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ScienceDirect

Journal of the European Ceramic Society 27 (2007) 1379–1387

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Influence of twin cations on zirconia composites stability

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Abstract

Last years the ternary stabilised zirconia systems attract a considerable attention as a source of materials for structural ceramics as well as for modern fuel cells.

The simultaneous influence of a pair of cations (twinned) such as: Mg^{2+}–Ca^{2+} and Sr^{2+}–Ca^{2+} on zirconia powders stabilisation process in 1550–1750 °C temperature range. Samples for investigations were performed by classical ceramic method. Comparative microstructure investigations were made by SEM on sample surfaces. The XRD, FTIR analysis and EDS spectra for the considered samples are in good agreement with the determined properties of the studied compositions.

Keywords: ZrO_2; CaO; MgO

1. Introduction

The stabilisation of ZrO_2 as well as the obtaining of zirconia products are now intensively studied domains as a result of their good mechanical and corrosion resistance at high temperatures.[1–3] This process leads to the fully or partially stabilisation of zirconia and may be achieved by inserting in ZrO_2 lattice some ions having close ion radius comparatively to that of Zr^{4+}. In such way the tetragonal (t) or cubic (c) polymorph become stable at room temperature.[4]

Stabilisation in binary systems is a very widely approached process, but in many cases the temperatures needed for its achievement are too high and sometimes, even if tetragonal solid solutions are formed, they are unstable and are changing into a monoclinic structure on cooling. Due to these reasons, the modern researches regarding the stabilisation process are focused towards ternary systems.[5–10] The high fracture toughness of optimally fabricated precipitation toughened partially stabilised ZrO_2's (PSZ's) is due to the stress induced martensitic transformation of tetragonal (t) precipitates to monoclinic (m) form in the stress fields of propagation crack. PSZ' s are two phase ZrO_2 alloys, the matrix phase is a solute rich cubic (c)-ZrO_2 solid solution, which contains fine tetragonal (t)-ZrO_2 precipitates of a lower solute content.

Consequently this paper aims the study of stabilisation in argon environment comparatively with oxidising temperature at 1550 °C of some ternary composition belonging to the ZrO_2–CaO–SrO and ZrO_2–CaO–MgO systems.

2. Experimental procedure

2.1. Starting materials

The raw materials characteristics are summarized in Table 1.

2.2. Fabrication and sintering

Zirconia (commercially available, Japan) and stabilising oxides mixtures batches were prepared according to Table 2, starting from monoclinic zirconia powder and 10, 15 and 20% CaO (by weight). MgO as secondary stabilising oxide (5 and 10% (weight) was added in an attritor with isopropyl alcohol, using zirconia balls, for 2 h. The $CaCO_3$ and $SrCO_3$ (Chimopar, Romania) and MgO (Ocna Mures, Romania) have had high purity (99.9, and 99.5%) (Table 1). After drying the powder mixtures (were dispersed by passing through a 0.5 mm sieve.

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doi:10.1016/j.jeurceramsoc.2006.08.003

Table 1
Characteristics of raw materials

Raw material	Chemical composition	Mineralogical phases	Density (g/cm^3)	dm[a] (μm)
Zirconia	Min. 99.5% $ZrO_2 + HfO_2$	Monoclinic ZrO_2	4.763	7.9
$CaCO_3$	99.9% $CaCO_3$	–	n.d.	22.7
$SrCO_3$	99.9% $SrCO_3$	–	n.d.	9.8
MgO	99.8%	Cubic	3.50	8.6

[a] dm: the median diameter determined by laser granulometry.

Table 2
The composition of monoclinic ZrO_2 and stabilising oxides mixtures

Specimens	ZrO_2 (wt.%)	CaO (wt.%)	MgO (wt.%)	SrO (wt.%)
Compositions in ZrO_2–CaO–MgO system				
A1	96	3	1	0
A2	94	5	1	0
A3	92	7	1	0
A4	90	9	1	0
A5	88	11	1	0
A6	94	4	2	0
A7	94	3	3	0
A8	94	2	4	0
Compositions in ZrO_2–CaO–SrO system				
S1	84	14	0	2
S2	84	12	0	4
S3	84	10	0	6
S4	79	19	0	2
S5	79	17	0	4
S6	79	15	0	6

The batches were pressed as cylinders ($d = 18$ mm). The specimens were treated at 1550 and 1750 °C in air in a kiln with methane gas – during 4 h of soaking. Samples with the same composition were sintered at 1550 °C in Argon in electrical furnace with (graphite electrodes) for 2 h at maximum temperature. The samples were cooled down with a rate of 5.5 °C/min.

2.3. Microstructure and ceramic properties

A TUR – four diffractometer with Cu Kα radiation was used to analyse the developed mineralogical phases. The particle size distribution of the powders was determined by using a laser granulometer (Fritsch). The sintering bulk density was measured by the hydrostatic method.

A Hitachi S 2600N scanning electron microscope (SEM) incorporating a microanalysis detector for energy dispersive X-rays (EDS) was used to observe the surface microstructure of samples.

2.4. Infrared powder transmission

As infrared grating spectrophotometer (Shimadzu FTIR 8400) was used for pellet spectra over 4000–400 cm^{-1} regions. Infrared transmission spectra were obtained from KBr pellets containing powdered sample material. Sample were first dry-grounded and blended with the KBr; 0.75 wt.% of samples was ordinarily used. Powder transmission method was used for IR spectra.

