

## DENSIFICATION AND GRAIN GROWTH OF SrO-DOPED ZnO

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*The grain growth kinetics in the 1, 2, 3 and 4 wt.% SrO doped ZnO was studied using the simplified phenomenological grain growth kinetics equation  $G^n - G_0^n = K_0 t \exp(-Q/RT)$  together with microstructure properties and densification of the sintered samples. The grain growth exponent values ( $n$ ) were found to be 5 for 1, 2, 3 and 4 wt.% SrO doped ZnO. The apparent activation energies for 1, 2, 3 and 4 wt.% SrO doped ZnO were found 780 kJ/mol, 709 kJ/mol, 764 kJ/mol and 744 kJ/mol, respectively. The apparent activation energy was increased with doping of SrO because of ZnSrO<sub>2</sub> phase at the grain boundaries. This ZnSrO<sub>2</sub> phase inhibited the grain growth of ZnO. But the increasing SrO level had no effect on the grain growth. Also, the increasing of SrO resulted in a slight reduction in densification at all temperatures.*

## 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 and contains several dopants, such as Bi, Sb, Mn, Cr, Co, Ti and Al [2].

The electrical properties of ZnO varistors directly dependent 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 doped ZnO systems, such as Bi<sub>2</sub>O<sub>3</sub>-doped ZnO [3,4], Sb<sub>2</sub>O<sub>3</sub>-doped ZnO [5], Al<sub>2</sub>O<sub>3</sub>-doped ZnO [1], PbO-doped ZnO [6], CuO-doped ZnO [7]. Among the numerous work 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<sub>2</sub>O<sub>3</sub>. In their work, Senda and Bradt [3] used simplified grain growth kinetics equation

$$G^n = k t \exp(-Q/RT) \quad (1)$$

where  $G$  is the average grain size at time  $t$ ,  $n$  is the kinetic grain growth exponent value,  $k$  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 value ( $n$ ) as 3 and apparent activation energy ( $Q$ ) as 224.16 kJ/mol in the sintering of the pure ZnO system.

The additions of MnO [8] and CoO [9] to the ZnO-6 wt.% Bi<sub>2</sub>O<sub>3</sub> system, the addition of MnO [10] to

the ZnO-6 wt.% Sb<sub>2</sub>O<sub>3</sub> system and the addition of PbO [6], CuO [7] and SiO<sub>2</sub> [11] to ZnO were studied by our group and the present work is the continuation of the previous works in the grain growth kinetics of ZnO varistors. The aim of the present work is also to study the effect of SrO addition on microstructure and the sintering behaviour of ZnO.

## EXPERIMENTAL

High purity ZnO (99.7 % Metal Bileşikleri A.Ş., Gebze, Turkey) and SrCO<sub>3</sub> powders (pure grade) were used in preparation of four basic compositions; ZnO containing 1, 2, 3 and 4 wt.% SrO. ZnO powders revealed a needle like fine crystal c. 0.5 μm in width and c. 0.5-2 μm in length. 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. After drying, the mixture were granulated in moist conditions and then semi-dry pressed at 100 MPa to prepared specimens at 10 mm diameter and 8 mm thick. The specimens were sintered at 1000, 1100, 1200 and 1300°C for 1, 3, 5 and 10 h using a heating rate of 5 PC/min. and were naturally cooled in a PID controlled 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<sub>α</sub> radiation. For the microstructural observations, both scanning electron microscopy (SEM) of the fracture surfaces and optical microscopy of polished and HCl etched surfaces were used.

Grain size measurements were carried out on the micrographs of the etched samples using the following equation,

$$G = 1.56 \bar{L} \quad (2)$$

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].

