

Investigation on the effect of sintering under oxygen atmosphere on microstructure and microwave dielectric properties of ZnNb₂O₆ ceramics

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The effect of sintering in air and oxygen atmospheres on microstructure and microwave dielectric properties of ZnNb₂O₆ ceramics has been investigated and compared. For most cases samples sintered in oxygen atmosphere exhibited higher density than those sintered in air atmosphere. The highest densities obtained for samples sintered in air and oxygen atmospheres were 93.6 and 95.2% of the theoretical value, respectively. The variation of relative permittivity (ϵ_r) values with temperature for samples sintered in air and oxygen atmospheres followed the variation in the density values. The highest values of ϵ_r for samples sintered in air and oxygen atmospheres were 22.6 and 23.5, respectively. A considerable improvement in $Q \times f$ (Q and f are quality factor and resonant frequency, respectively) was obtained for most sintering temperatures when sintering was performed in oxygen atmosphere. The highest $Q \times f$ obtained for samples sintered in air and oxygen atmospheres were 82,688 and 81,204 GHz, respectively. Temperature coefficient of resonant frequency (τ_f) values closer to the ideal value (0 ppm/°C) was exhibited by samples sintered in oxygen atmosphere. The best values of τ_f for air and oxygen sintering atmospheres are -59.4 and -48.6 ppm/°C, respectively.

1. Introduction: The rapid progress in microwave communication has created an increasing demand for dielectric materials in the microwave frequency region. High dielectric constant, low dielectric loss and near zero temperature coefficient of resonant frequency are the requirements for materials used as microwave dielectric resonators. Recently, ZnNb₂O₆ (ZN) ceramics have been paid much attention due to their promising microwave dielectric properties, low sintering temperature and low cost. The low sintering temperature makes ZN ceramics potentially attractive for low-temperature co-fired ceramic technology [1–3]. Typical properties for these ceramics are: $Q \times f$ of 83,700 GHz, ϵ_r of 25 and τ_f of -56 ppm/°C [4–7]. The first study on ZN composition was reported by Maeda *et al.* [8]. d’Astorg and Marinel [9] investigated the sintering behaviour of ZN ceramics under reducing atmosphere of Ar/H₂ 10%. This atmosphere was chosen because in multilayer ceramic capacitor (MLCC) technology the use of copper electrodes requires a reducing atmosphere to avoid oxidation of copper. The results showed that ZnO volatilises at about 900°C in Ar/H₂ atmosphere. This occurs when ZN decomposes to form Nb₂O₅ and ZnO. This is then followed by a partial reduction of Nb₂O₅ to Nb₂^{IV}Nb₁₀^VO₂₉. The decomposition and loss of ZnO from the material resulted in a significant degradation of dielectric properties. The properties of non-stoichiometric Zn_{1+x}Nb₂O_{6+x} ceramics were studied by Belous *et al.* [10]. It was found that for 0.005 ≤ x ≤ 0.03, there was a reduction in the porosity of the material which resulted in an increase in the microwave quality factor. The highest value of $Q \times f$, 120,000 GHz, was obtained for x = 0.01. The variation of ϵ_r values with zinc content was not considerable and ranged between 22 and 24. Wang *et al.* [11] investigated the effect of addition of ZnO and V₂O₅ on the microstructure and microwave dielectric properties of ZN ceramics as chemical formula Zn(Nb_{0.9}V_x)₂O_{5.5+5x}. It was shown that for 0 < x ≤ 0.1 sintering temperature was reduced from 1150°C to about 900–950°C. Addition of ZnO–V₂O₅ also resulted in rod-like grains. Ceramics with x = 0.05 exhibited excellent dielectric properties: ϵ_r = 24, $Q \times f$ = 72,800 GHz and τ_f = -63.5 ppm/°C. Quercioli *et al.* [12] studied the effect of the addition of B₂O₃–ZnO–SiO₂, B₂O₃–ZnO–Bi₂O₃ and B₂O₃–SiO₂–BaO glass frits on properties of ZN ceramics. All glass additives caused a reduction in sintering

temperature of ZN ceramics which make them suitable for MLCC technology. However, good microwave properties (ϵ_r = 24, $Q \times f$ = 23,070 GHz and τ_f = +147 ppm/°C) was only observed for ZN +5 wt% B₂O₃–ZnO–SiO₂ composition. All studies presented here describe methods which are used to alter the microstructure in order to achieve the required properties. In this Letter, the effect of sintering in an oxygen atmosphere on the microstructure and microwave dielectric properties has been investigated.

