

Grain growth of ZnO–V₂O₅ based varistor ceramics with different antimony dopants

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Abstract

Grain growth of 2 wt% V₂O₅/Sb₂O₃ precursor doped ZnO–V₂O₅ based ceramics was studied for sintering from 900 to 1050 °C. The results are discussed and compared with those of the conventional Sb₂O₃ doped ZnO–V₂O₅ based ones of the same stoichiometric ratio in terms of the phenomenological grain growth kinetics equation: $G^n - G_0^n = K_0 t \exp(-Q/RT)$. Grain growth exponent and apparent activation energy of the precursor doped ceramics are found to be 2.44 and about 218 kJ/mol, respectively, much lower than 4.03 and about 365 kJ/mol for the Sb₂O₃ doped samples. This result and the XRPD examination of the phase transformation within two extra batches of the precursor or the Sb₂O₃ slightly over-doped samples sintered at 550–900 °C for 1 h indicate the elimination of Sb₂O₃ related films contributes mainly to the observed noteworthy low temperature sintering (900 °C) of the precursor doped ZnO–V₂O₅ ceramics.

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1. Introduction

ZnO–V₂O₅ (ZnVO) based varistor ceramics are one group of newly developed ZnO based varistor ceramics, which have comparable electrical nonlinearity as that of previously developed ZnO–Bi₂O₃ (ZnBiO) based or ZnO–Pr₆O₁₁ (ZnPrO) based ones.¹ More interestingly, ZnVO based ceramics can be well sintered at 900 °C, a temperature much lower than that of ZnBiO based ceramics (~1200 °C) or ZnPrO based ceramics (~1300 °C).² This outstanding feature makes ZnVO based ceramics possible candidates for the fabrication of multi-layered chip varistor using pure Ag (m.p. 961 °C) as inner electrode instead of the expensive palladium or platinum metals. The electrical properties of ZnO based varistor ceramics are very sensitive to the microstructure because the varistor breakdown voltage is in direct proportion to the grain size. Therefore there have been numerous studies addressing the grain growth of pure ZnO,³ ZnBiO based ceramics,⁴ ZnPrO based ceramics⁵ and ZnVO based ceramics,⁶ as it is vital to the comprehension of the mechanism controlling the microstructure development of ZnO

based ceramics. It may also enable a researcher or manufacturer to tailor the microstructure of ZnO based varistor ceramics in a more efficient way according to the specific demands of application. The grain growth behavior can be profoundly affected by the dopants. For example, the addition of 1 mol% V₂O₅ promotes liquid-phase sintering and ZnO grain growth.⁶ Further addition of Sb₂O₃ hinders the grain growth significantly, elevating the sintering temperature as high as 1200 °C.⁷ Our previous study⁸ showed antimony doped ZnVO varistor ceramics can also be well sintered at 900 °C if the original 0.5 mol% Sb₂O₃ dopant has been substituted by equivalent amount of pre-synthesized V₂O₅/Sb₂O₃ (V/Sb) precursor, indicating a distinct sintering behavior change compared to that of Sb₂O₃ doped ones. Hence, present work further addresses the effects of antimony dopant form change from Sb₂O₃ to pre-synthesized V/Sb precursor on the sintering behavior of ZnVO based ceramics in a quantitative manner by using an activation analysis of the kinetic grain growth exponent and the apparent activation energy. These parameters can be determined by the well known phenomenological kinetic grain growth equation.

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

where G is the average grain size the as sintered ceramics at time t , G_0 is the original grain size of ZnO powders, the n value is the kinetic grain growth exponent, K_0 is the pre-exponential constant of the material, Q is the apparent activation energy, R is the universal gas constant, and T is the absolute temperature. In present study, G_0 is significantly smaller than G . Therefore, G_0 can be neglected, and Eq. (1) simplifies to

$$G^n = K_0 t \exp\left(\frac{-Q}{RT}\right) \quad (2)$$

which will be used throughout this study.

