

**Military Technical College
Kobry Elkobbah, Cairo,
Egypt.**



**4th International Conference
On
Chemical & Environmental
Engineering
27-29 May 2008**

EFFECT OF ZrO₂ ON The MECHANICAL PROPERTIES OF MODIFIED BASALT GLASS-CERAMICS

Fatma,H . Maragha, Salwa, A.M.Abdel-Hameed, Nagwa, A.Ghoniem *

ABSTRACT

This paper is mainly directed toward development of tough glass-ceramics by improving the mechanical properties of cordierite glass-ceramics from modified Egyptian basalt rocks using different amounts of zirconia (ZrO₂). Crystallization behavior of modified basalt glass was studied. X-ray diffraction (XRD) and scanning electron microscope (SEM) were used to study the phases developed and microstructure. Microhardness was measured for free and ZrO₂ containing glass-ceramics at different heat-treatments to study the effect of adding ZrO₂; on the hardness of these samples. Toughness increased with increasing amount of transformable ZrO₂, which process is probably caused by crack deflection due to the high stress field around the transformed ZrO₂.

KEY-WORDS

Glass-Ceramics, ZrO₂, cordierite, Basalt, Mechanical

* Glass Research Depart. National Research Center, 12622, El-Behous st. Doki, Cairo, Egypt

1. INTRODUCTION

Glass–ceramic materials have a number of outstanding characteristics in comparison with the traditional ceramics and glasses, which make them favorable for wear and corrosion resistant applications in advanced technology as well as in electronics and medicine ¹⁾. Glass-ceramics in general have superior mechanical properties including greater toughness compared to glasses.

In recent years, greater toughness is desired for glass-ceramics and many efforts are being made, including the formation of surface compressive stresses through ion exchange ⁽²⁻⁴⁾, fiber reinforcement using both brittle ^(5,6) and ductile ⁽⁷⁾ fibers, and the addition of titanium (Ti) particles to bioactive glass-ceramics ⁽⁸⁾. The best known direction is to develop glass-ceramic matrix composite materials.

Alternatively, there are methods to achieve glass-ceramics with higher toughness by modifying the microstructure of glass-ceramics primarily through crystallization. Chain silicate formation and zirconia (ZrO₂) precipitation are among such methods ⁽⁹⁾. In this process, usually metastable, tetragonal ZrO₂ (t-ZrO₂) particles are dispersed in a glass or glass-ceramic matrix and t-ZrO₂ phase particles transform to stable monoclinic ZrO₂ (m-ZrO₂) phase particles during fracture absorbing mechanical energy and thus increasing toughness of the material ⁽⁹⁾.

In general, ZrO₂-containing glass-ceramics have become of interest because of their high fracture toughness, which has been attributed to the stress-induced transformation of tetragonal ZrO₂. In the field of glass technology, ZrO₂ is used as a nucleating agent to make glass-ceramics. Tetragonal and cubic ZrO₂ were observed to precipitate during the crystallization together with other crystalline compounds ¹⁰⁾.

On the other hand, glass-ceramic based on cordierite phase (2MgO.2Al₂O₃.5SiO₂) has relatively high refractoriness and thermal stability, low coefficient of thermal expansion and excellent resistance to thermal chock as well as the high volume receptivity and low dielectric constants.

Several investigations have already been made to produce it via a glass-ceramic process ⁽¹¹⁻¹⁵⁾. Almost all these investigations used high purity chemical reagents or at least pure processed raw materials such as kaolin, magnetite and quartz sand as the starting batch materials.

Due to the high cost of some of the pure chemicals, and the high melting temperatures or special melting conditions, glass–ceramics are relatively expensive materials. The glass–ceramics produced from basalt, metallurgical slag and fly ash are cheaper than those from the elemental technical grade oxide powders. Therefore, the basalt was used as a starting material. The basalt is a grey to black fine grained volcanic rock, and chemically composed of major oxides: silica, alumina, iron oxide, calcium oxide, magnesia, and of lesser importance, soda, potassium oxide, titania and manganese, as well as trace amounts of other species ⁽¹⁶⁾

Due to these concepts, we aimed to increase hardness of glass ceramic, based on crystallization of cordierite from modified basalt rock, by adding different amounts of ZrO₂ and increasing the time of heat-treatment.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of materials

Base glass used in this study was a mixture of two raw materials; basalt and kaolin. Chemical composition of the base glass and raw materials used are shown in **Table 1**. The base composition was mixed with different amounts of ZrO₂ (5-30 wt.%). For simplicity, the prepared samples are labeled as B0, B5, B10, B15, B20 and B30

according to wt. % of ZrO₂ added. After well mixing 100gm of batch, materials were melted in a Pt crucible in an electrically heated Globar furnace at 1500°C for 3 h with occasional swirling every 30 min to ensure homogenization. The melt was then cast onto hot steel moulds in the form of discs (1cm thick) and rods (10×1×1 cm) which were then rapidly transferred to a muffle furnace for, annealing, adjusted at 550°C for 1 h and then switched off to obtain strain-free glass samples. Crystallization of prepared glass samples was performed by heat treatment at 1050°C for different times.

