curve shows an exothermic tendency between 233°C to 362°C, with two small exothermic peaks in this temperature range, with the decomposition temperature of tri-ammonium citrate and ammonium nitrate about 185°C; after 185°C they decompose rapidly. Therefore, these exothermic peaks are caused by the decomposition of citrates and nitrates [9]. The combustion decomposition of large molecular weight organics occurs in the range of 362°C to 556°C, which is well illustrated by the intense exothermic peak at 440°C. The rapid weight loss rate of xerogel from 190°C almost stops at 550°C in TGA curve, which is also well explained and corresponds to the exothermic peaks in that temperature range. There is no significant change in the TGA-DSC curves between 600°C and 1300°C. According to the ZrO_2-Y_2O_3 phase diagram, the phase transformation of 3YSZ from the tetragonal to the cubic phase occurs at around 1300°C, confirming that the endothermic peak at 1300°C is due to the phase transformation of ZrO_2. Therefore, it can be speculated that the decomposition of the 3YSZ precursor finishes at the temperature below 600°C, with further crystallization of 3YSZ characterized by XRD patterns.

3.2 Phase characterization by XRD

According to the TGA-DSC results, 3YSZ xerogel has been calcined at different temperatures (600°C, 700°C, 800°C, 900°C, and 1200°C) to obtain the best crystallization and phase distribution. The XRD patterns of 3YSZ calcined at these temperatures are shown in Figure 2. There are no obvious differences in the XRD patterns between sintering at 600°C and 700°C. However, as the calcination temperature increases, some new peaks occur around 30°, 35°, and 65°, and it becomes stronger under a higher calcination temperature. Figure 2 also shows that the XRD patterns become sharper as the calcination temperature increases.

