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Preparation and characterization of zirconia ceramics with oxides addition

A. Rittidech*, S. Wantrong and S. Chommi
Department of Physics, Faculty of Science Mahasarakham University, Mahasarakham 44150, Thailand

This research investigated the relationship between the quantitative phase crystal structure and mechanical properties of ZrO_2 ceramic addition of Y_2O_3, MgO and $BaCO_3$ at 0.0, 2.0, 4.0 and 6.0 mol%. Ceramic samples were prepared using mixed oxide method under normal sintering at 1,600 °C with dwell time for 120 min . ZrO_2-Y_2O_3 and ZrO_2-MgO ceramics were obtained with bulk densities values between 5.324-5.722 g/cm^3 while ZrO_2-$BaCO_3$ ceramic showed densification values about 4.412-4.827 g/cm^3. It was found that ZrO_2-Y_2O_3 and ZrO_2-MgO ceramic showed higher fracture toughness values than ZrO_2-$BaCO_3$ ceramics. Refinement of lattice parameter using Rietveld analysis in ceramic samples revealed the percentage of fraction phase ratios of *m*-ZrO_2, *t*-ZrO_2 and *c*-ZrO_2. The refinement parameters result in sample ceramic which are Y_2O_3 addition between 4-6 mol% obtained a high ratio of *t*-ZrO_2 phase and the result supported optimal mechanical properties. ZrO_2-Y_2O_3 ceramic showed a higher lattice stain value compared with the additions of other ZrO_2 oxides and it was found that lattice strain increase with high ratio of t-ZrO_2 phase. Sample ceramics had crystallite size values between 56.65-82.30 nm. SEM micrographs revealed morphology and average grain sizes. All samples grains were spherical in shape combined with irregular shape and were gray in color and were obtained with an average grain size between 0.63 -2.18 µm. It was found that the ZrO_2-Y_2O_3 ceramic showed small crystallize size and size of grains. The optimal condition for addition of oxide were found in ceramics of ZrO_2-Y_2O_3 and ZrO_2-MgO and confirmed that good mechanical properties were obtained from a high ratio of *t*-ZrO_2 phase and fine grain size.

Keywords: ZrO_2, Y_2O_3, MgO, $BaCO_3$, Rietveld refinement.

Introduction

ZrO_2 has attracted extensive attention for decades because it exhibit excellent characteristics such as low thermal conductivity and good mechanical properties under high temperature conditions. These properties have led to the use of zirconia-based components in many applications such as automobile engine part, medical devices and cutting tool. Zirconia is a polymorphic metastable material that exists in three crystallographic phases: monoclinic phase (up to 1,170 °C), tetragonal phase (1,170-2,370 °C), and cubic phase (2,370-2,680 °C) [1]. Zirconia is generally stable at room temperature in monoclinic phase. Zirconia in the tetragonal form at room temperature has the best mechanical properties among the forms [2]. The tetragonal (*t*-ZrO_2) to monoclinic (*m*-ZrO_2) martensitic transformation occurring during cooling after sintering is detrimental to sintered zirconia integrity as this process is accompanied by a large increase in volume, leading to disintegration by crack formation and propagation [3]. The high temperature polymorphs of pure zirconia cannot be retained by quenching to room temperature [4]. Many reports are attempt to synthesize for a metastable tetragonal phase formation in the zirconia at low temperature [5-7].

Stabilizing oxides such as CaO, Co, Y_2O_3 and MgO are used to stabilize in the cubic and tetragonal zirconia form at room temperature. Previous works reported [8-10] effects of zirconia ceramic stabilizing oxides on the phase structure, microstructure and mechanical properties. The mechanism of *t*-ZrO_2 to *m*-ZrO_2 transition is typical of partially stabilized zirconia and commonly supported by many studies of the transformation strength process, which has been widely, discussed [11, 12]. However, the study of the relationship of quantitative analysis in crystal zirconia stabilizing oxides ceramic with XRD patterns on its characteristics is of interest to study.

Therefor the aim of this research is to investigate effects of oxides doping on characterization of zirconia ceramics such as physical properties, phase composition, crystalline structure, microstructure, mechanical properties. Rietveld refinement was used to calculate significant quantities in crystal to describe the relationship between crystal structure and ceramics properties.