Before the heat treatments were carried out, the samples (15 x 10 x 5 mm slices) were polished to facilitate microhardness measurements. The polishing was conducted before the heat treatments to avoid the stress induced transformation of the crystallized tetragonal ZrO₂⁽¹⁰⁾.

2.2 Analytical methods

Identification of crystalline phases was carried out by X-ray diffraction (XRD, Rigaku Miniflex with graphite monochromator, Cu K α radiation). Surfaces of glass-ceramics samples were examined under scanning electron microscope (SEM, JEOL JSM-5200), after etching by hydrofluoric (HF) acid for 15 seconds, then coating with gold. Mechanical properties were measured on the polished glass-ceramics samples using a microhardness testing machine (Mitsutoyo, HM-100 series), and that by application of 0.2 kg (1.961 N) load.

Table 1. Chemical composition of base glass and raw materials used (wt.%.)

Oxide	Kaolin	Basalt	Base glass
SiO ₂	50.26	50.26	43.44
Al ₂ O ₃	42.93	14.73	27.39
Fe ₂ O ₃	1.06	3.96	0.00
MgO	0.59	6.25	3.7
CaO	0.93	10.79	6.51
Na ₂ O	1.31	2.46	1.49
K ₂ O	0.82	0.72	0.44
TiO ₂	2.10	3.46	10.43
FeO	0.00	7.37	6.60

3. Results and Discussion

3.1 XRD analysis

3.1.1 Investigation of the crystallization stage

XRD patterns of modified basalt glasses heat-treated at 1050°C for 3, 10, 20 and 30 hrs are shown in Figs. 1-4, respectively. For B0 (ZrO₂ = 0 wt.%), the identified crystalline phases were cordierite [Mg₂Al₄Si₅O₁₈], anorthite [CaAlSi₂O₈], pseudobrookite [Fe₂TiO₅] and spinel [MgAl₂O₄] after each heat-treatment.

Adding ZrO₂ with different quantities to the base glass led to crystallization of tetragonal and monoclinic (baddelite) ZrO₂ with different ratios according to the amount of ZrO₂ added and heat treatment time, in addition to the pre-mentioned

phases. It was noted that ZrO₂ didn't affect on the kinds of crystalline phases or their relative amounts.

The volume percent of crystalline phases present was $\geq 95\% \pm 5\%$ for samples of each composition, even after the shortest growth heat-treatment time. Therefore, any significant variation in properties with longer heat-treatment times is unlikely due to an increase in crystallinity of the samples.

It was reported that ferrous oxide (FeO) and ferric oxide (Fe₂O₃) in basalt oxidizes to magnetite (Fe₃O₄), which acts as a nucleating agent and crystal growth site⁽¹⁾. This behavior of basalt glass-ceramics gives advantages over other glass-ceramics where nucleating agents are necessary to obtain similar microstructure⁽¹⁶⁾.

3.1.2 Effect of ZrO₂ addition

The fracture of monoclinic and tetragonal zirconia of the total zirconia was evaluated from the intensities of their diffraction peaks and is shown in Fig. 5(a).

It is obvious that t-ZrO₂ formed with m-ZrO₂ by adding 5 wt.% ZrO₂. Increasing the amount of ZrO₂ led to an increase in tetragonal and monoclinic forms. They became almost equal in B15, B20 but after that t-ZrO₂ started to decrease while m-ZrO₂ continues to increase.

3.1.3 Effect of increasing time of heat treatment

Tetragonal ZrO₂ was formed with monoclinic form at 1050°C for 3 h as indicated in Fig. 5(b); then t-ZrO₂ decreased slightly while monoclinic form increased with increasing time of heat-treatment.

Increasing time of heat treatment might lead to an increase in the size of t-ZrO₂ particles which caused their spontaneous transformation to monoclinic zirconia⁽¹⁷⁾. Tetragonal ZrO₂ can be crystallized as dendrites, which, if large enough (~50 μm), can improve the fracture toughness⁽¹⁷⁾.

