



Effect of boron oxide on the cubic-to-monoclinic phase transition in yttria-stabilized zirconia

D.Z. de Florio, R. Muccillo*

*Centro Multidisciplinar para o Desenvolvimento de Materiais Cerâmicos,
CCTM-Instituto de Pesquisas Energéticas e Nucleares, CP 11049, Pinheiros, São Paulo, SP 05422-970, Brazil*

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Abstract

Specimens of yttria fully stabilized zirconia with different amounts of boron oxide have been studied by X-ray diffraction at room temperature and at higher temperatures up to 1250 °C. A boron oxide-assisted cubic-to-monoclinic phase transformation was determined in the temperature range 800–1250 °C. In situ high temperature X-ray diffraction experiments gave evidences of the dependence of the phase transformation on the heating rate. The possibility of tuning the cubic–monoclinic phase ratio by suitable addition of boron oxide before pressing and sintering is proposed.

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1. Introduction

The polymorphic nature of zirconia is well known. Zirconium oxide has at least three crystallographic phases at atmospheric pressure: fluorite-type cubic from its melting point (~ 2680 °C) down to ~ 2370 °C, tetragonal from that temperature to ~ 1150 °C, and monoclinic for lower temperatures [1]. After forming solid solution with aliovalent oxides (CaO, MgO, and Y_2O_3), the fluorite cubic structure is also detected at temperatures where pure zirconium oxide is monoclinic [1,2]. The zirconium oxide is then considered stabilized: the cubic phase that is stable in the pure oxide at high temperatures may now be found at room temperature due to solid solution formation after reaction with the aliovalent oxides. The extent of stabilization depends on the amount of the chosen stabilizer and can be determined from the binary phase diagram of the stabilizer oxide–zirconium oxide. The introduction of Me^{2+} ($Me = Ca, Mg$) or Me^{3+} ($Me = Y, Sc$, and rare earth ions) produces defective oxides with oxygen vacancies in the

* Corresponding author. Tel.: +55-11-3816-9343; fax: +55-11-3816-9343.

E-mail address: muccillo@usp.br (R. Muccillo).

fluorite structure. At temperatures higher than approximately 400 °C (depending on the dopant ion), the vacancies become mobile and the solid solution oxide behaves as an electrolyte, the charge carriers being the oxygen vacancies. An interesting variety of properties can be achieved with different zirconia–yttria compositions and heat treatments. Fine grained zirconia ceramics with 4–5 wt.% yttria have tetragonal structure and exhibit very high fracture toughness and high strength. For higher yttria contents (~8 wt.%) the structure is a mixture of cubic and tetragonal or monoclinic phases and these ceramics exhibit low thermal conductivity and good ionic conductivity. The phase equilibrium in zirconia–yttria systems is then of considerable interest. Different processing and heat treatment conditions lead to zirconia–yttria with metastable phases and a variety of microstructures [3]. To a large extent, the performance of devices based on stabilized zirconium oxide depends on the ability of these oxides to transport oxygen ions. The electrical behavior of stabilized zirconium oxides allows them to be used as electrochemical transducers in several applications: oxygen sensor in combustion engines, for controlling/optimizing fuel consumption [4]; oxygen sensors in the steel industry, for monitoring oxygen content in molten steels during steel production [4]; high temperature solid electrolytes in Solid Oxide Fuel Cell (SOFC) devices for producing environmental clean electrical energy [5]. Due to its wide technological applications, the stabilized zirconia has been extensively studied both theoretically and experimentally [6,7].

Yttrium, magnesium, and calcium oxides are the main stabilizers for zirconia found in commercial oxygen sensing devices. One of the requirements for stabilized zirconia to be used in these devices is the final density be higher than approximately 92% of the theoretical density to avoid oxygen molecule permeation through pores. That densification is usually reached after sintering the specimens at relatively high temperatures.