Experimental

Powders with ZrO_2 addition of Y_2O_3, MgO and $BaCO_3$ at 0.0, 2.0, 4.0 and 6.0 mol% were prepared from ZrO_2, MgO, Y_2O_3 and $BaCO_3$ as precursors and isopropyl alcohol as solvent. All the ten different batches were then ball milled for 24 h. After ball-milling, drying in electronic furnaces and sieving with

*Corresponding author:
Tel : +66 43 754379
Fax: +66 43 754379
E-mail: aurawan.r@msu.ac.th

120 mesh, the resulting powders were calcined at 1,200 ºC, with dwell times for 120 min and heating/cooling rates of 10 ºC/min. The powders were then pressed at 3 MPa into form pellets having 1.5 cm diameter using a hydraulic press and sintered in an alumina crucible at a temperature of 1,600 ºC for 120 min with heating rate of 10 ºC/min. The sintering experiments were carried out in an electrical furnace (Nabertherm, Germany). The bulk densities of sintered sample were calculated using Archimedes' method and measured percentage of linear shrinkages. Phase identification was then performed using an X-ray diffractometer (XRD; Bruker model D8 advance). Next, Rietveld refinement of the XRD patterns of all samples was carried out by TOPAS software. Microstructural analysis was performed by using Scanning Electron Microscopy (SEM) (JEOL JSM-840A) of sintered samples on a polished surface. The micro hardness of the bulk ceramics was measured using a micro scan from Vickers and Knoops (FM-700e type D, Future Tech., Japan).

Results and Discussion

The densification and shrinkage of ceramic samples which were doped with the three oxides are shown in Fig. 1 and 2. ZrO_2 ceramics with addition of Y_2O_3 at 0.0, 2.0, 4.0 and 6.0 mol% showed a density of between 4.93 and 5.51 g/cm^2 and percentage of linear shrinkage values between 10.54 and 14.52. ZrO_2 ceramics with addition of MgO at 0.0, 2.0, 4.0 and 6.0 mol% showed a density of between 4.93 and 5.75 g/cm^2 and percentage of shrinkage values between 10.54 and 16.01. ZrO_2 ceramics with addition of $BaCO_3$ at 0.0, 2.0, 4.0 and 6.0 mol% were showed a density of between 4.54 and 4.93 g/cm^2, percentage of shrinkage values between 9.60 and 10.54. Densities value of ZrO_2 ceramics with addition of Y_2O_3 and MgO tended to increase with increasing added oxides while density values of ZrO_2 ceramics with addition of $BaCO_3$ tended to decrease with increasing $BaCO_3$ content. This result may be due to the different ionic radius of Ba and Zr, therefor making it difficult for Ba^{2+} substitution of Zr^{4+}. The XRD patterns of ZrO_2 ceramics sample which were doped with the three oxides are shown in Fig. 3, 4 and 5. The three figures reveal the characteristic peaks of XRD patterns of ZrO_2 ceramics with different oxides contents. Fig. 3 shows XRD patterns of ZrO_2 ceramics with added 0.0-6.0 mol%Y_2O_3, which were identified using the main refraction of *m*-ZrO_2 (011) at 24.4º,

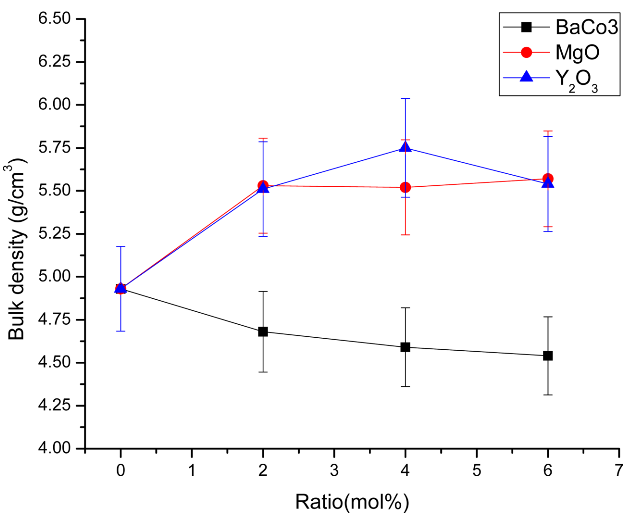

Fig. 1. Density of ZrO_2 ceramics with different stabilizing oxides additions.