Present paper also presents the result of an XRPD examination on the phase transformation within two additional batches of V/Sb precursor or Sb₂O₃ slightly doped samples during sintering to help clarify the effect of antimony dopant form change on the grain growth behavior of ZnO–V₂O₅ based varistor ceramics.

2. Experiment procedure

Analytical reagents of >99.5% purity were used. V/Sb precursor used in present study was synthesized by heating a mixture of Sb₂O₃ and V₂O₅ with a molar ratio of 4:1 at 650 °C for 1 h. This procedure is identical to that of our previous study; the product, as reviewed by X-ray powder diffraction (XRPD) test, is a mixture of Sb₂O₄ (JCPDS:80-0231) and SbVO₄ (JCPDS:88-0278) with a molar ratio of 3:2.⁸ Two batches of ceramic samples of following composition (in mole ratio): (balanced)ZnO + (0.5%)V₂O₅ + (0.15%)Mn₃O₄ + (0.25%)Co₂O₃ + (0.01%)Bi₂O₃ + (0.5%)Sb₂O₃ were prepared by a traditional oxide mixing approach respectively. Reagents were weighted and ball milled with zirconia balls and absolute alcohol in a polypropylene container for 24 h. After drying, the mixture was pressed into pellets of ∅12 mm × 1.5 mm under uniaxial pressure of 130 MPa. Then the pellets were sintered at temperatures of 900, 950, 1000 and 1050 °C for 4 h, and at 900 °C for 2, 6 and 8 h. Heating rate of 5 °C/min was used. After sintering, the furnace was turned off, allowing the sintered pellets to be cooled down naturally within the furnace. Samples of batch 1, using V/Sb precursor as the starting antimony dopant, were denoted as ZVSP. And those of Sb₂O₃ doped batch 2 were referred as ZVSS. Two additional batches with slightly over doped V/Sb precursor or Sb₂O₃ (10 wt%) were also prepared and denoted as ZVSP' and ZVSS', respectively to study the effect of the antimony dopant form change on the phase constituent evolution and grain growth controlling mechanism of ZnVO ceramics. These samples were sintered at 500 and 750 °C for 1 h and then directly quenched on the surface of a thick copper plate at room temperature to preserve the phase constituents at above mentioned high temperatures. An additional ZVSS' sample was sintered at 900 °C for 1 h and then quenched similarly to further extend the temperature range of above study of Sb₂O₃ doped ZnVO ceramics.

Phases characterization of the precursor, the sintered ceramics and the quenched samples was performed by X-ray powder diffraction (XRPD) in a X-ray diffractometer (Xpert, Netherlands) using Cu Kα₁ radiation (λ = 0.1541 nm).

Table 1
Average grain sizes of as sintered ZVSP and ZVSS samples (unit: μm).

	900 °C 2 h	900 °C 4 h	900 °C 6 h	900 °C 8 h	950 °C 4 h	1000 °C 4 h	1050 °C 4 h
ZVSP	1.98	2.56	3.11	3.47	3.31	5.43	6.86
ZVSS	1.50	1.81	2.01	2.15	2.60	4.21	6.17

Microstructures of polished and chemically etched specimens were examined by SEM (FEI Quanta 400). Density was decided from the weight and dimension of the ceramic body, and then relative density ρ_r was calculated with respect to the theoretical density of zinc oxide (5.675 g/cm³). The initial size G_0 of ZnO grains was examined by a X-ray granularity meter (Mastersizer 2000) after they had been ball-milled with other dopants for 24 h. Average grain size G was calculated by equation

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

where \bar{L} is the average grain-boundary intercept length of four random lines on the SEM photos.⁹

3. Results and discussions

Relative density variation is the most obvious macro indicator of a sintering process; therefore it has constantly been investigated in studies of the sintering behavior ceramics. The results of density measurements of the as sintered ZVSP and ZVSS ceramics are shown in Fig. 1. As revealed, the density variations over the studied sintering time or temperatures bears similar trends in general: becoming more densified with the increments of time or temperature. However, there are obvious differences between two batches of samples sintered at 900 °C for 2–4 h. The relative density of ZVSS sample is only 88% at 2 h, then slowly increases to around 94% at 4 h. This result is consistent with previously reported low densities of Sb₂O₃ doped ZnVO⁷ or ZnBiO¹⁰ based ceramics sintered at low temperatures. The densities of ZVSP samples, on the other hand, are all beyond 97% of the theoretical density of pure ZnO. The above results show that substituting Sb₂O₃ with pre-synthesized V/Sb precursor has brought about an obvious change on the sintering behavior of the studied ZnVO based ceramics.

