diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application
www.diffusion-fundamentals.org, ISSN 1862-4138; © 2005-2008

Structural Properties of Zirconia Doped with Some Oxides

Hussien Ahmed Abbas,[*,1,2] Fadwaa Fwad Hamad,[1] Atrees Khair Mohamad,[1]*
Zeinab Mohamad Hanafi,[1] Martin Kilo[2]

[1] National Research Center of Egypt, Inorganic Chemistry Department, Cairo, Egypt
[2] TU Clausthal, Fakultät für Natur- und Materialwissenschaften, Institut für Metallurgie, Robert-Koch-Str. 42, D-38678 Clausthal-Zellerfeld, Germany

E-Mail: hussien.abbas@tu-clausthal.de

Presented on the Bunsen Colloquium: Diffusion and Reactions in Advanced Materials
September 27th – 28th, 2007, Clausthal-Zellerfeld, Germany
Keywords: chemical synthesis, stabilized zirconia, X-ray diffraction, microstructure, CaO, Gd_2O_3, CeO_2

Abstract. Zirconia powders doped with different amounts of dopants (CeO_2, Gd_2O_3, and CaO) were synthesized by a citrate technique. X-ray diffraction for samples sintered at 1500 °C revealed that the zirconia ceramics were stabilized in the cubic phase above 12 mole % CaO and 10 mole % Gd_2O_3, while tetragonal zirconia is obtained above 15 mole % CeO_2. Relative densities up to 99.5% were obtained. The effect of dopant concentration on the lattice parameter, average crystallite size, microstrain was studied. The cubic lattice parameter increases nearly linearly with increasing the concentration in case of CaO and Gd_2O_3. The tetragonal lattice parameters a_t and c_t increase nearly linearly with increasing the concentration of CeO_2. The average crystallite size was found to be larger than 600 nm for the samples investigated.

1 Introduction

Pure, undoped zirconia can exist in three phases: monoclinic (T < 1170 °C), tetragonal (1170 < T < 2370 °C) and cubic (T > 2370 °C). Large volume change is associated with reverse phase transition between these phases on cooling/heating, and this affects the physical properties of zirconia. Being stabilized in the cubic or tetragonal phases, zirconia has a wide range of technological applications. However, different dopants have different influences on the phase diagram of ZrO_2-MeO_x. Both the stability of the cubic phase towards low temperatures, the position of the maximum of ionic conductivity and local ordering within the cubic phase are very sensitive to the doping. For example, Mg^{2+} stabilized zirconia (MgSZ) shows ordered phases, which are not known for Ca^{2+} stabilized zirconia (CSZ). Similarly, for Sc^{3+}

stabilized zirconia (ScSZ) there are oxygen-vacancy-ordered phases, which are not known for other phases like Y^{3+} or Gd^{3+} stabilized zirconia. These effects are explained either by charge effects [1] or by ionic size effects [2]: For the first, the charge differences between Zr^{4+} and stabilizer cations or between oxygen anion and oxygen vacancy are to be considered, while for the latter, the size differences between zirconium and the stabilizer cation on the one hand or the size difference between an oxygen anion and an oxygen vacancies are to be considered.

The present study aims to investigate the influence of the dopant valency and the dopant concentration on the structural properties of zirconia doped with different amounts of dopants such as tetravalent CeO_2, trivalent Gd_2O_3, and divalent CaO.

2 Experimental

Three ceramic oxides (CaO, Gd_2O_3, and CeO_2) were used to stabilize zirconia in the cubic or the tetragonal phases at room temperature. Samples were prepared by using the citrate technique for preparing nanosized powders, followed by uniaxial pressing and sintering to obtain > 99 % dense materials.