Because of the high melting point of zirconia (~2700 °C), its sintering requires temperatures as high as 1800 °C when the stabilization is achieved by mixing the stabilizer oxide to zirconia. Chemical synthesis, based on several solution techniques, provide very sinteractive powders, allowing for the fabrication of dense ceramic pieces at temperatures well below 1800 °C [8]. One alternative approach to lower the sintering temperature for the densification of zirconia-based ceramic materials is the use of additives or activators that could, via liquid-phase sintering, help to decrease the pore density via a capillary motion. These chemicals are named sintering aids. The introduction of low melting point oxides to the interparticle spaces during processing at different temperatures may result in chemical reactions between the zirconia–yttria matrix and the foreign oxide.

The effect of the densification of zirconia:8 mol% yttria solid electrolytes with the addition of boron oxide, which melts at 460 °C, was the initial basic idea of this work. Studies on densification of calcia-stabilized zirconia with borates showed that B₂O₃ is an effective sintering aid but led to destabilization of the cubic zirconia attributed to the depletion of CaO from the cubic ZrO₂ lattice by reaction with B₂O₃ to form low-melting calcium borate phases [9].

Destabilization of doped zirconium oxide is an interesting phenomenon. It has already been reported that thermal cycling of cubic zirconia components at high temperatures promotes their destabilization (FSZ to PSZ) and that the destabilization depends on the degree of purity of the samples: high-purity samples are less destabilized than less pure samples in similar temperature range [10–12]. The addition of zirconium diboride either to cubic calcia- or yttria-stabilized zirconia was found to destabilize the cubic zirconia after heating at 800 °C in air [13]. Phosphoric acid was also found to destabilize calcia- and yttria-stabilized zirconia. The effect of temperature, grain size, and chemical composition on the rate at which cubic zirconia is changed to monoclinic zirconia by phosphates was reported [14]. Both yttria- and lime-stabilized zirconia are destabilized by phosphoric acid addition, the former, at a slower

rate than the latter. Vanadium oxide also destabilizes cubic yttria-stabilized zirconia by reacting with the Y_2O_3 component to form YVO_4 [15]. The destabilization of $ZrO_2:9 \text{ mol}\% Y_2O_3$ by adding 3 wt.% H_3BO_3 was followed by X-ray diffraction after calcination in the range 600–1100 °C [16]. The main conclusion is that H_3BO_3 can produce very severe destabilization in fully stabilized zirconia when heated at temperatures higher than 800 °C, following the reactions [16]:



and



In this contribution, the effect of the addition of different amount of boron oxide to cubic zirconia:8 mol% yttria was studied by X-ray diffraction. Molten boron oxide readily dissolves metallic oxides to form borates that, on cooling, give glasses that are difficult to crystallize [11]. The destabilization of the cubic phase was detected by X-ray diffraction experiments.

2. Experimental

The yttria-stabilized cubic zirconia powder used was a commercially available powder TZ8Y from Tosoh, Japan. The boron oxide powder was 99.98% pure (Aldrich). The stabilized zirconia and the boron oxide powders were mixed to obtain boron oxide contents of 0, 10, 20, 30, 40, and 50 wt.%. The powder mixtures were wet (isopropyl alcohol) crushed and thoroughly mixed in an agate mortar. These powders were used for X-ray diffraction experiments, after annealing at different temperatures in the range 500–1200 °C, in a model D8 Advance Bruker-AXS Powder X-ray diffractometer with Ni-filtered $Cu \text{ } k_\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$), operating at 40 kV, 40 mA, in the Bragg–Brentano configuration. The slits used were 1° for the beam and 0.1° for the detector. Hot stage X-ray diffraction experiments were also carried out in mixtures (50 wt.%–50 wt.%) of YSZ and boron oxide in the same X-ray diffractometer equipped with an Anton Paar (Model HTK-16) high temperature sample chamber with a platinum resistive heating attachment, and a PSD X-ray detector. A Pt–10%RhPt thermocouple was used for temperature measurement and control within ~ 1 °C of the set temperature. A thin platinum strip was used as the sample holder, which was coated with 100–150 mg of the powder samples. The configuration with the PSD detector allowed for fast and reliable X-ray diffraction measurements in the 10–45° 2θ range. In that range are situated the main monoclinic, cubic, and tetragonal phases of zirconium oxide compounds.