3.1. Microstructure observation

Our deduction drawn on the base of density measurements was further confirmed by SEM examinations of the microstructure of these samples. The results are shown in Figs. 2 and 3. It is evident that ZVSS samples sintered at 900 °C for less than 4 h do bear a porous microstructure; whereas ZVSP samples all has far more densified microstructure. The average grain size of ZVSP sample, as summarized in Table 1, are generally larger than their ZVSS counterparts fabricated under the same conditions. However, samples of ZVSS and ZVSP ceramics do bear one similar microstructural feature: the homogeneity in microstructure. The abnormal grain growth, a common phenomena of ZnVO based varistor ceramics,¹¹ has been sufficiently suppressed by antimony related spinel particles, whose pres-

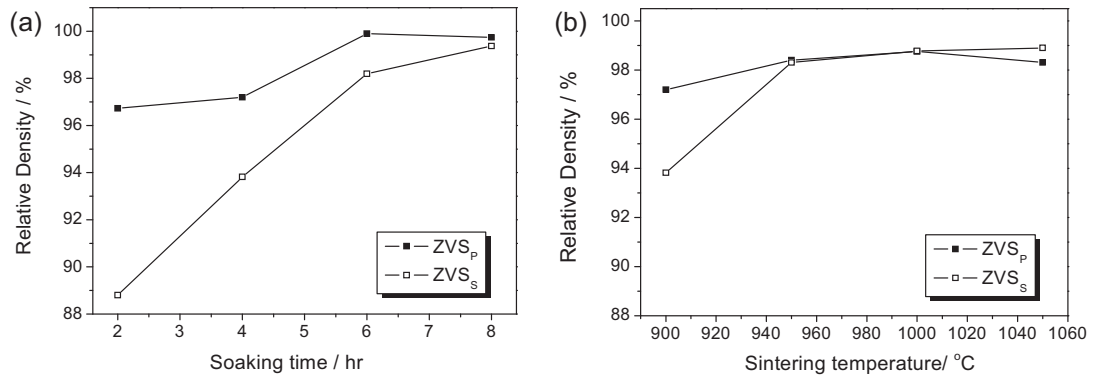


Fig. 1. Density variations of ZVSp and ZVSs ceramics: (a) with sintering time (sintered at 900°C) and (b) with sintering temperature (soaking time: 4 h).