Ce, Gd and Ca-doped zirconia can be prepared by several methods. Among these methods, mixed oxide, co-precipitation, sol-gel, and the citrate technique are the most popular**.** The citrate technique is a wet-chemical method and it is polymeric precursor route based on Pechini process [3]. This method can be used to synthesize various ceramic powders [4-8]. $ZrO(NO_3)_2 \cdot 2H_2O$ (99.9%, Alfa), $Ca(NO_3)_2 \cdot 4H_2O$ (99%, Aldrich), $Gd(NO_3)_3 \cdot 6H_2O$ (99.9%, Strem), $Ce(NO_3)_3 \cdot 6H_2O$(99.9%, Strem), $C_6H_8O_7$ (99.5%, Aldrich) and $C_2H_4(OH)_2$ (99%, ChemPur) were used as starting materials.

Aqueous zirconium and metal nitrate solutions were mixed in a beaker, considering the desired stoichiometry of the metal oxides in the final ceramic powder. On stirring, the mixture was heated to about 100 ºC. Citric acid (CA) was then added to chelate metal cations at the CA: $Me(NO_3)_x \cdot x\,H_2O$ molar ratio of 2:1. Me denotes Ca^{+2}, Gd^{+3}, Ce^{+4} in the final ceramic powder. After 15 min of reaction, ethylene glycol (EG) was added into solution at a CA : EG molar ratio of 60 : 40. The colourless solution thus obtained, was then heated up to 150 ºC, and kept under stirring to promote the esterification and polymerization reactions. After nitrous oxides and water elimination, a clear resin was obtained. The polymeric resin was charred at 250 ºC to remove organic substances. The brown powder thus produced was ball milled and calcined for 24 h at 600 ºC then for 24 h at 1000 ºC to obtain the ceramic powder. Pure zirconium oxide was also prepared using the above method for comparison. Chemical analysis was performed on the previously prepared samples to adjust the stoichiometry.

The effect of uniaxial pressing and ball milling time and sintering temperature and time were studied. It was observed that the time of ball milling as well as the pressure was found to be crucial for the quality of the final samples. The best ceramics were obtained when the powders were ball milled for 24 h then compacted using direct uniaxial pressing into cylindrical pellets with 8 mm diameter and 2 mm thickness under a pressure of 400 MPa and sintered at 1500 ºC for 5 h. The densities of the sintered samples were measured using Archimedes method. The theoretical density is calculated from the lattice parameters obtained from XRD. X-ray diffraction was measured for the sintered samples (Siemens D5000). The lattice parameter was calculated using program called UnitCell [9]. The average crystallite size and the microstrain were calculated from the peak width [10]. The pellets were polished and then thermally etched at 1450 ºC for 2h. SEM pictures of the samples were obtained using a CAMSCAN44 machine in the electron backscattering mode.

3 Results and Discussion

3.1 XRD Results

Especially at low stabiliser concentrations, two phases were found at room temperature. Typical XRD profile is given in (Fig. 1), together with a SEM picture of a fully sintered sample. The results of the data evaluation are summarised in Tables 1-3, also including information on calculated strain, on particle size, and on relative densities of the sintered samples.

Finally, in Fig. 2, a summary of all obtained lattice parameters and in Fig. 3 the lattice volumes are given, which allows to make comparisons between the different stabilisers.

Table 1: Microstructural parameter of ZrO_2-CaO system

monoclinic phase						cubic phase				relative density
CaO mol%	a [Å]	b [Å]	c [Å]	ß [º]	V [$Å^3$]	a [Å]	V [$Å^3$]	size [nm]	strain × 10^{-4}	
0	5.3146	5.2052	5.1503	99.255	140.622	–	–	–	–	87.1
5	5.3136	5.2018	5.1498	99.281	140.479	5.1232	134.471	850	53.3	–
12	–	–	–	–	–	5.1261	134.702	520	1.46	99.5
17	–	–	–	–	–	5.1311	135.093	650	17.2	98.5
20	–	–	–	–	–	5.1371	135.566	770	21.8	99.2

Table 2: Microstructure parameter of ZrO_2-Gd_2O_3 system

monoclinic phase						cubic phase				relative density
Gd_2O_3 mole %	a [Å]	b [Å]	c [Å]	ß [º]	V [$Å^3$]	a [Å]	V [$Å^3$]	size [nm]	strain × 10^{-4}	
0	5.3146	5.2052	5.1503	99.255	140.622	–	–	–	–	87.1
5	5.3084	5.2122	5.1597	99.238	140.907	5.1482	136.448	640	53.8	–
10	–	–	–	–	–	5.1591	137.313	830	25.5	97.4
15	–	–	–	–	–	5.1851	139.402	920	32.9	98.7
21	–	–	–	–	–	5.2002	140.628	710	17.3	98.2