3.3 Microstructure of obtained glass-ceramics

SEM micrographs of polished and etched surface glass-ceramic samples heat-treated at 3, and 30 h are presented in Figs. 6 and 7, respectively. In all samples, a fine interlocked volume crystallized microstructure was recognized, which is well desirable for good mechanical and physical properties⁽¹⁶⁾.

Comparing samples of the same ZrO₂ content but heat treated for different times (3, 10 and 30 h) indicate that the size of crystals increases with the increase of heat treatment time.

3.3 Mechanical properties

Figure 8 shows the Vickers hardness (in GPa) as a function of the zirconia content of the samples crystallized at 1050°C for 3, 10, 20, and 30 h. Measurement of the hardness of base glass (ZrO₂ = 0) heat-treated at 1050°C for 3 h, which include

cordierite, anorthite, pseudobrookite and spinel as crystallized phases [the existence of these crystalline phases seems to increase the micro-hardness of glass-ceramics⁽¹⁸⁾], gave 6.23 GPa this value increased to 6.8 GPa by adding 5 wt.% ZrO₂ and increased to 7.23 GPa by adding 30 wt.% ZrO₂. By increasing time of heat-treatment to 10, 20 and 30 hrs hardness were enhanced strongly as shown in Fig. 8 reaching 14.8 GPa (~1510 Hv) for the sample containing 30 wt.% ZrO₂ and heat-treated at 1050°C for 30hrs. According to Moh's scale these sample shows value as ~7.7 i.e. near topaz which has the highest value (8) in Moh's scale⁽¹⁹⁾.

The increase in hardness with the increase in ZrO₂ content could be attributed to the increase in number of m-ZrO₂ crystals; whereas its increase with time of heat treatment could be owed to the growth of t-ZrO₂ crystal size and its' transformation to m-ZrO₂ as mentioned above.

ZrO₂ grains act as impediments to microcrack extension by arresting these cracks, thereby limiting crack linkage. The higher ZrO₂ content makes this mechanism more effective⁽²⁰⁾.

As discussed in the literature⁽²¹⁾, the transformation of larger ZrO₂ particles from tetragonal to monoclinic phase is related to the size dependence of the Ms (martensitic transformation) temperature. Namely, as the size of t-ZrO₂ particles increase, the Ms temperature increases.

It clearly shows that, zirconia transformation in a rigid glass-ceramic matrix is accompanied by a large stress field and this can cause crack deflection and the observed hardness improvement. SEM of the fracture surface appeared to support the present interpretation, indicating a greater roughness with increasing monoclinic zirconia fraction⁽⁹⁾. Hardness of this glass-ceramic is increased by about 126% by adding 30 wt.% ZrO₂.

3. CONCLUSION

The production of highly hardness glass-ceramic materials from basalt rock is currently important for their properties inherent in these materials, such as high resistance, high chemical stability, low electrical conductivity, good mechanical strength and nearly zero-rated permeability. As a result of the present research, the increase in hardness can be attributed to the increase in m-zirconium crystal with increasing percentage of ZrO₂.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the support of Prof. Masafumi Okubo, department of electrical and mechanical engineering- faculty of science and technology, for this research.

REFERENCES

- [1] Yılmaz, S.; Bayrak, G.; Sen, S. and Sen, U., Materials and Design, in press, (2005).
- [2] Karsetter, B.R. and Voss, R.O., J. Am. Ceram. Soc., Vol. 50, pp. 133 (1967).
- [3] Beall, G.H.; Karsetter, B.R. and Ritter, H.L., J. Am. Ceram. Soc., Vol. 50, pp.