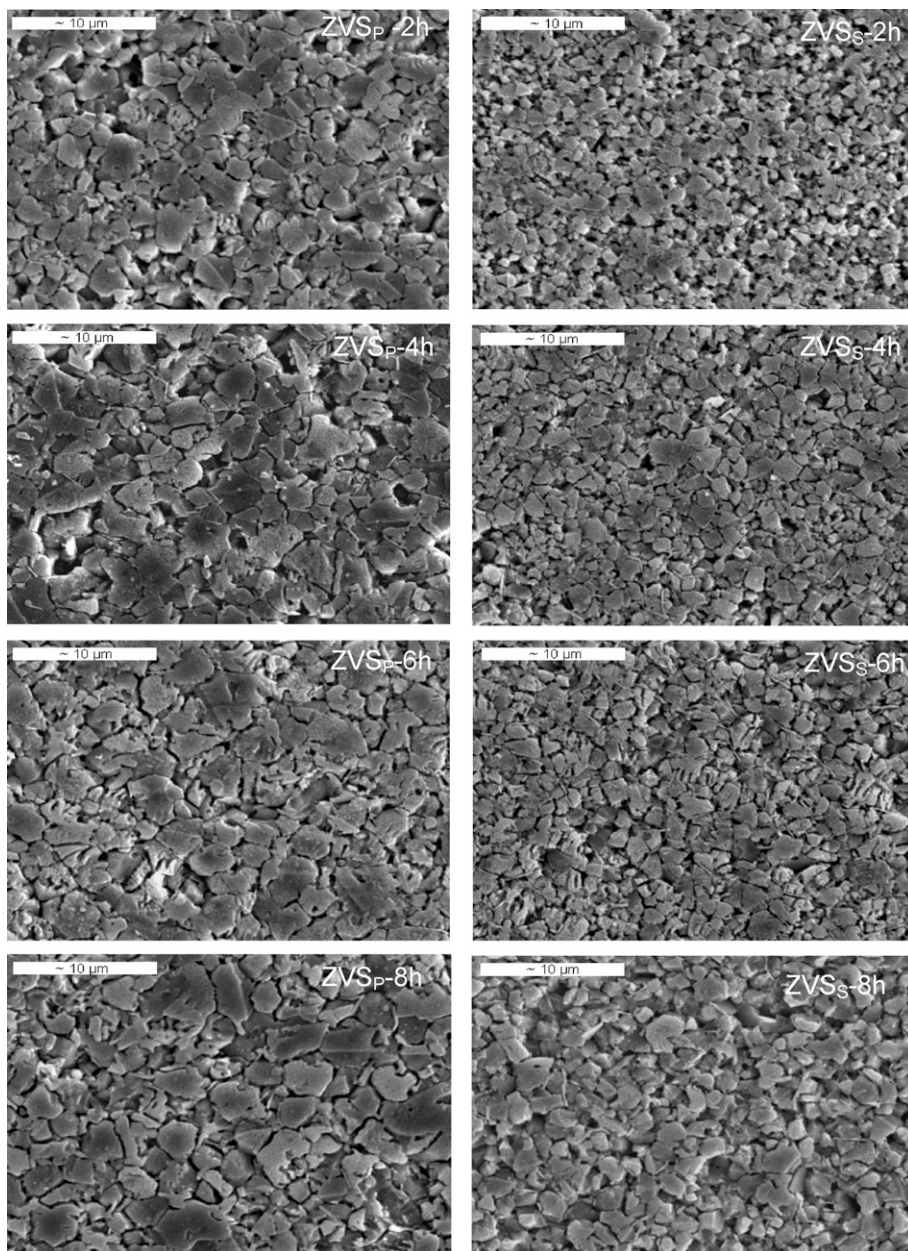


Fig. 2. SEM photos of ZVSp and ZVSs samples sintered at 900°C for 2–8 h.

