

Effect of Temperature on the Characteristics of Zinc Oxide with Cerium Oxide at Constant Frequency (20 kHz)

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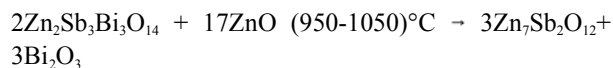
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Abstract: Zinc oxide ceramics, which contain rare earth oxides, have been developed. These bodies are widely used for low voltage surge protection devices and high voltage arrestors for electric power stations. The characteristics of ZnO ceramics with cerium oxide as principal additive are discussed. RCL circuit was used to measure the capacitance and resistance at different temperatures at constant frequency (20 KHz). The dielectric constant and conductivity were calculated. The change in resistivity with temperature was followed up to 523 K.

Key words: ZnO varistors • Electrical properties • Phases • X-ray diffraction • Microstructure

INTRODUCTION

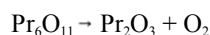
ZnO varistors are semiconducting ceramic resistors manufactured by sintering mixture of ZnO powder with other additives of small amount to enhance the nonlinearity and stability in addition to varistor-forming oxides, i.e. Bi₂O₃ and Pr₆O₁₁ [1-3]. The nonlinear V-I characteristics of ZnO varistors are attributed to a double Schottky barrier (DSB) formed to the grain boundaries, which are essentially formed by a segregation of varistor-forming oxides. In this system, the reaction sequence and the role of additives are now quite well understood. The key reaction is the following decomposition and recombination of Zn₂ Sb₃ Bi₃ O₁₄ pyrochlore on heating and in cooling, respectively, as was suggested by Inada [4]:



Pyrochlore forms below 700°C on heating by solid state reaction and reacts with additional ZnO to form grain boundary phases of Zn₇Sb₂O₁₂ Spinel particles and Bi-rich liquid at 1000°C. The former acting as a second phase inhibits rapid grain growth of ZnO, while the latter promotes densification and the grain growth of ZnO [5]. In the meantime, transition metal ions having dissolved to ZnO and pyrochlore redistribute among ZnO grains and the grain boundary phases and the chemical and micro structural homogeneities attain in high temperature sintering of the ceramic system [6]. There are many different methods for varistor fabrication, but there are still dilemmas and disagreements about role of additives and secondary phases, their influence on electrical properties and necessity of their presence. Ideal varistor should consist only of homogeneously distributed ZnO grains with highly resistive grain boundaries and without secondary phases [7]. The influences of Er₂O₃ content, Y₂O₃ content, sintering temperature and time and cooling

rate on electrical properties and stability of ZnO – Pr₆O₁₁ – CoO–Cr₂O₃–R₂O₃ (R=La₂O₃, Er, Y)-based varistors were diversely studied [8-16]. The α value is higher with the higher additive-content and the lower dopant/additive ratio and vice versa.

Muke[17] studied the effect of substituting Bi₂O₃ by praseodymium oxide to ZnO in the presence of Co₂O₃ and Cr₂O₃ and K₂CO₃. The Pr₂O₃ is formed during the sintering process accompanied by the evolution of O₂ according to the equation:



It is assumed that oxygen will be at ZnO grain boundaries. This oxygen is responsible for the generation of the electronic interface states out the grain boundaries. Also, cerium oxide is very similar to praseodymium and terbium oxides. The breakdown field E_{bk} is increased with the additive-content increasing and sintering temperature lowering at a given dopant-content. The grain size is increased with the increase in sintering temperature while the bismuth concentration decreased. The observed effects are related to the quality of grain boundaries and the conductivity of grains [18]. The dielectric spectra as a function of temperature yielded a thermal activation energy of 0.36 eV. Similar investigation yielded two thermal activation energies of 0.35 eV and 0.26 eV respectively for the traditional electro ceramic processed samples [19].