For dilatometric analysis, pellets of yttria-stabilized zirconia with addition of 10 mol% B_2O_3 were prepared by cold pressing $ZrO_2:8 \text{ mol}\% Y_2O_3$ mixed to B_2O_3 ceramic powders. Dilatometric analysis was carried out at ambient atmosphere from room temperature to 1500 °C at a heating rate of 10 °C min^{-1} .

3. Results and discussion

Fig. 1 shows results of linear shrinkage experiments carried out in two cold-pressed pellets: $ZrO_2:8 \text{ mol}\% Y_2O_3$ and $ZrO_2:8 \text{ mol}\% Y_2O_3$ with 10 mol% B_2O_3 addition. The heating rate was

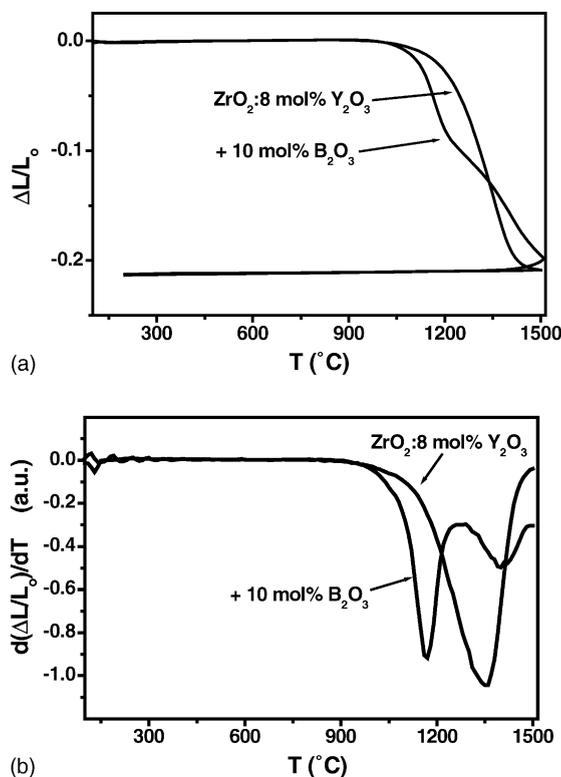


Fig. 1. (a) Linear shrinkage of cold-pressed $ZrO_2:8 \text{ mol\% } Y_2O_3$ and $ZrO_2:8 \text{ mol\% } Y_2O_3$ with addition of 10 mol% B_2O_3 as a function of temperature; (b) derivative of the curves shown in panel a.

$10 \text{ }^\circ\text{C min}^{-1}$ in air. A clear two-stage process is found for the specimen with boron oxide addition. The shrinkage starts at a lower temperature and finishes at a higher temperature in comparison with the specimen without the additive. The two stages are better seen in Fig. 1b, which shows the derivative with respect to the temperature of the curves depicted in Fig. 1a. While there is only one temperature of maximum shrinkage for the cubic zirconia–yttria specimen, approximately $1350 \text{ }^\circ\text{C}$, two are the maxima found for the shrinkage of the zirconia–yttria specimen prepared with addition of boron oxide, at approximately 1150 and $1400 \text{ }^\circ\text{C}$. One may conclude that boron oxide addition does change the sintering behavior of the yttria-stabilized zirconia. The shrinkage is faster for the specimen with boron oxide addition due to liquid sintering mechanism: the melting of the additive enhances pore elimination. As other mechanisms may play a role for enhancing sintering, these results will be discussed later after taking into account the results on X-ray diffraction of specimens heat treated at high temperatures.