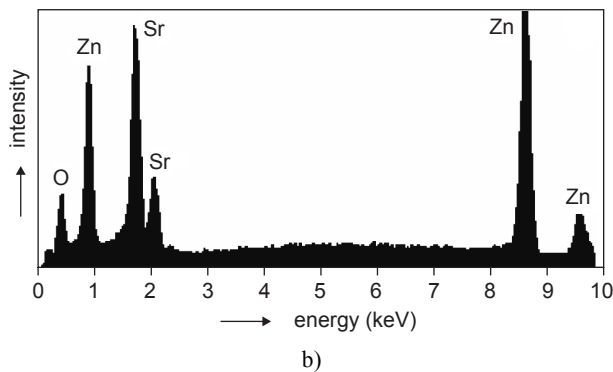
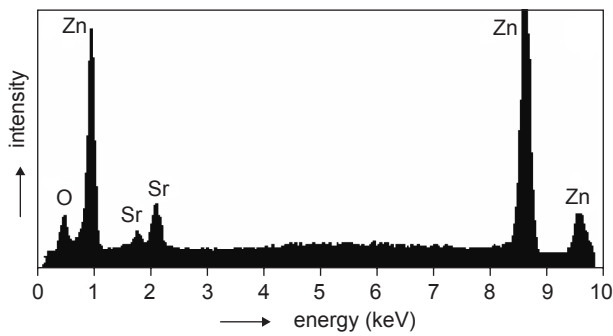
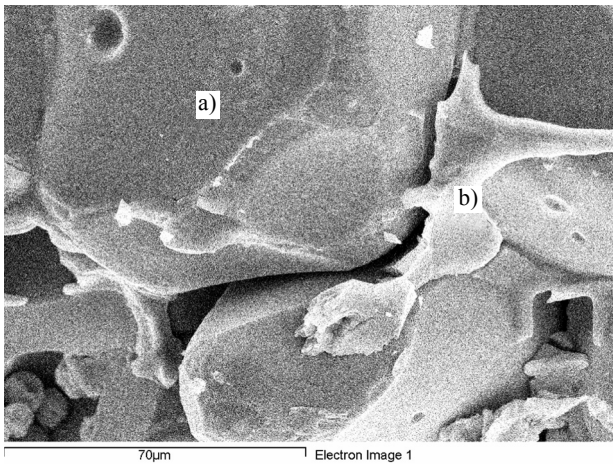
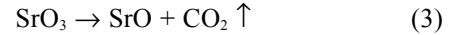


Figure 1. The backscattered electron images and EDS of the 4 wt.% SrO-doping ZnO sample sintered at 1300°C for 5 hours; a) ZnO phase, b) ZnSrO<sub>2</sub> phase.

## RESULTS AND DISCUSSION

### Physical properties of the sintered samples

It is determined the presence of ZnO (ASTM Card No: 5-0664) and SrCO<sub>3</sub> (ASTM Card No: 5-418) phases by using the X-ray powder diffraction of SrO-added all samples sintered only at 1000°C for different periods of time. According to equation (3), SrCO<sub>3</sub> decomposed at about 1000°C. SrCO<sub>3</sub> phase is determined by X-ray diffraction in all compositions sintered at 1000°C due to uncompleted decomposition reaction of SrCO<sub>3</sub>.



At the higher sintering temperatures, the X-ray powder diffraction study in the samples showed the presence of ZnO and ZnSrO<sub>2</sub> (ASTM Card No: 74-0134 or 72-0533). The backscattered electron images and energy dispersive x-ray spectrometer (EDS) of the 4 wt.% SrO-added ZnO samples sintered at 1300°C for 5 h are given in figure 1. The micrograph clearly shows the ZnSrO<sub>2</sub> phase as bright region between the ZnO grains. Watari and Bradt [13], have reported such a study in alkali oxide added ZnO system. It may be expected that the ions such as Li<sup>+</sup> (0.078 nm) and Na<sup>+</sup> (0.098 nm), which are very similar in size to Zn<sup>2+</sup> (0.071 nm), may experience significant solid solubility on the Zn<sup>2+</sup> lattice site within the ZnO wurtzite structure. However, the ions larger than Zn<sup>2+</sup> ion like K<sup>+</sup> (0,133 nm) and Sr<sup>2+</sup> (0.110 nm), will be considerably