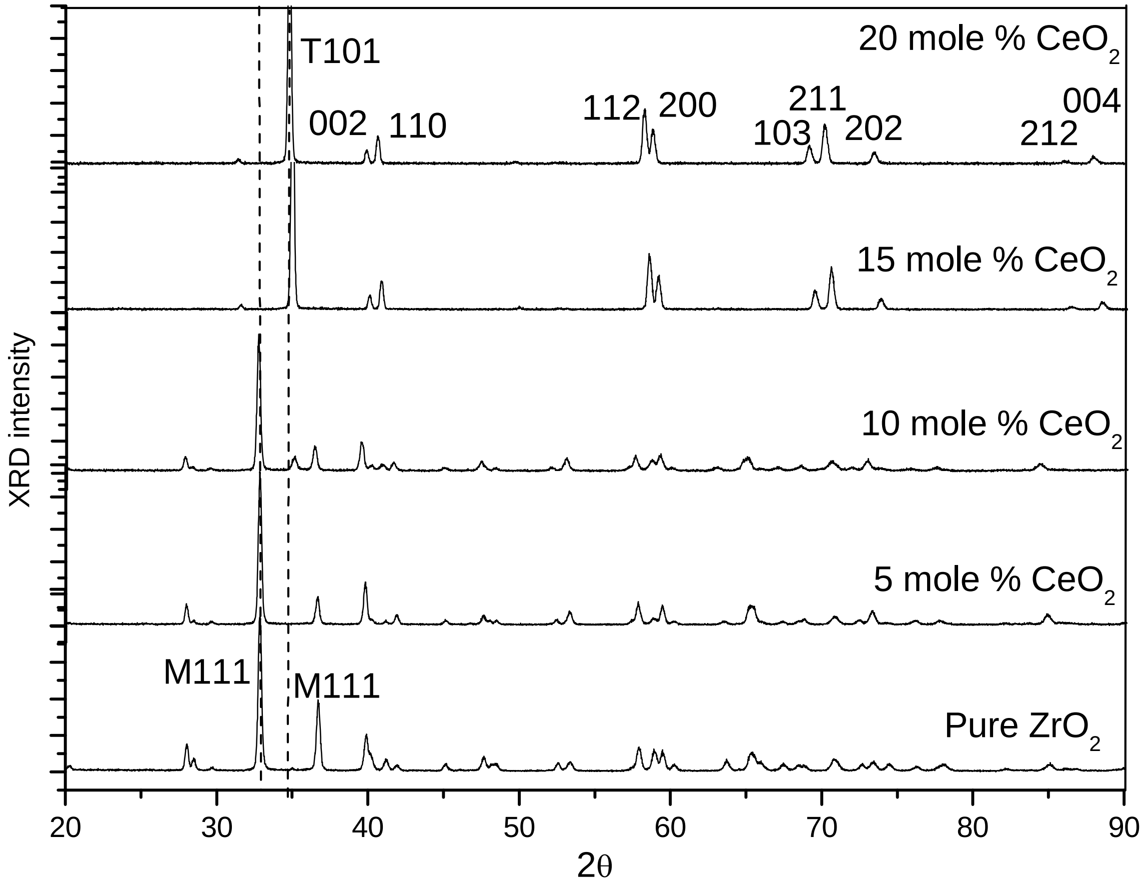
Table 3: Microstructure parameter of ZrO_2-CeO_2 system

monoclinic phase						tetragonal phase					rel. density
CeO_2 mole %	a [Å]	b [Å]	c [Å]	ß [º]	V [$Å^3$]	$\sqrt{2}\,a_t$ [Å]	c_t [Å]	V [$Å^3$]	size [nm]	strain × 10^{-4}	
0	5.3146	5.2052	5.1503	99.255	140.622	–	–	–	–	–	87.1
5	5.3270	5.2069	5.1662	99.128	141.482	–	–	–	–	–	89.8
10	5.3606	5.2159	5.1885	99.124	143.236	5.1274	5.2143	137.085	480	39.8	–
15	–	–	–	–	–	5.1325	5.2289	137.737	1040	43.1	95.0
20	–	–	–	–	–	5.1517	5.2448	139.193	890	40.6	87.8

