Ceramics International 30 (2004) 2137–2142

CERAMICS INTERNATIONAL

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Mechanochemical synthesis and thermal evolution of La^{3+}–ZrO_2 cubic solid solutions

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Received 22 May 2003; received in revised form 29 August 2003; accepted 20 November 2003

Abstract

The formation of cubic solid solutions in the system La_2O_3–ZrO_2 by mechanochemical activation of a mixture of the oxides (molar ratio ZrO_2 82%–La_2O_3 18%) is studied. After 6 h of activation at room temperature, a poorly crystalline cubic solid solution is formed, with ultimate crystallite sizes in the nanometer range. The mixtures activated during 1–3 h form the solid solution on subsequent heating at 1000 °C, while the non-activated mixture does not react, even after thermal treatment at 1200 °C. The solid solution obtained at room temperature undergoes partial structural ordering at temperatures between 800 and 1000 °C. Long time heating at temperatures of 1000 °C and above results in the formation of $La_2Zr_2O_7$ and rejection of the excess ZrO_2. Mechanochemical activation offers interesting possibilities for the synthesis of these materials at temperatures lower than those used in conventional processing, and for the control of their physicochemical and microstructural properties.

Keywords: D. ZrO_2; Mechanochemical activation; Solid solutions; La_2O_3

1. Introduction

At room pressure, three polymorphic forms of ZrO_2 are stable in different temperature ranges: monoclinic, tetragonal and cubic. In addition, a high-pressure orthorrombic form has been reported [1]. The successful production of pure ZrO_2 bodies is not possible because of the large volume change associated with the martensitic tetragonal–monoclinic transformation. This fact restricts the applications of this material, in spite of its excellent mechanical and thermal properties. However, the stabilization of the high temperature polymorphs at room temperature as metastable phases is made possible by addition of suitable dopants. Fully stabilized (cubic) ZrO_2 and partially stabilized (tetragonal) ZrO_2 show interesting properties, and are widely used as ionic conductors, coatings, gas sensors, elements in solid oxide fuel cells, and structural applications [2].

Most frequently used dopants include Y^{3+}, Ca^{2+}, Mg^{2+} and Ce^{4+} oxides, although other oxides, such as those of rare earth elements, can also act as stabilizers of the high temperature structures. The incorporation of aliovalent cations to the lattice, forming substitutional solid solutions, allows to control the concentration of anionic vacancies in the structure. This aspect is particularly important in designing ionic conductors [3], and is also determinant in the stabilization process [4].

Stabilized zirconias are usually prepared by solid state reaction between the oxides at high temperatures (>1400 °C). Also, coprecipitation and sol–gel methods have been developed; however, additional thermal treatments are required to produce solid solutions with high-temperature structures. This also makes difficult to control microstructural characteristics; for this reason, the development of processes to obtain these phases in conditions milder than those required by conventional methods is of particular importance.

In addition to the possibility of stabilization of high temperature structures, the ZrO_2–La_2O_3 system includes the existence, at high temperatures, of $La_2Zr_2O_7$, with pyrochloric structure [5,6]. This compound finds application as catalyst

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doi:10.1016/j.ceramint.2003.11.020

[7], and as thermal barrier [8]. It can be synthesized by solid state reaction between the oxides at 1500–1600 °C, or by the sol–gel process [9].

Mechanochemical activation of crystalline solids has become a valuable tool for the synthesis of nanostructured solids, including stabilized tetragonal and cubic zirconium oxides (e.g. see [10–12]). Mechanochemical activation of the reacting systems takes place through the transfer of mechanical energy from the milling media to the solid. This excess energy is stored as plastic deformation of crystals, crystalline defects and new surfaces. This builds up in the solid high reactivity regions, making possible the development of solid state processes, and the synthesis of metastable phases which cannot be obtained by conventional thermal methods.

In this work, the synthesis at room temperature of La^{3+}–ZrO_2 cubic solid solutions by mechanochemical activation of the starting oxides is studied, together with their thermal evolution up to the formation of $La_2Zr_2O_7$.

2. Experimental

The starting oxides were monoclinic ZrO_2 (baddeleyite) (BDH, 99.99%) and La_2O_3 (Anedra, 99.99%). They were mixed in a molar ratio ZrO_2 82%–La_2O_3 18%. According to previous studies [5,6] this composition is located, at high temperatures (>1900 °C) into the stability field of the cubic solid solution.