3. Results and discussions

3.1. Ceramic properties

3.1.1. ZrO_2–CaO–SrO systems

The ceramic properties-bulk density and open porosity-of zirconia powders (S1–S6) belonging to ZrO_2–CaO–SrO system after sintering at 1550 and 1750 °C in air and at 1550 °C in argon, respectively are plotted in Fig. 1(a) and (b). All samples fired at 1550 °C in Argon present a lower densification process, comparatively with the firing in air at the same temperature.

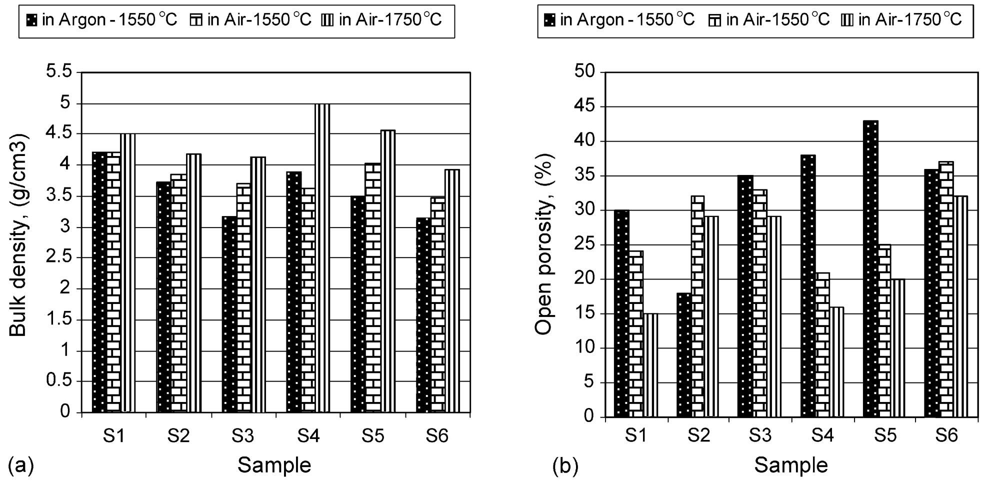

Fig. 1. Evolution of bulk density (a) and open porosity (b) of ZrO_2–CaO–SrO powders after sintering at 1550 and 1750 °C in air and at 1550 °C in argon, respectively.

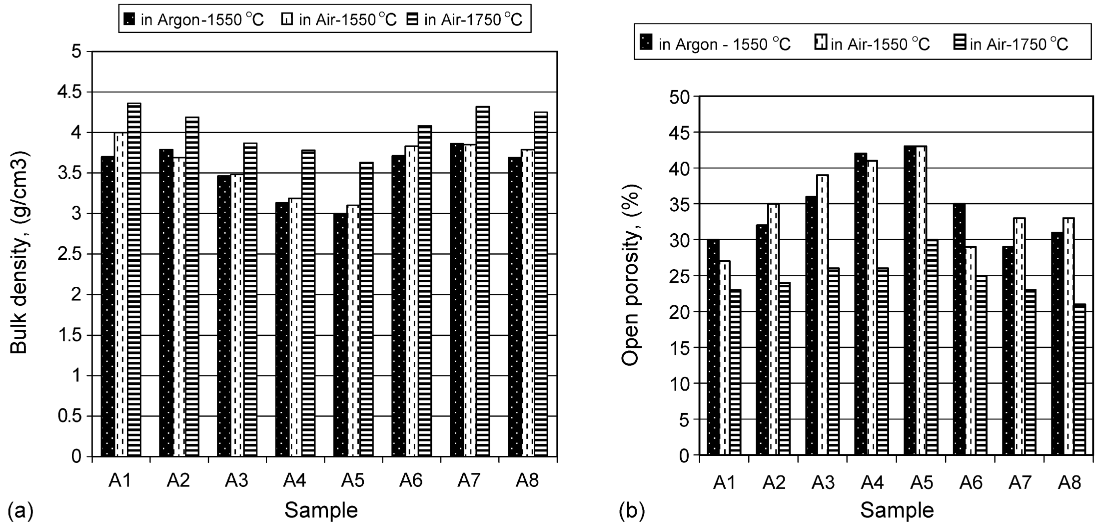

Fig. 2. Evolution of bulk density (a) and open porosity (b) of ZrO_2–CaO–MgO powders after sintering at 1550 and 1750 °C in air and at 1550 °C in argon, respectively.

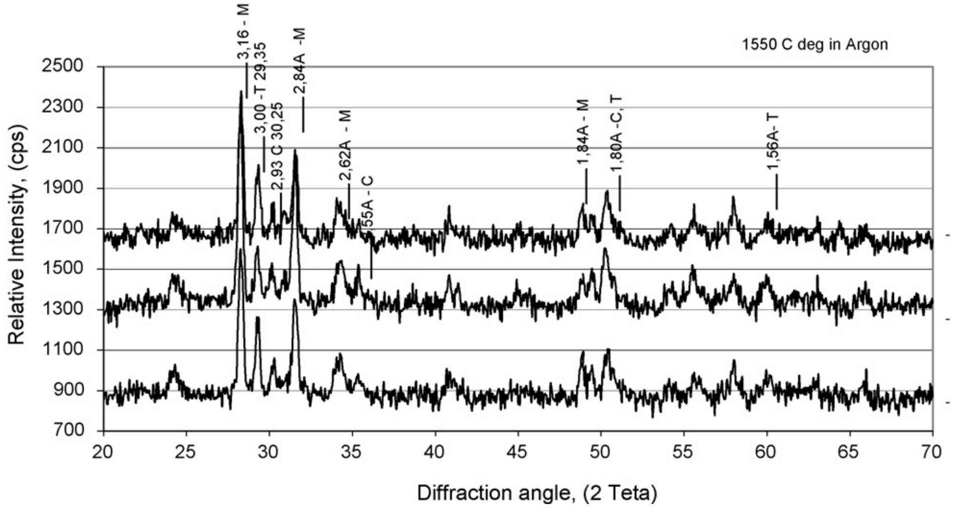

Fig. 3. XRD patterns of S1, S3, and S5 compositions in ZrO_2–CaO–SrO system fired in Argon at 1550 °C.

