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Densification and grain growth of TiO_2-doped ZnO

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The kinetics of grain growth in 1–4 wt. % TiO_2-doped ZnO was studied using the simplified phenomenological grain growth kinetics equation together with examination of microstructure and densification of the sintered samples. The grain growth exponent values *n* were found to be 3 for 1 and 2 wt. % TiO_2-doped ZnO, 5 for 3 and 4 wt. % TiO_2-doped ZnO. The apparent activation energy of 435 kJ/mol was found for 1 and 2 wt. % of TiO_2 in ZnO. It was found to be 608 kJ/mol and 615 kJ/mol for 3 and 4 wt. % TiO_2, respectively. The apparent activation energy increased with TiO_2 content due to formation of spinel Zn_2TiO_4 phase at the grain boundaries which inhibited the grain growth of ZnO. Also densification decreased with increasing TiO_2 content.

Key words: *ZnO; TiO_2 doping; grain growth kinetics; densification*

1. Introduction

ZnO-based materials have been developed for various technological applications, such as varistors, gas sensors, and optoelectronic devices due to their electrical and optical properties [1]. A typical ZnO-based varistor is a very complex chemical system containing several dopants, such as Bi, Sb, Mn, Cr, Co, Ti and Al [2].

The electrical properties of ZnO varistors directly depend on the composition and microstructural characteristics such as grain size, density, morphology and the distribution of second phases. Many studies have been conducted on the sintering of several ZnO systems doped with Bi_2O_3 [3, 4], Sb_2O_3 [5], Al_2O_3 [1], PbO [6] and CuO [7]. Among numerous papers published on the subject, Senda and Bradt [3] presented the most detailed study covering the grain growth kinetics in ZnO ceramics containing up to 4 wt. % Bi_2O_3. They used a simplified grain growth kinetics equation

$$G^n = K_0 t \exp\left(-\frac{Q}{RT}\right) \tag{1}$$

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where G is the average grain size at time t, n is the kinetic grain growth exponent, K_0 is a constant, Q is the apparent activation energy, R is the gas constant and T is the absolute temperature. Using this equation, Senda and Bradt have calculated the grain growth exponent $n = 3$ and apparent activation energy $Q = 224\pm16$ kJ/mol in the sintering of the pure ZnO system.

The additions of MnO [8] and CoO [9] to the ZnO–Bi_2O_3 6 wt. % system, the addition of MnO [10] to the ZnO–Sb_2O_3 system and the addition of PbO [6], CuO [7] and SiO_2 [11] to ZnO have been studied by our group. The aim of the present work is to study the effect of TiO_2 addition on microstructure and the sintering behaviour of ZnO.

2. Experimental

High purity ZnO (99.7 % Metal Bile□ikleri A.□, Gebze, Turkey) and TiO_2 powders (pure grade) were used in preparation of four basic compositions – ZnO containing 1, 2, 3 and 4 wt. % TiO_2. ZnO powders contained a needle like fine crystals 0.5 μm wide and 0.5–2 μm long. The calculated amounts of oxides for the indicated compositions were ball milled in ashless rubber lined ceramic jars for 6 h using zirconia balls and distilled water as the milling media. The mixtures were dried to 10–15% moisture content and then granulated. Samples of 10 mm in diameter and 8 mm thick were prepared by semi-dry pressing of the granules of (150±75) μm in size range at the pressure of 100 MPa. The specimens were sintered at 1000, 1100, 1200 and 1300 ºC for 1, 2, 3 and 5 h with the heating rate of 5 ºC/min, then were naturally cooled in the furnace.

The bulk densities of the samples were calculated from their weights and dimensions. Characterizations of the phases in the sintered specimens were carried out by X-ray diffraction using CuK_α radiation. For the microstructural observations, both scanning electron microscopy (SEM) of the fracture surfaces and optical microscopy of polished and etched surfaces were used. Grain size measurements were carried out on the micrographs of the etched samples using the following equation,