- 181 (1967).
- [4] Duke, D.A.; Macdowell, J.F. and Karsetter, B.R., *J. Am. Ceram. Soc.*, Vol. 50, pp. 67 (1967).
 - [5] Aveston, J., "The Properties of Fiber Composite", CIPC Science and Technology press, London (1972).
 - [6] Sambell, R.A.J.; Bowen, D.H. and Phillips, D.C., *J. Mater. Sci.*, Vol. 7, pp. 663 (1972).
 - [7] Sambell, R.A.J.; Bowen, D.H. and Phillips, D.C., *J. Mater. Sci.*, Vol. 7, pp. 676 (1972).
 - [8] Troczynski, T.B. and Nicholson, P.S., *J. Am. Ceram. Soc.*, Vol. 74, pp. 1803 (1991).
 - [9] Tomozawa, M. and Sarno, R.D., *Chemistry Express*, Vol.6, pp.949 (1991).
 - [10] Dal Maschio, R. and Scardi, P., *Ceramics International*, Vol. 17, pp. 31 (1991).
 - [11] El-Shennawi, A.W.A.; Morsi, M.M. and Abdel-Hameed, S.A.M. *Journal of the European Ceramic Society*, In Press, Corrected Proof, Available online 11 July (2006).
 - [12] Gregory, A.G. and Veasey, T.J., *J. Mater. Sci.*, Vol. 6, pp. 1312 (1971).
 - [13] Zdaniewski, W., *J. Material Sci.*, Vol. 8, pp.192 (1973).
 - [14] Morell, R., *Proc. Brit. Ceram. Soc*, Vol. 28, pp. 53 (1979).
 - [15] Barry, T.I., Cox, J.M. and Morell, R., *J. Material Sci.*, Vol. 13, pp. 594 (1978).
 - [16] Senol Y., Osman T., Ozkan and Volkan G., *Ceram Inter.*, Vol. 22, pp. 417 (1996).
 - [17] McCoy M., Lee W.E. and Heuer A.H., *J. Am. Ceram. Soc.*, Vol. 69, pp. 292 (1986).
 - [18] Bijan Eftekhari Yekta, Parvin Alizadeh and Leila Rezazadeh (2006) *Journal of the European Ceramic Society*, in press.
 - [19] Tayler, E.W., *J. Soc. Glass. Tech.*, 34, 69T (1950).
 - [20] Sarno, R.D. and Tomozawa M., *J. Mater. Sci.*, Vol. 30, pp. 4380 (1995).
 - [21] Heuer, H.A., Claussen, N., Kriven M.W. and Ruhle M., *J. Am. Ceram. Soc.*, Vol. 65, pp. 642 (1982).