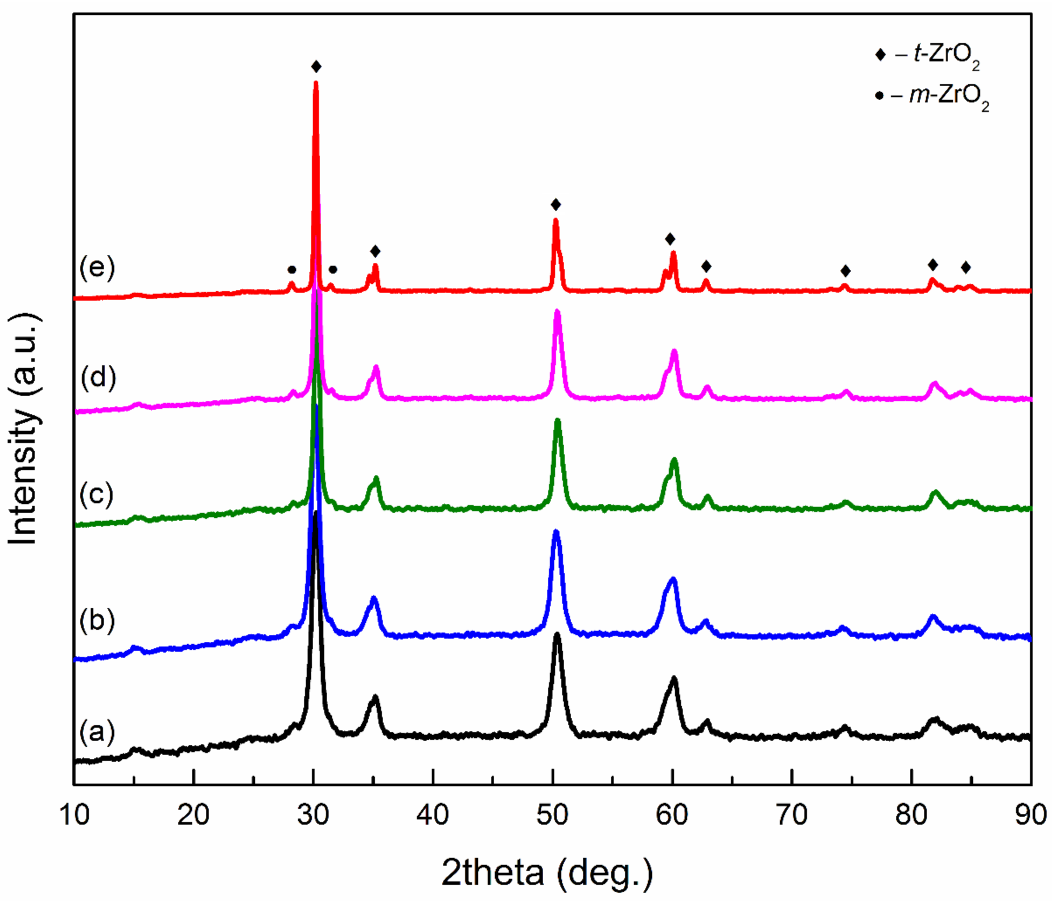

FIGURE 2 XRD PATTERNS OF 3YSZ CALCINED AT DIFFERENT TEMPERATURE: (a) 600°C, (b) 700°C, (c) 800°C, (d) 900°C, (e) 1200°C

The major phase of 3YSZ calcined at 600^{o}C is the tetragonal phase, without any monoclinic phase and free yttria trace, which means the Y^{3+} cations have gone into the crystal lattice of ZrO_2 and substitutes Zr^{4+} cations successfully. With a higher heat-treatment temperature, the width and intensity of the XRD peaks become narrow, with phase transformation from the tetragonal to monoclinic phase observed at a temperature higher than 700^{o}C, corresponding to the new peaks around 30°. The behaviour of the characteristic doublets of tetragonal peaks clearly observed in the XRD patterns of the sample calcined at 1200^{o}C indicates larger and less distorted 3YSZ crystallites. The peaks representing the monoclinic phase are negligible at 600^{o}C and 700^{o}C, but can be seen more clearly by increasing the calcination temperature. Table 1 shows the crystallization status of 3YSZ calcined at different temperatures in detail. The percentage for the monoclinic phase (x_m) is calculated by the following Equation (2):

$$x_m = \frac{I_{m(-111)} + I_{m(111)}}{I_{m(-111)} + I_{m(111)} + I_{t(101)}} \qquad (2)$$

where $I_{m(-111)}$, $I_{m(111)}$ are the intensity of the peaks representing the crystal orientation (-111) and (111) of m-ZrO_2, and $I_{t(111)}$ is the intensity of t-ZrO_2 with the crystal orientation of (101). The calculated results are 2.9 %, 4.7 %, and 5.7 % at 800^{o}C, 900^{o}C, and 1200^{o}C, respectively. The crystallite size of 3YSZ at different calcination temperatures show a normal tendency, increasing by increasing the calcination temperature, from 10.7nm at 600^{o}C to 36.9nm at 1200^{o}C, as calculated by the Scherrer formula [equation (3)] [10-12]:

$$B_p(2\theta) = \frac{\kappa\lambda}{D\cos\theta} \qquad (3)$$

where κ is a constant with a value of 0.89, D is apparent crystallite size (nm), θ is the Bragg diffraction angle, λ is the wavelength of X-rays (normally 0.154nm), and B_p (2θ) is the additional broadening at half maximum intensity (FWHM), which should be converted to radian(rad) during calculation.

According to the XRD results, it hard to distinguish the tetragonal and monoclinic phases for those calcined at 600^{o}C, 700^{o}C, and 800^{o}C, with the crystallite size becoming much larger at 1200^{o}C. Therefore, 900^{o}C is the most suitable calcination temperature for YSZ due to the reasonable crystallite size and crystallization situation.

TABLE 1 PHASE DISTRIBUTION AND CRYSTALLIZATION SITUATION OF 3YSZ CALCINED AT DIFFERENT TEMPERATURE

Calcination temperature	Monoclinic phase (%)	Tetragonal phase (%)	Crystallinity (%)	Crystallite size (nm)
600^{o}C	0	100	94.48	10.7
700^{o}C	0	100	96.02	12.5
800^{o}C	2.9	97.1	100	16.1
900^{o}C	4.7	95.3	100	19.2
1200^{o}C	5.7	94.3	100	36.9

Figure 3 shows that 3YSZ does not consist of a complete tetragonal phase after calcined at 900^{o}C and above; thus, in order to obtain 100% tetragonal phase ZrO_2 at room temperature, more stabilizer content has been used to stabilize ZrO_2 (3.5YSZ and 4YSZ), with further more stabilizer, cubic ZrO_2 will be generated that is unexpected [13].