X-ray diffraction patterns of a mixture of 50 wt.% $ZrO_2:8 \text{ mol\% } Y_2O_3$ and 50 wt.% B_2O_3 powders, after thermal treatments at different temperatures in the room temperature, $1200 \text{ }^\circ\text{C}$, were obtained at room temperature in the $10\text{--}45^\circ 2\theta$ range. Fig. 2 shows the results in the range $950\text{--}1200 \text{ }^\circ\text{C}$. In these experiments the powder mixture was placed inside an alumina boat, which was inserted into a tubular furnace set to heat (20 min^{-1}) the powder to the chosen temperature and turn the furnace off after reaching that temperature. For comparison purposes, the intensities of all reflections have been normalized to the maximum amplitude of the 100% intensity reflection. At temperatures higher than

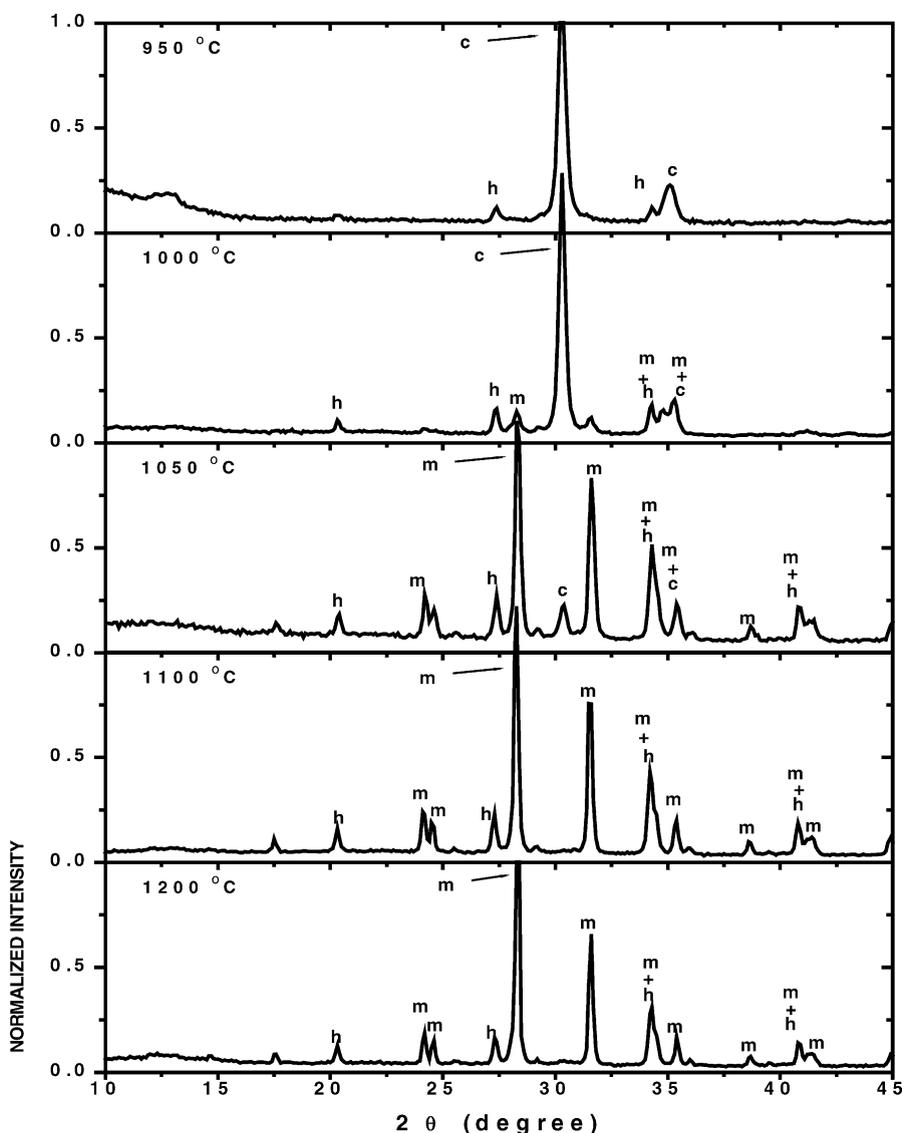


Fig. 2. X-ray diffraction patterns of $\text{ZrO}_2:8 \text{ mol\% Y}_2\text{O}_3 + \text{B}_2\text{O}_3$ (50 wt.%–50 wt.%) ceramic powder mixtures at room temperature and after heat treating at 950, 1000, 1050, 1100, and 1200 °C; m: monoclinic ZrO_2 , c: cubic ZrO_2 , and h: hexagonal YBO_3 .

950 °C the reflections of monoclinic zirconia are detected. Up to 1000 °C the (1 1 1) reflection of cubic zirconia predominates. For the powder mixture heat treated at 1050 °C, a substantial decrease in the main cubic zirconia reflections is noticed, while the reflection of monoclinic zirconia predominates. The cubic-to-monoclinic transformation is complete at 1100 °C. In addition, some other reflections are detected and ascribed to YBO_3 at $2\theta = 28^\circ$, Miller index (1 0 0), 35° (1 0 2), and 41° (0 0 4) [16].

The destabilization of the cubic phase of the $\text{ZrO}_2:8 \text{ mol\% Y}_2\text{O}_3$ powders is clearly seen, in agreement with the results reported by Guo for $\text{ZrO}_2:9 \text{ mol\% Y}_2\text{O}_3$ with 3 wt.% H_2BO_3 addition [16].