The aim of the present work is to investigate the characteristics of ZnO ceramics with cerium oxide as principal additive. The change in resistivity and dielectric constant with temperature will be studied at constant frequency of 20 kHz.

MATERIALS AND METHODS

Sintered polycrystalline samples were prepared by conventional ceramic fabrication procedures. Reagent – grade ZnO Ce₆O₁₁, CoO, Cr₂O₃ and Bi₂O₃ powders were used in preparation of basic compositions., ZnO containing 0.03, 0.08, 0.1, 0.2 and 0.4 mol % Ce₆O₁₁ alone group I (M) or plus 0.25 mol % CoO and 0.25 mol % Cr₂O₃ group II (Z) and a constant proportion of 0.5 mol % of Bi₂O₃ group III (B) respectively, the powders were mixed by wet ball- malling using deionized water. Disc specimens with the following dimensions, diameter either 1.2 Cm or 5 Cm and thickness 0.3 Cm were processed

under a force of 70 KN, dried and then fired at 1150°C / 30 minutes. Specimens were first polished with different grades of diamond paste thoroughly washed in an ultrasonic bath dried then thermally etched at 1000°C for 30 minutes. Microstructure developed was examined under SEM type Philips XL 30 provided with EDAX, after sputtering with gold. The PM6304 programmable automatic RCL meter was used for precise measurements of resistance, capacitance and inductance. From the measured values of capacitance, the dielectric constant at all temperature from 313 K to 523K was calculated at 20 kHz and the respective permittivity (ϵ) and conductivity (σ) were calculated according to the relation

$$\epsilon = C \cdot d \epsilon_0 / A$$

where C is capacitance in Farad, d is the thickness of specimen in m, ϵ_0 is the dielectric constant of vacuum (8.8×10^{-12} F/m). Also, from the values of resistance (R), the resistivity (ρ) and conductivity (σ) were calculated by using the relation:

$$\rho = RA / d$$

RESULTS AND DISCUSSION

The XRD patterns of the respective mixes fired at 1150°C for 30 minutes, showed a shift in the d – spacing equivalent to 0.03 – 0.04°A in the main peak, indicating a kind of limited solid solution of Ce₆O₁₁ in the oxide. A maximum shift of 0.04°A was recorded in mix containing 0.4-mol% cerium oxide, Fig. 1 XRD results showed that no binary compound was formed. Also, the shift in ZnO peaks did not exceed the recorded value .The melting point of ZnO is about 1300°C. Therefore, the addition of cerium oxide to it probably lower the temperature of liquid formation to 1150 – 1200°C. As a result the liquid phase rich in ZnO is formed and partly dissolved the cerium first precipitate along the grain boundaries as small spots then accumulates intragranularly. Part of cerium oxide entered the lattice of ZnO. This view coincides with that reported by Morris [5] in case of Bi₂O₃ as it cannot form a solid solution with ZnO but undoubtedly it disso lies to some extent. Bi⁺³ and Ce⁺³ would not be expected to fit easily into the ZnO lattice either substituting or interstitially. The dielectric properties and temperature dependence of conductivity at constant frequency of 20 kHz may be due to the increase in the number of dipoles.

