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The effect of CuO on the grain growth of ZnO

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The grain growth kinetics in the 1, 2, 3 and 4 wt.% CuO doped ZnO was studied using the simplified phenomenological grain growth kinetics equation $G^n - G_0^n = K_0 \cdot t \cdot \exp(-Q/RT)$ together with microstructure properties of the sintered samples. The grain growth exponent value (n) was found to be 3 for 1, 2 and 3 wt.% CuO doped ZnO and 5.5 for 4 wt.% CuO doped ZnO. The apparent activation energy was decreased with CuO doping up to 3 wt.% from 250 kJ/mol to 150 kJ/mol but it was not changed significantly (155 kJ/mol) by 4 wt.% CuO doping. CuO doping up to 3 wt.% promoted the grain growth of ZnO whereas 4 wt.% CuO doping inhibited the grain growth of ZnO because of formation of Cu-rich secondary phase in the grain boundaries.

1. Introduction

ZnO based varistor ceramics have become technologically important because of their highly non-linear electrical characteristics enabling them to be used as reversible, solid state switches with large energy-handling capabilities [1].

Commercial ZnO varistor ceramics are compositionally designed to contain several metal oxides, which modify the sintering and electrical properties of these ceramics which show unique electrical properties. Additions may include Bi_2O_3, Pr_6O_{11}, Sb_2O_3, Cr_2O_3, SiO_2, CoO/Co_3O_4, MnO/MnO_2 and other oxides, each of which makes specific contribution to the microstructural evolution of the ZnO during sintering as well as to the electrical characteristics of the fired ZnO based ceramic varistor [2]. Since the electrical properties of these polycrystalline ceramics are directly dependent on the microstructure, as the grain size affect the varistor breakdown voltage per unit thickness. Other properties of polycrystalline ceramics also depend on the microstructure, so that it is important in a general sense to fundamentally understand the microstructural development of ZnO ceramics [3]. Therefore, it is important to study in a systematic way the effect of these additives on the microstructural development and the grain growth kinetics of the materials.

Senda and Bradt [3], have reviewed the grain growth of pure ZnO and described the role of Bi_2O_3 in the liquid phase sintering of ZnO varistor ceramics. In their work, they used the phenomenological kinetic grain growth equation:

$$G^n - G_0^n = K_0 \cdot t \cdot \exp\left(-\frac{Q}{RT}\right) \qquad (1)$$

where G_0 is the initial grain size of the ZnO, G is the average grain size at the time t, the n is grain growth exponent, K_0 is a kinetic constant, Q is the apparent activation energy for grain growth, R is the gas constant and T is the absolute temperature. Using this equation, Senda and Bradt 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.

Many studies have been conducted on the sintering of several doped ZnO system, with additives such as Sb_2O_3 [4], Bi_2O_3 [3], MnO [5], BaO [6], and Al_2O_3 [7]. In a previous study, it was observed that the gradual addition of CuO decreased the leakage current, but increased the breakdown electric field of the CuO-doped ZnO ceramics because of the segregation of a second phase containing excess CuO precipitated from ZnO matrix. However the microstructure was not clearly understood [8].

In the present work, the effect of CuO doping on the grain growth of ZnO is investigated. This study was performed by isothermal sintering of ZnO doped with CuO in the range of 1–4 wt.%.

2. Experimental procedures

Reagent grade ZnO powders (>99.8%, Metal Bileşikleri A.Ş. Gebze, Kocaeli, Turkey) and $CuSO_4.5H_2O$ were used to prepare the compositions of ZnO with 1, 2, 3 and 4 wt.% CuO added. To dope with CuO, the solution of $CuSO_4{\cdot}5H_2O$ was prepared and rapidly mixed with NaOH solution and, the following reaction occured [9]

$$Cu^{+2} + 2(OH)^- \rightarrow Cu(OH)_2 \downarrow \qquad (2)$$

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The $Cu(OH)_2$ and ZnO powders were ball milled in an ashless rubber lined ceramic jars for 6 h using zirconia balls and distilled water as the milling media. The slurry was dried, the powders were calcined at 500°C for 2 h and then isostatically pressed (100 MPa) into cylindrical pellets. The specimens were sintered in air at 1000°, 1100°, 1200° and 1300°C for 1, 2, 3 and 5 h with a heating rate of 10°C/min. and were naturally cooled in a PID controlled furnace.

