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Phase stabilization and structural studies of nanocrystalline La_2O_3-ZrO_2

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La_2O_3 doped nanocrystalline zirconia (ZrO_2) has been prepared by chemical co-precipitation method for various dopant concentrations, varying from 3 to 30 mol%. Structural phases have been characterized by X-ray diffraction technique. All the as-synthesized samples were found to be in monoclinic phase. Annealing of the samples at different temperatures from 400 to 1000°C stabilized ZrO_2 either partially or fully the tetragonal/cubic phases. When they were annealed at 1200°C, the monoclinic phase appeared again with a new cubic pyrochlore structured $La_2Zr_2O_7$ at the expense of stabilized tetragonal phase. Formability of the tetragonal/cubic phase has been influenced by the dopant concentration and the annealing temperature. Sample with 8 mol% La_2O_3 has been stabilized completely in tetragonal/cubic phase after annealing at 900°C for 1 h. Smallness of the grain in these nanocrystalline materials may also have assisted in the formation of La_2O_3-ZrO_2 solid solution.

Introduction

Zirconia based compounds have been actively studied [1, 2] because of their enormous applications in electrochemical devices such as oxygen pumps [3], oxygen sensors and solid state electrolyte in fuel cells [4]. As the zirconia based compounds are used in solid oxide fuel cells (SOFC), its electrolytic properties are very significant and they can be suitably modified by doping with appropriate mixed valence cations [4]. Pure zirconia exists in three allotropic forms *viz.* monoclinic, tetragonal and cubic. Even though the phase boundaries are not exactly known yet as a function of temperature, many reports have been found to define the temperature range of these phase boundaries [1, 5]. Mostly, pure ZrO_2 exists in the monoclinic form up to 1170°C and above that it transforms into tetragonal phase. Cubic fluorite phase is obtained above 2300°C [6]. As this material finds huge applications from structural constructions to oxygen sensors in its cubic form, it has been an interesting research field to study their cubic phase stabilization. Mostly, this cubic phase stabilization has been achieved by a suitable dopant. Some of the dopants used to stabilize the cubic phase of ZrO_2 are CaO [5], Y_2O_3 [7], Gd_2O_3 [8], Sc_2O_3 [9] etc. In this series, some of the lanthanide series oxides such as Er_2O_3, Dy_2O_3 etc. [10] have also been used as a stabilizer. There are literatures which reported that the La^{3+} ion is too large to form cubic fluorite solid solutions [11] in this system. In the present study, the authors have chosen La^{3+} to stabilize ZrO_2 in the nanocrystalline form. The selection of this ion is due to the following two reasons: One is the crystal chemistry model. The process of stabilization with larger ionic radii dopants is rationalized by the crystal chemistry model [5], that describes the dopant cations as typical stabilizer when they have larger ionic size, lower charged state and higher ionicity than Zr^{4+}. The ionic radius of Zr^{4+} is 0.79 Å and that for La^{3+} is 1.016 Å [12]. The second reason is the absence of any reasonable knowledge on the performance of nanocrystalline materials in this system. The properties such as cubic formation [13], annealing effects [7] and ionic conductivity [14] have been studied on nanocrystalline ZrO_2 with other stabilizing dopants. Because of the interest to study the formability of tetragonal/cubic phase solid solution in nanocrystalline La_2O_3-ZrO_2 system with the annealing temperature and dopant concentration, in the present work, La_2O_3-ZrO_2 has been prepared in nanocrystalline form with different dopant concentrations and studied. The influence of the dopant concentration, annealing temperature and grain size in the phase stabilization is also discussed in this work.