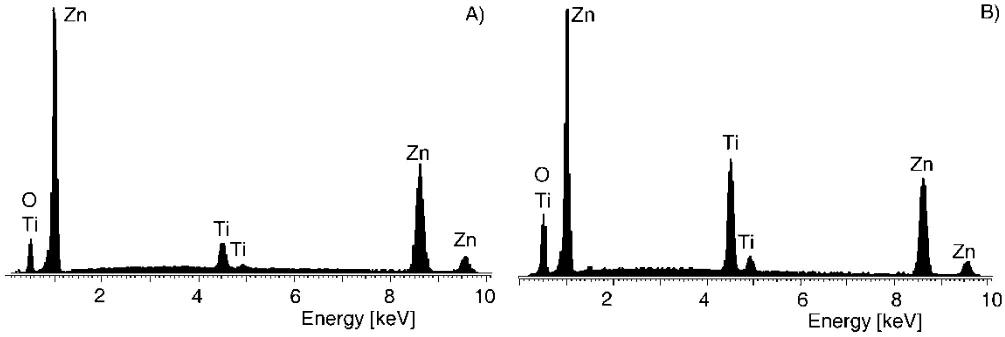
$$G = 1.56\bar{L} \tag{2}$$

where G is the average grain size, $\bar{L}$ is the average grain boundary intercept length of four random lines on two different micrographs of each sample [12].

3. Results and discussion

3.1. Physical properties of the sintered samples

The presence of ZnO (ASTM Card No. 5-0664) and Zn_2TiO_4 (ASTM Card No. 18-1487) phases was determined using of the X-ray powder diffraction of the TiO_2 -doped samples sintered at various temperatures and various periods of time. TiO_2 formed a spinel phase (Zn_2TiO_4) with ZnO as expected from the phase diagram of the



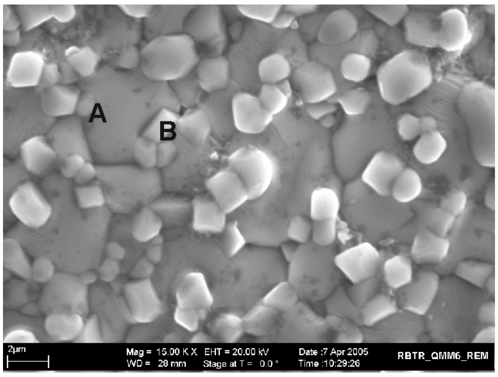


Fig. 1. The backscattered electron images and EDS of the 3 wt. % TiO_2-doped ZnO sample sintered at 1300 ºC for 5 h

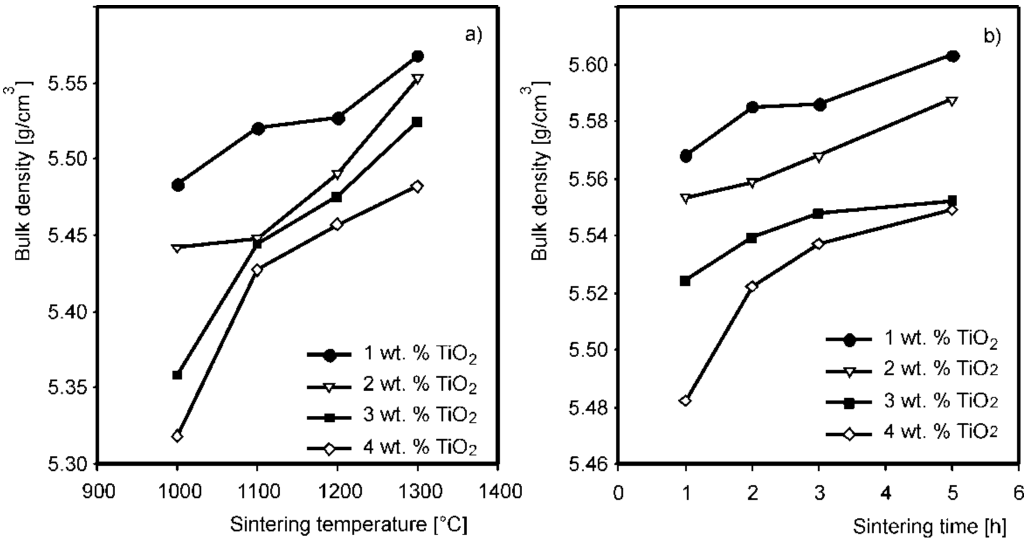


Fig. 2. The bulk density vs. sintering temperature (a) and the bulk density vs. sintering time (b) for TiO_2 doped ZnO

ZnO–TiO_2 binary system [13]. The backscattered electron and energy dispersive X-Ray spectrometer (EDS) images of 3 wt. % TiO_2-added ZnO samples sintered at

1300 ºC for 5 h are shown in Fig. 1. The micrograph clearly shows spinel phases (Zn_2TiO_4) as bright regions between ZnO grains.