The characterisation of sintered specimens was 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 (in a 10% HCl acid-distilled water solution) surfaces were used. Grain size measurements were carried out on micrographs of the etched samples using the following equation,

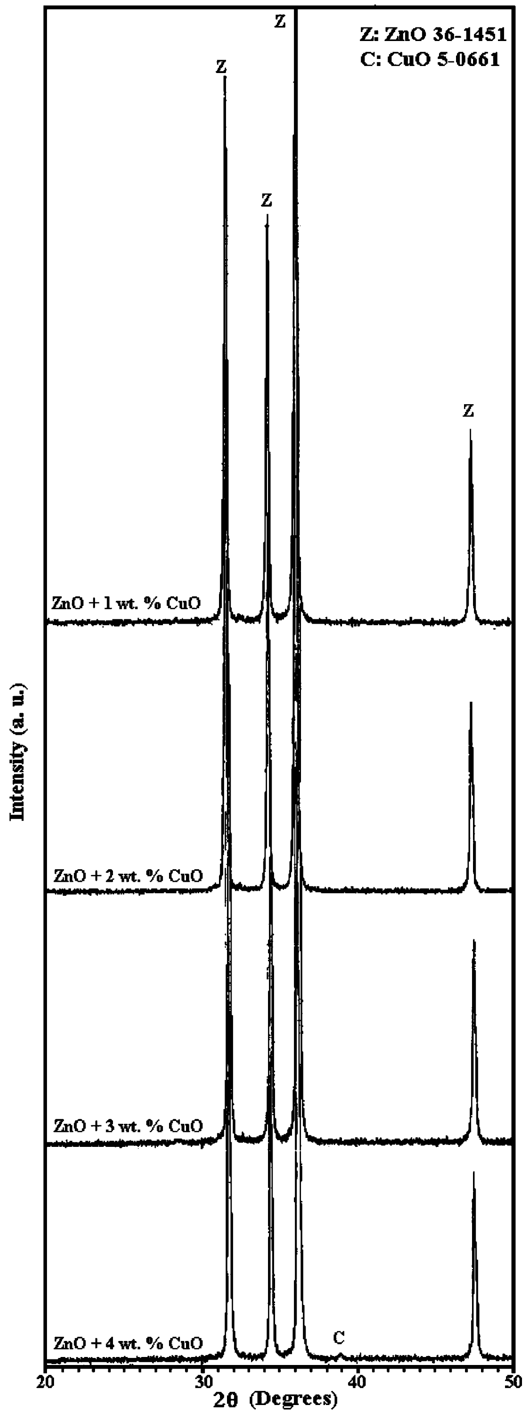


Figure 1 XRD spectra of crashed pellets obtained from samples of x wt.% CuO doped ZnO (x = 1, 2, 3 and 4) sintered at 1000°C for 1 h.