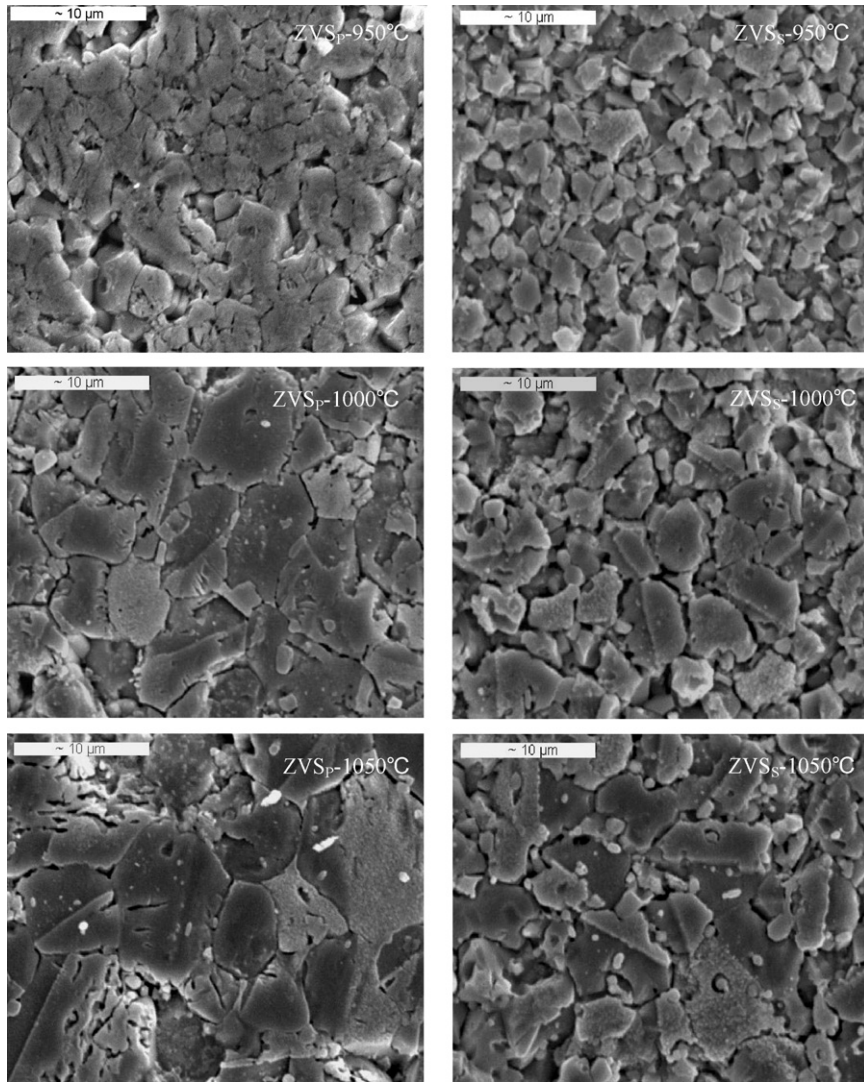


Fig. 3. SEM photos of ZVS_p and ZVS_s samples sintered at 950, 1000 and 1050 °C for 4 h.

ence were both confirmed by our previous study and the XRPD result of the quenched ZVS_p' and ZVS_s' samples, present in the latter part of this article. This microstructural feature makes the V/Sb precursor doped ZnVO based ceramics more favorable candidates for the fabrication of multilayered chip varistors with high surge energy handling ability, where in the homogeneity in ceramic's microstructure is a must feature that ensures an uniform distribution of currents over whole ceramic body between two electrodes.¹²

3.2. Activation analysis of kinetic grain-growth parameters

In order to reveal the sintering behavior difference between these two different batches of ZnVO based ceramics, Eq. (1) was expressed in the form of

$$\log G = \frac{1}{n} \log t + \frac{1}{n} \left[\log K_0 0.434 \left(\frac{Q}{RT} \right) \right] \quad (4)$$

The n value can be determined from the inverse of the slope of the $\log(G)$ versus $\log(t)$ plot (Fig. 4) constructed on the base of

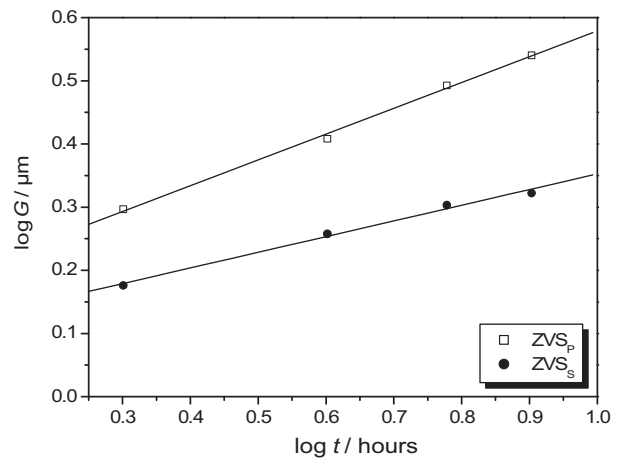


Fig. 4. Grain growth of ZVS_p and ZVS_s ceramics sintered at 900 °C for various sintering times.