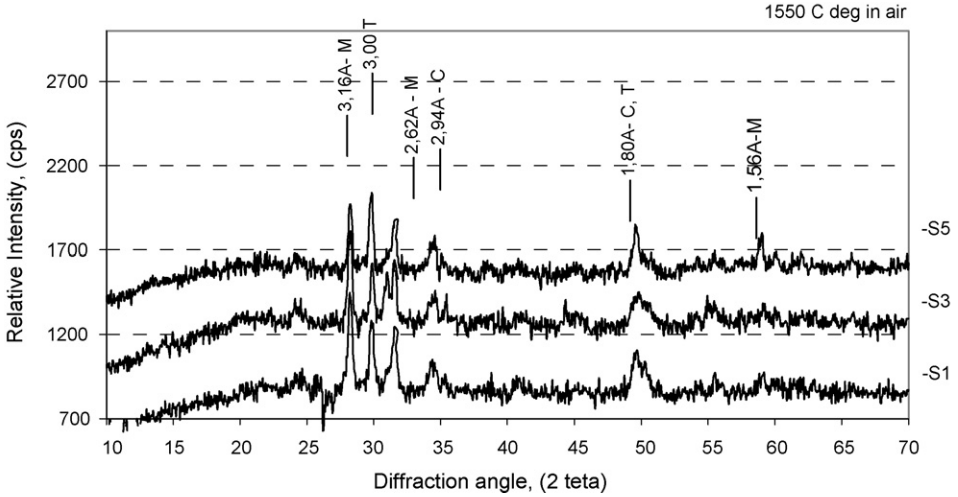

Fig. 4. XRD patterns of S1, S3, and S5 compositions in ZrO_2–CaO–SrO system fired in air at 1550 °C.

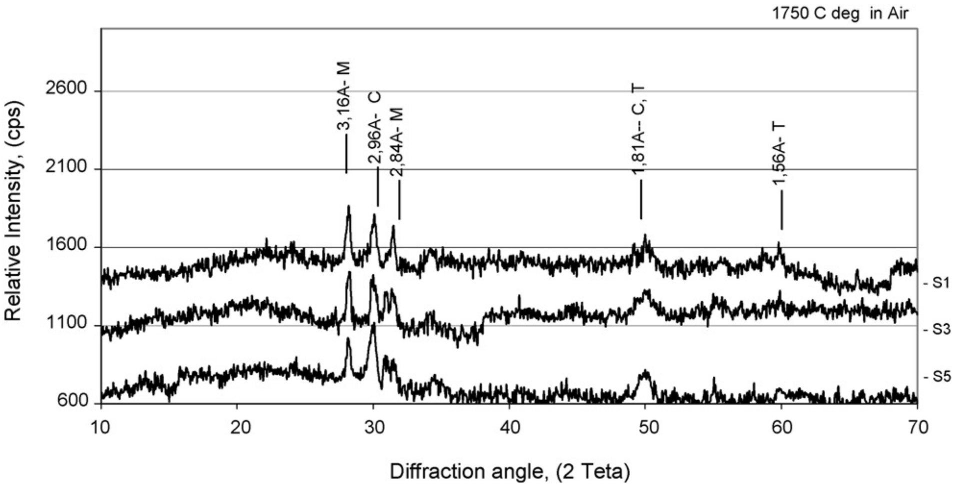

Fig. 5. XRD patterns of S1, S3, and S5 compositions in ZrO_2–CaO–SrO system fired in air at 1750 °C.

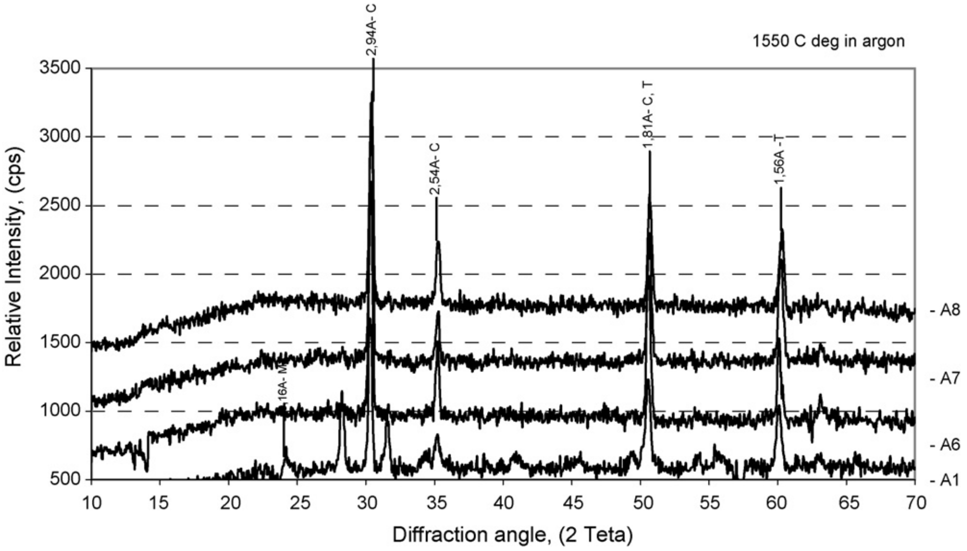

Fig. 6. XRD patterns of A1, A6, A7 and A8 compositions in ZrO_2–CaO–MgO system fired in Argon at 1550 °C.