3.2 Comparison of Systems

After addition of 5 mole% of the stabilisers CaO and Gd_2O_3 to zirconia, mixtures of monoclinic and cubic phases are obtained. Fully cubic stabilized zirconia ceramic was obtained after addition of 12 mole % of CaO, or 10 mole% Gd_2O_3. Battacharya and Agrawal [11] stabilized zirconia samples containing ≥ 9.5 mole % Gd_2O_3 in the cubic phase. Muccillo *et al.* [4] prepared zirconia-16 mole% calcia in the cubic structure. However, the tetragonal phase was not observed in the Ca- and Gd-stabilised systems investigated. Tetragonal stabilized zirconia ceramic is obtained at 15 mole % CeO_2. Zirconia containing 20 mole % ceria is also fully stabilized in the tetragonal phase and this result is in agreement to that of Torng *et al.* [12]

In all cases, the volume decreases significantly when going from the monoclinic to the next phase with higher symmetry. It is remarkable that for all phases, the effect of Ca stabilisation on lattice parameter is smallest, and the effect of CeO_2 incorporation is the highest: Within the monoclinic phase, the lattice volume is almost constant when adding more CaO, while for the Gd_2O_3- and CeO_2-stabilised systems, the lattice volume is increasing, with increasing slope. The same effect is observed at higher dopant concentrations in the cubic/tetragonal phases: Cubic ZrO_2-CaO has a, small, only slightly with dopant increasing unit cell volume, while ZrO_2-Gd_2O_3 and ZrO_2-CeO_2 have higher, stronger with dopant concentration increasing lattice volumes (Fig. 3). It is also interesting to note that this effect is only due to changes in the lattice constant c, while a is constant for ZrO_2-CeO_2 (Fig. 2).



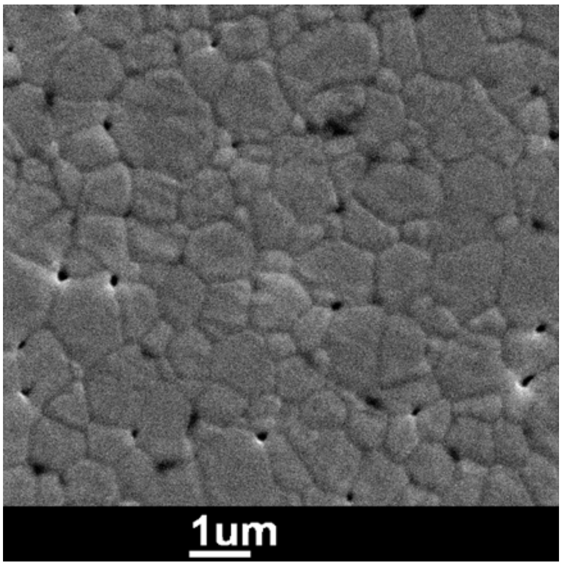


Fig. 1: Top: X-ray diffraction patterns of ZrO_2-CeO_2 sintered at 1500 °C / 5 h, obtained at room temperature. Left: SEM image of the sample containing 15 mol% CeO_2.