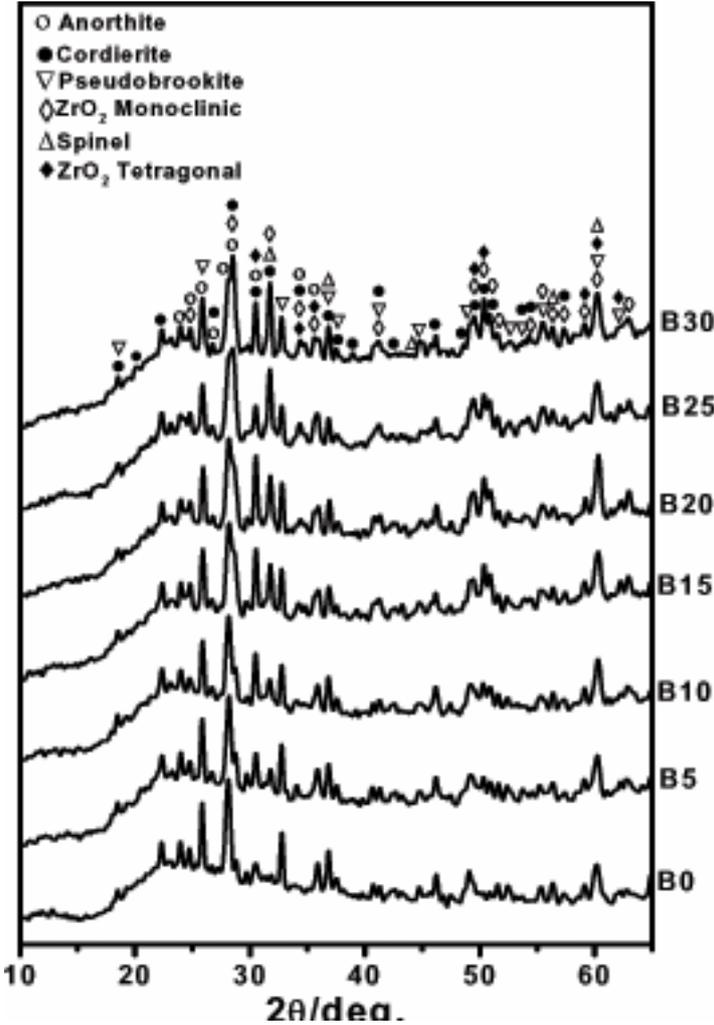


Fig. 1. XRD patterns of basalt glasses heat-treated at 1050°C for 3 h

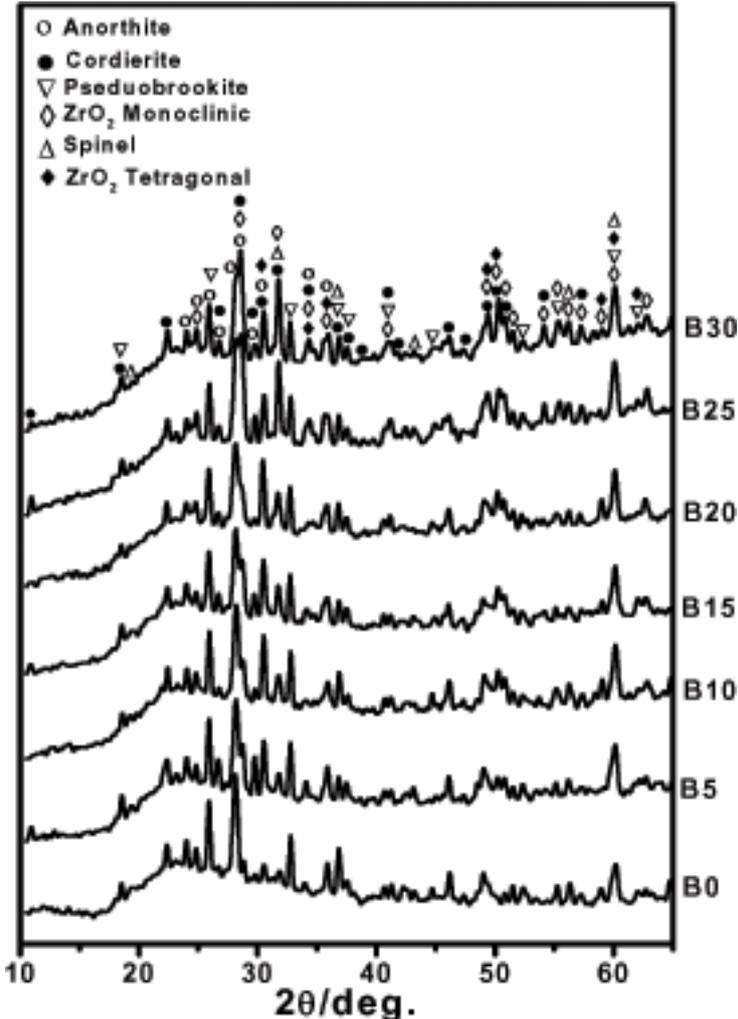


Fig. 2. XRD patterns of basalt glasses heat-treated at 1050°C for 10 h

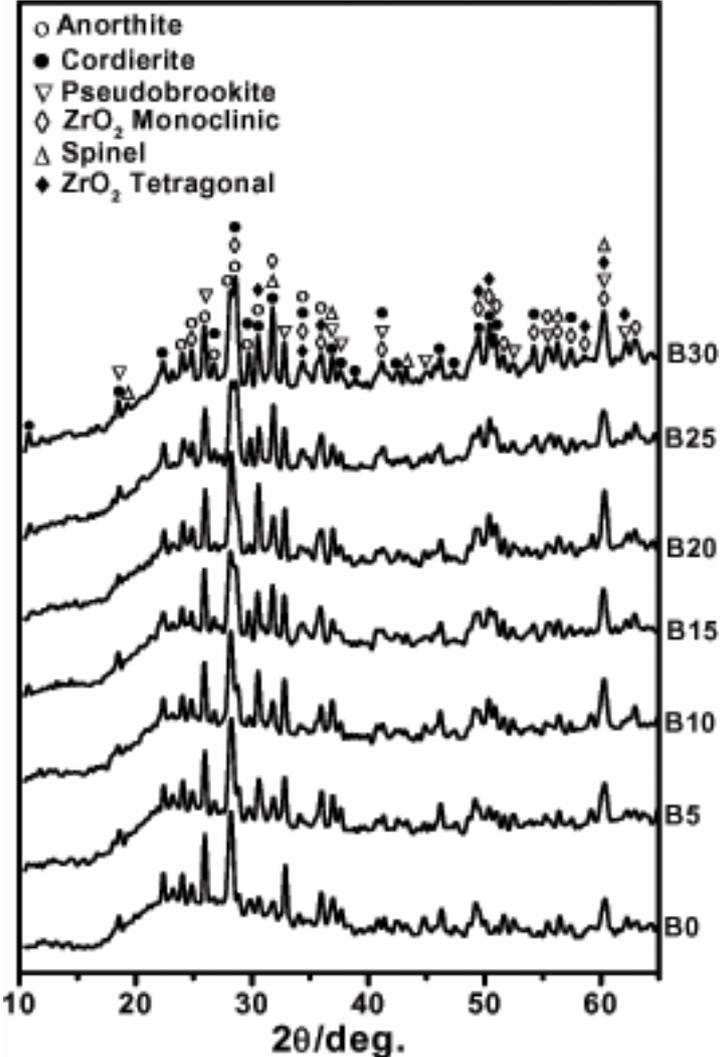


Fig. 3. XRD patterns of basalt glasses heat-treated at 1050°C for 20 h