Mechanochemical treatments were performed with a planetary mill Fritsch Pulverisette 7, with TZP (tetragonal ZrO_2 polycrystal) vials (45 ml) and balls (7 balls of 1.5 cm diameter). Five grams of mixture were loaded in each vial, resulting in a milling media to powder mass ratio of 15:1. The treatments were done in air atmosphere at 1500 rpm, during measured times up to 6 h, in 15-min increments, between which the vials were allowed to cool. The obtained samples were labeled LZ*t*, where *t* is the activation time in h.

Thermal treatments were done in an electric furnace with Kanthal heating elements (Indef) for the temperature range 600–1000 °C, and in an electric furnace with $MoSi_2$ heating elements (Carbolite) for the temperature range 1000–1300 °C. The treated samples were named LZ*t*-*x*-*y*, where *x* is the treatment temperature (°C) and *y* is the soaking time (h).

The obtained materials were characterized by X-ray diffraction (XRD) (Philips PW 1830/00, Cu-K_α radiation and Ni filter, at 40 kV and 30 mA), differential thermal analysis (DTA) (Shimadzu DTA 50H, at 10 °C/min in air) and scanning electron microscopy (SEM) (Philips 505).

3. Results and discussion

Fig. 1 shows the diffractograms of the series of activated samples LZ0–LZ6. The diffraction peaks of La_2O_3 disappear at short times because of the loss in crystallinity caused by the activation, while the intensity loss is gradual for ZrO_2, reaching 60% of the initial intensity after 3 h of activation. In LZ3, only baddeleyite peaks are observed, much wider than those of LZ0. The crystallite size of LZ3, estimated using the Scherrer equation [13] is about 37 nm. In LZ6, a very wide band centered about $2\theta = 29°$ appears superposed to the baddeleyite peaks, the intensity of which is clearly lower than in LZ3. This shows that mechanochemical activation has produced, at room temperature, a new structure which is either the solid solution or a low-crystalline phase precursor of it.

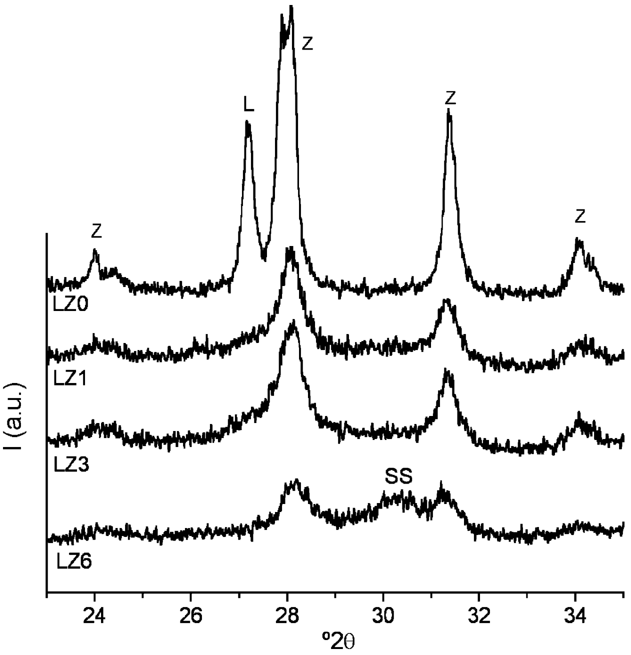
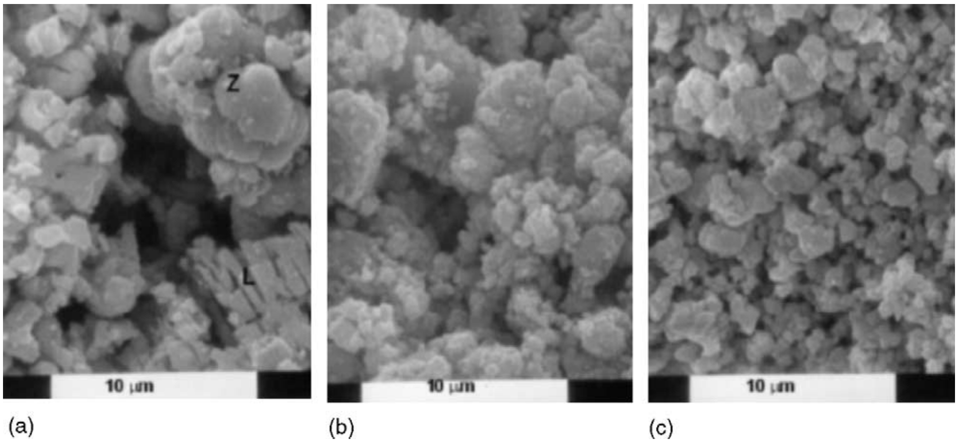