Figure 3 shows the general and specific range of the XRD pattern for ZrO_2 stabilized with different Y_2O_3 content. Figure 3 (A) clearly shows that there are some small peaks around 30° in the XRD patterns for 3YSZ and 3.5YSZ while there are no similar peaks in the XRD pattern for 4YSZ. Another difference of those XRD patterns is the behaviour of the characteristic doublets of the tetragonal peaks that become more apparent by increasing the Y_2O_3 content, especially around 60°. It is hard to distinguish the cubic and tetragonal phases in the XRD patterns due to the overlapping Bragg reflections. In order to confirm the phase composition of YSZ, it is necessary to make a correct judgment by analyzing the XRD patterns around

72°-75° [14, 15]. The two peaks representing tetragonal phase ZrO_2 are all shown in Figure 3 (B) with little differences, only becoming more independent when compared to the background noise.

Although the primary phase of these three compositions is the tetragonal phase, as mentioned above, the small peaks around 30° for 3YSZ and 3.5YSZ represent the monoclinic phase, 4.7% and 3.7% for 3YSZ and 3.5YSZ, respectively. There are no peaks matching the monoclinic phase in the 4YSZ XRD patterns that lead to the formation of a non-transformable tetragonal zirconia phase. The better behaviour of the characteristic doublets of the tetragonal peaks with increasing yttria content implies better crystallization of YSZ. In summary, 3YSZ and 3.5YSZ show a mixture of the tetragonal and monoclinic phases, with 4YSZ exhibiting a non-transformable tetragonal phase below a certain temperature.