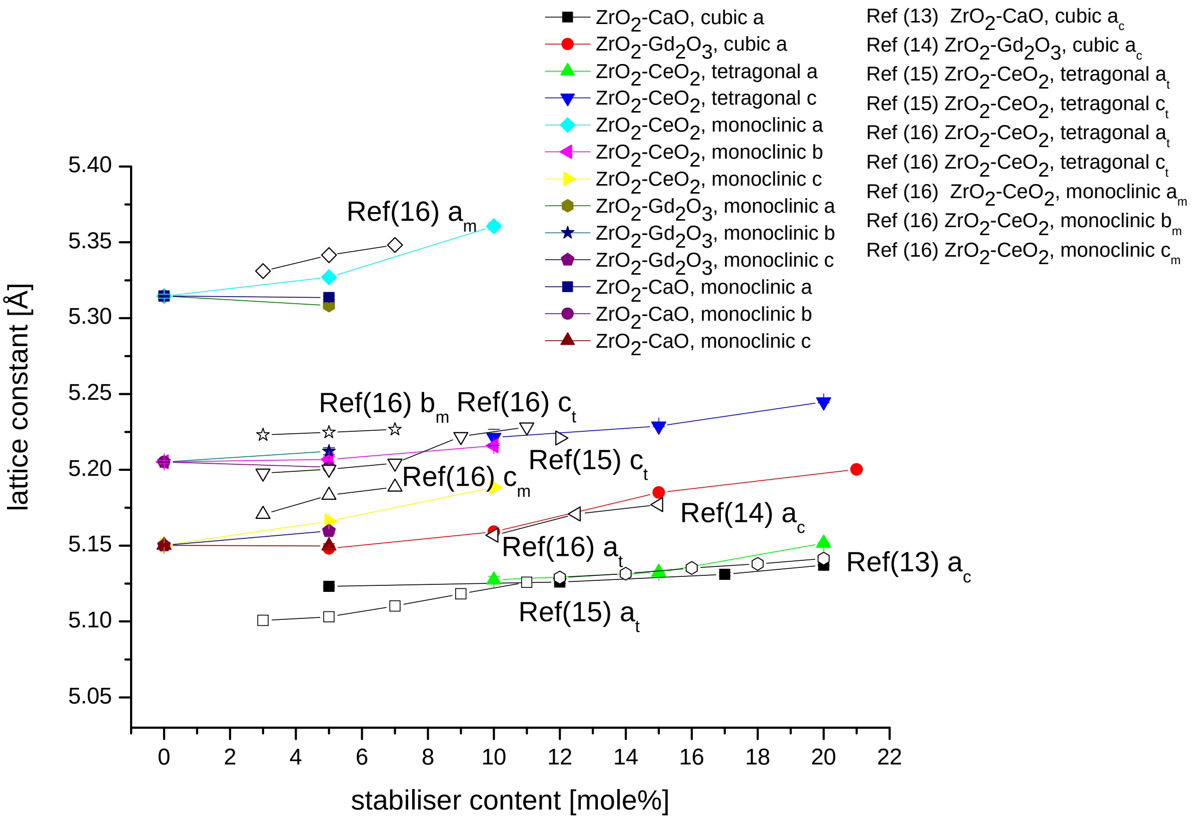


Fig. 2: Lattice constants for the investigated systems. For comparison, literature results are also included.

From Fig. 2, it can be seen that for ZrO_2-CaO and ZrO_2-Gd_2O_3 the cubic lattice parameter a increases nearly linearly with increasing CaO and Gd_2O_3 content. This is in agreement with refs. [13] and [14], respectively. The tetragonal a and c parameters for ZrO_2-CeO_2 are in agreement with those of refs. [15] and [16], respectively, whereas the monoclinic a, b and c parameters are slightly smaller than reported in ref. [16].

When going from monoclinic to tetragonal to cubic phases, the distortion defined by the difference between the a and c parameters is not strongly decreased when increasing the stabiliser content. It is remarkable to note that the tetragonal a-parameters for ZrO_2-CeO_2 and cubic a-parameter for ZrO_2-CaO are almost identical.

The lattice volume of the tetragonal ZrO_2-CeO_2 is in agreement with that of ref. [16] whereas the monoclinic lattice volume of the ZrO_2-CeO_2 is smaller than given in ref. [16] (Fig. 3). One reason for this could be that the particle size and strain in our samples is different than those in [16], where samples of grain sizes well below 100 nm were investigated and an interdependency between the growth of monoclinic and tetragonal particles was observed. According to Lin and Duh [16], powders of grain size around 10 nm show rapid grain growth above 1300 °C, independent of the stabiliser type.