Experimental procedure

Nanocrystalline La_2O_3 doped ZrO_2 was prepared by chemical co-precipitation method with different concentrations of La_2O_3. The dopant concentration was varied from 3 to 30 mol% (3, 5, 8, 10, 15, 20 and

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30 mol%). Aqueous solution of zirconyl oxychloride was taken with appropriate mol% of lanthanum nitrate and hydrolyzed for 72 h in a reflux condenser at a temperature of ∼130°C. Initial pH value of the precursor solution was in the range 2 to 4. After hydrolysis the solution was neutralized by ammonia solution. White coloured precipitate was formed and that was washed with double distilled water to remove the unnecessary adsorbents, dried at 150°C for 1 h and subsequently ground into powder in an agate mortar. The prepared powder samples were annealed at different temperatures such as 400, 600, 700, 800, 900, 1000 and 1200°C for 1 h in air and furnace cooled to room temperature. Structural phases were identified from the X-ray diffraction patterns taken in a high resolution Seifert Guinier X-ray power diffractometer, using Cu-$k_{\alpha 1}$ radiation with quartz monochromator. Silicon with (111) plane was used as calibration standard. Average grain sizes were calculated using Scherrer formula [15] and their deviations were also calculated. Only the widths of the 100% peaks, after profile fitting, of the XRD patterns have been used for grain size estimation. Hence the estimated grain size is either for monoclinic or tetragonal.

Results and discussion

Structural analyses have been performed by fitting the X-ray diffraction (XRD) patterns taken for all the as-synthesized and annealed samples using PEAKFIT, a graphical tool. Typical XRD patterns for the 8, 10 and 15 mol% doped La_2O_3-ZrO_2 with different annealing conditions are presented in Figs 1a, b and c. Annealing temperatures and the phases present are given against each pattern. In these figures. m, t, c and p refer to monoclinic, tetragonal, cubic and pyrochlore phases respectively. All the patterns are indexed and the corresponding diffraction planes are marked against each peak. The chemical formula of pyrochlore is $La_2Zr_2O_7$. Calculated grain sizes for 8, 10, 15 and 20 mol% dopant are given in Fig. 2. It is observed that the grain size increases with the annealing temperature. The standard deviation in the grain sizes is less than 1 nm except for the three samples having dopant concentration 20 and 30 mol% for which the deviation is around 1.5 nm.

Invariably all the as-prepared La_2O_3-ZrO_2 samples are found to be in the monoclinic phase. This may be due to two reasons. One is that there may be some strains formed in the ZrO_2 lattice during synthesis. The other may be that tetragonal/cubic solid solution could not have been formed in the as-synthesized conditions [7, 13]. One of the factors for the origin of strain in the host lattice may be the difference in the ionic radius between the host and the dopant ions. As cited in the introduction, ionic radii of Zr^{4+} and La^{3+} are 0.79 Å and 1.016 Å respectively [12]. It is observed that other than 3 mol% doped La_2O_3-ZrO_2, all the other samples annealed at 400°C or onwards (i.e., for all other compositions of La_2O_3) show the partial or total stabilization of tetragonal/cubic phase. The quantitative determination of the volume fraction of tetragonal phase (Γ) in the mixture of both monoclinic and tetragonal phases was made by using the formula [7, 16]

$$\Gamma = I(111)_t/\{I(\bar{1}11)_m + I(111)_m + I(111)_t\} \quad (1)$$

where the subscripts m and t refer to the monoclinic and tetragonal phases and $I(hkl)$ refers to the X-ray intensity of the corresponding peaks. Thus estimated tetragonal volume fractions in nanocrystalline La_2O_3-ZrO_2 annealed at 600°C are given in Fig. 3. The fraction of the tetragonal phase increases up to 15 mol% dopant content and then saturates with further increase of dopant. This shows that the tetragonal phase is unstable with higher La^{3+} loading at this annealing temperature.