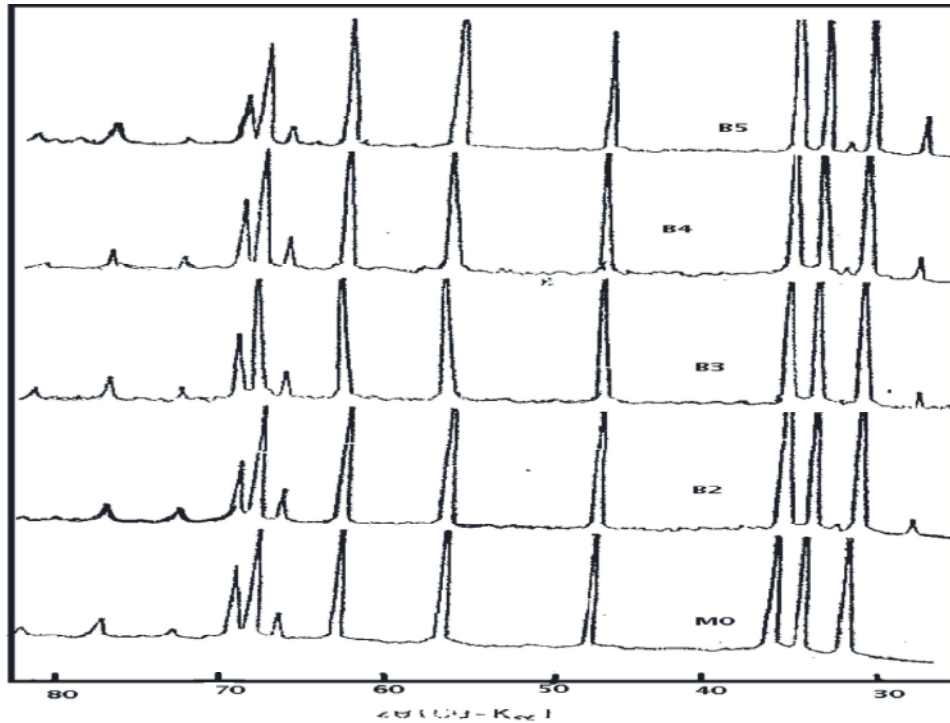


Fig. 1: X-ray diffraction patterns of group III

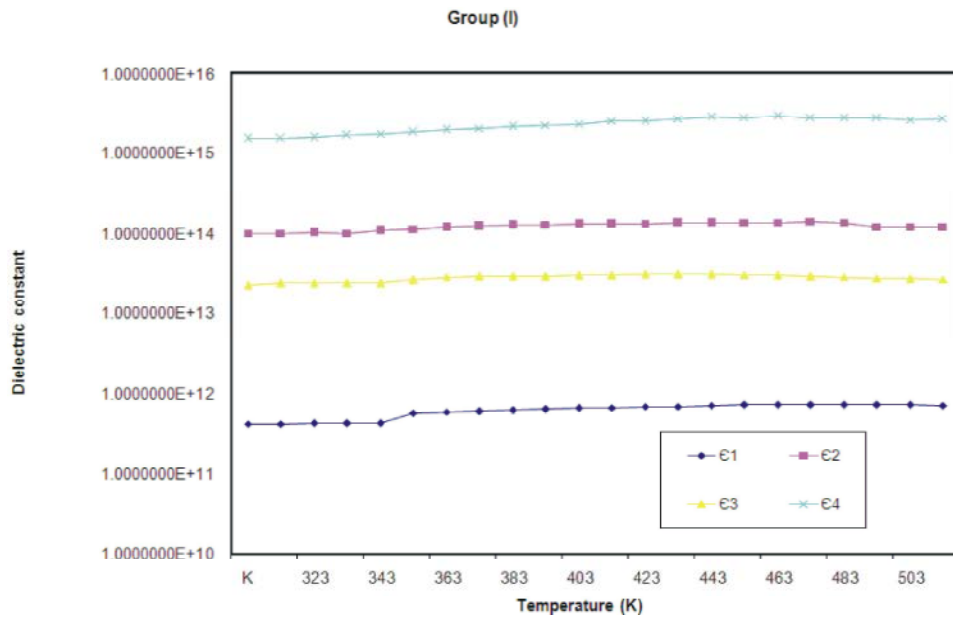


Fig. 2: Relation between dielectric constant of group I versus temperature at 20 kHz

Figures 2-4 show the relation between dielectric constant $[\epsilon]$ and temperature at spot frequency of 20 kHz. The observed dielectric constant of different mixes was variably affected by increasing temperature from 323 to 523 K. Generally $[\epsilon]$ appears to be constant with

rise temperature and slightly increases in the higher range. The increase of temperature raised the dielectric constant because it increase the ionic response to the field again this is related to the intergranular material at any particular frequency. Presumably these effects are associated with