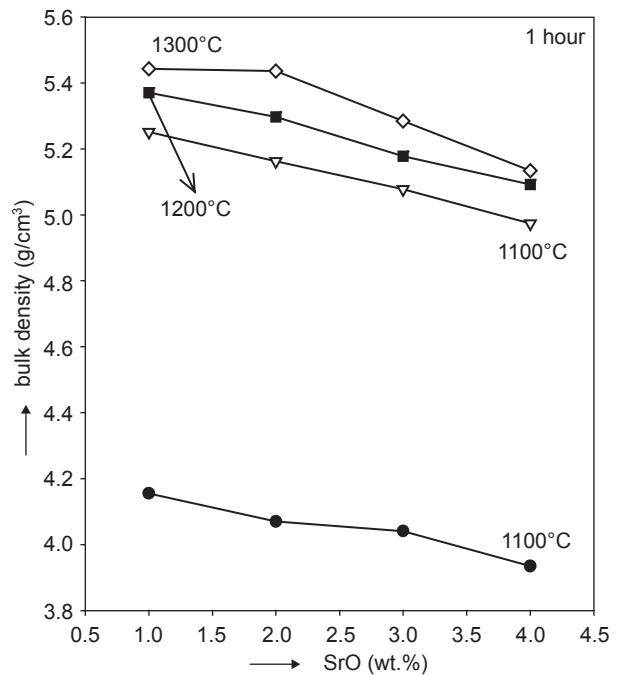
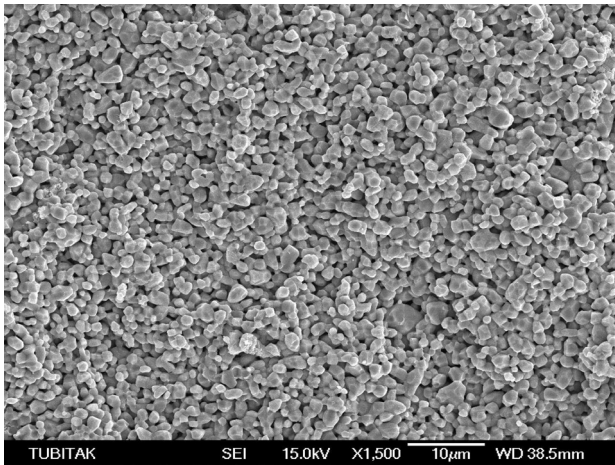
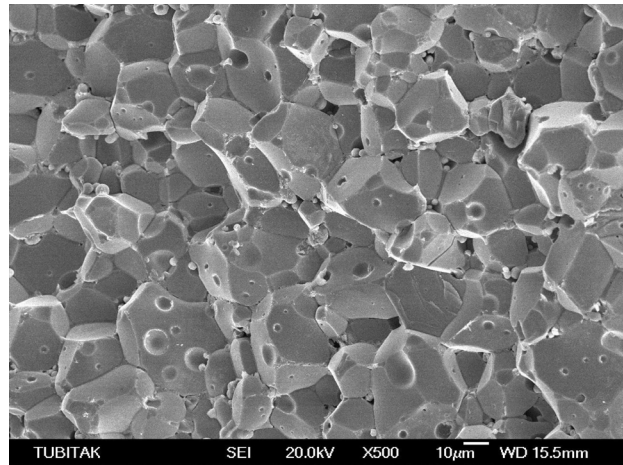


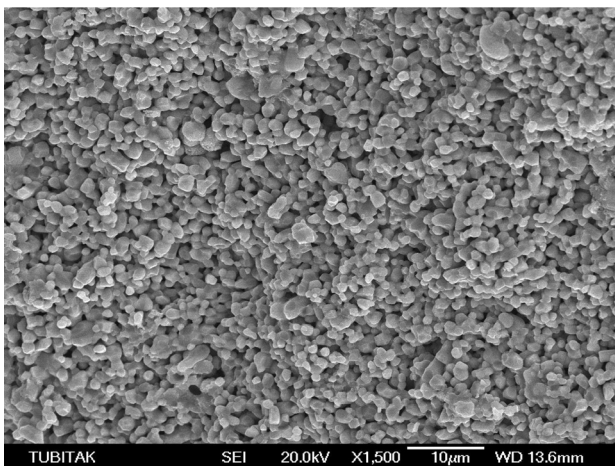
Figure 2. The effects of SrO on densification of the samples at different sintering temperatures for 1 hour.