The effects of sintering temperatures and sintering time on the bulk densities of the specimens with different TiO_2 contents are shown in Fig. 2. The highest densifications are obtained at high sintering temperatures and high sintering times. The calculated density of Zn_2TiO_4 spinel phase is about 5.28 g/cm^3. The amount of Zn_2TiO_4 spinel phase increased with increasing TiO_2 content. This resulted in decreasing of the bulk density.

3.2. Kinetics of grain growth

The SEM micrographs of the fracture surfaces of the samples with 1, 2, 3 and 4 wt. % of TiO_2 sintered at 1000 and 1300 ºC for 1 h are shown in Fig. 3. The samples sintered at 1000 °C for 1 h resulted in a porous and fine (<1 μm) crystalline microstructure. The sintering at 1300 °C caused a sudden grain growth, which in turn entrapped porosity within and among grains. Also the average grain size of each sample increased with increasing sintering temperature from 1000 °C to 1300 °C. As seen in Fig. 3, the grain growth of ZnO is inhibited with increasing TiO_2 doping. This is because of the formation of Zn_2TiO_4 phase in the grain boundaries, as seen in Fig.1. The relationship between the average grain size and the level of TiO_2-doping for the samples sintered at 1200 ºC and 1300 ºC for 1 h is shown in Fig. 4. As seen from this figure, the average grain size of undoped ZnO is about 17.5 μm at 1200 ºC for 1 h sintering and about 20 μm at 1300 ºC for 1 h [3]. The average grain size of ZnO decreases with TiO_2 content. A sharp decrease in the grain size of the samples sintered at 1200 °C for 1 h is observed. The grain growth of ZnO occurred with the solid-state diffusion of Zn^{2+} cations. The solid-state diffusion of Zn^{2+} cations [3] is strongly inhibited by the formation of Zn_2TiO_4 phase in the grain boundaries at the sintering of 1200 ºC (the grain size of ZnO is 6.3 μm in the 1 wt. % TiO_2-doped sample). But the same situation is not observed at the sintering of 1300 °C. The grain size of ZnO is 11.8 μm in the 1 wt. % TiO_2-doped sample.

The grain growth kinetics can be determined using a simplified phenomenological kinetics (Eq. (1)). The value of the grain growth exponent n in the equation can be found at isothermal conditions where the kinetic equation is expressed in the form of

$$n \log G = \log t + \log K_0 - 0.434\left(\frac{Q}{RT}\right) \tag{3}$$

The n value can be calculated from the slope of the log(grain size) versus log(time) plot which is equal to ($1/n$). Such plots were made for isothermal conditions employed at the sintering temperatures and the n values were calculated by the method of linear regression. Figs. 5a, b show the plots of log$G$ vs. log$t$ for various TiO_2 contents at 1200 ºC and 1300 ºC and the calculated n values are listed in Table 1. Similar plots