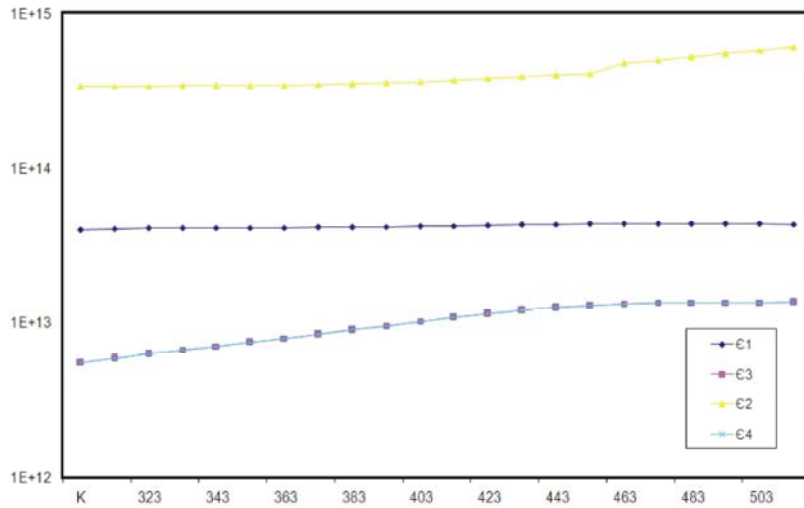


Fig. 3: Relation between dielectric constant of group II versus temperature at 20 kHz

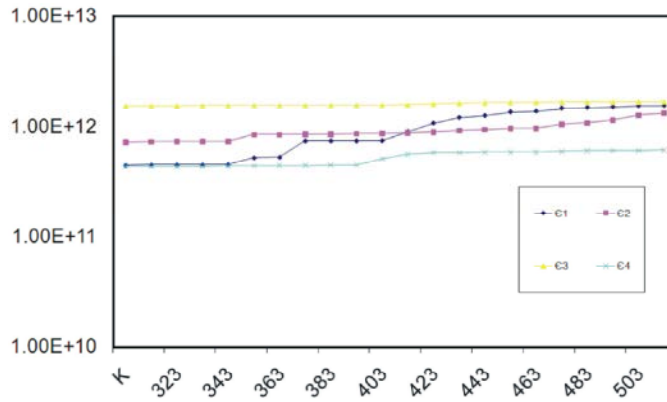


Fig. 4: Relation between dielectric constant of group III versus temperature at 20 kHz

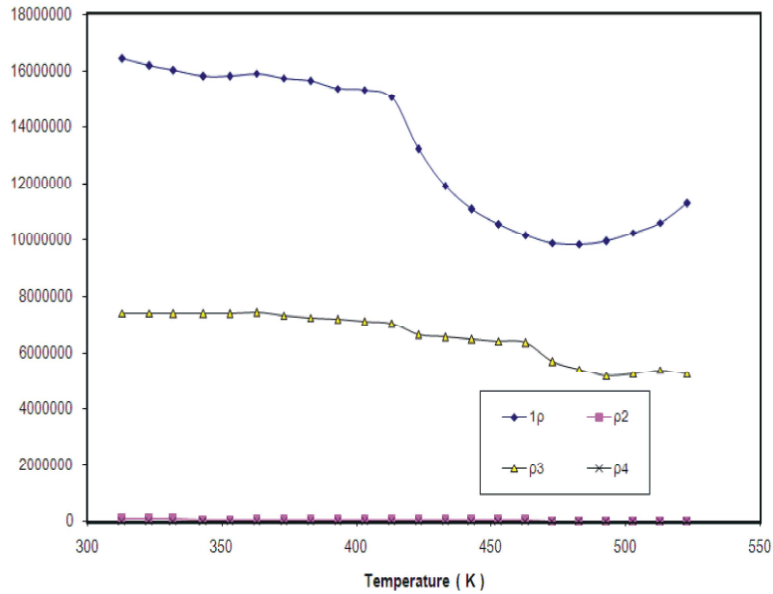


Fig. 5: Variation of the resistivity of group I as function of temperature measured at 20 kHz