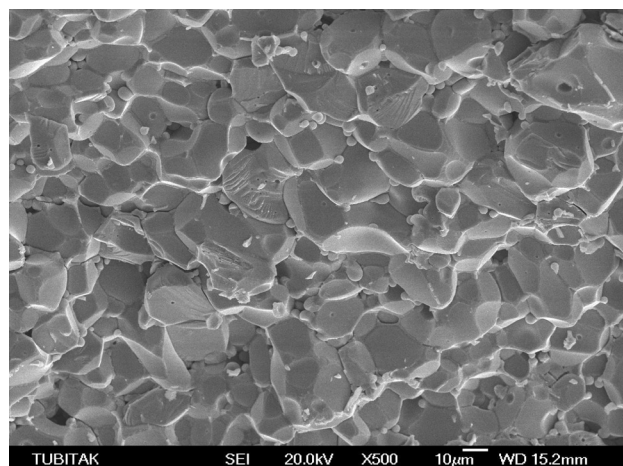
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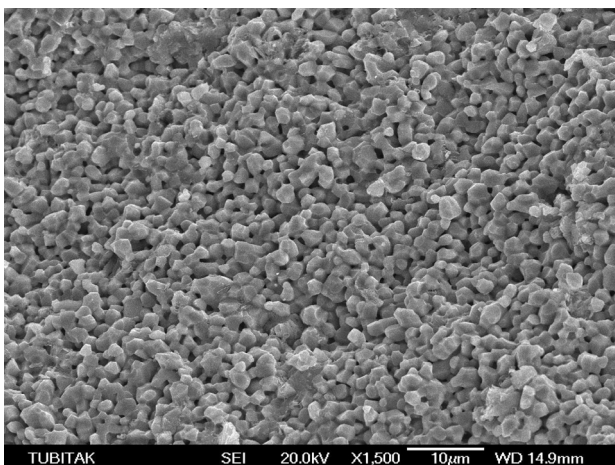
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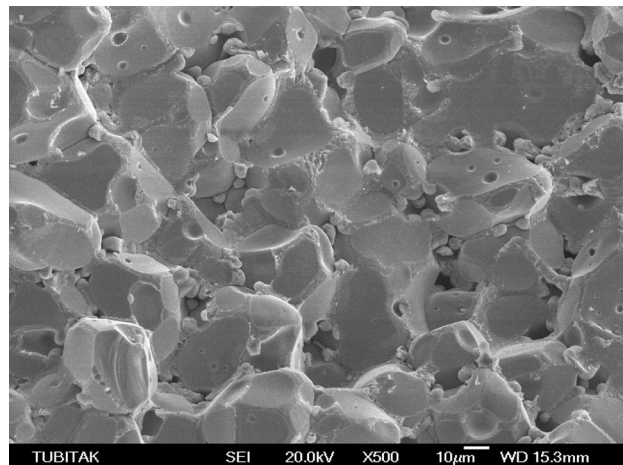
c)



d)



e)



f)

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

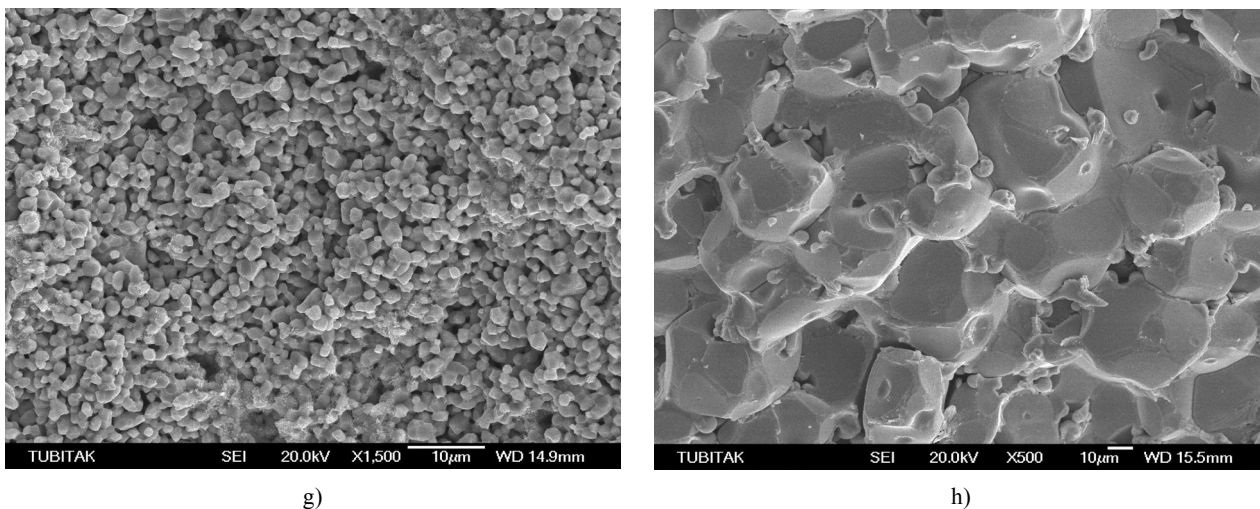
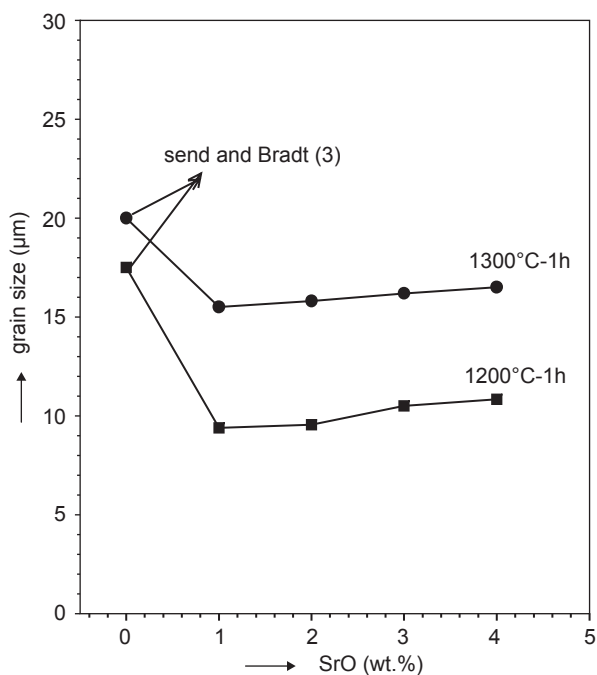
Figure 3. *continue.*