The X-ray diffraction patterns for the nanocrystalline La_2O_3-ZrO_2 annealed at 900°C are given in Fig. 4. Sample descriptions are given against each pattern. It can be observed that the annealing at 900°C leads to good formability of the tetragonal/cubic phase solid solution. Even then, 3 and 5 mol% samples contain both monoclinic and tetragonal phases. In the 8, 10 and 15 mol% doped samples, it seems that there are no splitting in the (200), (220) and (311) peaks. These XRD patterns do not show clearly whether the crystal structure is cubic or tetragonal. This may be due to the merging of the (002), (202) and (113) peaks of tetragonal phase respectively with (200), (220) and (311) peaks of cubic phase (The latter three peaks can be identified as due to tetragonal phase also). Because of the line broadening there may be an overlap and they could not have been resolved for tetragonal and cubic phases with clarity. Therefore these peaks have been indexed to both tetragonal and cubic phases. As far as the tetragonal phases are concerned, the (202) and (220) peaks have been profile fitted and indexed. One such fitting is given in Fig. 5. Therefore all the samples represented by t/c in XRD patterns contain a mixture of tetragonal and cubic phases. The XRD patterns of 8 mol% sample can be indexed only to the tetragonal and cubic phases and there is no monoclinic phase. The volume fractions of the tetragonal phase present for the 600, 700, 800 and 900°C annealed La_2O_3-ZrO_2 system are given in Fig. 6. It is observed from the Fig. 6 that the maximum of volume fraction of the tetragonal phase shifts to the lower dopant content with increase in annealing temperature. The 900°C annealed La_2O_3-ZrO_2 shows the maximum of this fraction for 8 mol% of La_2O_3. This figure also explains the stability of the tetragonal phase with the dopant content. When the La^{3+} loading is more such as 20 and 30 mol%, the XRD peaks for 900°C annealed La_2O_3-ZrO_2 are found to contain asymmetry. This asymmetry may be due to the presence of some other phases in addition to the stabilized phases. One usually expects the formation of pyrochlore structured $La_2Zr_2O_7$ phase in La_2O_3-ZrO_2. Trombe *et al.* [17] have observed this system with $La_2Zr_2O_7$ phase when the concentration of La_2O_3 lies between 15 and 30%. In order to check the formation of such a phase in the samples having 20 and 30 mol% of La_2O_3, the 100% peaks of the XRD patterns for those two concentrations have been carefully profile fitted with deconvolution of peaks. These deconvoluted peaks are presented in Figs. 7a and b. It may