2. Materials and methods: ZnO (Sigma-Aldrich Co., USA, >99.5%) and Nb₂O₅ (Alfa-Aesar Co., UK, >99.5%) powders were weighed according to ZN formula. Milling was carried out in a vibratory mill for 30 h using deionised water with zirconia balls. The slurry was then dried at 100°C for 2 h, and the calcination of the powder mixture was performed in an electric furnace at 800°C for 2 h. The method described above was also used for milling the calcined powder. Pellets were prepared using uniaxial pressing in a steel die at a pressure of 187 MPa. Sintering was performed in an electric furnace under air and oxygen atmospheres from 1100 to 1300°C with 50°C intervals for 2 h soaking time, heating rate was 10°C/min whereas the samples were cooled naturally from the maximum temperature. Archimedes method (according to C 373-88 ASTM) was used for measuring bulk densities of the sintered samples. Crystal structure of samples was studied through X-ray diffraction method (XRD, Philips X-ray diffractometer, 3710, CuK_α radiation). Microstructural investigations of the samples were carried out by scanning electron microscope (SEM, Cambridge, Stereoscan 360, England). The average grain size was estimated by the linear intercept method. Microwave dielectric properties of samples were measured by a network analyser (Hewlett Packard, 8510CRFRB) [13, 14].

3. Results and discussion: Fig. 1 shows XRD patterns for the samples sintered at 1150°C for 2 h in air and oxygen atmospheres. Both samples exhibit single-phase ZN phase with no second phases present. Similar patterns were also observed for samples sintered at other temperatures in air and oxygen atmospheres.

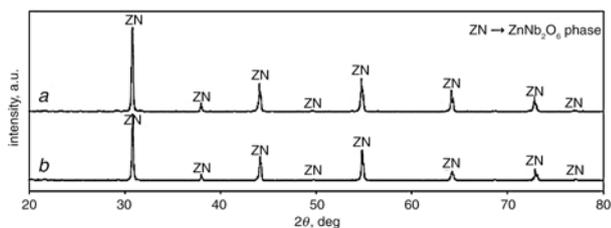
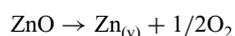


Fig. 1 XRD patterns for ZN ceramics sintered in
a Air
b Oxygen atmospheres at 1150°C

Relative density results for samples sintered at different temperatures in air and oxygen atmospheres are illustrated in Fig. 2. As can be seen, in both cases there is an increase in density with sintering temperature up to a maximum which for both cases occurs at 1150°C. Further increase in sintering temperature resulted in a decrease in density for both air and oxygen atmospheres. The increase in density up to 1150°C for both cases can be explained by the improvement in densification when sintering temperature increased. A vast difference exists between the density of samples sintered at 1100°C in air and oxygen atmospheres. As sintering is a process controlled through diffusion and therefore point defects, the inferiority of density due to oxygen atmosphere at this temperature may be related to the lower amount of vacancies after sintering under oxygen as oxygen from atmosphere has entered the ZN lattice and occupied its own position. Also the decrease in density for both cases for sintering temperatures higher than 1150°C can be attributed to ZnO volatilisation [15]. In fact at temperatures higher than 1150°C the decrease in density due to ZnO loss dominates the increase in density relating to higher sintering temperatures. As can be seen, for most cases the density values for samples sintered in oxygen atmosphere are higher than those sintered in air atmosphere. This can be explained by lower ZnO loss under oxygen atmosphere. The mechanism for loss of ZnO is as follows [11]



The release of the gaseous species according to the above mechanism opposes sintering process and results in lower densities when air atmosphere is used.