Figure 4. The relationship between the average grain size and the level of SrO-doping for the samples sintered at 1200°C and 1300°C for 1 hour.

Table 1. Calculated grain growth exponent ( $n$ ), apparent activation energy ( $Q$ ) and preexponential constant ( $K_0$ ) values

SrO content (wt.%)	$n$ values used in Arrhenius plots	$\log K_0$	$Q$ (kJ/mol)
1	≈5	30.26	780
2	≈5	29.68	709
3	≈5	31.85	764
4	≈5	31.35	744

less soluble within ZnO wurtzite structure and may be preferably segregated to the ZnO grain boundaries. Therefore, SrO formed  $\text{ZnSrO}_2$  phase with ZnO and segregated to the ZnO grain boundaries.

The effects of SrO on densification of the samples is given in figure 2. Similarly, the SEM micrographs of the fracture surfaced of samples with 1, 2, 3 and 4 wt.% SrO content sintered at 1000°C and 1300°C for 1 h were compared in figure 3a-h. The sintering at 1000°C for 1 h did not show any significant effect on the densification. The sinterings at this temperature resulted in a porous and fine ( $< 1 \mu\text{m}$ ) crystalline microstructure. The highest densifications are obtained at high sintering temperatures and high sintering times. The addition of SrO results in a slight reduction in the bulk densities of the samples at all temperatures. The reduction mainly arises from the differences between the densities of ZnO ( $5.68 \text{ g/cm}^3$ ) and SrO ( $5.1 \text{ g/cm}^3$ ).

#### Grain growth kinetics

The relationship between the average grain size and the level of SrO-doping for samples sintered at 1200 and 1300°C for 1 h is given in figure 4. As seen from this figure, the average grain size of undoped ZnO is about  $17.5 \mu\text{m}$  at 1200°C for 1 h sintering and about  $20 \mu\text{m}$  at 1300°C for 1 h [3]. The average grain size of ZnO decreases sharply with the SrO additions at the both sintering temperatures. The grain growth of ZnO is occurred with the solid-state diffusion of  $\text{Zn}^{2+}$  cations. The solid-state diffusion of  $\text{Zn}^{2+}$  cations is strongly inhibited by the formation of  $\text{ZnSrO}_2$  phase in the grain boundaries at the both sintering temperatures. However the increased SrO additions have no any significant effect on the grain growth of ZnO, as it is seen from the micrographs given in figure 3a-h.