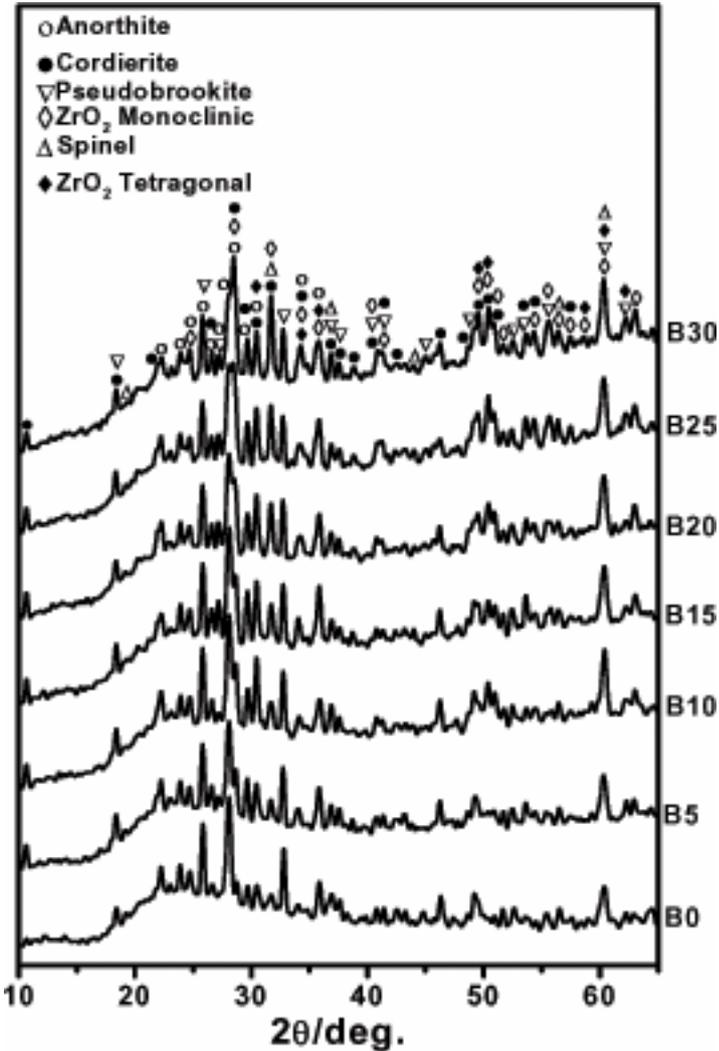


Fig. 4. XRD patterns of basalt glasses heat-treated at 1050°C for 30 h

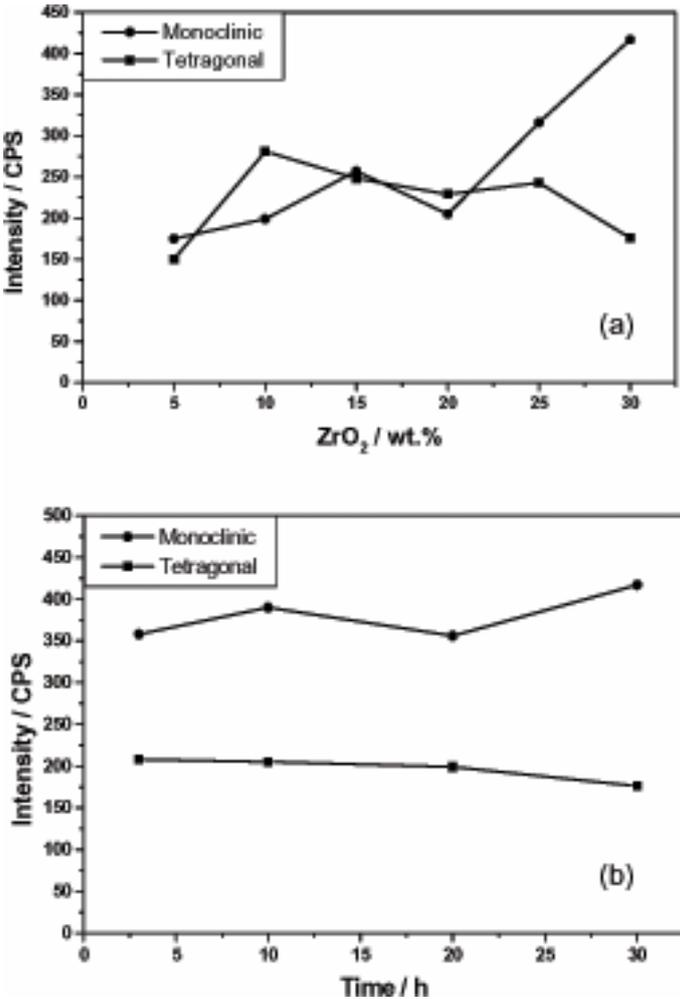


Fig. 5. Fracture of monoclinic and tetragonal zirconia with increasing (a) amounts of ZrO₂ addition and (b) time of heat-treatment.

