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Solubility Limits of Ceria-Zirconia-Lanthana Solid-Solutions

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Abstract

We demonstrate, the solubility limits of Ceria-Zirconia-Lanthana (CZLa) solid-solutions with the increase in heat-treatment temperature from 600°C to 1300°C. CZLa nano-crystalline samples were successfully synthesized by EDTA-Citrate complex method and were characterized by Raman Spectroscopy (RS) and Transmission Electron Microscopy (TEM) analysis. With an increase in temperature, it is noticed that the solubility limit is decreased in CZLa system. At 600°C, a very good solubility is observed in CZLa system and is confirmed from RS analysis. At higher heat-treatment temperatures (1000 and 1300°C), with an increase in La content, Zr precipitated in the CZLa system and is confirmed from RS analysis. The reason for such kind of behavior in this CZLa system is clearly explained in this work.

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Keywords: Ceria-Zirconia Lanthana; solubility limit; XRD; Raman Spectroscopy; EDTA-Citrate method

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1. Introduction

For more than three decades, CeO_2 (cerium dioxide) emerged as a promising materials for environmental and energy sectors [1]. Oxygen vacancy defects, which are important in catalytic applications, can be enhanced by ceria lattice with metal oxides having lower oxidation state than Ce^{4+} [2,3] and can also lead to increased ionic conductivity. In 1950s, an early phase diagram of CZO was established[4] and later Yoshima et al.[5], gave an in-depth analysis of phase diagram for this binary system. In recent years, ternary oxide system of CZO system doped with rare earth (RE) elements gained a huge attention due to the fact that RE element addition enhances the oxygen vacancy defects and thus increases the OSC and oxygen ion mobility[6,7] and also may have a significant impact on conductivity behaviour.

The present contribution focuses on the solubility limit of La in CZO oxides at various heat treatment temperatures (600°C, 1000°C and 1300°C) and the samples were characterized using XRD, Raman Spectroscopy (RS) and TEM analysis.

2. Experimental

The Lanthanum doped Ceria-Zirconia Solid-solution ($Ce_{0.75-x}Zr_{0.25}La_xO_{2-\delta}$, for x from 0.05 to 0.40 mol %) was successfully prepared by EDTA Citrate complex method[8-10]. In order to find out the solubility limits of CZLa system, the nano-powder heat-treated at 600°C/5h, 1000°C/5h and 1300°C/5h are analysed using XRD, Raman spectroscopy and TEM characterization techniques.

3. Results and Discussions

From XRD plot, the solubility limits in CZLa samples and lattice constants are calculated and depicted in Fig. 1. At 600°C, a linear increase in lattice constant with an increase in La content are observed and shows that Vegard's rule is applicable at this heat-treatment temperature for CZLa system. As the temperature is increased from 600°C to 1000°C and 1300°C a clear difference in the slope is observed at 1000°C (15 mol% La) and 1300°C (10 mol% La). Thus in CZLa system the solubility limit changes with an increase in heat-treatment temperatures.