Fig. 1. X-ray diffractograms of samples LZ0, LZl, LZ3 and LZ6. Z: monoclinic ZrO_2; L: La_2O_3; SS: solid solution.

The SEM micrographs of LZ0, LZ1 and LZ6 are shown in Fig. 2. In LZ0, the crystals of both oxides can be observed, with grain sizes lower than 10 μm. In LZ1, the decrease in size and the loss of the original morphology are evident, mainly for La_2O_3, with production of irregular round-edged particles showing a strong tendency to agglomeration, as a consequence of their small size and high surface energy. Finally, the EPMA of LZ6 determined that the individual particles of the sample contained both cations, showing a fine and homogeneous microstructure (∼1 μm). On the other hand, the tendency to agglomeration is weaker than in LZ1, suggesting a lower surface energy. In all cases, the particles are made up of aggregates of nanometric crystals.

With the aim of developing the crystalline structure of the obtained materials, the samples were heated during 1 h at temperatures between 600 and 1000 °C for LZ6 and between 800 and 1200 °C for LZ1 and LZ3, and subsequently analyzed by XRD (Figs. 3 and 4, respectively).

In Fig. 3, no differences are observed between LZ6-700-7 and LZ6. In LZ6-800-1, however, the diffraction band at $2\theta = 29°$ narrows, and a new band appears at about $2\theta = 34°$. These bands correspond to the (1 1 1) and (2 0 0)



(a) (b) (c)

Fig. 2. SEM micrographs of (a) LZ0; (b) LZI; (c) LZ6. Z: monoclinic ZrO_2; L: La_2O_3.

planes of the cubic solid solution, respectively. The ultimate crystallite sizes are 3 nm at 700 °C, 4 nm at 800 °C and 8 nm at 1000 °C. The angular position of the (1 1 1) band of LZ6-1000-1 corresponds to a lattice parameter $a \approx 0.53$ nm. In cubic ZrO_2, the size of the unit cell is $a = 0.51$ nm [14]. The difference between both values may be adscribed to the larger ionic radius of La^{3+} (104 pm) with respect to Zr^{4+} (70 pm) and to the low crystallinity of the solid solution. The size of La^{3+} causes the solid solution to be substitutional, with cubic fluorite structure [5,15].

In agreement with these results, DTA of LZ6 shows a small exothermic effect at 850 °C, which can be related to the establishment of some structural ordering of the coordination polyhedra, from the disordered structure of LZ6. This aspect was studied by Li et al. [16], who reported that in the solid solution, the individual coordination polyhedra are defective, because of the high concentration of anionic vacancies produced to maintain electrical neutrality. These vacancies concentrate in the immediate vicinity of Zr^{4+} ions; for this reason, the coordination polyhedra can be described as LaO_8 and ZrO_{8-x}. Also, although the individual polyhedra are highly distorted, their long range ordering is well developed, maintaining the cubic symmetry of the solid solution.

The same authors establish that the stabilization of the cubic structure occurs when large trivalent cations are added to ZrO_2 in high concentration (>11 mol%). This reduces the Zr^{4+} average coordination number, and when it reaches about 7.5, the high temperature cubic structure is stabilized.