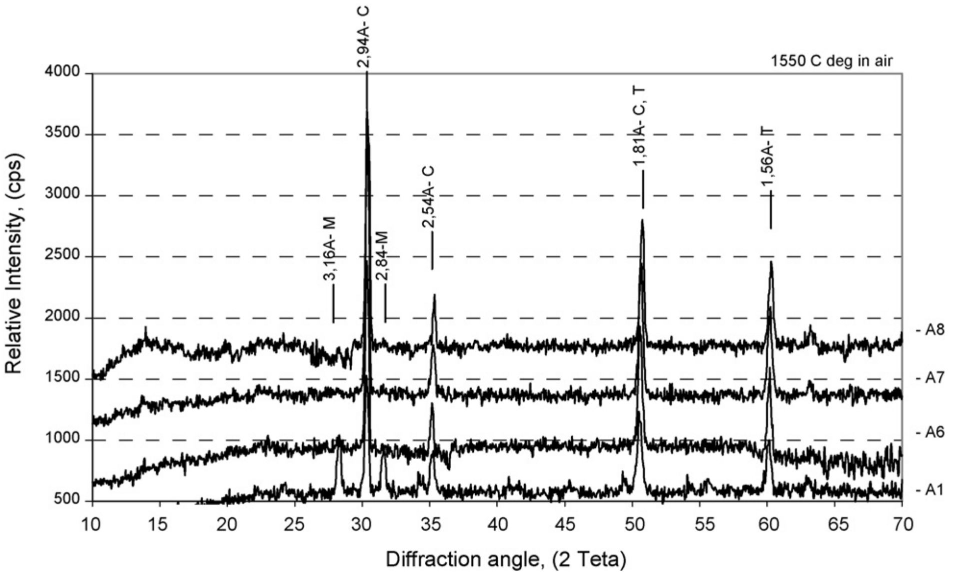

Fig. 7. XRD patterns of A1, A6, A7 and A8 compositions in ZrO_2–CaO–MgO system fired in air at 1550 °C.

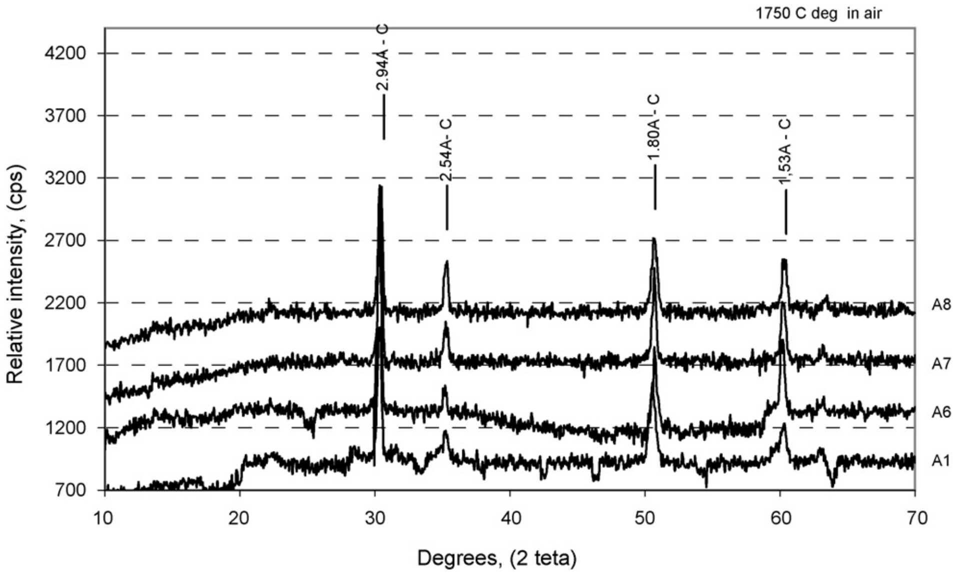

Fig. 8. XRD patterns of A1, A6, A7 and A8 compositions in ZrO_2–CaO–MgO system fired in air at 1750 °C.