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

$$n \log G = \log t + [\log K_0 - 0.434 (Q/R T)] \quad (4)$$

The  $n$  value can be calculated from the slope of the log (grain size) versus log (time) line 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 from the slopes of the plots constructed by the linear regression method. Figure 5a-d depicts the log  $G$  vs log  $t$  plots for different SrO

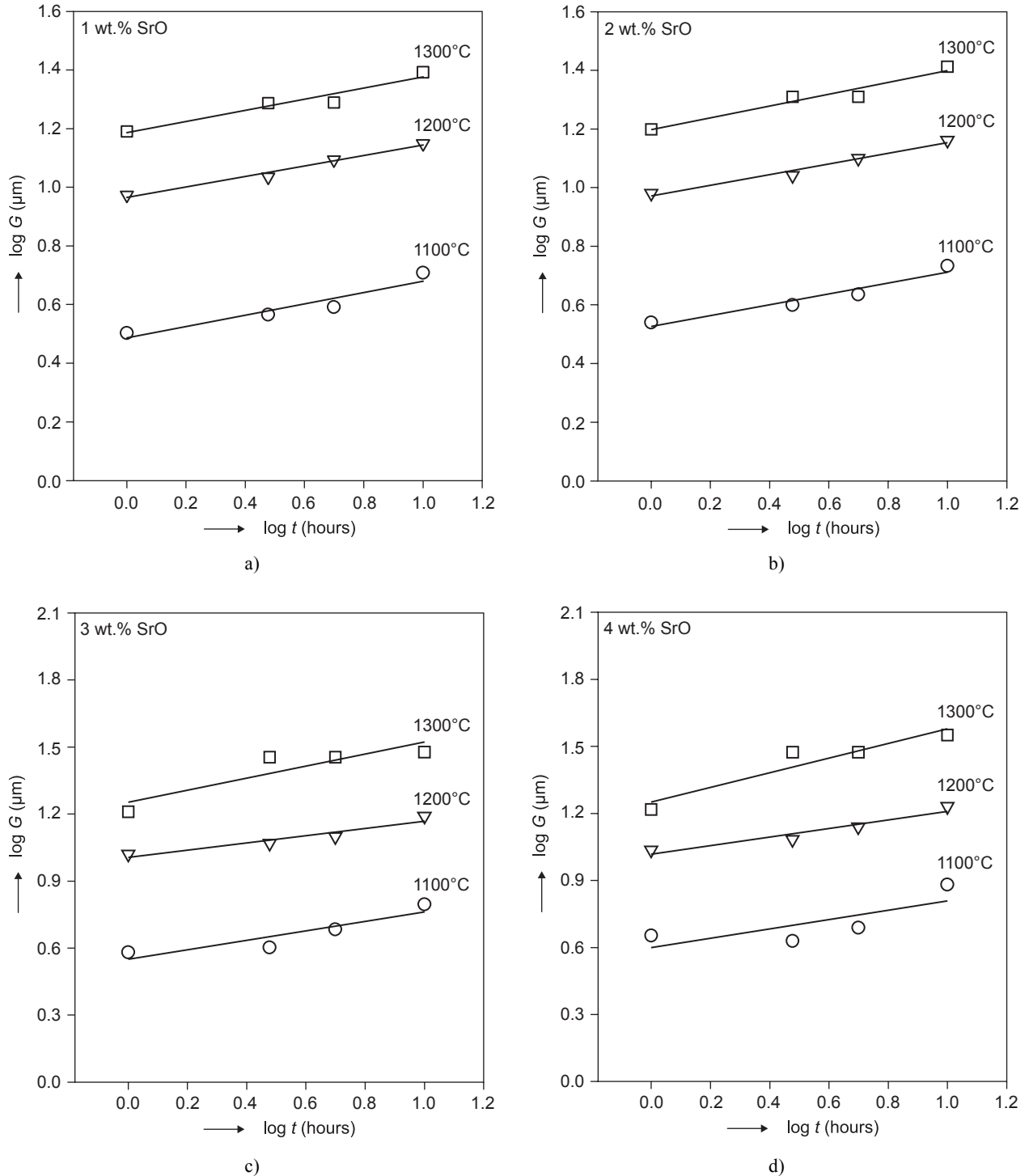


Figure 5. Isothermal grain growth of ZnO with doping (a) 1 (b) 2 (c) 3 and (d) 4 wt.% SrO at different sintered temperatures.

contents at the 1100, 1200 and 1300°C temperatures and the calculated ( $n$ ) values are listed in table 1. Similar plots could not be constructed for isothermal sintering at 1000°C, since the samples had a fine crystalline size ( $\leq 1 \mu\text{m}$ ) and a very porous microstructure, which gave rise to a large amount of grain pull-outs in the sample polishing process for optical microscopy.

Some researchers [3-5] have reported the  $n$  values for ZnO and ZnO-2.38 wt.%  $\text{Sb}_2\text{O}_3$  system as 3 and 6, respectively. They also pointed out that  $n$  value in a system indicated a grain growth inhibition mechanism. The  $n$  values for grain growth of the ZnO- 1, 2, 3 and 4 wt.% SrO system studied in this work were found to be 5.