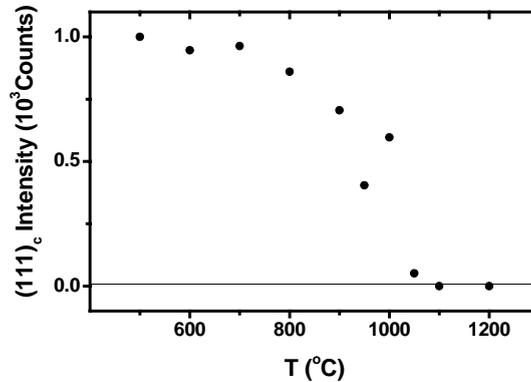


Fig. 3. Relative intensity of the main cubic phase X-ray diffraction line of ZrO_2 :8 mol% $\text{Y}_2\text{O}_3 + \text{B}_2\text{O}_3$ (50 wt.%–50 wt.%) ceramic powder mixtures, after heat treating at several temperatures in the range 500–1200 °C.

The destabilization of ZrO_2 :8 mol% Y_2O_3 by addition of B_2O_3 was then carefully analyzed as a function of temperature as well as of boron oxide content.

Fig. 3 shows the dependence of the intensity of the main X-ray reflection of the cubic phase on the temperature in the range 500–1200 °C. These data were obtained from the results partially shown in Fig. 2. The degree of destabilization increases with increasing temperature. The destabilization is probably due to the acidic nature of B_2O_3 , which would promote the boron removal of yttrium ions from the yttria-stabilized zirconia. The removal of yttrium leads to the formation of YBO_3 and the monoclinic phase of zirconia, which is the stable phase of pure zirconia. The deviation at 1000 °C shows the competition between the $c \rightarrow m$ destabilization provoked by the boron oxide addition and the increase in the cubic phase content probably due to solubilization of the yttrium ion from the intergranular sites to intragranular regions of the sample. We will be back to discussion of this result after the in situ high temperature X-ray diffraction measurements.

The study of the destabilization as a function of the amount of boron oxide addition was performed by preparing specimens with different B_2O_3 content and heat-treating at 1200 °C. That temperature was chosen to be sure that the reaction of boron oxide with zirconia–yttria is complete.