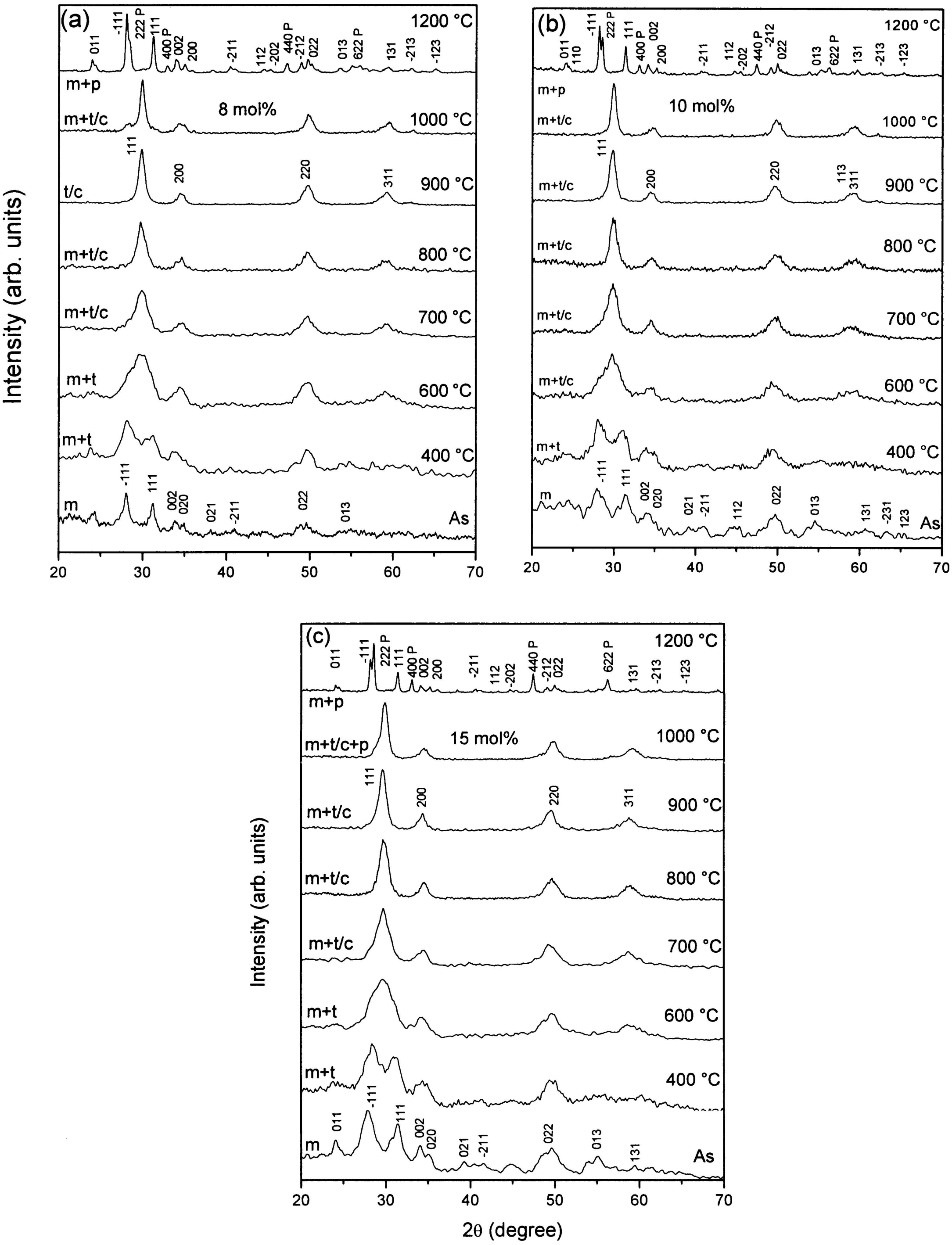

Figure 1 XRD patterns for the nanocrystalline La_2O_3-ZrO_2 system with (a) 8, (b) 10 and (c) 15 mol% dopant concentration. Annealing temperature and the phases present are given against each pattern. The letters *m*, *t*, *c* and *p* refer to monoclinic, tetragonal, cubic and pyrochlore phases respectively.

be noted that for 30 mol% of La_2O_3, the formation of pyrochlore is more compared that for 20 mol%. These two samples contain monoclinic as well as pyrochlore structured $La_2Zr_2O_7$ in addition to the tetragonal phase. It is worth to note that the concentration of the dopant plays a major role in the stabilization of the tetragonal phase solid solution in this system. The samples with other dopant concentrations, less than 20 mol%, do not exhibit the pyrochlore phase in the 900°C annealing condition. But when they were annealed at 1000°C, the stabilized tetragonal phase starts to destabilize with the appearance of monoclinic and pyrochlore phases. This can be observed from the XRD patterns in Fig. 1. Out of all the dopant concentrations studied in this research, 8 mol% La_2O_3 seems to be a better concentration to stabilize ZrO_2 in tetragonal/cubic phases.

In order to find the effect of annealing temperature in the tetragonal/cubic phase stabilization, volume fractions of the tetragonal phase present in 8 to 20 mol% La_2O_3-ZrO_2 as a function of annealing temperature have been plotted in Fig. 8. This shows that the tetragonal phase formation increases up to 900°C and then decreases with annealing temperature. When the samples of La_2O_3-ZrO_2 were annealed at 1200°C, they have been completely transformed into monoclinic phase with the presence of $La_2Zr_2O_7$ phase. This can be seen from the XRD patterns shown in Fig. 1. Similar observations were made in all the other samples

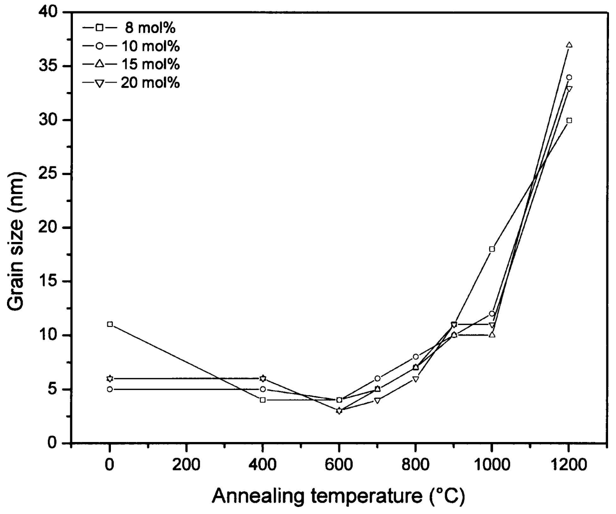

Figure 2 Grain size variation with annealing temperature for 8, 10, 15 and 20 mol% La_2O_3-ZrO_2. Lines are guide to the eye.