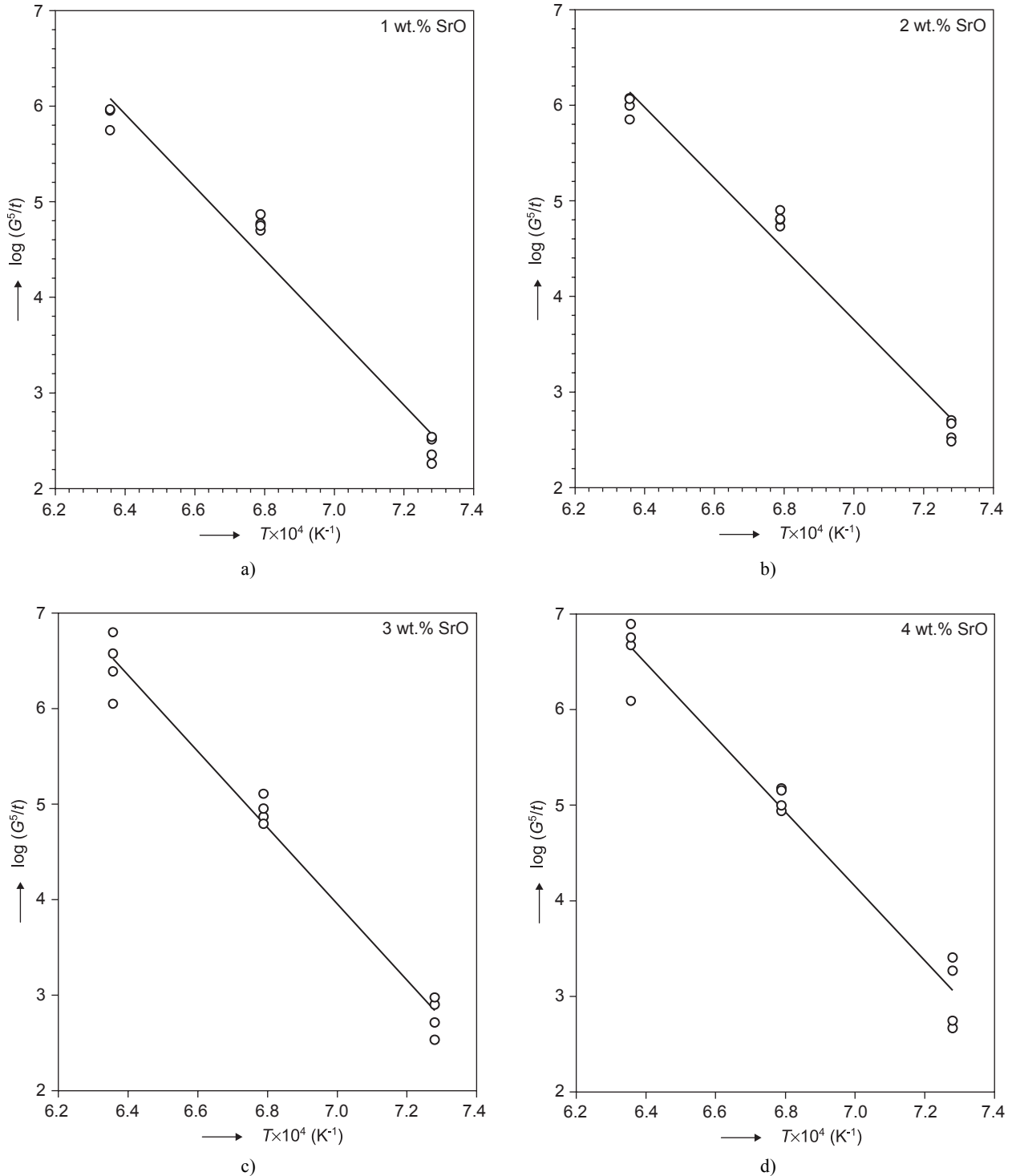


Figure 6. Arrhenius plots for the grain growth of ZnO with doping (a) 1 (b) 2 (c) 3 and (d) 4 wt.% SrO.