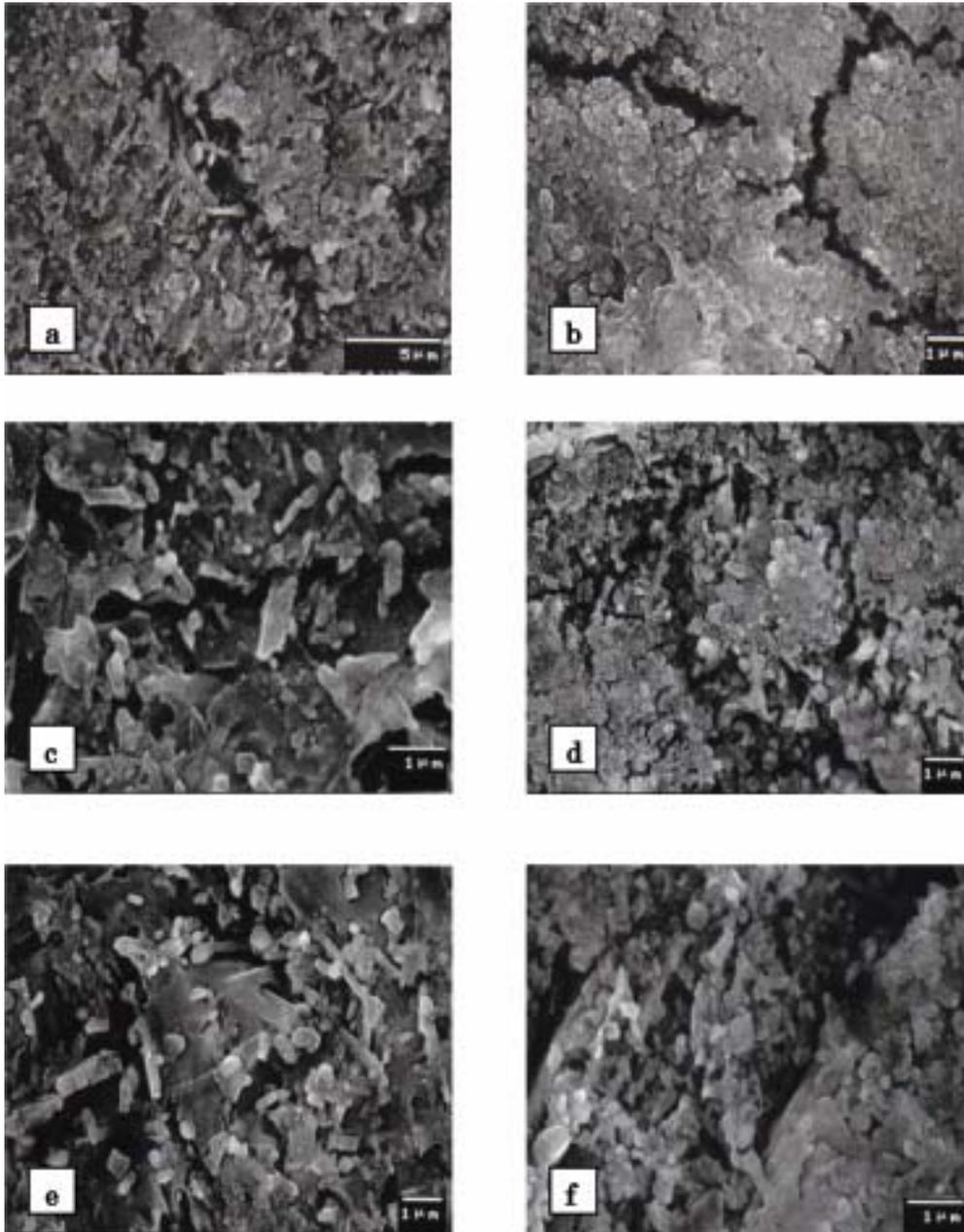


Fig. 6. SEM photographs of (a) B5, (b) B10, (c) B15, (d) B20, (e) B25 and (f) B30 after heat-treated at 1050°C for 3 h.