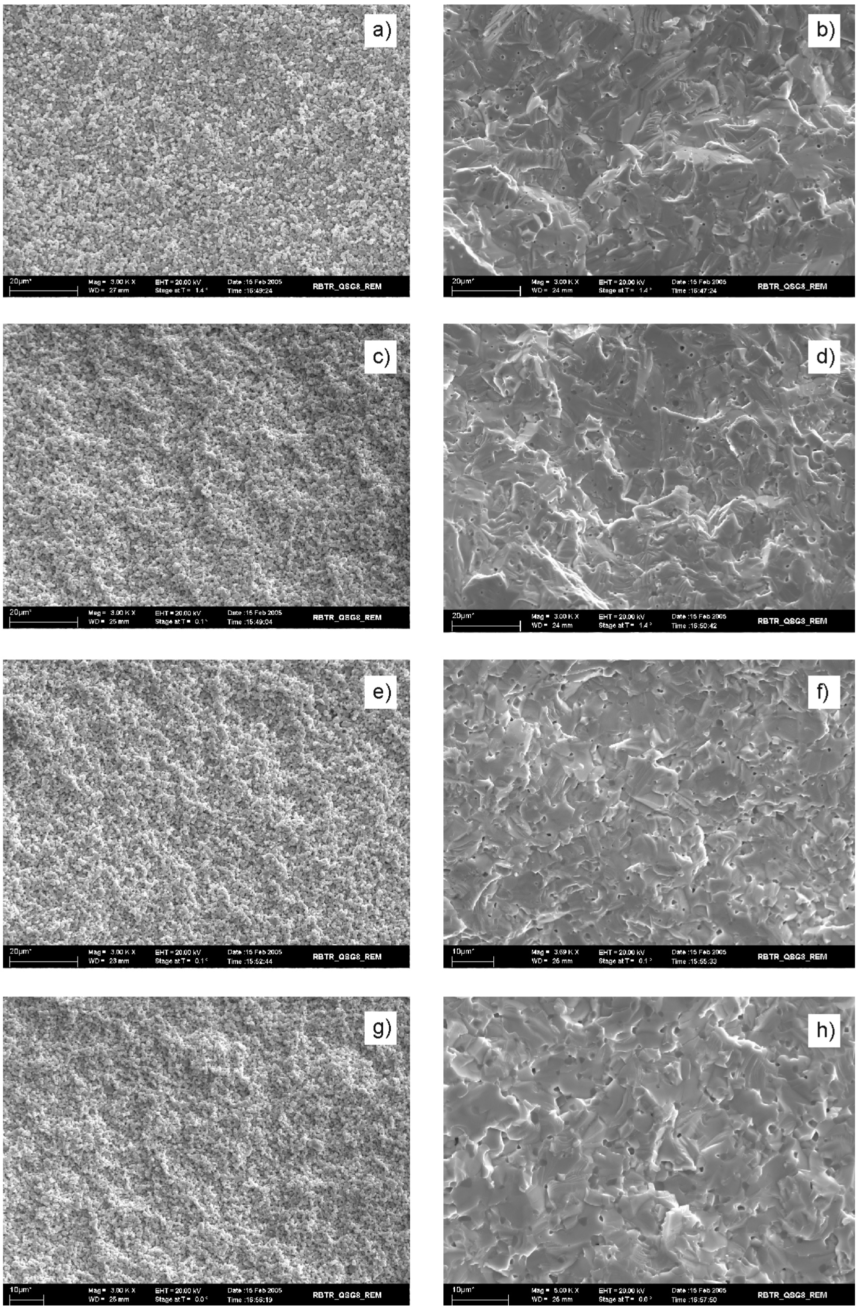


Fig. 3. SEM micrographs of the fracture surfaces of samples with 1, 2, 3 and 4 wt. $\%TiO_2$ doping sintered at 1000 °C /1 h (a, c, e, g) and 1300 ºC/1 h (b, d, f, h)

could not be constructed for isothermal sintering at 1000 and 1100 ºC, since the samples had a fine crystalline size (<1 μm) and very porous microstructure which gave rise to a large amount of grain pull-outs in the sample polishing process for optical microscopy. Therefore the grain sizes used as starting points for plots in the evaluation of the activation energies were deduced from the SEM micrographs in the samples sintered at 1000 ºC.

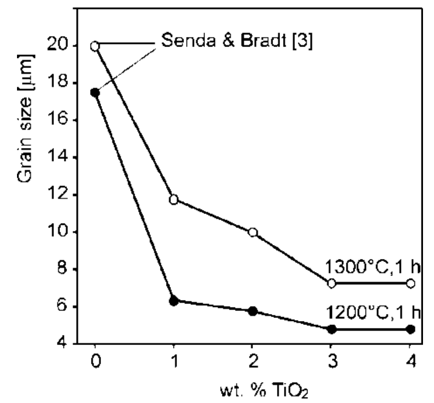


Fig. 4. The relationship between the average grain size and the level of TiO_2 doping for samples sintered at 1200 ºC and 1300 ºC for 1 h