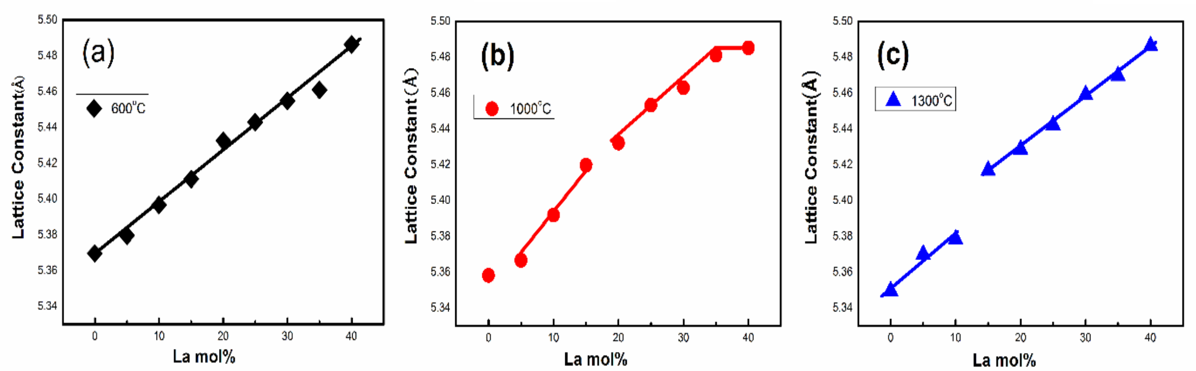

Fig. 1.Variation of Lattice constant with an increase in La mol % of CZLa samples heat-treated at (a) 600^0C, (b) 1000^0C and (c) 1300^0C.

Fig.2 depicts the Raman spectra of CZLa samples heat-treated at 600°C, 1000°C and 1300°C, respectively. The peak centered at 465cm^{-1} can be attributed to ceria (cubic fluorite structure) with a symmetric breathing mode (O-Ce-O) [11]. A shoulder peak centered at 590cm^{-1} is observed for the CZLa samples and is assigned to non-degenerate longitudinal optical (LO) mode and is related to the oxygen vacancies present in the ceria lattice[12]. In Fig. 2(a), the intensity of this shoulder peak increases with the increase of La doping and it indicates that the oxygen vacancies also increase in the same order.

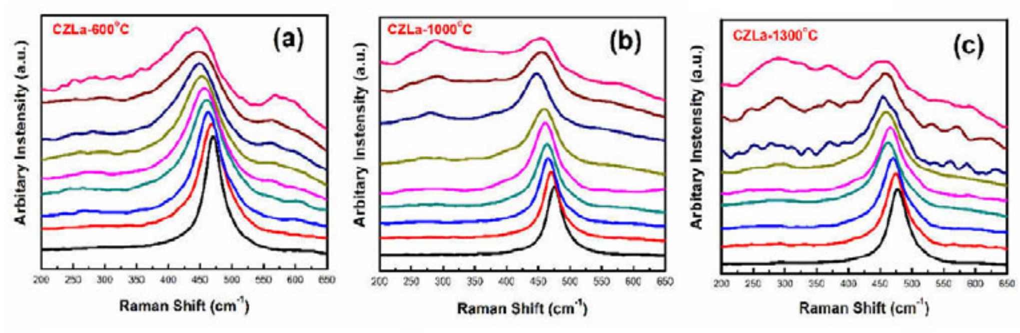

Fig. 2 Raman spectra of CZLa samples heat-treated at (a) 600^{0}C (b) 1000^{0}C and (c) 1300^{0}C.

It is quite interesting to observe the Raman spectra of the CZLa samples heat-treated at 1000°C (Fig. 2(b)). For 1000°C heat-treated CZLa samples (La < 0.20), the Raman spectra is very similar to that of 600°C heat-treated samples but as the La content increases (La≥0.20) a secondary phase is detected and the peak can be clearly noticed at 275cm^{-1}. This peak can be assigned to tetragonal phase of Zirconia [13,14]. From figure, it is concluded that as La content increases in CZLa samples Zr comes out as a secondary. Fig. 2(c) demonstrates the Raman spectra of 1300°C heat-treated CZLa samples and it clearly shows the secondary phase as Zirconia for La≥0.15.