When comparing dopant influence on the cubic lattice parameter, the value for ZrO_2-CaO is significantly smaller than that of cubic ZrO_2-Gd_2O_3 and that of tetragonal ZrO_2-CeO_2. This might be explained by effects of ionic size: Zr^{4+} has an ionic size of 84 pm, Ca^{2+} 112 pm, Gd^{3+} 105 pm and Ce^{4+} 97 pm [17]. For Ca^{2+} doping, each cation is accompanied with one oxygen vacancy, while for Gd^{3+} two cations are accompanied with one oxygen vacancy, while for Ce^{4+} no oxygen vacancies should be formed due to doping. Since the volume effect of doping on CSZ is strongest, it can be suggested that the volume of an O^{2-} vacancy in zirconia is smaller than the volume of an oxygen anion, which is 144 pm. This means that the effective

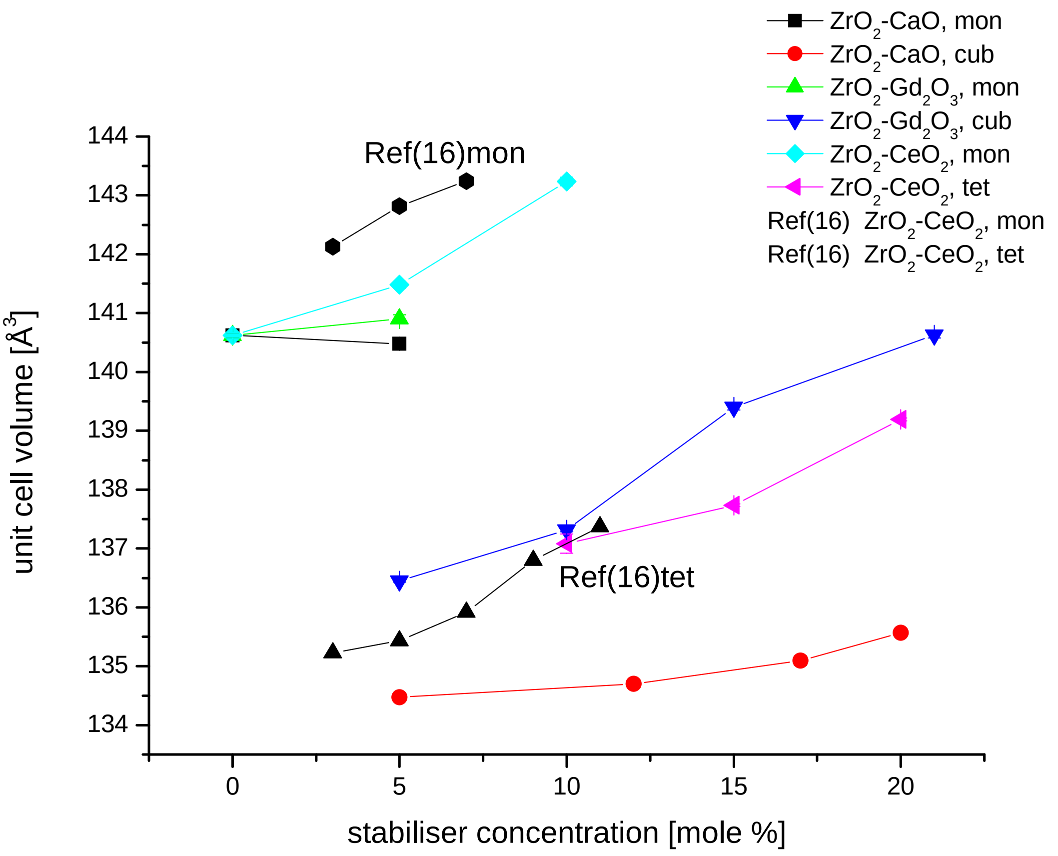


Fig. 3: Lattice volume for the investigated systems.

volume is decreasing on removing oxygen ions, but increasing because of the accompanying introduction of cations.