The effect of the amount of boron oxide as destabilizer on the degree of destabilization is shown in Fig. 4. The monoclinic volume fraction V_m was determined using the following equations [17]:

$$V_m = \frac{1.3X_m}{1 - 0.3X_m}, \quad \text{for}$$

$$X_m = \frac{I_m(-111) + I_m(111)}{I_m(111) + I_m(111) + I_c(111)}$$

The addition of approximately 15 wt.% of boron oxide is required to transform the fully cubic structure of ZrO_2 :8 mol% Y_2O_3 to fully monoclinic. The transition from cubic to monoclinic is not sharp, namely, it is possible to choose cubic-to-monoclinic phase ratios just by adding the proper amount of B_2O_3 to ZrO_2 :8 mol% Y_2O_3 . The modification of the cubic–monoclinic phase ratio by changing the Y_2O_3 content would promote also the formation of the tetragonal phase. The following advantage of this result is foreseen: if one takes into account that cubic zirconia has higher ionic

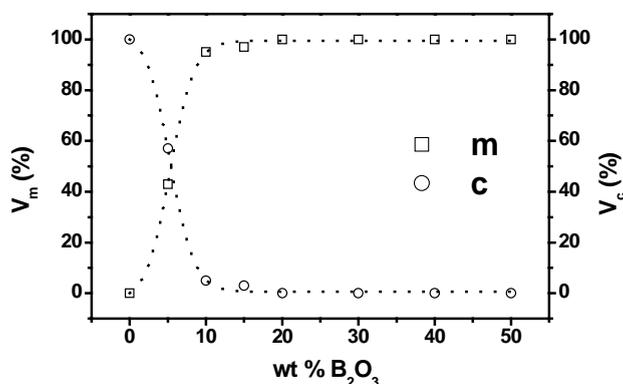


Fig. 4. Cubic and monoclinic volume fractions of $\text{ZrO}_2:8 \text{ mol\% Y}_2\text{O}_3 + \text{B}_2\text{O}_3$ ceramic powder mixtures after heat treating at 1200°C ($20^\circ\text{C min}^{-1}$ heating and cooling rates) as a function of the B_2O_3 content.

conductivity than monoclinic zirconia and that, on the other hand, cubic–monoclinic partially stabilized zirconia has better mechanical strength and better thermal shock resistance than cubic zirconia, the addition of boron oxide could be a way to choose cubic-to-monoclinic phase ratio suitable to prerequisites of good ionic conductivity and acceptable thermal shock resistance (enhanced mechanical properties), when designing zirconia-based solid electrolytes for specific applications.

To determine more accurately the temperatures of destabilization of yttria-stabilized zirconia by addition of boron oxide, and also to evaluate the kinetics effect (the dependence of the monoclinic-to-cubic ratio on the heating rate), hot stage X-ray diffraction experiments were carried out. The $\text{ZrO}_2:8 \text{ mol\% Y}_2\text{O}_3 + \text{B}_2\text{O}_3$ 50 wt.%–50 wt.% powder mixture (that proportion was chosen to guarantee that the reaction of boron oxide with the cubic yttrium oxide powders take place) was placed on the platinum strip of the sample chamber and heated to 1250°C at several heating rates in the range $1\text{--}4^\circ\text{C s}^{-1}$, the X-ray diffraction data being collected at different temperatures using a fast detection mode (1 min for the whole $10\text{--}45^\circ 2\theta$ range) with a position sensitive detector.

Fig. 5a shows the diffraction patterns of the powder mixture at 27, 500, 600, 700, 800, 850, 900, 950, 1000, 1050, 1100, 1150, 1200, and 1250°C . The data were collected at a 4°C s^{-1} heating rate. The destabilization of the cubic yttria-stabilized zirconia starts at approximately 1100°C and is almost complete at approximately 1250°C . All diffraction patterns show a reflection at approximately $2\theta = 49.8^\circ$, which corresponds to the (1 1 1) X-ray diffraction peak of platinum. To be sure that the destabilization occurs only because of the addition of boron oxide to the cubic zirconia ceramic powders, X-ray diffraction experiments were carried out under the same experimental conditions with powders without boron oxide addition. The results are shown in Fig. 5b. No destabilization occurs, the main diffraction lines being ascribed to cubic yttria-stabilized zirconia.