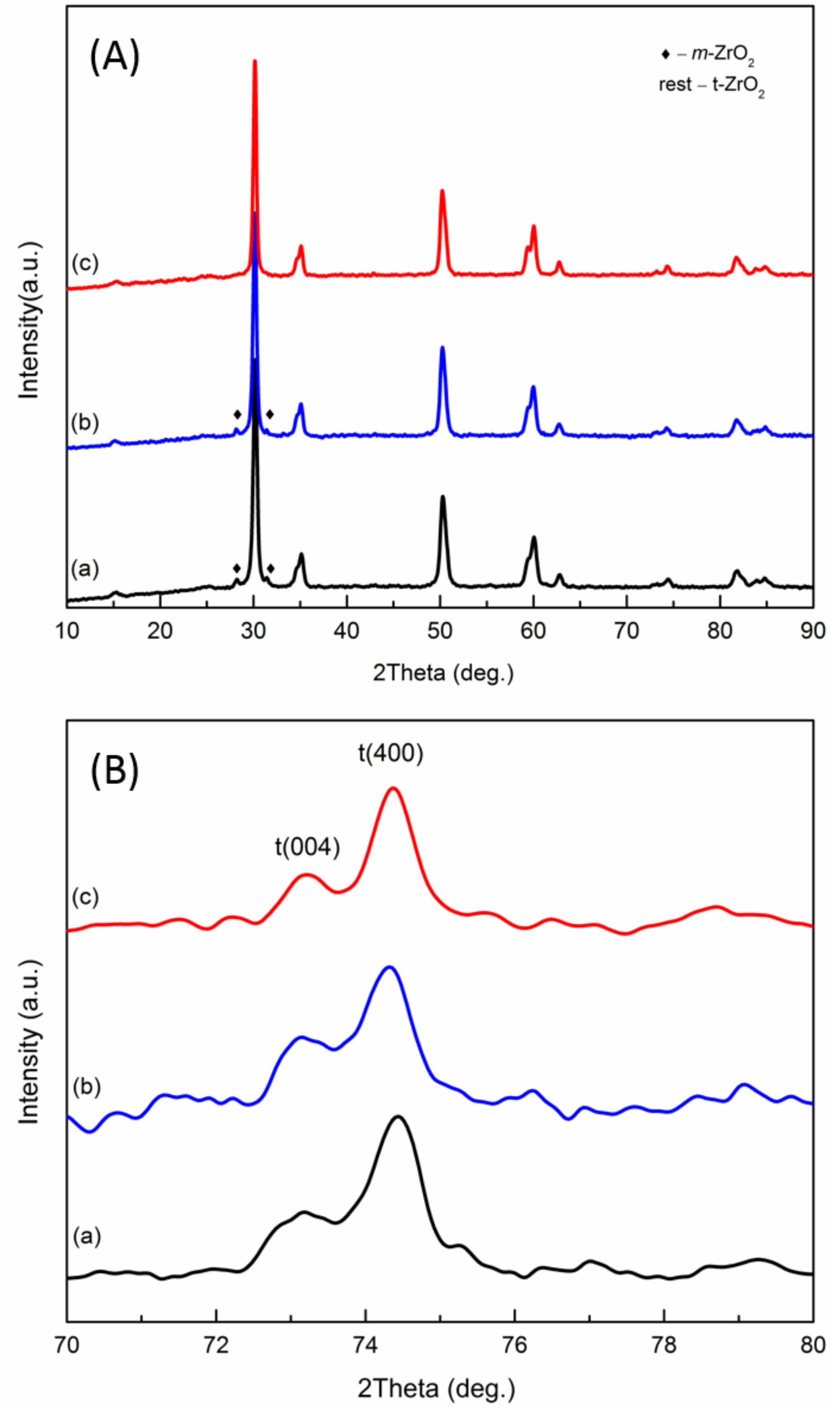

FIGURE 3 (A) XRD PATTERNS OF ZrO_2 WITH DIFFERENT CONTENT OF STABILIZER Y_2O_3 CALCINED AT 900°C, (B) SPECIFIC RANGE (70°-80°) OF XRD PATTERNS OF (A): (A) 3YSZ, (B) 3.5YSZ, (C) 4YSZ