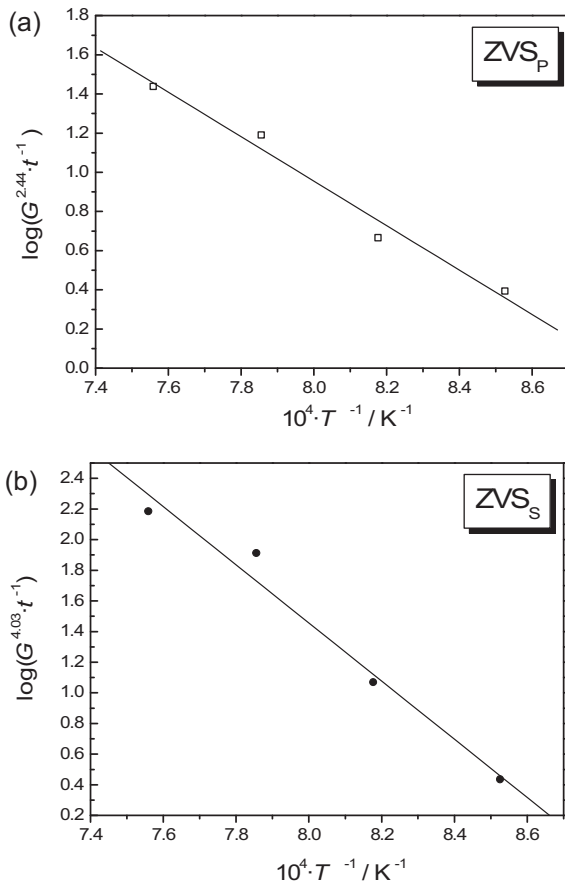


Fig. 5. Arrhenius plots for grain growth of ZVS_P and ZVS_S ceramics: (a) $\log(G^{2.44} \cdot t^{-1})$ versus $10^4 \cdot T^{-1}/K^{-1}$; (b) $\log(G^{4.03} \cdot t^{-1})$ versus $10^4 \cdot T^{-1}/K^{-1}$.

the isothermal grain growth data listed in Table 1. The obtained n values for ZVS_P and ZVS_S ceramics are 2.44 and 4.03, respectively.

Eq. (1) can also be rearranged as

$$\log\left(\frac{G^n}{t}\right) = \log K_0 \frac{0.434Q}{R} \left(\frac{1}{T}\right) \quad (5)$$

The apparent activation energy Q for the grain growth process can be calculated from the gradient of the Arrhenius plot of $\log(G^n/t)$ versus $(1/T)$ (Fig. 5). The results for above two batches of ceramics are 218 and 365 kJ/mol, respectively.

It is well known that small values of grain growth exponent and apparent activation energy are indicative of the faster coarsening speed of ceramic microstructures. These two kinetic parameters may also pave the way for our appreciation of rate controlling mechanism of grain growth. For example, the grain growth exponent and apparent activation energy of ZnO–V₂O₅ binary system with less than 2 mol% V₂O₅ are only ~ 1.6 and ~ 90 kJ/mol, respectively,⁶ even smaller than 3 and ~ 224 kJ/mol for pure ZnO ceramic.³ And, it has been postulated that the rate controlling mechanism has changed from solid-state diffusion of Zn²⁺ within the lattice for pure ZnO,³ to a much faster solution–precipitation liquid phase sintering for V₂O₅-doped ZnO.⁶ Further addition of 2 mol% Sb₂O₃ shows a dramatic retarding effect on the grain growth of the ceramics