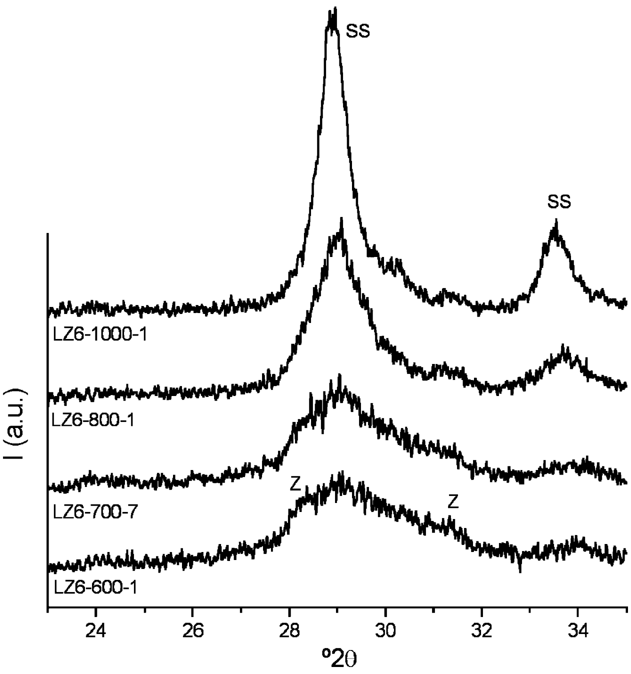


Fig. 3. X-ray diffractograms of samples LZ6-600-1, LZ6-700-7, LZ6-800-1 and LZ6-l000-1. Z: monoclinic ZrO_2; SS: solid solution.

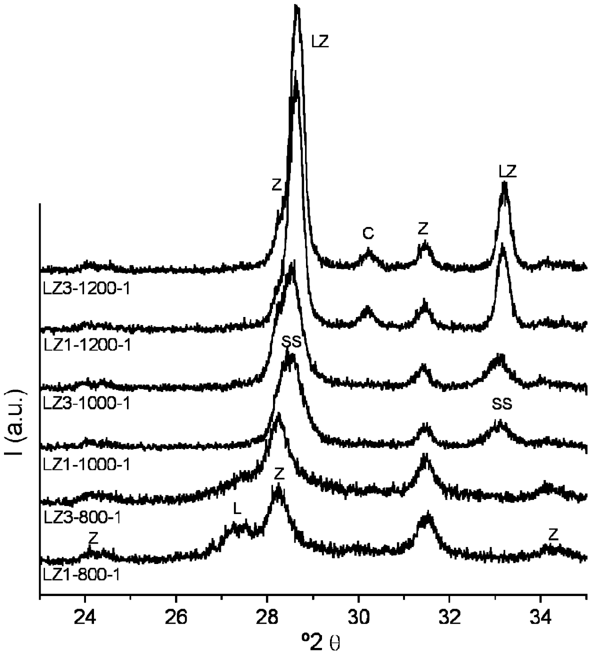


Fig. 4. X-ray diffractograms of samples LZ1 and LZ3 heated for 1 h at 800, 1000 and l200 °C. Z: monoclinic ZrO_2; L: La_2O_3; SS: solid solution; LZ: lanthanum zirconate; C: contamination solid solution.

In our case, assuming that all the anionic vacancies are nearest neighbors of Zr^{4+} ions, the global composition results in an average polyhedron $ZrO_{7.55}$.

In Fig. 4, the presence of the starting oxides is observed for LZ1-800-1 and LZ3-800-1. Their crystallinity is improved in relation to LZ1 and LZ3 (Fig. 1), and there is no evidence of the presence of solid solution. Only at 1000 °C, the (1 1 1) peak of the solid solution, overlapped with the monoclinic ZrO_2 peak at $2\theta = 28.1°$, and the (2 0 0) peak, appear. At 1200 °C, a slight shift towards higher angles and a noticeable narrowing of the two most intense peaks suggest the formation of lanthanum zirconate. A new peak is also observed at $2\theta = 30.3°$, due to contamination from the milling media, which contain Mg^{2+} as stabilizer, resulting in a tetragonal structure having slightly different lattice parameters. In agreement with this observation, XRD analysis of the milling vials shows the most intense peak at $2\theta = 30.3°$.

In the case of LZ0, no reaction was observed, even at 1200 °C, where the phase transformations of both oxides could have produced regions of higher reactivity in the solid. The sample LZ0-1200-1 is still a mixture of the starting oxides.

From these results, sample LZ6 was selected to perform thermal treatments in the temperature range up to 1300 °C, in order to assess the thermal stability of the solid solution. It has been reported that with some stabilizers, such as MgO, the solid solution decomposes at temperatures above 1100 °C in MgO and ZrO_2, which has monoclinic structure at room temperature [10].