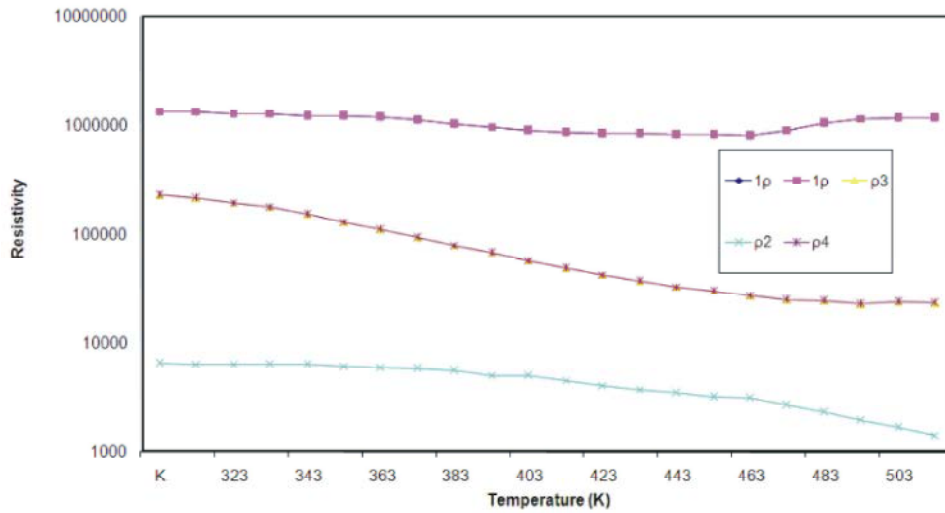


Fig. 6: Variation of the resistivity of group II as function of temperature measured at 20 kHz

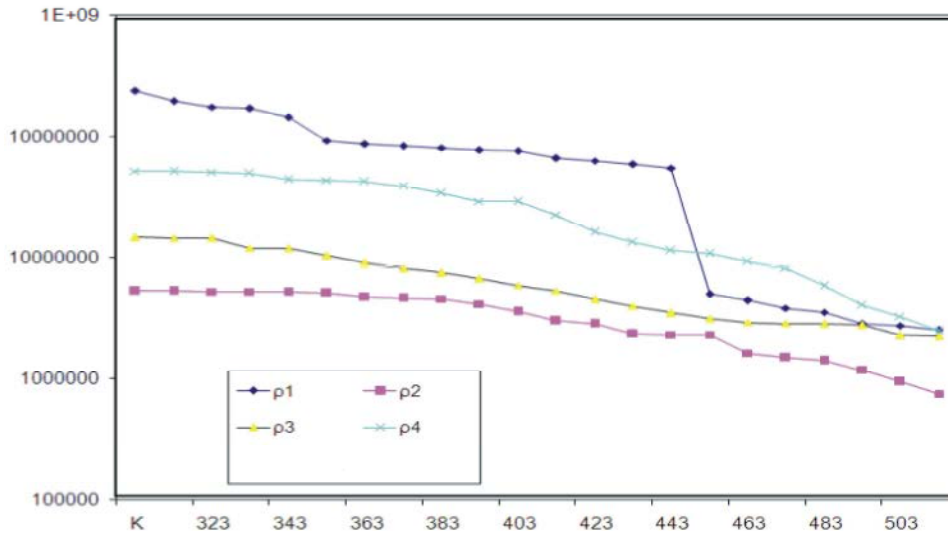


Fig. 7: Variation of the resistivity of group III as function of temperature measured at 20 kHz

polarization currents arising from trapping states of various kinds and densities. According to Levinson and Philipp [1], the theory for conduction in the non-ohmic region must be related to grossly intrinsic electronic features which exist in such intergranular materials or interfaces. In the ZnO-intergranular material interface, the states lying possibly in the transition region (interface) between ZnO and intergranular material.