The data taken from Fig. 5a and b were analyzed and the intensities of the main cubic (1 1 1) reflection were plotted as a function of the temperature the diffraction patterns were measured. The results, normalized to the intensity measured at room temperature, are shown in Fig. 6.

The decrease in the cubic phase content at the expenses of the increase in the monoclinic phase content is seen in the specimen with boron oxide addition. Moreover, the intensity of the main cubic reflection of the $\text{ZrO}_2:8 \text{ mol\% Y}_2\text{O}_3$ without B_2O_3 addition show a sharp increase at the same temperature boron oxide destabilizes the cubic phase in the sample with boron oxide addition. That

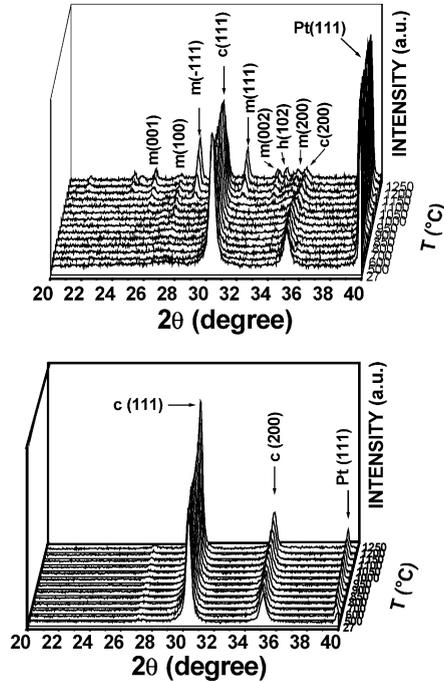


Fig. 5. In situ high temperature (RT–1250 °C range) X-ray diffraction patterns of (a) $\text{ZrO}_2:8 \text{ mol\% } \text{Y}_2\text{O}_3$ and (b) $\text{ZrO}_2:8 \text{ mol\% } \text{Y}_2\text{O}_3 + \text{B}_2\text{O}_3$ (50 wt.%–50 wt.%) ceramic powders.

increase might be due to the solubilization (solid solution formation) of the yttrium ions, known to have a minor content located at the grain boundaries in yttria-stabilized zirconia compounds. A question remains to be solved: As the destabilization temperature is in the range of the cubic-to-tetragonal transformation temperature, the tetragonal phase should be taken into account in the determinations of phase content. Lattice parameter calculations were carried out using available softwares [18].

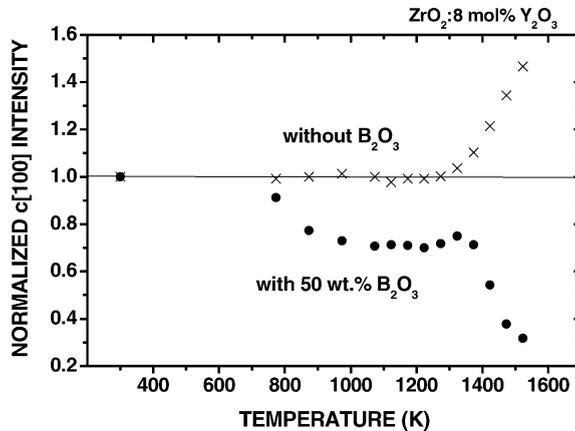


Fig. 6. Variation with temperature of the intensity of the cubic phase of $\text{ZrO}_2:8 \text{ mol\% } \text{Y}_2\text{O}_3$ and $\text{ZrO}_2:8 \text{ mol\% } \text{Y}_2\text{O}_3 + \text{B}_2\text{O}_3$ (50 wt.%–50 wt.%) ceramic powders determined by in situ X-ray diffraction measurements.