Fig. 5 shows the X-ray diffractograms of the samples heated at temperatures between 800 and 1000 °C. At higher temperatures and longer times, the most intense peaks are slightly displaced towards lower angles. This could indicate the formation of the $La_2Zr_2O_7$ phase, which has pyrochloric structure [17]. This agrees with the results reported by Kido et al. [9], who observed the formation of this phase after 6 h at 1000 °C from powders obtained by the sol–gel method; also, Mitterdorfer and Gauckler [18] reported the formation of $La_2Zr_2O_7$ at $T \geq 1100$ °C in a system containing Sr, Mn and Y. The X-ray diffractogram of the solid solution is quite similar to that of $La_2Zr_2O_7$; for this reason, the unequivocal identification of the zirconate by XRD is difficult when this phase is in low concentration and has low crystallinity. With longer heating times (7 and 45 h) at 1000 °C, the solid solution due to contamination, detected only at 1200 °C in LZ1 and LZ3, is also observed.

It should be mentioned here that a sample of pure ZrO_2, mechanochemically activated during 6 h and heated 1 h at 1000 °C, also showed the presence of the contamination solid solution. This difference in behaviour may be explained considering that in sample LZ6-1000-1, the zirconium oxide is forming the solid solution and thus not available until the formation of zirconate at longer times, while in pure ZrO_2 it is already free to be stabilized by the contaminating Mg.

At higher temperatures (Fig. 6), the lanthanum zirconate formation process allows the weaker peaks of the

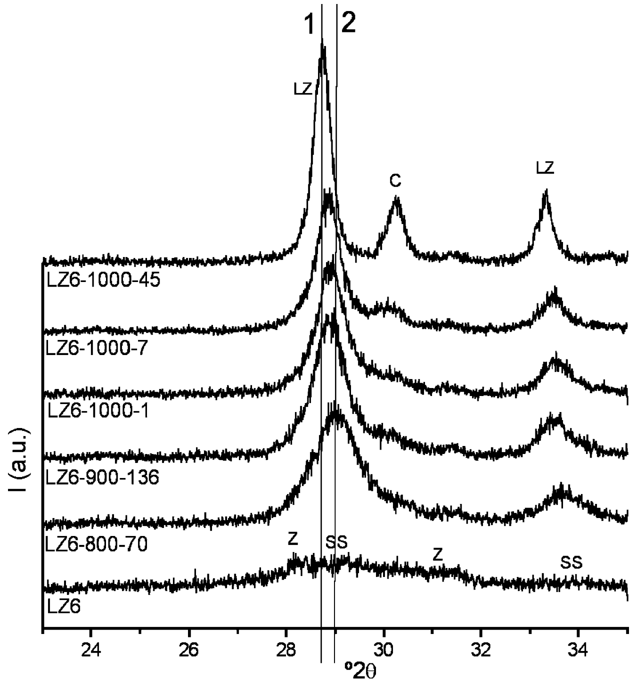


Fig. 5. X-ray diffractograms of samples LZ6, LZ6-800-70, LZ6-900-136, LZ6-1000-1, LZ6-1000-7 and LZ6-1000-45. Z: monoclinic ZrO_2; SS: solid solution; LZ: lanthanum zirconate; C: contamination solid solution. Line 1: angular position of most intense peak of lanthanum zirconate. Line 2: angular position of most intense peak of cubic solid solution.