Also lower density of the sample sintered at 1300°C in oxygen atmosphere compared with that for the sample sintered in air may be explained by the fact that samples sintered in oxygen atmosphere exhibit higher grain sizes (Fig. 5) compared with those sintered in air. This suggests that abnormal grain growth may have taken

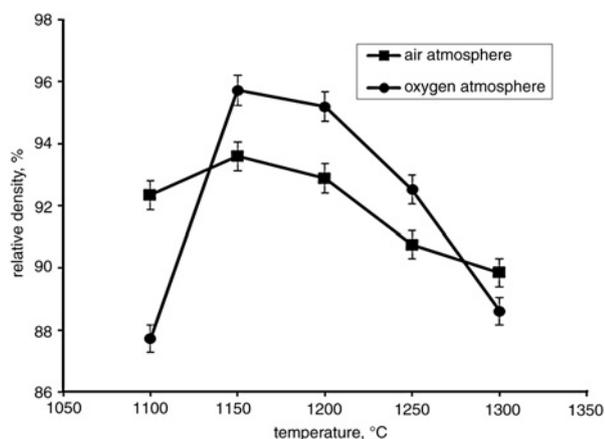
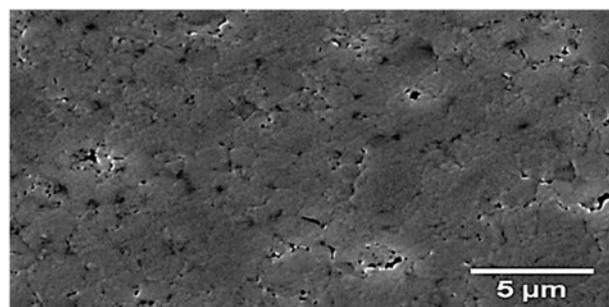
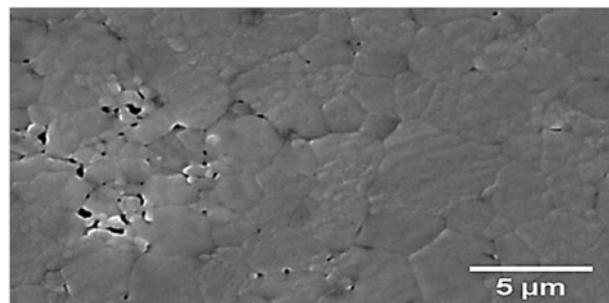


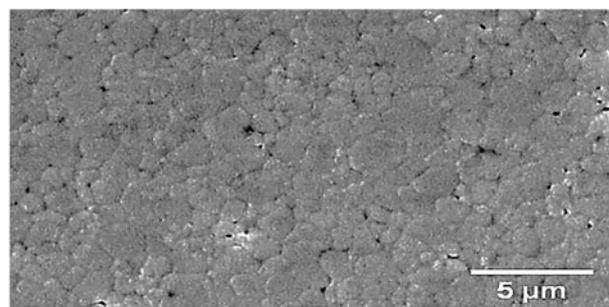
Fig. 2 Variation of relative density with sintering temperature for ZN ceramics sintered in air and oxygen atmospheres



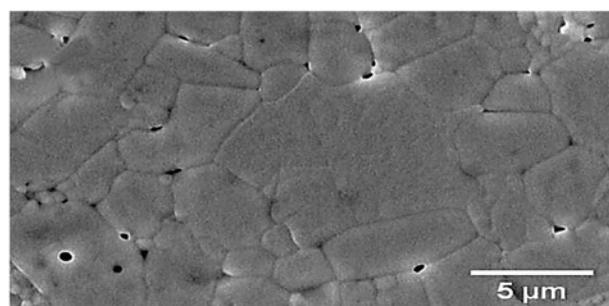
a



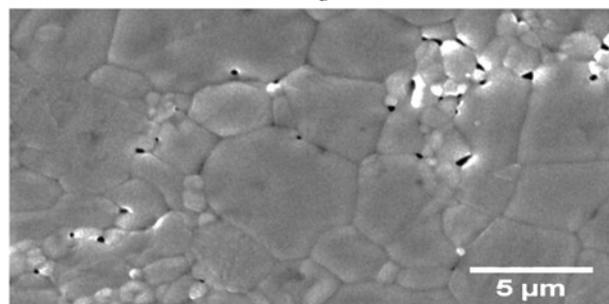
b



c



d



e

Fig. 3 SEM micrographs for ZN ceramics sintered under air atmosphere at
a 1100°C
b 1150°C
c 1200°C
d 1250°C
e 1300°C