of ZnO–V₂O₅ binary system, resulting in an obvious elevation of sintering temperature from 900 °C to as high as 1200 °C.⁷ Unfortunately, the authors of above mentioned paper did not perform the activation energy analysis for the ceramic. As a result, grain growth exponent n and apparent activation energy Q are not available for such Sb₂O₃ doped ZnO–V₂O₅ ceramics. However Senda et al. did carry out an activation energy analysis for 0.29–2.38 wt% Sb₂O₃ doped ZnO and reported large values of 6 and 600 kJ/mol for the grain growth exponent and apparent activation energy, indicating the grain growth of Sb₂O₃ doped ZnO is much slower than that of pure ZnO or ZnO–V₂O₅ binary system. They concluded that the as observed zinc-antimony spinel particles on the boundary area and Sb₂O₃ induced twins within ZnO grains are responsible for the retarded grain growth of ZnO grains.¹³ A transmission electron microscope study of Sb₂O₃ over-doped (2–10 mol%) ZnO, on the other hand, proved the existence of amorphous Sb₂O₃ induced non-crystalline films on the surfaces of ZnO grains at temperatures below 700 °C, which then crystallize and finally transform into stable Zn₇Sb₂O₁₂ (Zn_{2.33}Sb_{0.67}O₄) spinel films within the temperature range of 700–900 °C; such films are more likely the main reason responsible for the retarded grain growth observed in Sb₂O₃ doped ZnO.¹⁴

In present study, the grain growth exponent and apparent activation energy for ZVS_P and ZVS_S samples are generally larger than those of ZnO–V₂O₅ binary system, but much smaller than those obtained for Sb₂O₃ doped ZnO ceramics, indicating the grain growth controlling mechanisms of studied ZVS_P and ZVS_S ceramics should be the combinations of solution–precipitation liquid phase sintering mechanism for V₂O₅-doped ZnO and a retarded grain growth mechanism dominated by Sb-rich films and spinel particles for Sb₂O₃ doped ZnO ceramics. However, this deduction is still not enough to explain the effect of antimony dopant form change on the grain growth controlling mechanisms between the studied ZnVO based ceramics.

To clarify the specific mechanisms controlling the grain growth of ZVS_P and ZVS_S ceramics, ZVS_P' and ZVS_S' samples were sintered at 500 and 750 °C for 1 h and then directly quenched on the surface of a thick copper plate at room temperature. One additional ZVS_S' sample was further sintered at 900 °C for 1 h and then quenched by the same method. The phase constituents of those samples were determined latterly using a standard XRPD technique. The XRPD patterns are present in Fig. 6, and the as identified phase constituents are summarized in Table 2. As it presents clearly in Table 2, there is clearly no Sb₂O₃ detected in all V/Sb precursor over doped ZVS_P' samples, indicating the absence of Sb₂O₃ related films and their hindering effect on the grain growth of ZVS_P ceramics during the sintering process. Therefore, the ZnO grains of ZVS_P ceramics can grow at a much faster speed compared to that of ZVS_S samples, resulting in smaller grain growth exponent and apparent activation energy values for this batch of samples. Above XRPD results also confirms the general existence of ZnSb spinel phase within samples sintered at temperatures above 700 °C. Thus these spinels, generally in forms of particles, may hinder the grain growth of ZVS_S and ZVS_P samples.