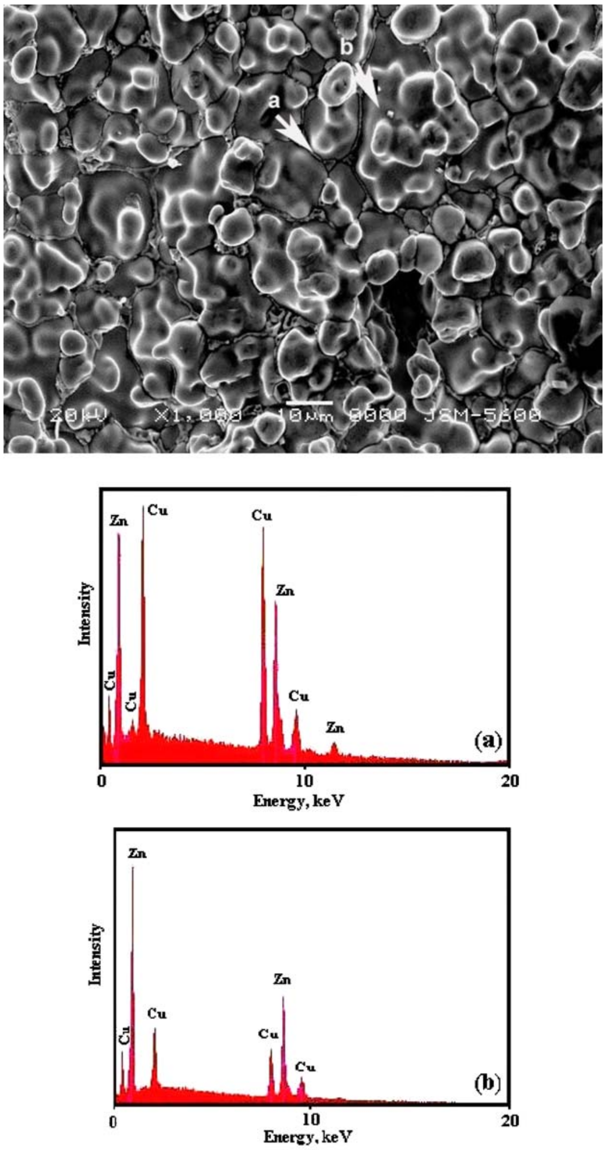


Figure 2 A higher magnification backscattered electron SEM image and EDS spectra of 4 wt.% CuO doped ZnO sintered at 1000°C for 1 h.

$$\bar{G} = 1.56 * \bar{L} \quad (3)$$

where, $\bar{G}$ is the average grain size, $\bar{L}$ is the average grain boundary intercept-length of random lines on two different micrographs for each sample [10].