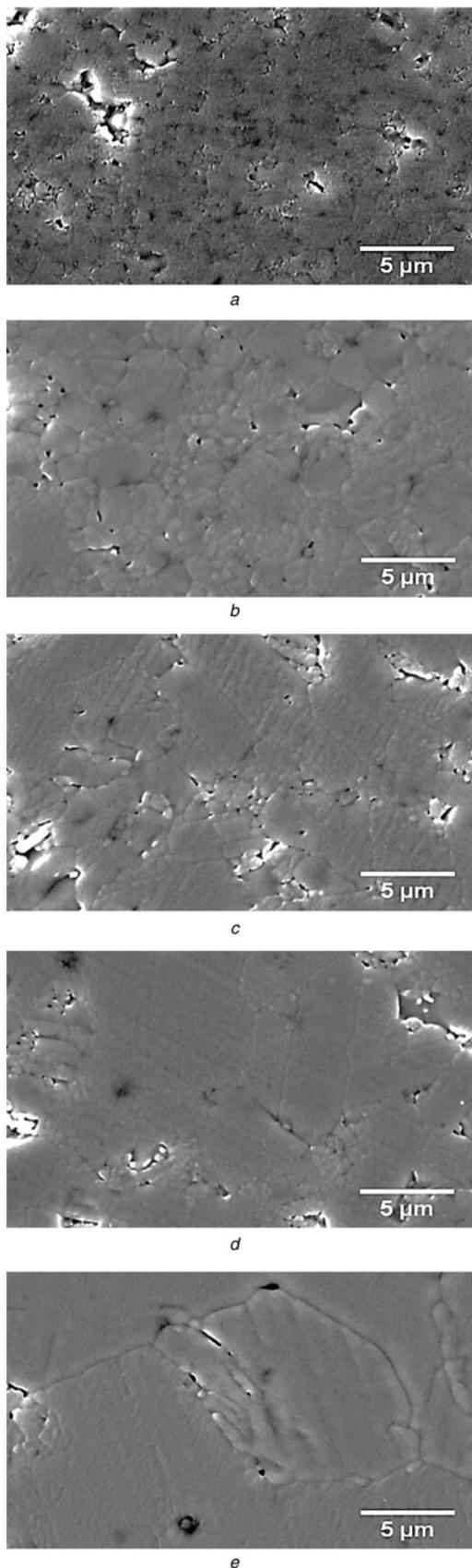


Fig. 4 SEM micrographs for ZnO ceramics sintered under oxygen atmosphere at
 a 1100°C
 b 1150°C
 c 1200°C
 d 1250°C
 e 1300°C

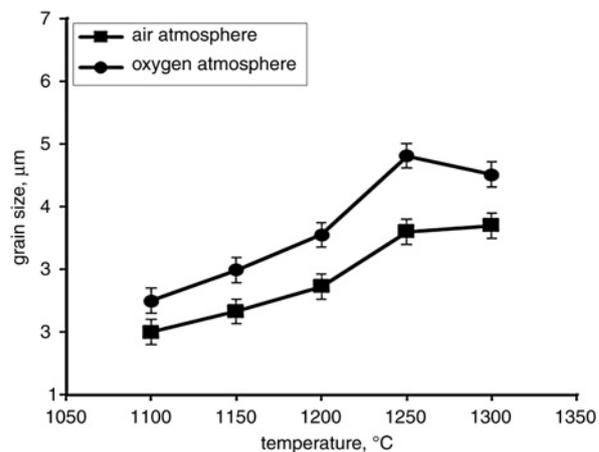


Fig. 5 Variation of grain size with sintering temperature for ZnO ceramics sintered in air and oxygen atmospheres

place especially for the sample sintered at 1300°C in oxygen which can result in lower density values.

The maximum relative densities for samples sintered in air and oxygen atmospheres were 93.6 and 95.2%, respectively.

SEM micrographs of samples sintered at different temperatures for 2 h in air atmosphere are shown in Fig. 3. In Fig. 4, the SEM micrographs for samples sintered at different temperatures for 2 h in oxygen atmosphere are presented. In both cases, an increase in grain size is the common feature. The variation in grain size for samples sintered in air and oxygen atmospheres at different temperatures is shown in Fig. 5. As can be seen, there is an increase in grain size in both cases with increasing sintering temperature except for the sample sintered at 1300°C in oxygen atmosphere which shows a lower grain size value compared with the sample sintered under the same atmosphere at 1250°C. It is also evident that samples sintered in oxygen atmosphere exhibit higher grain sizes compared with those sintered in air at the same temperature.