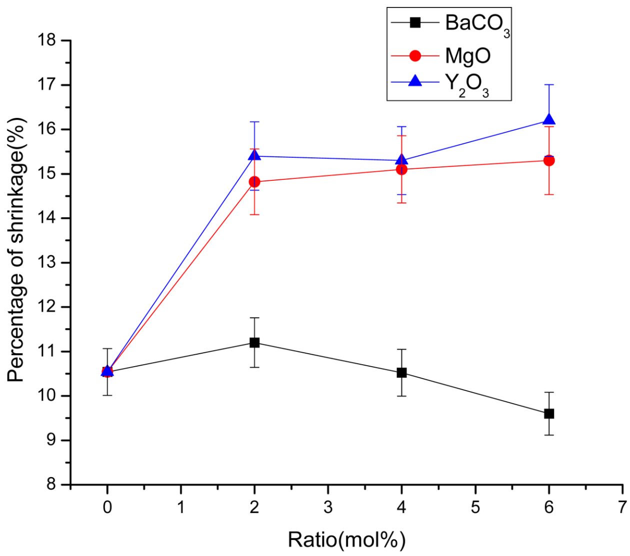

Fig. 2. Shrinkage ZrO_2 ceramics with different stabilizing oxides additions.

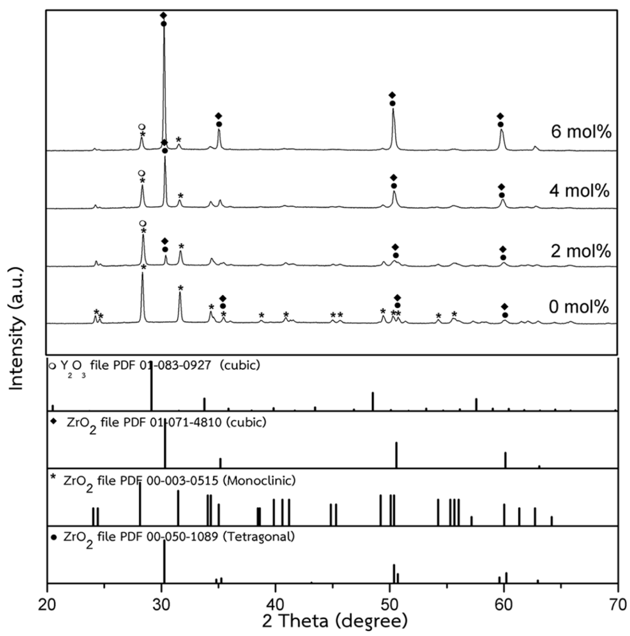

Fig. 3. XRD patterns of ZrO_2 ceramics with added 0.0-6.0 mol% Y_2O_3.

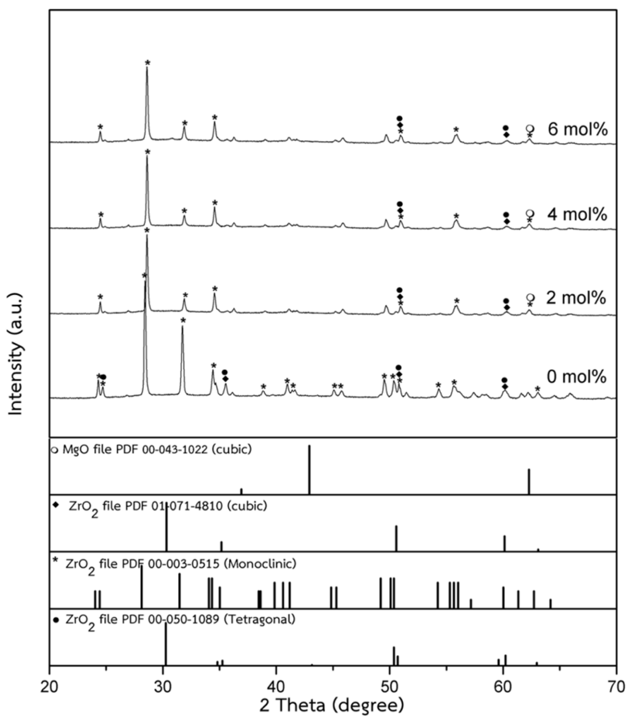

Fig. 4. XRD patterns of ZrO_2 ceramics with added 0.0-6.0 mol% MgO.