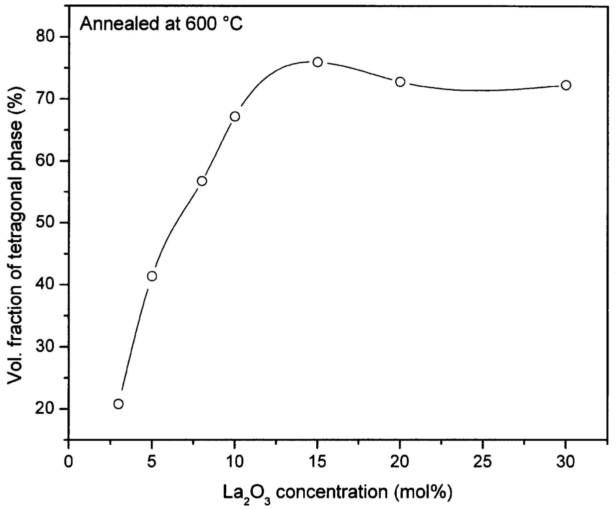

Figure 3 Volume fraction of tetragonal phase in the 600°C annealed samples of nanocrystalline La_2O_3-ZrO_2 for various dopant concentrations. Line is guide to the eye.

also. At high temperatures such as 1200°C, the stabilizer might have been diffused out with the formation of the $La_2Zr_2O_7$ phase and hence the tetragonal phase is destabilized.

By comparing the earlier discussions, it can also be derived that the 900°C annealing would have assisted the process of stabilization of the tetragonal/cubic phases. Hence the dopant content of 8 mol% and the annealing temperature of 900°C appears to be better stabilizing conditions in nanocrystalline La_2O_3-ZrO_2. In addition to these, grain size of the materials may also have played an indirect role in phase stabilization. There are strong experimental evidences for the role of grain size in phase stabilization [7, 13]. And hence the smallness of the grains in nanocrystalline La_2O_3-ZrO_2 might have assisted the formation tetragonal/cubic solid solutions. The grain sizes of all the samples annealed at 900°C vary from 10 to 13 nm, which may be conducive for the formation of these solid solutions. Also many parameters such as ionic radii, electronegativity etc. contribute to the tetragonal phase stabilization in zirconia based systems.

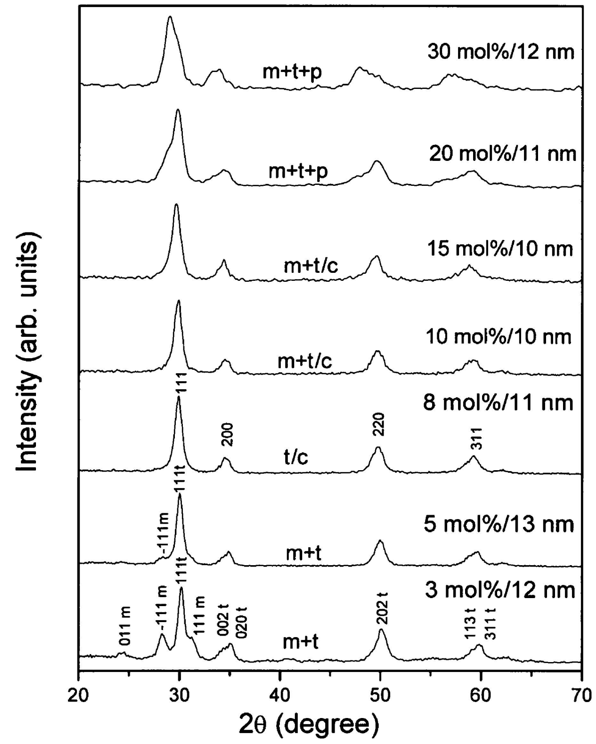

Figure 4 XRD patterns for the 900°C annealed nanocrystalline La_2O_3-ZrO_2. Dopant concentration and grain size are given against each pattern. [*t*-tetragonal, *m*-monoclinic, *c*-cubic and *p*-pyrochlore phases].