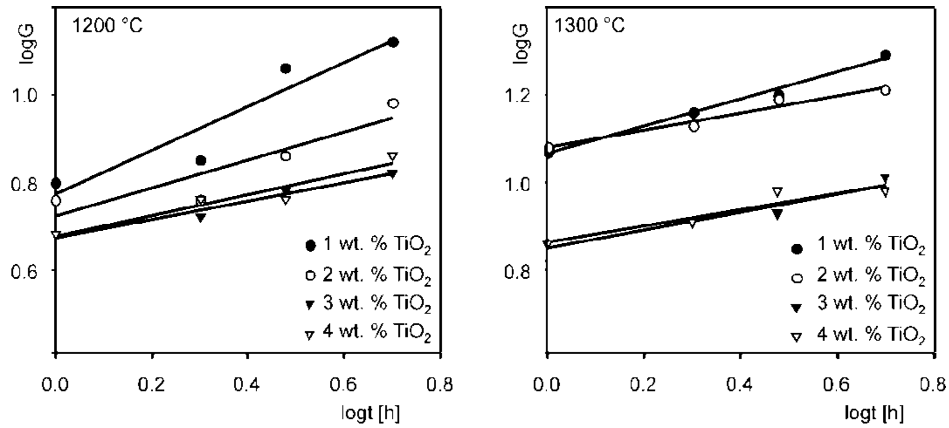


Fig. 5. Isothermal grain growth of ZnO with doping 1–4 wt. % TiO_2 sintered at: 1200 °C and 1300 °C

Senda and Bradt [3–5] reported the n values for ZnO and ZnO–2.38 wt. % Sb_2O_3 as 3 and 6, respectively. They also pointed out that the n value in the system indicated the mechanism of inhibition of grain growth. The n values for grain growth of the ZnO–TiO_2 1–4 wt. % studied in this work were found to be 3, 3, 5 and 5, respectively. They were affected by the high level of TiO_2 addition. If Eq. (2) is expressed as

$$\log\left(\frac{G^n}{t}\right) = \log K_0 - 0.434\left(\frac{Q}{RT}\right) \tag{4}$$

the apparent activation energy Q of the grain growth process can be calculated from the gradient of the Arrhenius plot of $\log(G^n/t)$ vs. $1/T$ (K^{-1}). Such plots for the studied system are given in Fig. 6. In Table 1, the *n* values accepted in the construction of these plots are given together with the calculated values of the logarithm of rate constants and the apparent activation energies.

Table 1. Values of grain size, calculated grain growth exponent *n*, apparent activation energy *Q* and preexponential constant K_0

TiO_2 content [wt. %]	Grain size [μm]		*n*	$\log K_0$	*Q* [kJ/mol]
	1200 ºC, 1 h	1300 ºC, 1 h			
0 [3]	17.5	20	3	11.49	225
1	6.3	11.8	3	17.47	435
2	5.7	10	3	17.85	435
3	4.8	7.3	5	24.65	608
4	4.8	7.3	5	24.95	615

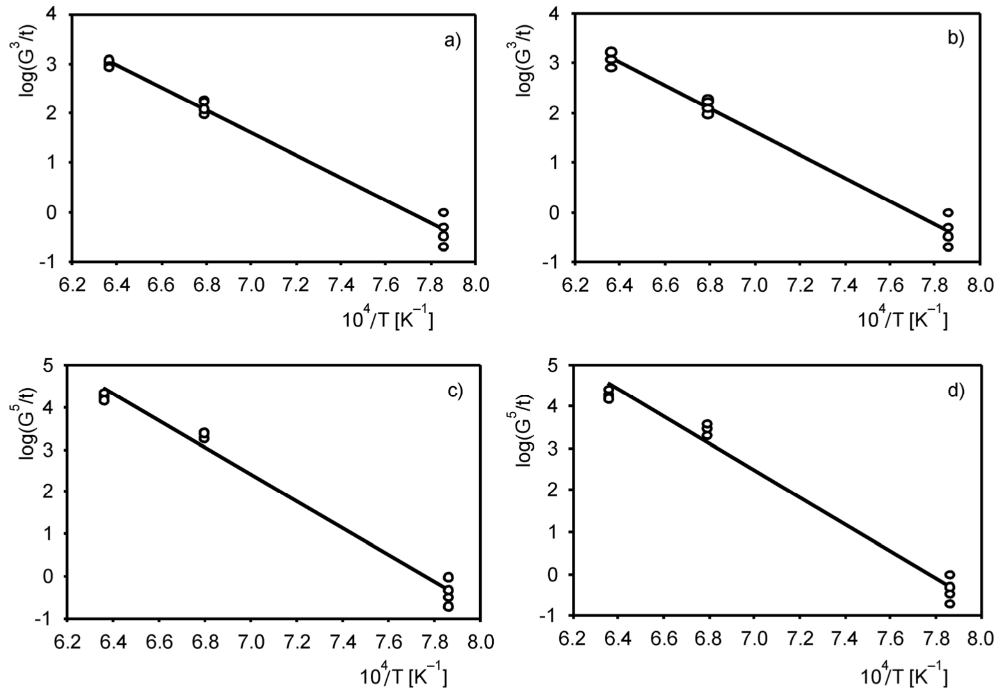


Fig. 6. Arrhenius plots for the grain growth of ZnO with TiO_2: a) 1 wt. % of TiO_2, Q = 435 kJ/mol, b) 2 wt. % of TiO_2, Q = 435 kJ/mol, c) 3 wt. % of TiO_2, Q = 608 kJ/mol, d) 4 wt. % of TiO_2, Q = 615 kJ/mol