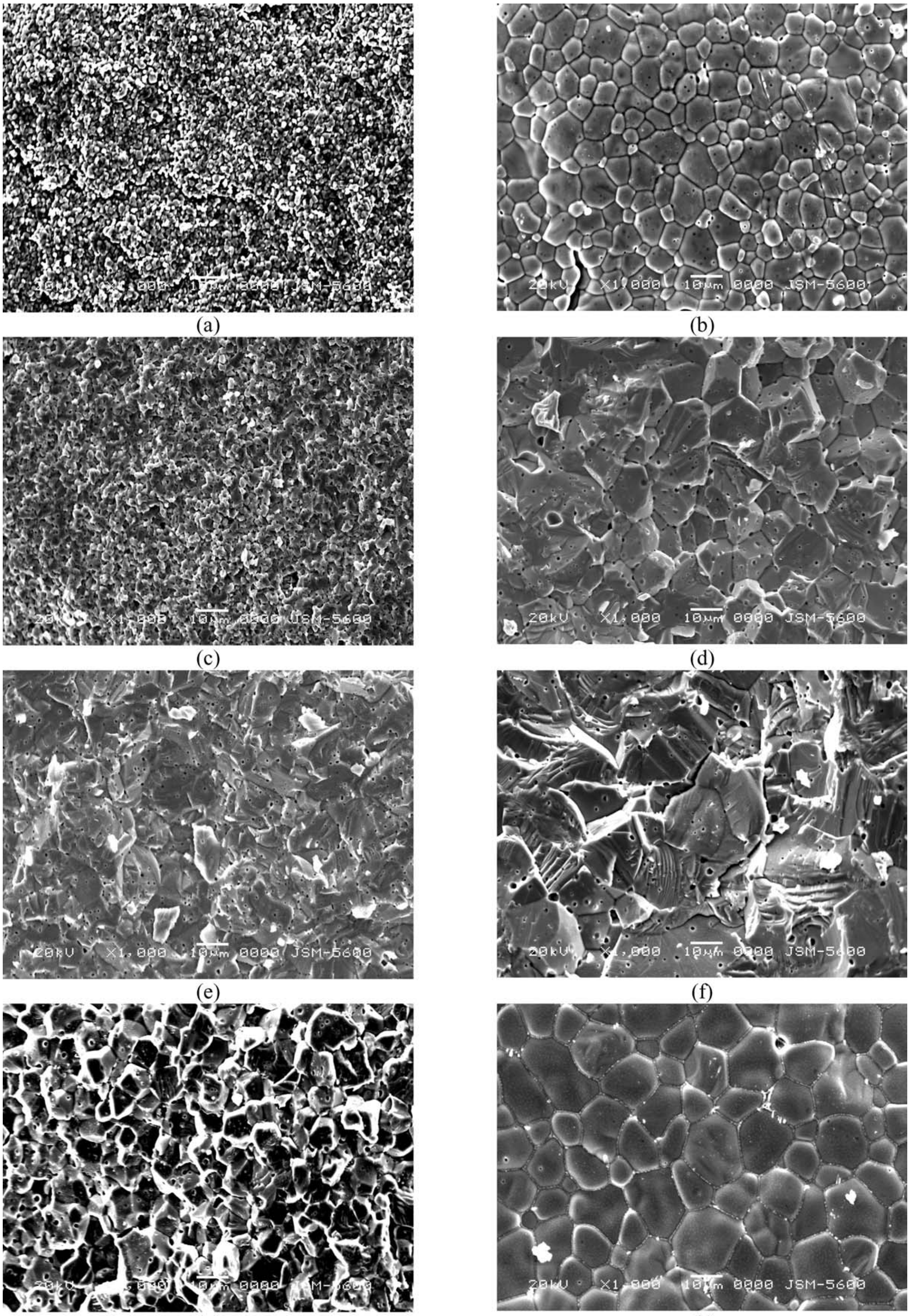
3. Result and discussions

3.1. Microstructure

Fig. 1 shows the powder XRD spectra of crushed pellets obtained from samples of x wt.% CuO doped ZnO ($x = 1, 2, 3$ and 4) sintered at 1000°C for 1 h. For ZnO-x wt.% CuO ($x = 1, 2$ and 3) only the ZnO phase (ASTM Card No: 36-1451) is observed. This shows that CuO forms solid solution with ZnO. The X-ray powder diffraction study in the addition of 4 wt.% CuO shows the presence of ZnO and CuO (ASTM Card No: 5-0551). Thus, for this composition, the XRD spectrum presents traces of

CuO as secondary phase (insoluble CuO). Also Fig. 2 shows a higher magnification backscattered electron SEM image of 4 wt.% CuO doped sample sintered at 1000°C for 1 h revealing the dark grey ZnO grains and the lighter grey CuO phases located at grain junctions as confirmed by the EDS spectra. The results are in agreement with the results of Bellini and co-workers [8].

The SEM micrographs of the fracture surfaces of the samples with 1, 2, 3 and 4 wt.% CuO doping sintered



(a) (b)

(c) (d)

(e) (f)

(g) (h)

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

at 1000°C and 1300°C for 1 h are given in Fig. 3a–h. The samples with 1 and 2 wt.% CuO doping sintered at 1000°C for 1 h resulted in a porous and fine crystalline microstructure (Fig. 3a and c). More additions (Fig. 3e and g) cause a sudden grain growth, which in turn entraps porosity within and among the grains. The sinterings at 1300°C result in the decreasing of these pores (Fig. 3b, d, f and h). Also, the average grain size of each sample increases with increasing sintering temperature from 1000° to 1300°C. The average grain size of ZnO increases with the CuO doping up to 3 wt.%. In the case of 4 wt.% CuO doping, the average grain size is inhibited because of the formation of Cu-rich secondary phase in the grain boundaries.

3.2. Grain growth kinetics

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 when the kinetic equation is expressed in the form of

$$n \log G = \log t + \{\log K_0 - 0.434(Q/RT)\} \quad (4)$$

The n value can be calculated from the slope of the log(grain size) vs. log(time) line plot which is equal to ($1/n$). Fig. 4a–d shows such plots for isothermal sintering at 1000°–1100°–1200° and 1300°C and the calculated n values are listed in Table I. In 1 and 2 wt.% CuO doping samples, similar plots could not be constructed for isothermal sinterings at 1000°C, since the samples had a fine crystalline size and very porous microstructure, which gave rise to a large amount of grain pull-outs in the sample polishing process for the optical microscopy. The grain growth exponent value of 3 determined for the 1, 2 and 3 wt.% CuO doped-ZnO systems is same to n value obtained by Senda and Bradt [3], Gupta and Coble [11], and Nicholson [12] for pure ZnO. But the 4 wt.% CuO doping gave the n value of 5.5.

TABLE I Calculated grain growth exponent (n), apparent activation energy (Q) and Preexponential constant (K_0) values

CuO (wt.%)	n	logK_0	Q (kJ/mol)
1	3	12.49	250 ± 24
2	3	11.77	220 ± 20
3	3	9.83	150 ± 13
4	5.5	12.61	155 ± 13