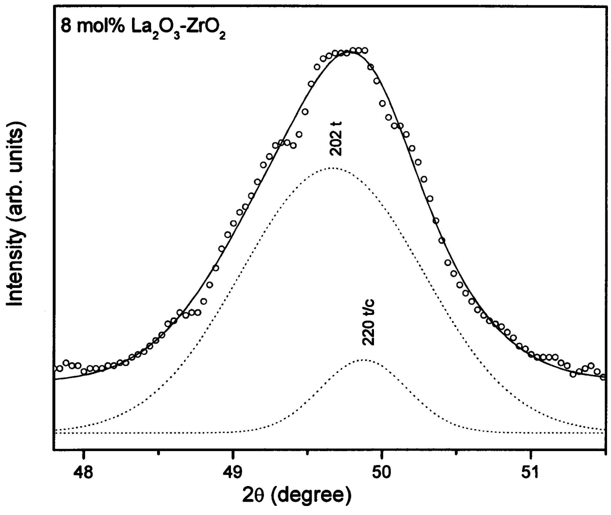

Figure 5 Deconvoluted (220) peak of 8 mol% doped nanocrystalline La_2O_3-ZrO_2 annealed at 900°C. The (202) peak corresponds to tetragonal phase. However, the (220) peak can be identified with both cubic and tetragonal phases.

During the initial study of this system, La_2O_3-ZrO_2, it was shown that the cubic fluorite solid solution could be formed for 10 to 35% La_2O_3 after melting, 25 to 42% La_2O_3 at 2000°C and 40% La_2O_3 at 1000°C [1, 18]. Even though the $La_2Zr_2O_7$ phase is expected in this system, fluorite phase was observed to be stable above 1800°C [19] and extends from 6 to 16% La_2O_3 near liquidus temperatures. It has been prepared metastably at only 800°C via co-precipitation in the amorphous state, but above 1450°C, decomposed rapidly to a tetragonal ZrO_2 solid solutions and $La_2Zr_2O_7$ [20]. Fluorite structure has been observed at about 14% La_2O_3 by Lin and Yu [21]. All these studies have been performed on the

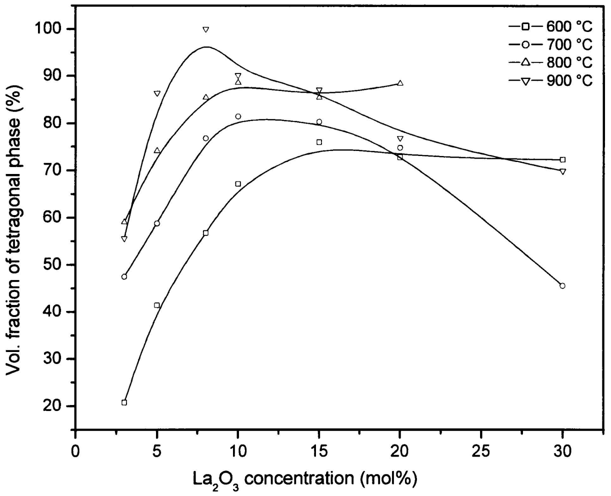

Figure 6 Volume fraction of metastable phase in nanocrystalline La_2O_3-ZrO_2 for various dopant concentrations annealed at different temperatures. Lines are guide to the eye.