Fig.3 demonstrates the TEM images of CZLa (La = 25 mol%) samples heat-treated at 600 and 1000°C. From Fig. 3(a), the 600°C heat-treated sample clearly indicated a high crystalline nature and has a particle size in the range of 5-10nm. From the figure, it is noticed that the lattice fringes can be easily identified and the corresponding SAED patterns are depicted in Fig. 3(b). The diffraction rings in Fig. 3(b) also confirms that the crystallites have different planes. Fig. 3(c) and Fig. 3(d) shows sample heat-treated at 1000°C and noticed that the particle size increased from 5-10 nm to 60-70 nm when the temperature increased from 600 to 1000°C. For the 1000°C heat-treated sample, it was a bit difficult to identify the secondary phase and this can be due to the amount of sample that is analyzed for TEM analysis than compared to RS analysis. Further analysis using electron energy loss spectroscopy (EELS) and secondary ion mass spectroscopy (SIMS) can give a clue on the concentrations of Zirconia (Secondary phase as identified from RS analysis) at the grain boundaries relative to the adjacent grains and SIMS analysis on the fracture surfaces can give an idea on the depth profiles of Ceria, Zirconia and Lanthanum. These studies will be reported in the forthcoming paper.

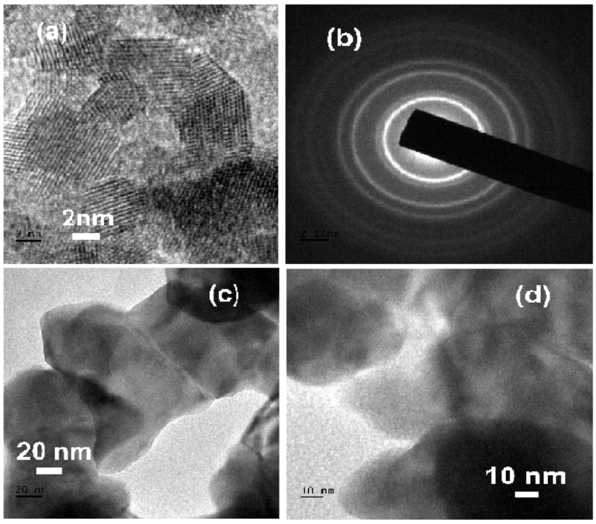

Fig. 3 TEM Micrographs of CZLa samples heat-treated at (a) 600^{0}C (b) corresponding SAED image (c) & (d) 1000^{0}C

3.1. Reasons for secondary phase precipitation

For CZLa sample heat-treated at 600°C, the number of grains and grain boundaries will be high when compared to the samples heat-treated at 1000°C and 1300°C, hence Zr (Zr^{4+} = 0.87Å) has completely dissolved in bulk ceria near the grain boundaries. As the heat-treatment temperature increased from 600°C to 1000°C, an increase in grain size on the expanse of number of grain boundaries is expected. As the number of grain boundaries decreases the smaller ionic radius dopant tries to precipitate out and is successfully identified in RS analysis. With the increase of the heat-treatment temperature further from 1000°C to 1300°C a further decrease in the solubility is expected and is observed in CZLa system. Similar results were reported by Ping Li et al.[15], where 3vol% of Fe is stable as tetragonal solid-solution at 600°C and while they de-mix forming hematite and monoclinic Zirconia at 1300°C. Ross et al.[16], demonstrated that a small addition (0.15wt%) of Alumina resulted in segregation of Al^{3+} and Y^{3+} at the grain boundaries in 5.2 wt% of Yttria stabilized tetragonal ploycrstals. Since the difference in the ionic sizes is much larger in case of ceria with fluorite structure the de-mixing of Zr is not surprising in CZLa system and this further supports the experimental evidences observed by Ping Li et al.,[15], and by Ross et al.,[16].

Conclusion

The solubility limit of CZLa systems synthesized by EDTA Citrate complex with increasing heat treatment temperatures were identified. From XRD and Raman Spectroscopy it was confirmed that the solubility limit is decreased with an increase in heat-treatment temperature. The solubility limit is decreased from 15 mol% La to 10 mol% with an increase in heat-treatment temperature from 1000°C to 1300°C. Zirconia is precipitated as a secondary phase and the reason for the precipitation is confirmed through Raman spectroscopy. The ionic radius is smaller when compared to its counterparts, which acts as a driving force for precipitation at the grain boundary regions.

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