The SEM images as well as the density measurements confirmed that the cubic samples do not contain open pores. The few remaining pores are isolated, closed pores meaning that it was possible to obtain dense ceramics. Grain sizes observed using SEM are up to 1 µm, i.e, in the same range as observed with XRD.

3.3 Effect of Crystallite Size and Microstrain

Fig. 4 shows the average grain size and lattice strain, as obtained according to [10], for the cubic or tetragonal phases. The grain size is around 750 nm, varying between 500 and 1100 nm. It is almost independent of the dopant type and concentration, meaning that the sintering process was in the intermediate stage dominated mainly by compaction but only minor grain growth. However, cubic samples show larger grains (around 1 µm) than monoclinic or tetragonal samples. The X-ray microstrain is the highest in case of ZrO_2-CeO_2 system which is in the tetragonal phase and it is the lowest in case of ZrO_2-CaO which has the cubic phase. This is remarkably opposite to the size difference of the ions, which is smallest for Ce^{4+} and largest for Ca^{2+}.

In the future, the oxygen ion conductivity of these samples should be measured and the bulk as well as grain boundary effects should be separated.

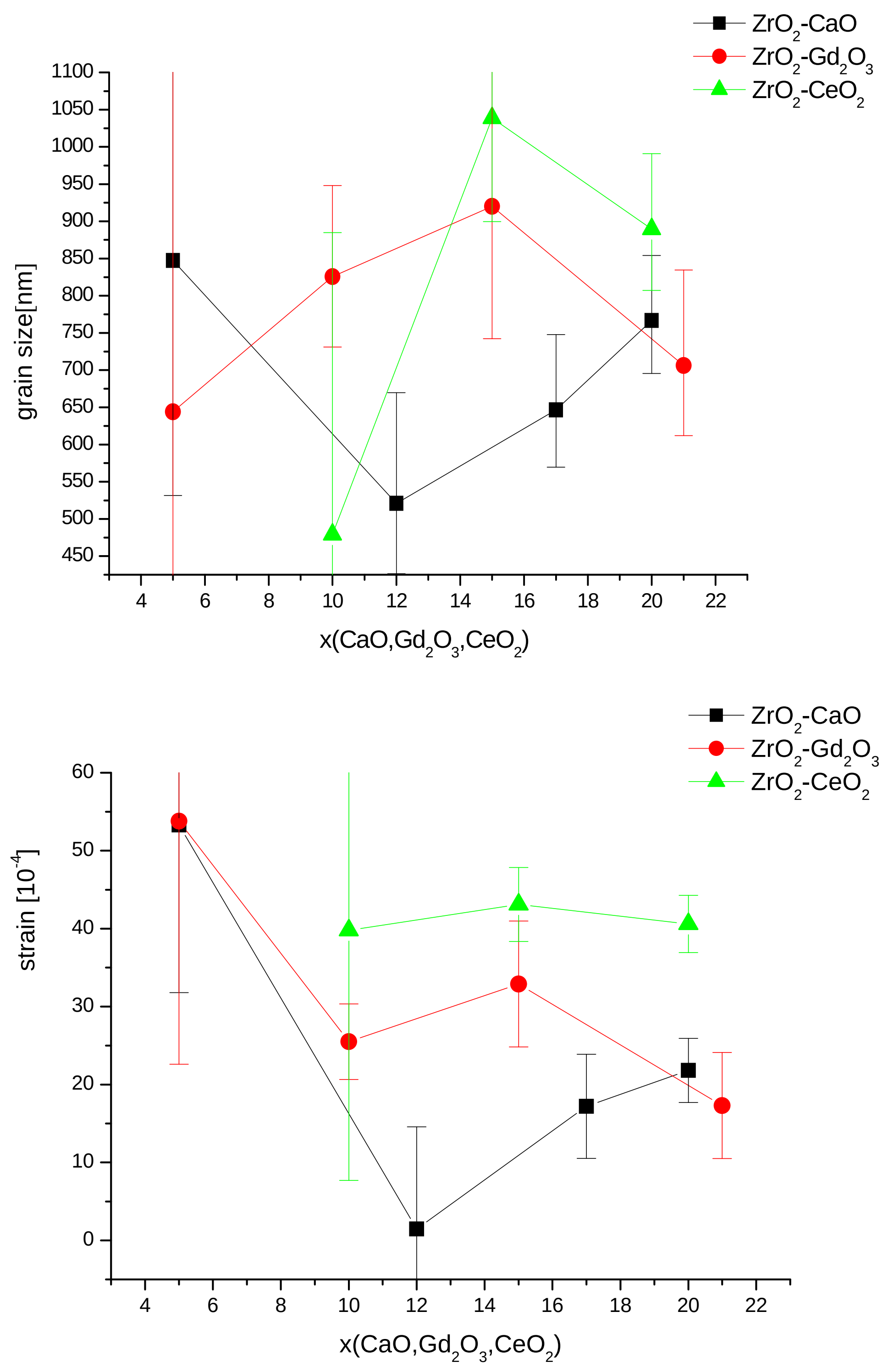


Fig. 4: Average grain size (top) and lattice strain (bottom) for the investigated systems.

4 Conclusions

Zirconia stabilized with different amounts of dopants (CaO, Gd_2O_3 and CeO_2) prepared using the citrate technique was studied with particular interest in the dopant vacancy and dopant concentration**.