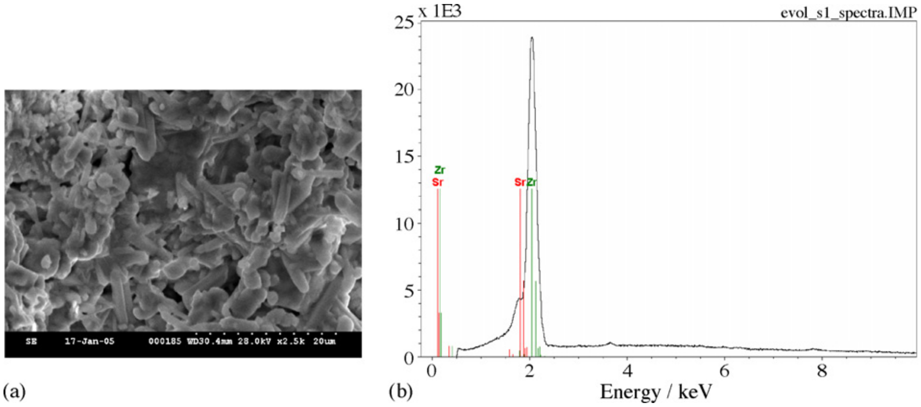

Fig. 9. SEM micrograph (a) and EDS signals on S1 (14% CaO + 2% SrO) sample surface (b) fired at 1550 °C in Argon.

3.1.2. ZrO_2–CaO–MgO systems

In Fig. 2(a) and (b) are presented the ceramic properties-bulk density (a) and open porosity (b)-of zirconia samples (A1–A8) belonging to ZrO_2–CaO–MgO system after sintering at 1550 and 1750 °C in air and at 1550 °C in argon and the same behaviour of the samples is registered like in ZrO_2–CaO–MgO system.

3.2. Microstructure

3.2.1. ZrO_2–CaO–SrO systems

XRD patterns of S1, S3, and S5 ternary zirconia powders stabilised in Argon atmosphere are given in Fig. 3 and in oxidising atmosphere at 1550 °C are shown in Fig. 4. XRD patterns of the

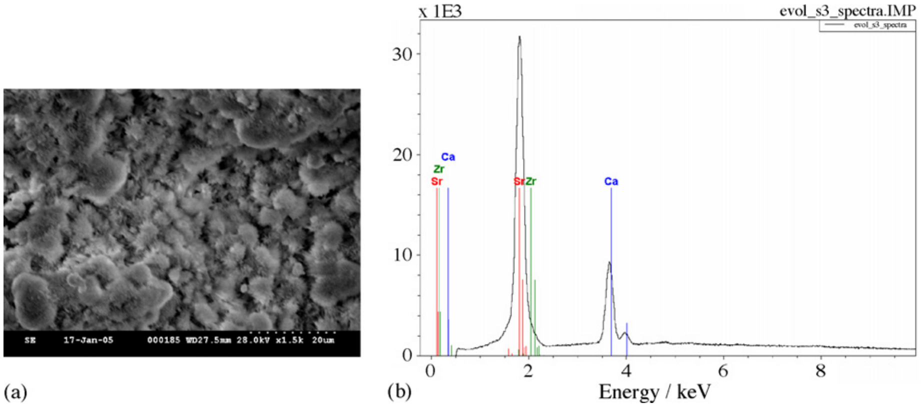

Fig. 10. SEM micrograph (a) and EDS signals on S3 (10% CaO + 6% SrO) sample surface (b) fired at 1550 °C in Argon.

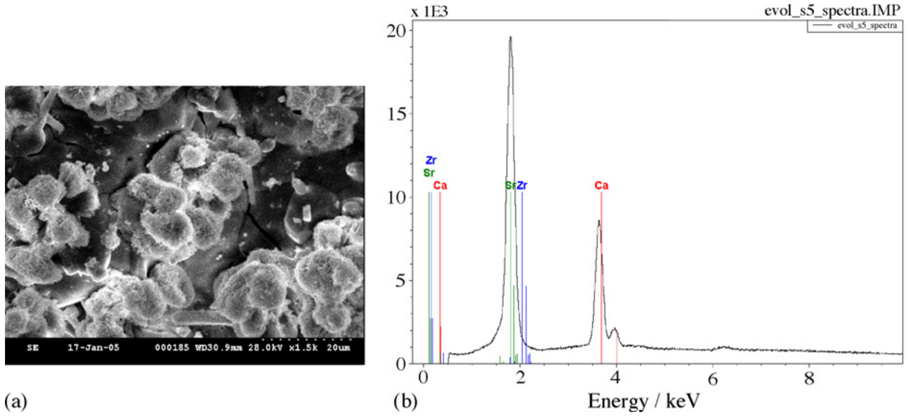

Fig. 11. SEM micrograph (a) and EDS signals on S5 (17% CaO + 4% SrO) sample surface (b) fired at 1550 °C in Argon.

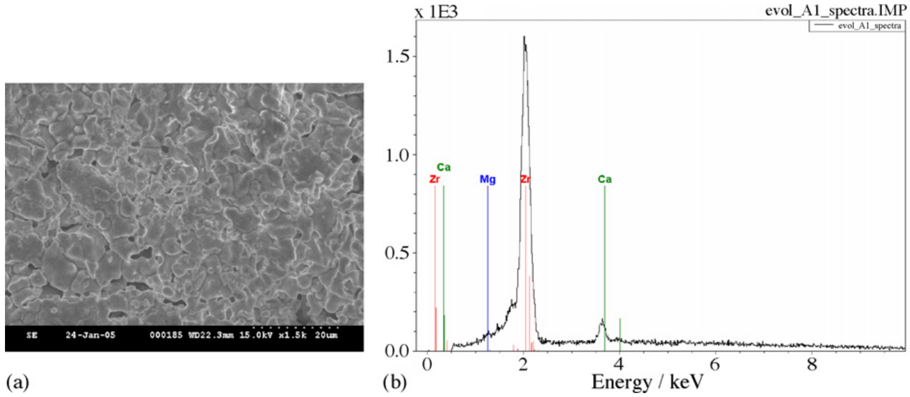

Fig. 12. SEM micrograph (a) and EDS signals on A1 (3% CaO + 1% MgO) sample surface (b) fired at 1550 °C in Argon.