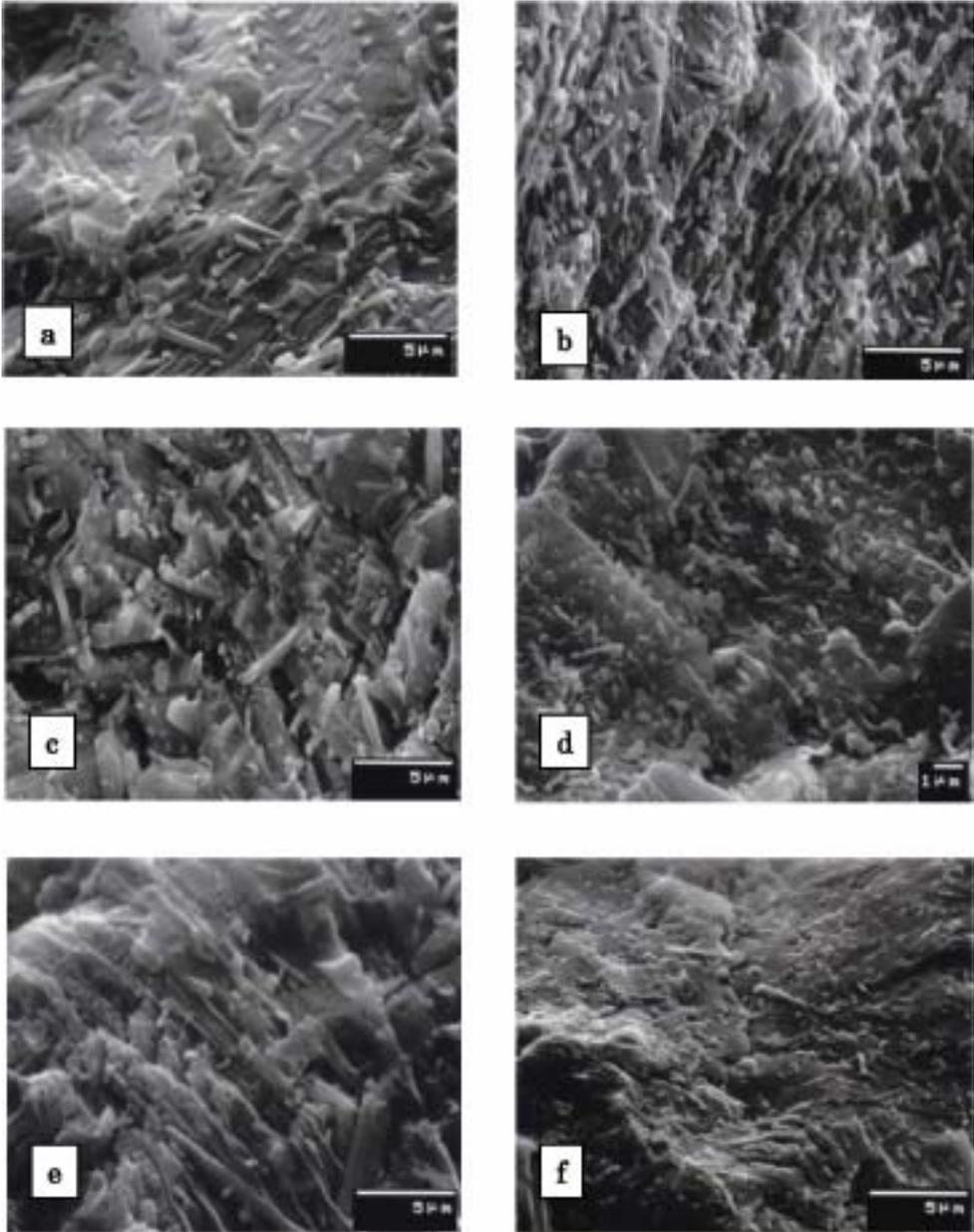


Fig. 7. SEM photographs of (a) B5, (b) B10, (c) B15, (d) B20, (e) B25 and (f) B30 after heat-treated at 1050°C for 30 h.

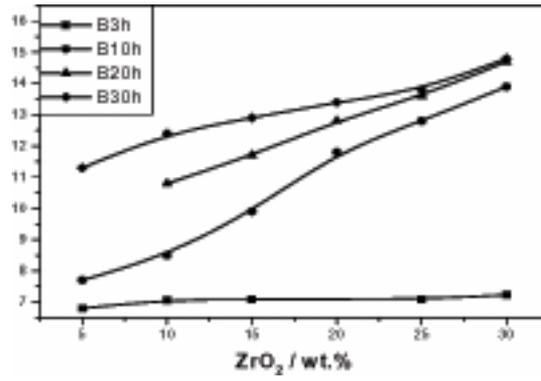


Fig. 8. Hardness of ZrO₂ contained basalt glass-ceramics heat-treated at 1050°C for 3, 10, 20 and 30 h