** Using the Pechini method, fully cubic stabilized zirconia ceramics were obtained in case of ZrO_2-CaO and ZrO_2-Gd_2O_3 whereas fully tetragonal stabilized zirconia ceramics were obtained in case of ZrO_2-CeO_2. Fully dense, ceramic samples of zirconia stabilised with different amounts of CaO, Gd_2O_3 and CeO_2 were prepared. It is recommended to ball mill the powders prepared by the Pechini method in order to obtain dense ceramics. It was found that in all the systems the addition of different amounts of dopants (CaO, Gd_2O_3 and CeO_2) to zirconia had a remarkable effect on the lattice parameter, unit cell volume and microstrain. The lattice parameters increase with increasing stabilizer content and are changing when going from Ca^{2+} via Gd^{3+} to Ce^{4+} doping.

References

[1] M. Weller, Z. Metallkunde 84 (1993) 381.
[2] S. P. S. Badwal, Solid State Ionics 52 (1992) 23.
[3] M. Pechini, US patent 3,330,697 (1967).
[4] R. Muccillo, R. C. Buissa Netto, E. N. S. Muccillo, Mater. Lett. 49 (2001) 197.
[5] E. N. S. Muccillo, R. A. Rocha, R. Muccillo, Mater. Lett. 53 (2002) 353.
[6] J. Kaspar, P. Fornasiero, G. Balducci, R. Di Monte, N. Hickey, V. Sergo, Inorg. Chim. Acta 349 (2003) 217.
[7] A. L. Quinelato, E. Longo, L. A. Perazolli, J. A. Varela, J. Europ. Ceram. Soc. 20 (2000) 1077.
[8] M. Kakihana, S. Kato, M. Yashim, M. Yoshimura, J. Alloys Cpds. 280 (1998) 125.
[9] T. J. B. Holland, S. A. T. Redfern, Mineralogical Magazine 61 (1997) 65.
[10] M. A. Carpenter, European J. Mineralogy 10 (1998) 619.
[11] S. Bhattacharyya, D. C. Agrawal, J. Mater. Sci. 37 (2002) 1387.
[12] S. Torng, K. Miyazawa, T. Sakuma, Ceramics International 22 (1996) 309.
[13] T. Y Tien, E. C. Subbarao, J. Chem Phys. 39 (1963) 1041.
[14] T. -K Kang, T. Nagasaki, N. Igawa, K. Il-Hiun, H. Ohno, J. Am. Ceram. Soc. 75 (1992) 2297.
[15] T. Hirata, E. Asari, M. Kitajima, J. Solid State Chem. 110 (1994) 201.
[16] J. -D. Lin, J.-G. Duh, J. Am. Ceram. Soc. 81 (1998) 853.
[17] R .D. Shannon, Acta Cryst. A 32 (1976) 751.