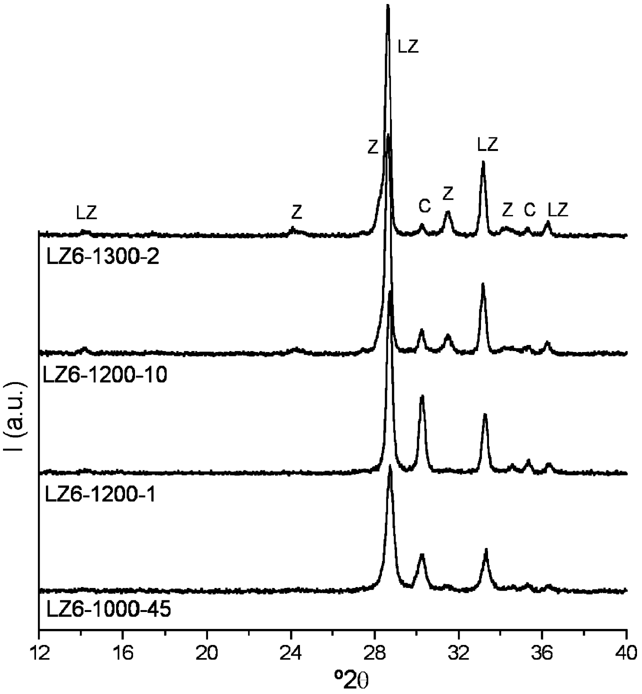


Fig. 6. X-ray diffiactograms of samples LZ6-100045, LZ6-1200-1, LZ6-1200-10 and LZ6-1300-2. Z: monoclinic ZrO_2; LZ: lanthanum zirconate; C: contamination solid solution.

pyrochloric phase (1 1 1) at $2\theta = 14.2^\circ$, (3 3 1) at $2\theta = 36.3^\circ$, and (5 1 1) at $2\theta = 43.6^\circ$ to be observed, and also to assign the angular shifts observed in Fig. 5 (from $2\theta = 29.0$ to 28.6°) to the formation of $La_2Zr_2O_7$. It is worth noting that the temperature at which the development of this phase is produced, is much lower than that required with conventional thermal treatments (1600 °C) [9]. Also, since the global composition of LZ6 is richer in Zr than $La_2Zr_2O_7$, the excess ZrO_2 is released and incorporated by the contamination solid solution, as can be seen by the increase of intensity of the peaks at $2\theta = 30.3^\circ$ (1 1 1) and about $2\theta = 35^\circ$ (2 0 0), in sample LZ6-1200-1. At longer times at 1200 °C, and at 1300 °C (LZ6-1200-10 and LZ6-1300-2), this solid solution decomposes, and ZrO_2 is observed as monoclinic at room temperature.

The sequence of transformations can be explained considering that the mechanochemically activated material is highly disordered, and at low temperature has a cubic structure with La^{3+} and Zr^{4+} cations randomly distributed in the cationic sublattice. The solid solution, homogeneous at atomic level, has a high concentration of structural defects. At high temperatures (≥1000 °C) the thermal energy is high enough for ionic diffusion to become significant, and the material develops the pyrochloric structure, with both types of cations located in specific lattice sites. This does not happen in the non-activated sample, where the longer diffusion paths and the high energy necessary for the solid state reaction require higher temperatures and longer times for the formation of the zirconate structure. The formation of the zirconate in this temperature range suggests that the stability field of this compound extends down to at least 1000 °C, according to previous reports [9] which state that $La_2Zr_2O_7$ is thermodynamically stable from room temperature, but the complexity of its crystal structure imposes kinetic limitations for the reaction.

The pyrochloric structure can be described as two different interpenetrating structures [19]. One of them is an array of cation-centered ZrO_6 octahedra, and the second is built of anion-centered La_4O tetrahedra, both sets of polyhedra sharing corners. Two octahedral blocks and one tetrahedral block combine to give $La_2Zr_2O_7$, with La^{3+} cations placed in the hexagonal windows of the octahedral lattice.

The ionic conduction characteristics of the solid solutions, which depend on the existence of a high concentration of mobile anionic vacancies, are also affected when the zirconate is formed, because this process involves long-range ordering and loss of mobility of the oxygen vacancies [20]. This part of the study has been published elsewhere [21].

4. Conclusions

Cubic La^{3+}/ZrO_2 solid solutions are obtained, by mechanochemical activation, after 6 h at room temperature, and in samples activated 1 and 3 h after thermal treatment at 1000 °C. Non-activated samples did not form the solid solution, even after thermal treatment at 1200 °C. The obtained solid solutions are composed of crystallites with sizes smaller than 10 nm.

The crystallinity of the cubic solid solution improves at temperatures ≥800 °C, through the spatial ordering of the oxygen-defective coordination polyhedra.

At 1000 °C and higher temperatures, the solid solution transforms into $La_2Zr_2O_7$. This suggests that the stability field of $La_2Zr_2O_7$ extends at least down to 1000 °C.

Mechanochemical activation is a valuable alternative method for the preparation of cubic La^{3+}/ZrO_2 solid solutions under processing conditions milder than those required by conventional thermal methods. This technique offers new possibilities for the design and control of the microstructural and physicochemical properties of these materials.

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