If equation (1) is expressed in the form of

$$\log(G^n/t) = [\log K_0 - 0.434 (Q/R T)] \quad (5)$$

the apparent activation energy  $Q$  of a 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 figure 6a-d. Table 1 also listed the  $n$  values accepted in the construction of these plots along with the calculated values of the logarithm of rate constants and the apparent activation energies. The numerous studies out on the grain growth kinetics 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, an increasing sharply in the apparent activation energy to values of 780, 709, 764 and 744 kJ/mol was found for 1, 2, 3 and 4 wt.% SrO added system, respectively.

The grain growths of several doped ZnO systems have been previously investigated. The same increase of the apparent activation energy and retardation of ZnO grain growth are observed in the  $Sb_2O_3$ -doped ZnO ( $Q = \approx 600$  kJ/mol) [5],  $K_2O$ -doped ZnO ( $Q = \approx 560$  kJ/mol) [13],  $Na_2O$ -doped ZnO ( $Q = \approx 310$  kJ/mol) [13],  $Al_2O_3$ -doped ZnO ( $Q = \approx 400$  kJ/mol) [1] and  $SiO_2$ -doped ZnO ( $Q = \approx 900$  kJ/mol) [11] systems. Watari and Bradt [13] reported that metal oxide additions inhibit the grain growth of ZnO by two different mechanisms; (1) the reduction of  $Zn^{2+}$  diffusion in the ZnO wurtzite structure by the reduction of the number of lattice cation vacancy sites and the occupation of interstitial sites, and (2) the reduction of the ZnO grain boundary mobility by segregation of the second phases like  $Zn_7Sb_2O_{12}$ ,  $ZnAl_2O_4$  and  $Zn_2SiO_4$  to grain boundaries. It is suggested that SrO dominates through the second mechanism. Since the microstructural and phase analysis of SrO containing ZnO ceramics indicates the presence of the  $ZnSrO_2$  phase as distinct crystals at the grain boundaries, inhibition of the ZnO grain growth must be considered to be related to presence of those second phase 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],  $ZnO-Al_2O_3$  ( $ZnAl_2O_4$ ) [1],  $ZnO-SiO_2$  ( $Zn_2SiO_4$ ) [11].

## CONCLUSION

The effect of SrO additions of 1-4 wt.% on sintering behaviour and grain growth mechanism of ZnO were studied. The highest densifications were obtained at high sintering temperatures and high sintering times. Also the increasing addition of SrO resulted in a slight reduction in densification at all temperatures.

The apparent activation energy of 225 kJ/mol was reported for the undoped ZnO in literature. A sharply increasing in the apparent activation energy to a value of 780 kJ/mol, 709 kJ/mol, 764 kJ/mol and 744 kJ/mol

was found for 1, 2, 3 and 4 wt.% SrO added system, respectively. The addition of SrO inhibited strongly the grain growth of ZnO. When SrO is added to ZnO,  $ZnSrO_2$  phase particles form at the grain boundaries. It appears to be dominated by a grain boundary particles drag mechanism that is related to the formation of second phase  $ZnSrO_2$  particles. But the increasing SrO levels to ZnO have no effect on the grain growth of ZnO and the apparent activation energies.

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## ZHUTŇOVÁNÍ A RŮST ZRNA ZnO LEGOVANÉHO POMOCÍ SrO

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Byla studována kinetika růstu zrna v 1, 2, 3 a 4 hmotnostních ZnO legovaného pomocí SrO pomocí zjednodušené fenomenologické rovnice kinetiky růstu zrna  $G^n - G_0^n = K_0 \cdot t \cdot \exp(-Q/R \cdot T)$  společně s mikrostrukturálními vlastnostmi a zhutňováním slinovaných vzorků. Byly nalezeny hodnoty exponentu růstu zrna ( $n$ ) - hodnota 5 pro 1, 2, 3 a 4 % hmotnostních ZnO legovaného pomocí SrO. Zdánlivá energie aktivace pro 1, 2, 3 a 4 % hmotnostních ZnO legovaného pomocí SrO byla zjištěna na hodnotě 780 kJ/mol, 709 kJ/mol, 764 kJ/mol a 744 kJ/mol. Zdánlivá energie aktivace byla zvýšena legováním pomocí SrO v důsledku fáze  $ZnSrO_2$  na hranicích zrna. Tato fáze  $ZnSrO_2$  zabraňovala růstu zrna ZnO. Zvýšení úrovně SrO však nemělo žádný účinek na růst zrna. Zvýšení SrO vedlo k redukci zhutnění při všech teplotách.