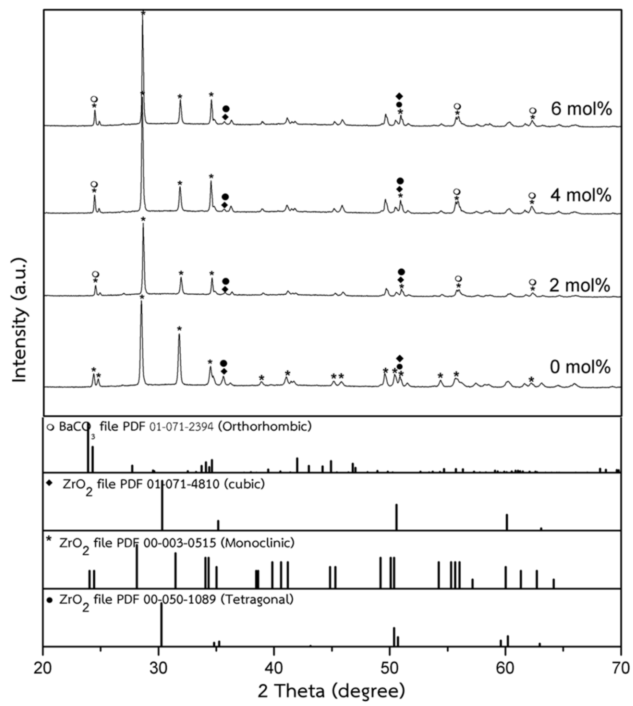

Fig. 5. XRD patterns of ZrO_2 ceramics with added 0.0-6.0 mol% $BaCO_3$.

(-111) at 28.2°, (111) at 31.45°, (020) at 34.70° and *t*-ZrO_2 (101) at 30.41°, (002) at 34.81°, (110) at 35.10° and *c*-ZrO_2 (010) at 30.10°. Fig. 4 shows XRD patterns of ZrO_2 ceramics with added 0.0-6.0 wt% MgO, which were identified as the main refraction of *m*-ZrO_2 (011) at 24.4°, (111) at 31.45°, (020) at 34.70° and *t*-ZrO_2 (101) at 35.10°. Fig. 5 shows XRD patterns of ZrO_2 ceramics with added 0.0-6.0 mol% $BaCO_3$, which are identified using the main refraction of *m*-ZrO_2 (011) at 24.4°, (-111) at 28.2°, (111) at 31.45°, (020) at 34.70° and *t*-ZrO_2 (110) at 35.10°. The results indicated the appearance of ZrO_2 polymorphous crystalline phase consistent with previous reports [8, 13, 14]. The intensity of ZrO_2 peaks in three polymorphous are the result of different oxides addition at varies proportions of dopants. It was found that XRD patterns in Fig. 4 and Fig. 5 are nearly similar patterns. Full pattern matching refinement of XRD patterns was performed using the TOPAS program based on the Rietveld method to obtain more detailed information on crystallographic spectra of ZrO_2 ceramics with three oxides addition (Y_2O_3 , MgO, $BaCO_3$) using 0.0, 2.0, 4.0 and 6.0 mol%

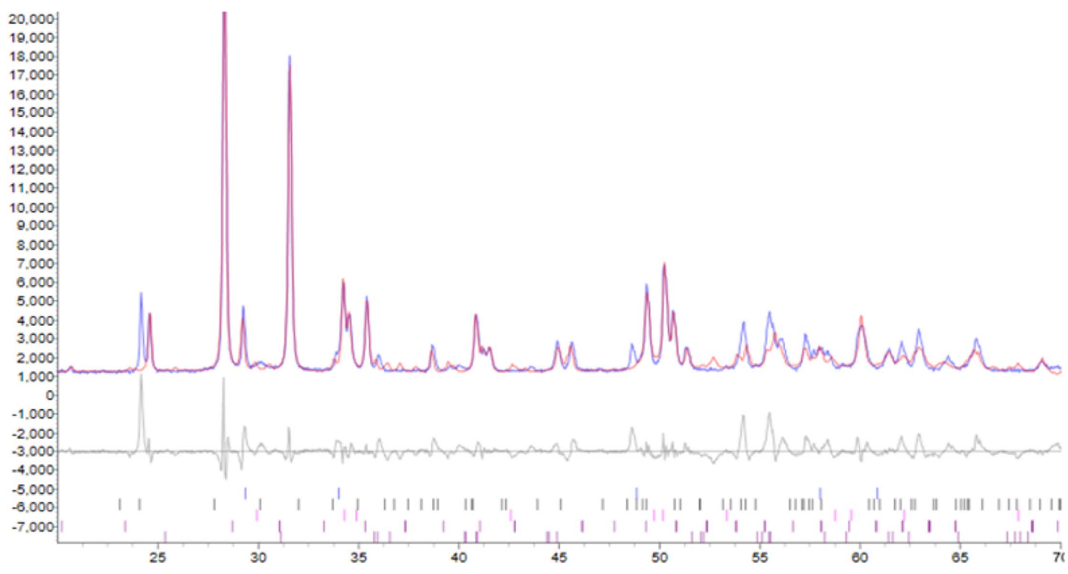

Fig. 6. Rietveld refinement of ZrO_2 ceramics with added 4.0 mol% Y_2O_3.