Figures 5-7 show the relation between resistivity (Ωm) and temperature at constant frequency (20 kHz). The variation of capacitance and resistance with temperature is thought to be associated with dielectric relaxation. Increasing the concentration of Ce_6O_{11} leads

to a gradual decrease of $[\rho]$ as a function of temperature, due to the fact that the increase of temperature activates the mobility of ions and increases the carrier density and as a result the conductivity. This may be explained in the light of the microstructure developed, formed at the semi-conductive ZnO grains surrounded by an insulating glassy phase which is similar to that of grain boundary layer capacitors. As a result, the observed dielectric constant increased with an increase in cerium oxide. Microstructure of ZnO varistors plays an important role in the electric characteristic displayed. There are two models postulated to describe the microstructure of ZnO depending on constitution. A three-phase model comprising grains, intergranular material and particles.

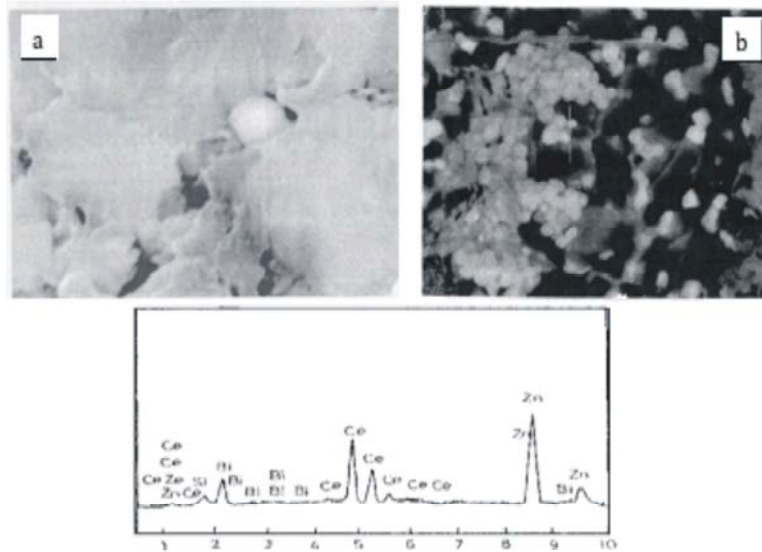
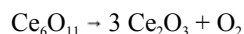


Fig. 8: SEM of mix B4. (a) Chemical etched shows oval shape Ce – rich phase x= 25000, (b)Chemical etched show accumulation of oval shape of Ce – rich grains in patches between ZnO grains, (c) EDAX of oval shape, showing the distribution of Zn, Ce and Bi

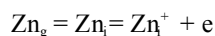
And two model comprising the first two only. The addition of Ce_6O_{11} leads to a two phase microstructure; well crystalline ZnO grains showing grain growth in preferred orientation, ZnO crystallizes in hexagonal system, it is characterized by perfect cleavage plane along (001) which was distinct in SEM of ZnO with different additives.

The SEM of mix B4 presented in Fig. 8 shows the inter-granular phase having an oval shape of various sizes ranging between 0.1 to 0.2 μm situated at the triple points between the ZnO grains. EDAX indicates of Bi and Ce in these grains, this means that the dissolution of Ce_6O_{11} in ZnO is limited. Part of Ce_6O_{11} enter in the lattice of ZnO . Higher addition of Ce_6O_{11} to ZnO caused the exsolution of the doped Zn + Ce to intergranular . The presence of Bi enhanced the dissolution of cerium causing its enrichment in the intergranular phase.