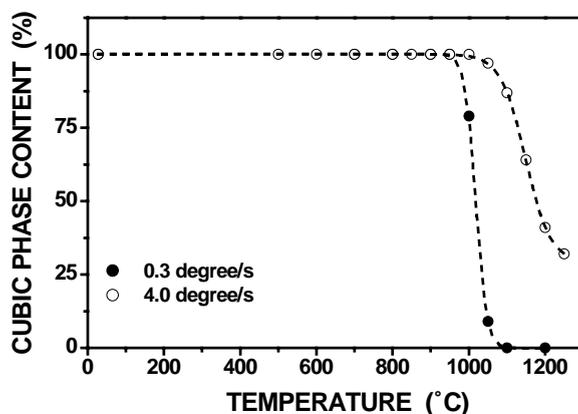


Fig. 7. Cubic phase content in $\text{ZrO}_2:8 \text{ mol\% Y}_2\text{O}_3 + \text{B}_2\text{O}_3$ (50 wt.%–50 wt.%) ceramic powders as a function of the annealing temperature; heating rates: (a) $0.3 \text{ }^\circ\text{C s}^{-1}$ and (b) $4.0 \text{ }^\circ\text{C s}^{-1}$.

The results do not converge if one assumes that the data represents a tetragonal phase, but do converge for the assumption of a cubic phase. Further experimental work is required to look for evidence that the destabilization occurs via the cubic \rightarrow tetragonal \rightarrow monoclinic transformation path. Experiments utilizing the micro Raman laser technique are under way to clarify this point.

Fig. 7 shows the cubic phase content as a function of temperature using the data of Fig. 5a ($4 \text{ }^\circ\text{C s}^{-1}$ heating rate) and of another experiment collecting the X-ray data at the same temperatures but with a slower heating rate ($0.3 \text{ }^\circ\text{C s}^{-1}$). The temperature where the maximum destabilization occurs depends on the heating rate. The higher is the heating rate, the higher is the temperature of maximum destabilization and the lower is the destabilization rate.

The destabilization of $\text{ZrO}_2:8 \text{ mol\% Y}_2\text{O}_3$ with B_2O_3 addition depends then on the B_2O_3 content, on the temperature the mixture is heat treated, and on the heating rate the mixture is heated. One can then find an explanation for the shrinkage behavior shown in Fig. 1: the specimen with boron oxide undergoes the cubic–monoclinic transition at a temperature lower than that of the specimen without boron oxide due to the destabilization phenomenon described above. At that temperature there is a volume variation known to occur at that transition, producing consequently the shrinkage of the specimen. Further experimental work, probably requiring TEM to look for intergranular glassy phase (due to boron oxide reaction with intergranular second phases) which could inhibit densification, is necessary to explain the second peak of Fig. 1b. Another possibility is that it represents the shrinkage rate of monoclinic zirconia because at this stage, most of the cubic zirconia has already been transformed in monoclinic zirconia.

4. Conclusions

X-ray diffraction experiments show that the addition of boron oxide to 8 mol% yttria-stabilized zirconia promotes the destabilization of the cubic zirconia to partially stabilized (cubic and monoclinic) or fully destabilized (monoclinic) depending on the boron oxide content and the temperature of reaction of both compounds. The destabilization is also found to depend on the heating rate to reach the temperature of reaction. Preliminary results show that the destabilization process occurs also in other

(magnesia and calcia) stabilized zirconias, meaning that this is a concept with far reaching implications. For solving the thermal shock problem, for example, the concept of adding boron oxide to the solid oxide powder before sintering will allow us to tune the cubic–monoclinic content ratio and systematically adjust the thermal shock resistance in solid electrolytes used in high temperature sensor devices. Boron oxide is then proposed as an additive for preparing zirconia ceramic bodies with different cubic-to-monoclinic phase ratios.

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