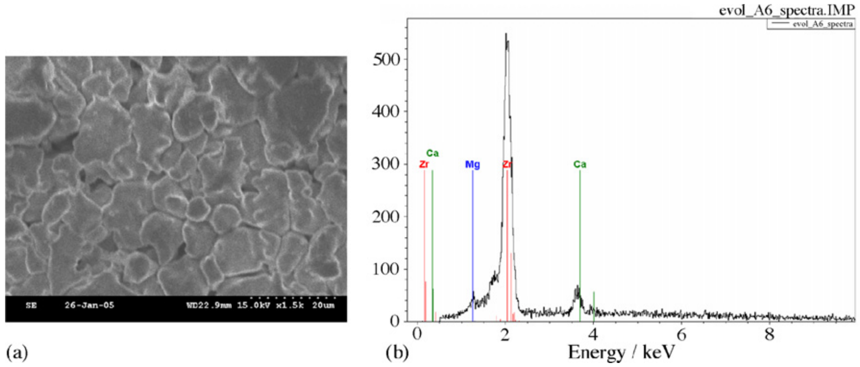

Fig. 13. SEM micrograph (a) and EDS signals on A6 (4% CaO + 2% MgO) sample surface (b) fired at 1550 °C in Argon.

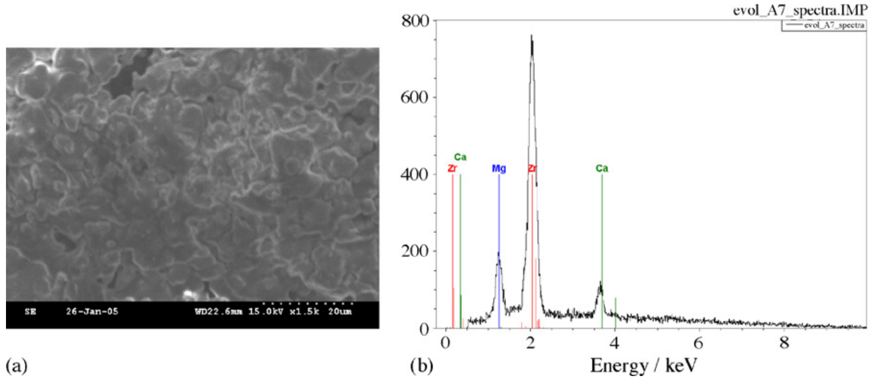

Fig. 14. SEM micrograph (a) and EDS signals on A7 (3% CaO + 3% MgO) sample surface (b) fired at 1550 °C in Argon.

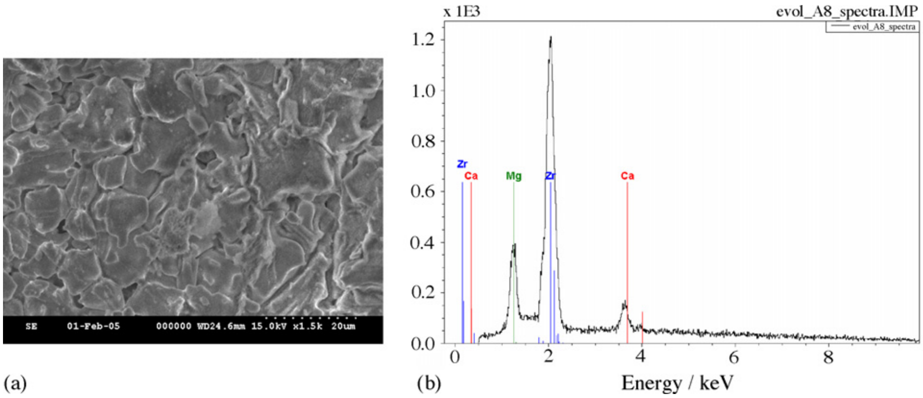

Fig. 15. SEM micrograph (a) and EDS signals on A8 (2% CaO + 4% MgO) sample surface (b) fired at 1550 °C in Argon.

same samples stabilised in oxidising atmosphere at 1750 °C are shown in Fig. 5. The X-ray diffraction on the samples S1, S3, and S5 fired in argon at 1550 °C (Fig. 3) emphasised partially stabilisation process of zirconia when a major amount of tetragonal solid solution is present among the cubic and monoclinic polymorphs. The formation of tetragonal ZrO_2 is extremely interesting for development of high toughness ceramic materials. The firing in air at 1550 °C (Fig. 4) and 1750 °C (Fig. 5)