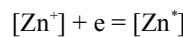
The role played by cerium oxide in this case is during firing the valancy state of cerium is change into Ce_2O_3 with the evolution of oxygen. This oxygen is responsible for the generation of electronic interface states out the grain boundaries.



The electrical conduction in ZnO is the interstitial Zn_i that can be ionized as follows:



The interstitial cations occupy a shallow donor level (at ≈ 0.05 eV) close to the conduction band and are completely ionized to Zn^+ ions and electrons. The positively charged interstitial Zn^+ in the depletion region migrates to the grain boundary and neutralizes the negative charge at the grain boundary interface (recombination) forming a neutral interstitial zinc ion.



Since there are two depletion regions, migration occurs on both sides of the grain boundary interface with alternation of field polarity [20].

Charge neutralization thus occurs in both depletion layers resulting in asymmetrical lowering of barrier height [21]. The variation of capacitance and resistance with temperature was thought to be associated with relation but on plotting the frequency as ϵ'' versus ϵ' , the usually semi- circle of cole – cole diagram was not obtained. This result implies that the dielectric loss is not caused by simple relaxation. The addition of Cr_2O_3 and CoO slightly increases its wettability.

CONCLUSIONS

Zinc oxide ceramics, which contain rare earth oxides, have been developed. The typical ZnO-based system of ZnO– Sb_2O_3 – Bi_2O_3 – MtrO (Mtr=3d-transition elements) is known to have excellent varistor characteristics: high

nonlinear coefficient (α) over 50; low leakage current (IL) below 10 mA/cm²; large surge absorbing capability over 200 J/cm³.

REFERENCES

1. Levinson, L.M. and H.R. Pilipp, 1986. Am. Ceram. Soc. Bull., 65: 639.
2. Gupta, T.K., 1990. J. Am. Ceram. Soc., 73: 18172.
3. Gupta, T.K., 1990. J. Am. Ceram. Soc., 73: 1817.
4. Inada, M., 1980. J. Appl. Phys, 19: 409.
5. Kim, J.H., T. Kimura and T.J. Yamaguchi, 1989. Am. Ceram. Soc., 72: 1390.
6. Hong, Y.W., J.H Kim and J. Kor, 2000. Ceram. Soc., 37: 651.
7. Bernik, S., N. Daneu and A. Recnik, 2004. J. Eur. Ceram. Soc., 24: 3703.
8. Nahm, C.W., H.S. Yoon and J.S. Ryu, 2001. J. Mater. Sci. Lett., 20: 393.
9. Nahm, C.W., 2001. Mater. Lett., 47: 182.
10. Nahm, C.W., 2002. J. Mater. Sci. Lett., 21: 201.
11. Nahm, C.W. and J.S. Ryu, 2002. Mater. Lett., 53: 110.
12. Nahm, C.W. and B.C. Shin, 2002. J. Mater. Sci., Mater. Electron., 12: 111.
13. Nahm, C.W., H.-S. Kim, 2003. Mater. Lett., 47: 1544.
14. Nahm, C.W., B.-C. Shin, 2003. Mater. Lett., 57: 1322.
15. Nahm, C.W., 2003. Mater. Lett., 57: 1317.
16. Nahm, C.W., 2006. Mater. Lett., 60: 3311 .
17. Mukae, M., 1987. Ceramic bulletin, 66 (9): 1329.
18. Lin, C., W. Lee, C. Sun and W.H. Whu, 2007. Composites: Part B, 38: 338.
19. Alim, M., S. Li, D. Zhai, Bo. Li and L. Jianying, 2006. J. Appl. Phys., 39: 4969.
20. Gupta, T.K., W.G. Carlson and P.I. Hower, 1981. J. Appl. Phys., 52: 4104.
21. Eda, K., A. Iga, M. Matsuoka, J. Appl. Phys, 18: 997.