When Equation 1 is expressed in the form;

$$\log(G^n/t) = \log K_0 - (0.434Q/R)(1/T) \quad (5)$$

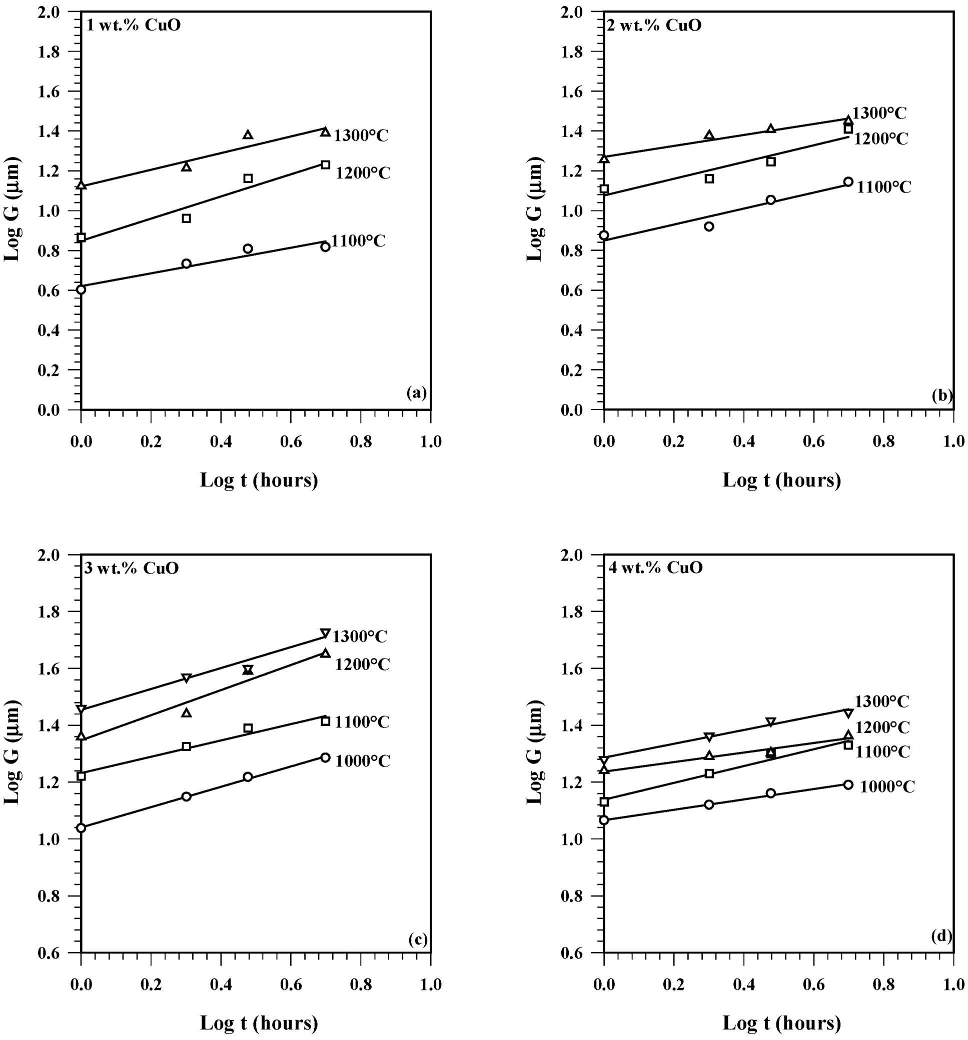


Figure 4 Isothermal grain growth of (a) 1, (b) 2, (c) 3 and (d) 4 wt.% CuO doped ZnO at different sintering temperature