and selected sample with added 4.0 mol%Y_2O_3, shown as the XRD refinement pattern in Fig. 6. The fitted patterns of ZrO_2 ceramics with added three oxides are in good agreement with the respective experiment data, denoted by R_p, R_{wp} and GOF factors listed below Table 1. ZrO_2 ceramics with added 4.0 mol%Y_2O_3 had a larger lattice parameter compared to ZrO_2 ceramics with added MgO and $BaCO_3$ ¸which may be attributed to substitution to Zr^{4+}site due to the addition of substances with similar ion sizes in agreement with the studies of M.T. Vinas et al. [9], M. Borik et al. [10]. This is clearly seen from the result of the higher tetragonality (*c/a*) and strain lattice in ZrO_2 ceramics with added Y_2O_3. Moreover, when considering the percentage ratio of tetragonal phase, it was obviously related to crystallize size and average grain size of ZrO_2 ceramics with oxides addition. The high tetragonal fraction of ZrO_2 ceramics with small crystallize size and fine grains was found in ZrO_2 ceramics with added Y_2O_3, supporting previous works [15-17]. The micro-structure of ZrO_2 ceramics is shown in Fig. 7, where Fig. 7(a) is a micrograph of pure ZrO_2 ceramic and Fig. 7(b-d) are micrographs of ZrO_2 ceramics with three different oxides addition using a ratio of 4.0 mol%.

Table 1. Parameters obtained from Rietveld analysis, percentage of fraction phase, lattice parameter, lattice strain, crystallize size and average grain sizes of ZrO_2 ceramics with added 4.0 mol% stabilizing oxides.

Oxides contents 4.0 mol%	Phase present	Lattice parameter				Phase content (%)	Lattice strain ($x10^{-1}$)	Crystallite size (nm)	Average grain size
		a (nm)	*b* (nm)	*c* (nm)	β (°)				(μm)
Y_2O_3	m-ZrO_2	0.5653	0.5342	0.5144	97.31	4.16	15.24	60.13	0.78
	t-ZrO_2	0.3628	0.3628	0.5107		77.60			
	c-ZrO_2	0.5237				3.71			
MgO	m-ZrO_2	0.5330	0.5211	0.5151	96.89	60.41	4.95	67.28	1.49
	t-ZrO_2	0.3591	0.3591	0.5372		33.96			
	c-ZrO_2	0.5203				4.44			
$BaCO_3$	m-ZrO_2	0.5526	0.5215	0.5049	96.91	57.45	2.56	75.86	1.84
	t-ZrO_2	0.3593	0.3593	0.5364		25.09			
	c-ZrO_2	0.5207				0.15			