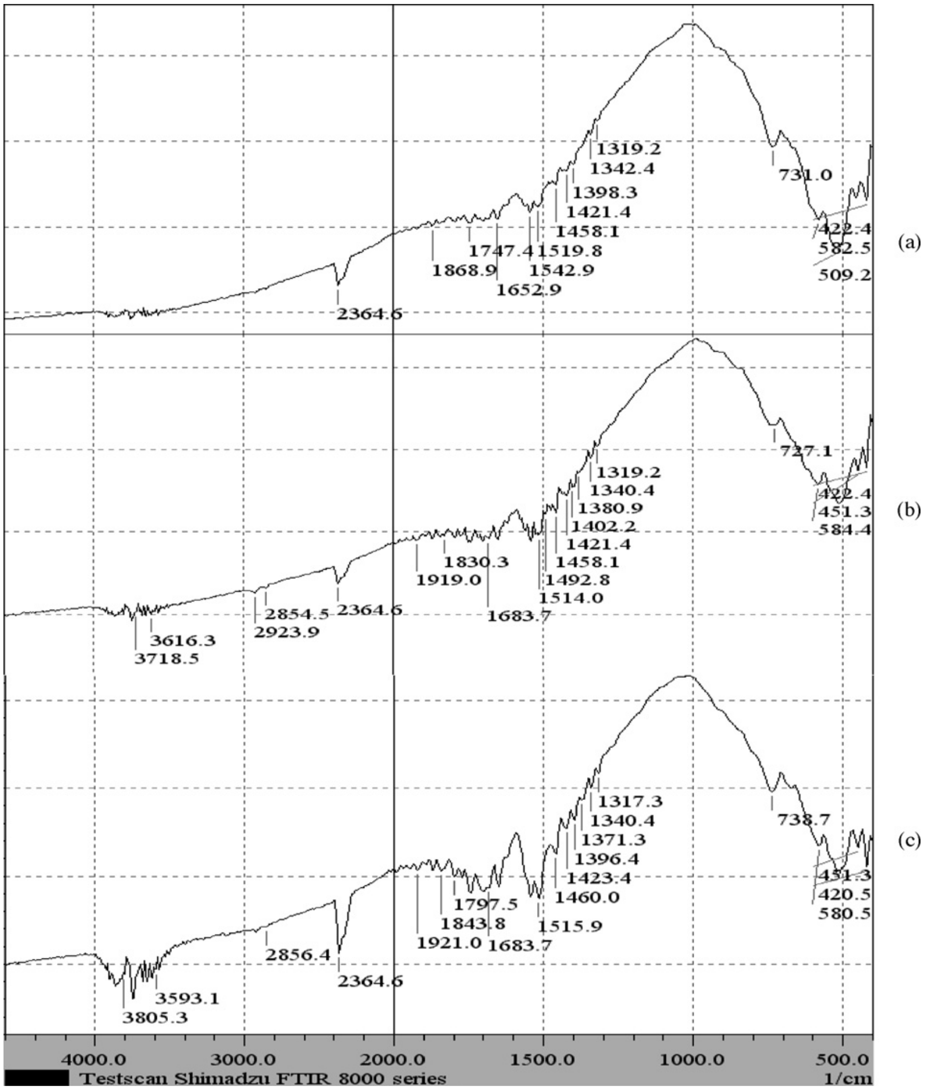

Fig. 16. Powder transmission FTIR spectra of zirconias fired at 1550 °C in Argon (a) sample S1 with 14% CaO + 2% SrO; (b) sample S3 (10% CaO + 6% SrO); (c) sample S5 with 17% CaO + 4% SrO.