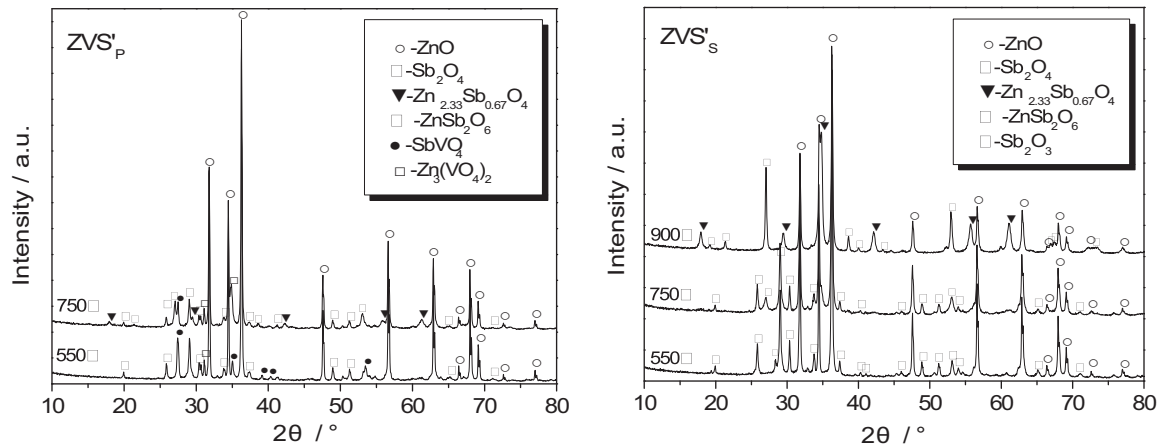


Fig. 6. XRPD patterns of quenched ZVS'_P and ZVS'_S samples sintered at 550–900 °C for 1 h.

Table 2
Phase constituents of V/Sb precursor or Sb_2O_3 over doped ZnVO based ceramics over the temperature range of 500–900 °C.

Temperature	ZVS'_P	ZVS'_S
550 °C	ZnO, Sb_2O_4 , SbVO ₄ , $Zn_3(VO_4)_2$	ZnO, Sb_2O_4 , Sb_2O_3
750 °C	ZnO, Sb_2O_4 , SbVO ₄ , $Zn_3(VO_4)_2$, $ZnSb_2O_6$, $Zn_{2.33}Sb_{0.67}O_4$	ZnO, Sb_2O_4 , $ZnSb_2O_6$
900 °C	–	ZnO, $ZnSb_2O_6$, $Zn_{2.33}Sb_{0.67}O_4$

More interestingly, the result of present study also enables us to compare the general magnitude of the hindering effect of zinc antimony spinel particles and Sb_2O_3 related films on the grain growth of ZnVO based ceramics. As above mentioned, the apparent activation energy of ZnO– V_2O_5 binary system with less than 2 mol% V_2O_5 is only around 90 kJ/mol.⁶ Using this activation energy as the comparing basement, all the spinel particles can only result in an increment of 128 kJ/mol ($218 - 90 = 128$ kJ/mol) in the activation energy for ZVS'_P samples. Therefore, the increment in activation energy caused by the existence of Sb_2O_3 related films in ZVS'_S samples could be decided as 147 kJ/mol ($365 - 228 = 147$ kJ/mol). That is, in general, Sb_2O_3 related films are the main reason responsible for the hindering effect of Sb_2O_3 on ZnVO based ceramics.

4. Conclusion

Grain growth of the V_2O_5/Sb_2O_3 precursor or the Sb_2O_3 doped ZnVO based ceramics of the same stoichiometric composition were investigated by means of phenomenological grain growth kinetics analysis. The microstructure homogeneity of the ZnVO ceramics can be generally improved by both antimony dopants. However, the sintering behavior of the studied ZnVO based ceramics varies remarkably with the antimony dopant form changes. The V/Sb precursor doped ZnVO ceramics can be well sintered at all studied sintering temperatures and sintering times, including at 900 °C for 2 h and 4 h. In contrast, the Sb_2O_3 doped ones have to be sintered for a longer

time or at a higher temperature in order to obtain the similar density. The kinetic grain growth exponent n and the apparent activation energy Q for the V/Sb precursor doped ZnVO based ceramics were 2.44 and 218 kJ/mol, much lower than 4.03 and 365 kJ/mol of the Sb_2O_3 doped ones. The grain growth of the V/Sb precursor doped ceramics is mainly dominated by combinational mechanism of liquid phase assisting of ZnVO ceramic and spinel particles pinning of ZnO– Sb_2O_3 ceramic. While in Sb_2O_3 doped samples, the grain growth of ZnO grains is further retarded by the Sb_2O_3 related films. This kind of specific films, in general, contributes mainly to the poor densification of Sb_2O_3 doped ZnVO based ceramics. The results of present study present a way to fabricate Sb_2O_3 doped ZnVO based ceramics at low temperature of 900 °C, simply by pre-heating V_2O_5 with Sb_2O_3 to form V/Sb precursor, and then using it as the substitute for the original Sb_2O_3 .

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