Numerous studies on the kinetics of grain growth of ZnO have revealed that the rate controlling mechanism is the solid-state diffusion of Zn^{2+} cations. The apparent activation energy for this process is about 225 kJ/mol. As indicated in Table 1, the apparent activation energy of 435 kJ/mol was found for 1 and 2 wt. % TiO_2 content in the system. A sharp increase in the apparent activation energy to the value of 608 and 615 kJ/mol was found for 3 and 4 wt. % of TiO_2, respectively.

Since the microstructural and phase analysis of ZnO ceramics containing TiO_2 indicates the presence of Zn_2TiO_4 spinels as distinct crystals at the grain boundaries, inhibition of the ZnO grain growth must be considered related to presence of those spinel grains. The type of grain growth inhibition has been previously reported for other ZnO systems such as ZnO–Sb_2O_3 ($Zn_7Sb_2O_{12}$) [5] and ZnO–Al_2O_3 ($ZnAl_2O_4$) [1].

4. Conclusions

The effects of TiO_2 additions on the grain growth of ZnO were studied. Samples containing TiO_2 additions from 1 to 4 wt. % were sintered in air at 1000–1300 °C for 1–5 h. The resulting microstructures were observed by optical and electron microscopy methods and the phases were identified by the X-ray diffraction.

The apparent activation energy of 435 kJ/mol was found for samples containing 1 and 2 wt. % of TiO_2. A sharp increase in the apparent activation energy to the value of 608 and 615 kJ/mol was found for 3 and 4 wt. % of TiO_2, respectively. The apparent activation energy increased upon increasing content of TiO_2. The addition of TiO_2 to ZnO inhibits strongly the grain growth of ZnO. The inhibition is dependent on TiO_2 content, so higher contents of TiO_2 yield finer average ZnO grain sizes. When TiO_2 is added to ZnO, Zn_2TiO_4 spinel particles form at the grain boundaries. The process appears to be dominated by a grain boundary particle drag mechanism that is related to the formation of second-phase Zn_2TiO_4 spinel particles. The TiO_2 additions reduce the densification in the initial stages of sintering.

References

[1] HAN J., MANTAS P.Q., SENOS A.M.R., J. Mater. Res., 16 (2001), 459.
[2] HAN J., MANTAS P.Q., SENOS A.M.R., J. Europ. Ceram. Soc., 20 (2000), 2753.
[3] SENDA T., BRADT R.C., J. Am. Ceram. Soc., 73 (1990), 106.
[4] DEY D., BRADT R.C., J. Am. Ceram. Soc., 75 (1992), 2529.
[5] SENDA T., BRADT R.C., J. Am. Ceram. Soc., 74 (1991), 1296.
[6] TOPLAN H.Ö., ERKALFA H., ÖZKAN O.T., Ceramics-Silikaty, 47 (2003), 116.
[7] APAYDIN F., TOPLAN H.Ö., YILDIZ K., J. Mater. Sci., 40 (2005), 677.
[8] ÖZKAN O.T., AVCI M., OKTAY E., ERKALFA H., Ceram. Int., 24 (1988), 151.
[9] GÜNAY V., GELECEK-SULAN O., ÖZKAN O.T., Ceram. Int., 30 (2004), 105.
[10] TOPLAN Ö., GÜNAY V., ÖZKAN O.T., Ceram. Int., 23 (1997), 251.
[11] CANIKOĞLU N., TOPLAN N., YILDIZ K., TOPLAN H.Ö., Ceram. Int., 32 (2006), 127.
[12] *Metals Handbooks*, Vol. 8, 8th Ed., The American Society for Metals, PA, USA, 1973.
[13] LEVIN E.M., ROBBINS C., MC MURDIE F., *Phase Diagrams for Ceramics*, The American Ceramic Society Inc., Columbus, OH, 1965.

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