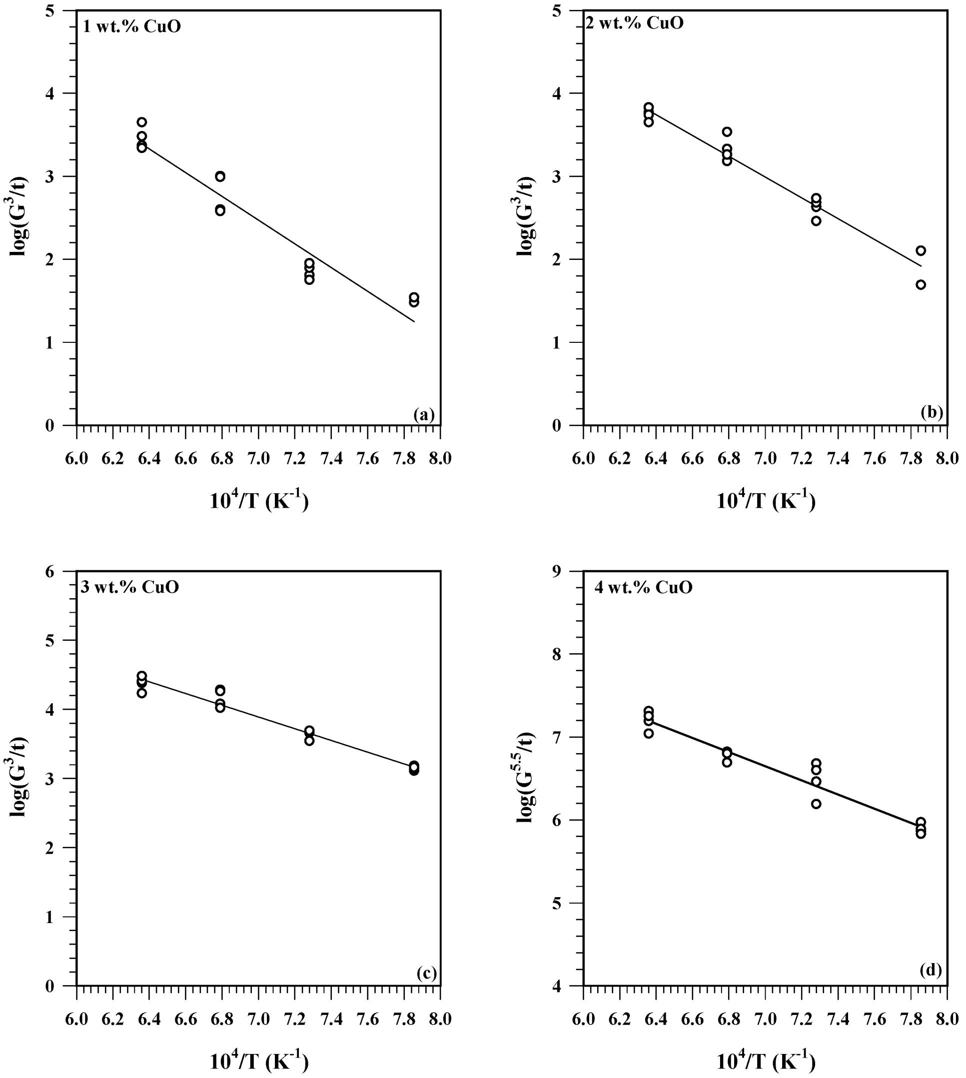


Figure 5 Arrhenius plots for the grain growth of (a) 1, (b) 2, (c) 3 and (d) 4 wt.% CuO doped.

the apparent activation energy Q for the grain growth process can be calculated from the gradient of the Arrhenius plot of $\log(G^n/t)$ vs. $(1/T)$. Such plots were constructed for the system studied are shown in Fig. 5a–d and the calculated apparent activation energies along with the logarithm of preexponential constant K_0 are also listed in Table I.

The numerous studies carried out on the grain growth kinetics of ZnO have revealed that the rate-controlling mechanism is the solid state diffusion of the Zn^{+2} cations. The apparent activation energy for this process is about 225 ± 16 [3]–250 ± 42 kJ/mol [11].

In this study it was observed that CuO doping up to 3 wt.% reduced the apparent activation energy from 250 ± 24 kJ/mol to 150 ± 13 kJ/mol. This reduction of activation energy for ZnO grain growth in the presence of CuO also implies that CuO doping promotes the grain growth of ZnO. These results indicate that CuO doping up to 3 wt.% in ZnO promotes the grain boundary transport for grain growth. But more CuO additions (4 wt.%) inhibited the grain growth of ZnO because of secondary phase (Cu-rich) in grain boundaries, as seen in Figs 1 and 2.

4. Conclusion

Isothermal sintering of ZnO doped with CuO from 1 wt.% to 4 wt.% was performed in the range of 1000° to 1300°C in air. The effect of CuO doping on the grain growth of ZnO was investigated. CuO doping up to 3 wt.% promotes ZnO grain growth during sinterings. At 4 wt.% CuO doping, grain growth of ZnO is inhibited because of the formation of Cu-rich secondary phase in grain boundaries. The grain growth exponent (n) for ZnO-x wt.% CuO ($x = 1$, 2 and 3) is 3 and apparent activation energy is reduced from 250 ± 24 kJ/mol to 150 ± 13 kJ/mol. The n value and apparent activation energy for ZnO-4 wt.% CuO is 5.5 and 155±13 kJ/mol, respectively.

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