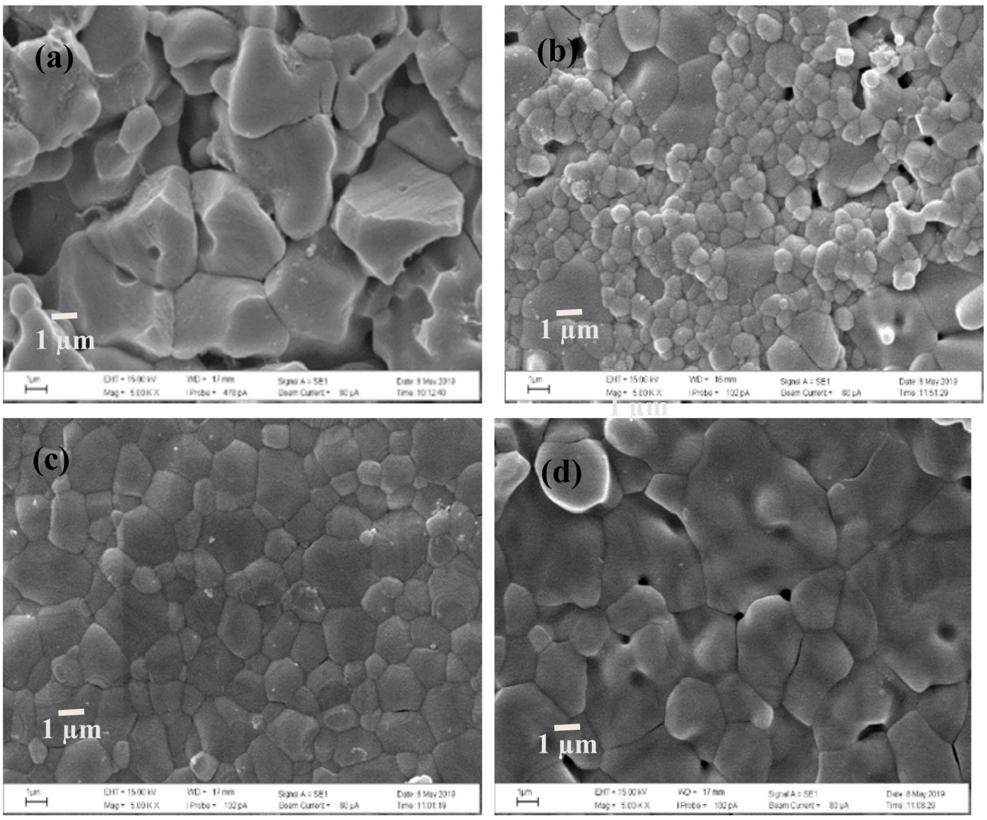

Fig. 7. SEM micrographs of ZrO_2 ceramics with oxides added: (a) 0.0 mol%, (b) 4.0 mol% Y_2O_3 (c) 4.0 mol% MgO (d) 4.0 mol% $BaCO_3$.

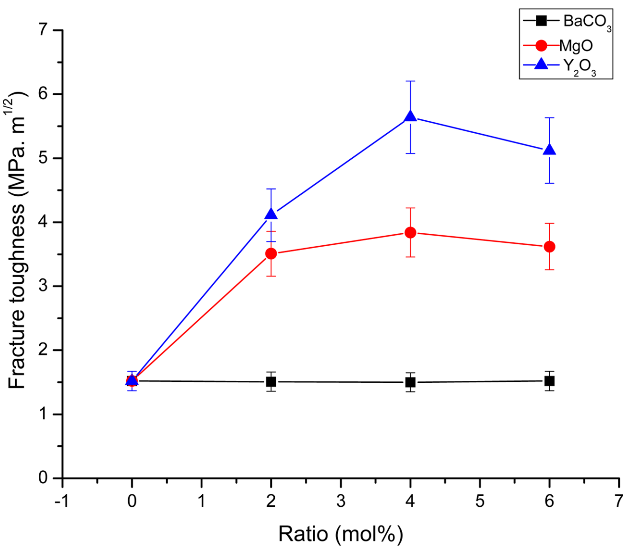

Fig. 8. Fracture toughness of ZrO_2 ceramics with different stabilizing oxides additions.

Microstructural evaluation was performed, i.e., uniformly sized grains with well-packed, continuous grain structure and spherical shape combined with irregular shape in gray color. By applying the linear intercept method [18] to these SEM images, grain sizes were estimated for these samples as given in Table 1. It can be seen that ZrO_2 ceramics with no added oxide exhibited large grains with average grain sizes in the range of 2.65-2.91 mm. While, ZrO_2 ceramics with addition of the three oxides showed average grain sizes between 0.63-2.18 mm. Comparing the grain sizes of pure ZrO_2 ceramics and ZrO_2 ceramics added oxides, it is found that the grain of ZrO_2 ceramics with addition of oxides had smaller sizes than grain sizes of pure ZrO_2 ceramics. Thus, the optimal contents and type of stabilizing oxides is an important parameter for development of ceramic microstructures. The mechanical properties of ZrO_2 ceramics were investigated by measuring microhardness by Knoop and Vickers techniques and then calculating the fracture toughness values. The fracture toughness of ZrO_2 ceramics as a function of different type and concentration of oxide additions is shown in Fig. 8. The toughness values of ZrO_2 ceramics with additions of Y_2O_3 and MgO were in the range 3.51-5.64 MPa $m^{1/2}$. Pure ZrO_2 ceramics and ZrO_2 ceramics with additions of $BaCO_3$ had toughness values that were not much different and in the range 1.52-1.58 MPa $m^{1/2}$. This result indicated that the mechanical properties are related to grain size and phase transformation, which increase as grain size decrease and high fraction of tetragonal phase, in agreement with previous reports by J. Vleugels et al. [19] and Chun-Feng Hu et al. [20]. The highest of fracture toughness value was found in ZrO_2 ceramics with 4 mol% Y_2O_3 added, which corresponds to high ratio of tetragonal phase by XRD refinements and optimal microstructure.