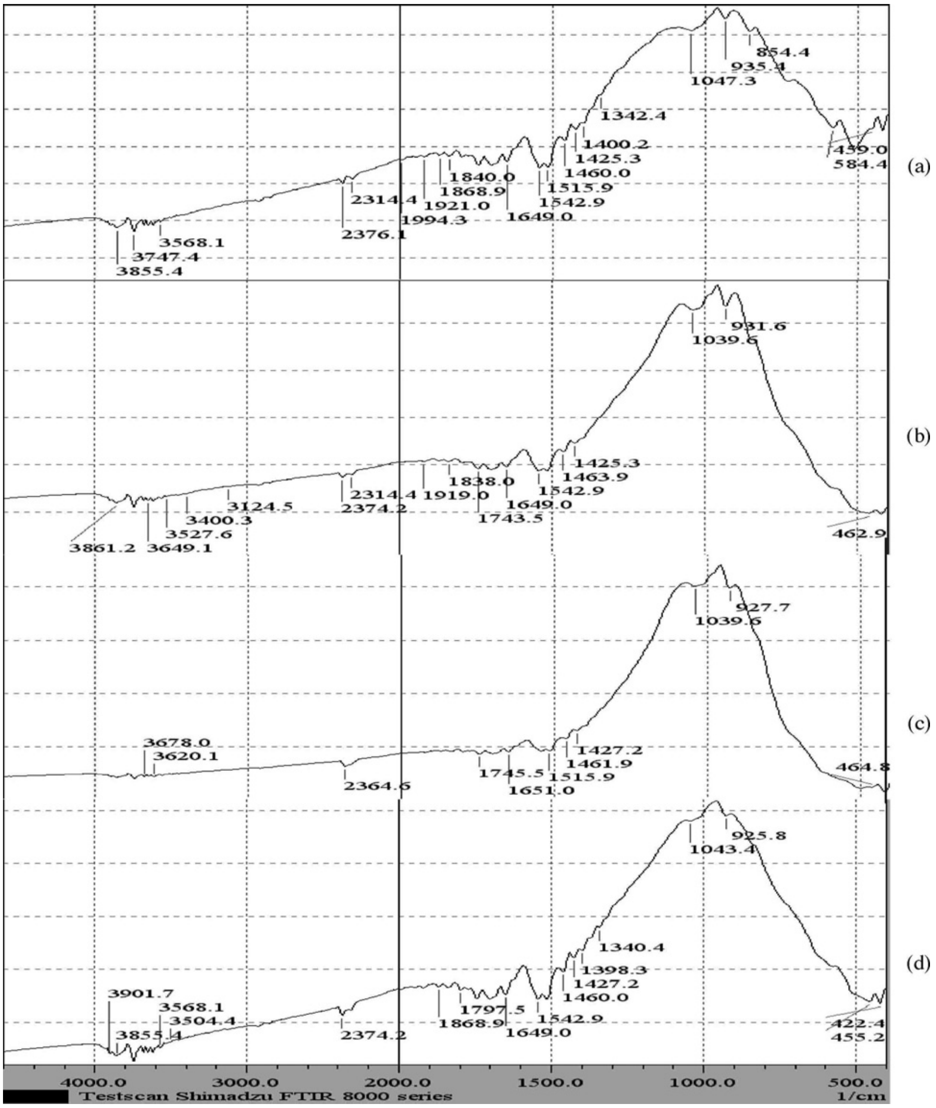

Fig. 17. Powder transmission FTIR spectra of zirconias fired at 1550 °C in Argon (a) sample A1 with 3% CaO + 1% MgO; (b) sample A6 (4% CaO + 2% MgO); (c) sample A7 with 3% CaO + 3% MgO); (d) A8 (2% CaO + 4% MgO).

during 4 h at maximum temperature leads to the developing of partially stabilised zirconia consisting of cubic solid solutions as major phase, tetragonal phase in low amount and monoclinic polymorph. This finding makes plausible the assumption that equilibrium is not yet reached during the heat treatment. The sintering conditions (in air or in argon) seem to have a great influence and determine major changes on ratio between zirconia polymorphs.

3.2.2. ZrO_2–CaO–MgO systems

XRD patterns of A1, A6, A7 and A8 ternary zirconia powders stabilised in Argon atmosphere are given in Fig. 6 and in oxidising atmosphere at 1550 °C are shown in Fig. 7. XRD patterns of the same samples stabilised in oxidising atmosphere at 1750 °C are shown in Fig. 8. The X-ray diffraction on the samples A1, A6, A7 and A8 fired in argon at 1550 °C (Fig. 6) emphasised totally stabilisation process of zirconia when cubic and tetragonal solid solutions are present. The firing of same samples in air at 1550 °C (Fig. 7) leads to the developing of partially stabilised zirconia consisting of cubic solid solutions as major phase, tetragonal phase in low amount and monoclinic polymorph while at 1750 °C in air (Fig. 8), only the cubic zirconia was detected. Also in this system, the sintering conditions (in air or in argon) seem to have a great influence and determine major changes on ratio between zirconia polymorphs.

SEM micrographs and EDS signals from the samples S1, S3 and S5 fired in Argon at 1550 °C are shown in Figs. 9–11. The stabilising element Sr and Ca are revealed on samples surface.

SEM micrographs and EDS signals from the samples A1, A6, A7 and A8 fired in Argon at 1550 °C are shown in Figs. 12–15. The stabilising element Mg and Ca are revealed on samples surface.

3.3. Infrared powder transmission spectra analysis

3.3.1. ZrO_2–CaO–SrO system

Fig. 16 illustrates the powder transmission spectra of dry-ground samples S1, S3 and S5 stabilised with SrO and CaO and fired in argon. No significant differences attributable to the type or concentration of stabilising agent were detected.

The broad band in the 3500–3700 cm^{-1} region may result from atmospheric moisture retained by the KBr pellet. The bands in the 1900–1000 cm^{-1} region were found in all investigated samples: 1843, 1787, 1633, 1515, 1460, 1423, 1396, 1371, 1340, and 1317 cm^{-1}. Their intensities have a small variation; they were affected by stabilising additives amount. Broad bands in this region are commonly observed in spectra of metal oxides powders with adsorbed CO_2 and are assigned to surface carbonate groups which are variable with respect to temperature and crystal structure of the oxide.[8,9] Therefore, similar bands in the ZrO_2 spectra are attributed to impurities formed from absorbed atmospheric CO_2.

The 425 cm^{-1} band is distinctive for the monoclinic zirconia,[8] and their appearance was revealed in all investigated samples (S1, S3, S5). The stabilised polymorphs were identified also corresponding to cubic zirconia by the bands around 480 cm^{-1} and to tetragonal phase a band around 435 cm^{-1} was apparent.

3.3.2. ZrO_2–CaO–MgO system

Fig. 17 illustrates the powder transmission spectra of dry-ground samples A1, A6, A7 and A8 stabilised with MgO and CaO and fired in argon. No significant differences attributable to the type or concentration of stabilising agent were detected.

The cubic polymorph may be assigned to 462 and 584 cm^{-1} bands and this finding is in good accordance with the X-ray diffraction analysis results.

4. Conclusions

The results highlighted the possibility of fully or partially stabilisation of some compositions belonging to ZrO_2–CaO–SrO and ZrO_2–CaO–MgO systems, cured in air and in Argon at 1550 °C.

The sintering conditions (in air or in argon) seem to have a great influence and determine major changes on ratio between zirconia polymorphs.

The argon protective environment at 1550 °C induces in the composites belonging to ZrO_2–CaO–SrO system the decreases of cubic and tetragonal polymorphs of zirconia, while the oxidising heating at same temperature leads to the decreases of monoclinic polymorph.

For compositions belonging to the ZrO_2–CaO–MgO system and stabilised in argon protective environment at 1550 °C a totally stabilisation process was effective.

Acknowledgement

Part of this work has been performed in the framework Romanian National R&D Programme, CERES project (nr. 4-78/2004).

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