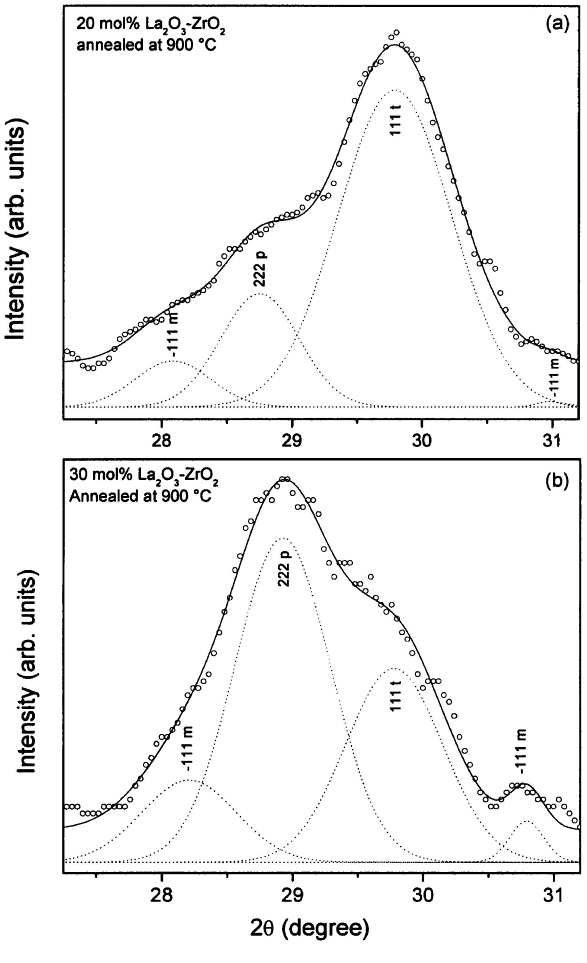

Figure 7 Deconvoluted 100% XRD peaks for the 900°C annealed nanocrystalline La_2O_3-ZrO_2 with (a) 20 mol% and (b) 30 mol% dopant concentration. The letters *t*, *m* and *p* refer to the tetragonal, monoclinic phases of ZrO_2 and pyrochlore ($La_2Zr_2O_7$) phase respectively.

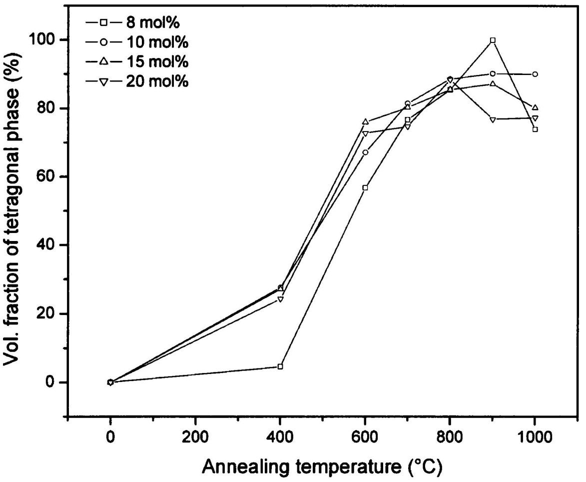

Figure 8 Volume fraction of tetragonal phase with annealing temperature for the 8, 10, 15 and 20 mol% doped nanocrystalline La_2O_3-ZrO_2.

coarse-grained bulk ZrO_2. Cubic solid solution formation was dependent on the sintering temperature also. Generally cubic fluorite phase of ZrO_2 doped with 2 to 8 mol% La_2O_3 could be stabilized by sintering the samples at 2000°C [22]. In this work, tetragonal/cubic phase stabilization was achieved with 8 mol% of dopant under the annealing temperature of 900°C. It is also worth to note that even 600°C annealing partially stabilizes the tetragonal phase and the volume fraction of tetragonal phase increases with annealing temperature up to 900°C. It is important to note that we are dealing with the nanocrystalline form of La_2O_3-ZrO_2 in this study rather than the coarse grained bulk materials as found in the previous literatures.

Summary

Structural analysis of the chemically prepared La_2O_3-ZrO_2 system by XRD has shown that the stabilization of tetragonal/cubic phase can be achieved with suitable heat treatment and dopant concentration. Even though the as-prepared samples contain only monoclinic phase for all concentrations of the dopant, the tetragonal/cubic phase can be stabilized by choosing suitable dopant concentration and annealing temperature. In this work, it is found that the appropriate stabilizing parameters are 8 mol% dopant content and an annealing temperature of 900°C. Annealing at 1200°C results in the formation of $La_2Zr_2O_7$ phase with destabilization of the tetragonal phase. The salient feature of the paper, apart from the above results, is that the present results show that even with low concentration of La_2O_3 (8 mol%), the tetragonal phase of ZrO_2 can be stabilized at lower annealing temperatures compared to the reported values in the literature. This may be because of the nanocrystalline nature of the system La_2O_3-ZrO_2 in this work.

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