3.3 RAMAN of nYSZ

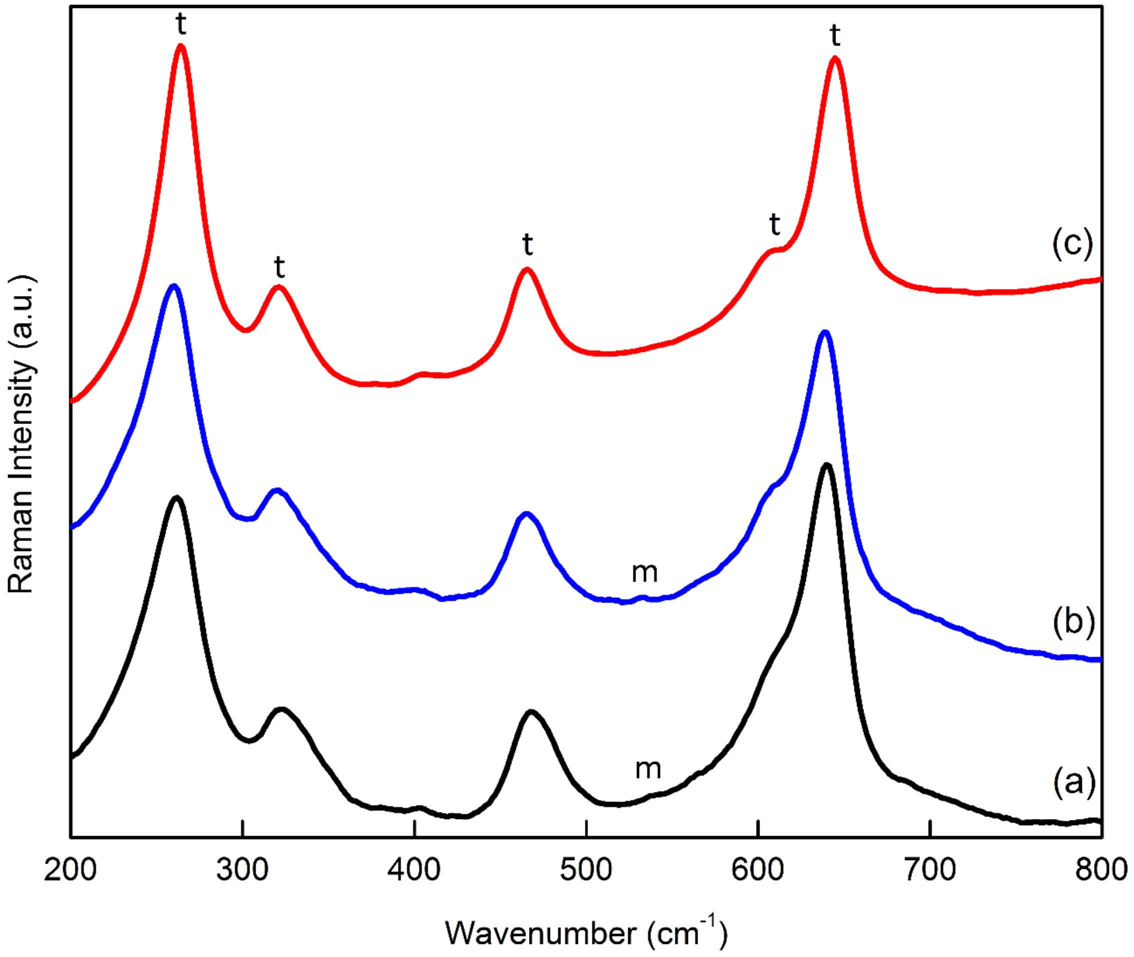

FIGURE 4 RAMAN SPECTRA OF ZrO_2 STABILIZED BY DIFFERENT CONTENT OF Y_2O_3: (A) 3YSZ, (B) 3.5YSZ, (C) 4YSZ

After being characterized by XRD, the structural information of sol-gel synthesized nYSZ (n=3, 3.5, 4) has been obtained by Raman spectra (see Figure 4). Figure 4 shows that the shape of the Raman spectra of nYSZ is almost the same apart from the peak around 520 and 600 cm^{-1}, with the spectra shifting slightly with different Y_2O_3 content. According to XRD characterization, nYSZ mainly consists of tetragonal phase and a little or no monoclinic phase. Thus the predominant peaks shown in the Raman spectra correspond to the tetragonal structure, which is an agreement with the XRD analysis. Tetragonal ZrO_2 (t-ZrO_2) belongs to the $P4_2$lnmc space group which has six Raman active vibrations at 148, 270, 315, 468, 600, and 646 cm^{-1} [16-19]. The pure tetragonal structure of 4YSZ is readily achieved and evidenced by the set of characteristic bands shown in the Raman spectrum of 4YSZ in **Error! Reference source not found.**. Compared to the vibration modes of pure t-ZrO_2, the Raman spectrum of 4YSZ shifts a little, showing bands at 265, 320, 465, 605, and 644 cm^{-1} (the band around 148 cm^{-1} is out of the test range). This shift is due to the lattice distortion caused by doped Y_2O_3, with no bands attributed to the monoclinic ZrO_2 (m-ZrO_2) observed in this spectrum. However, the t-ZrO_2 bands are predominant in the other two 3YSZ and 3.5YSZ Raman spectra. There are still some weak m-ZrO_2 Raman bands shown at around 540 cm^{-1}, with the band at 600 cm^{-1} not apparent, indicating that pure t-ZrO_2 has not been obtained in the composition of 3YSZ and 3.5YSZ. Therefore, it can be concluded that 4YSZ consists of a pure t-ZrO_2, which accords with the XRD results.

IV. CONCLUSION

Tetragonal phase ZrO_2 is usually used as a toughening agent due to the Martensitic phase transformation of ZrO_2 from the tetragonal phase to the monoclinic phase. However, the single tetragonal phase cannot exist at room temperature. In this paper, Y_2O_3 was selected as a stabilizer to stabilize ZrO_2 with different content. YSZ was synthesized by a sol-gel route. The major findings are listed below:

(1) The calcination mechanism of YSZ was determined by TGA-DSC analysis. Results indicated that the decomposition of YSZ xerogel completed at below 550^{o}C, the crystallization of YSZ started at above 600^{o}C.
(2) XRD results showed that the best calcination temperature for 3YSZ xerogel was 900^{o}C. 3YSZ consisted of monoclinic phase and tetragonal phase. With more content stabilizer, 4YSZ can keep single tetragonal phase at room temperature.
(3) Raman spectrum accorded with XRD results that 4YSZ consisted of pure tetragonal phase at room temperature.

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