Conclusions

In the present work, ZrO_2 ceramics with addition of three oxides (Y_2O_3, MgO, $BaCO_3$) at 0.0, 2.0, 4.0 and 6.0 mol% were prepared by solid state reaction method. The effects of addition of different oxides and concentrations on the properties of ZrO_2 ceramics were studied. This samples had phase compositions of polymorphous combine with *t*-, *c*- and *m*- ZrO_2 phases. Quantitative analysis from XRD pattern using Rietveld technique was performed to explain the crystal structure. The relationship between the tetragonal phase ratio, densification, grain size and mechanical properties is discussed.

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References

1. A. Behbahani, S. Rowshanzamir, and A. Esmaeilifar, Proced. Engin. 42 (2012) 908-917.
2. M. Ruehle, Adv. Mater. 9[3] (1997) 195-217.
3. M. Matei, E.A. Voinea, R. Rica, H. Manolea, L. Mogoanta, A. Salan, A. Rica. V.C. Dinescu, and N. Cioatera, Ceram. Inter. 45[12] (2019) 14859-14866.
4. T. Chraska, A.H. King, and C.C. Berndt, Mater. Sci. and Eng. A 286[1] (2000) 169-178.
5. M.G. Shahri, A. Shafyei, A. Saidi, and K. Abtahi, Ceram. Inter. 40[8] (2014) 13217-13221.
6. O. Gorban, S. Synyakina, G. Volkova, S. Gorban, T. Konstanyiova, and S. Lyubchik, J. Sol. Stat. Chem. 232 (2015) 249-255.
7. K.H. Lee, S.H. Ahn, and K.W. Nam, J. Ceram. Process. Res. 19[3] (2018) 183-188.
8. G.P. Cousland, X.Y. Cui, A.E. Smith, A.P.J. Stampfl, and C.M. Stampfl, J. Phys. and Chem. of Sol. 122 (2018) 51-71.
9. M.T. Vinas, F. Zhang, J. Vleugels, and M. Anglada, J. Eur. Ceram. Soc. 38[6] (2018) 2621-2631.
10. M. Borik, M. Gerasimov, E. Lomonova, F. Milovich, V. Myzina, P. Ryabochkina, N. Sidorova, and N. Tabbachkova, Mat. Chem. Phys. 232 (2019) 28-33.
11. B. Basu, Int. Mater. Rev. 50[4] (2005) 239-256.
12. J. Chevalier, L. Gremillardw, A.V. Virka, and D.R. Clarke, J. Am. Ceram. Soc. 92[9] (2009) 1901-1920.
13. Z. Zeng, Y. Liu, F. Qian, J. Guo, and M. Wu, J. Eur. Ceram. Soc. 39[14] (2019) 4338-4346.
14. N.F. Amat, A. Muchtar, M.S. Amril, M.J. Ghazali, and N. Yahaya, J. Mater. Res. Technol. 8[1] (2019) 1092-1101.
15. C. Piconi, W. Burger, H.R. Richter, A. Cittadini, G. Maccauro, V. Covacci, N. Bruzzesse, G. A. Ricci, and E. Marmo, Biomat. 19[16] (1998) 1489-1494.
16. C. Piconi, and G. Maccauro, Biomat. 20[1] (1999) 1-25.
17. S.T. Aruna, and K.S. Rajam, Mat. Res. Bull. 39[2] (2004) 157-167.
18. W.E. Lee, and W.M. Rainforth, in "Ceramics Microstructure Property Control by Processing" (Chapman&Hall, 1994) p.220.
19. J. Vleugels, Z.X. Yuan, and O.V. Der Biest, J. Eur. Ceram. Soc. 22[6] (2002) 873-881.
20. C.F. Hu, B.N. Kim, Y.J. Park, K. Morita, H. Yoshida, S. Grasso, H.B. Zhang, S.Q. Guo, and Y. Sakka, J. Ceram. Process. Res. 16[3] (2015) 281-286.