The variation of relative permittivity values with sintering temperature for samples sintered in air and oxygen atmospheres is shown in Fig. 6. As can be seen for most cases the variation of relative permittivities with temperature follows the variation of density with temperature for both air and oxygen atmospheres (Fig. 2). Other researchers have also reported this relationship [16]. The highest values for relative permittivity for samples sintered in air and oxygen atmospheres which occur at 1150°C were 22.6 and 23.5, respectively.

These relative permittivity values are comparable to those reported in the previous literature, for example Barzegar *et al.* [17] and Pullar *et al.* [18] obtained relative permittivity values of 23.6 and 23.2 for samples sintered at 1000°C for 30 min and 1200°C for 2 h, respectively.

The variation of $Q \times f$ with sintering temperature for samples sintered in air and oxygen atmospheres is shown in Fig. 7. It is evident that for most cases sintering in oxygen atmosphere results in a considerable improvement in $Q \times f$ compared with air atmosphere. Observation of higher $Q \times f$ values (for most cases) for samples sintered in oxygen atmosphere can be attributed to the reduction in loss of ZnO from the material under oxygen atmosphere. This is because the loss of ZnO results in a lower value of density and higher level of defects in the ZnO lattice which are both detrimental to quality factor. For samples sintered in oxygen atmosphere the highest $Q \times f$ value (81,204 GHz) is observed at a lower sintering temperature of 1150°C, whereas the maximum $Q \times f$ for samples sintered in air (82,688 GHz) occurs at 1300°C. Two different trends can be observed for the variation of $Q \times f$ with sintering temperature for the two atmospheres used. When sintering was performed in air it seems that the variation of $Q \times f$ with sintering

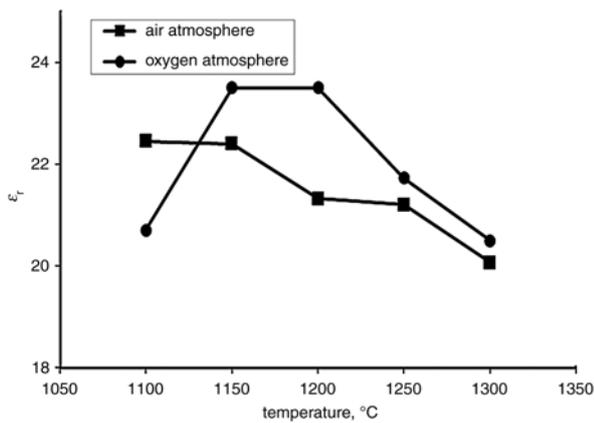


Fig. 6 Variation of ϵ_r with sintering temperature for ZN ceramics sintered in air and oxygen atmospheres

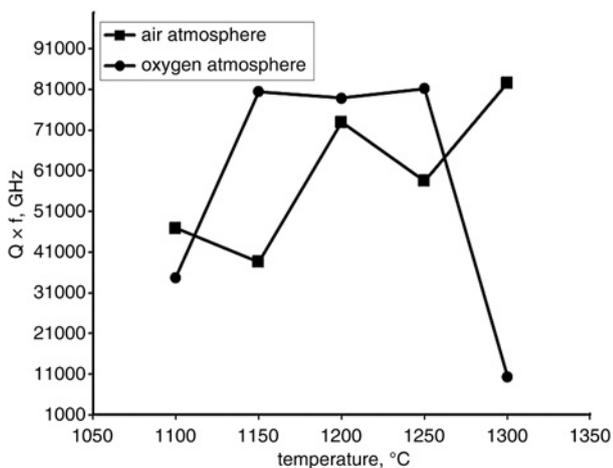


Fig. 7 Variation of $Q \times f$ with sintering temperature for ZN ceramics sintered in air and oxygen atmospheres

temperature mainly follows that of grain size (Fig. 5). This relationship has also been reported in our previous work where microwave sintering was used for preparation of ZN ceramics [19]. A different trend is observed for samples sintered in oxygen atmosphere

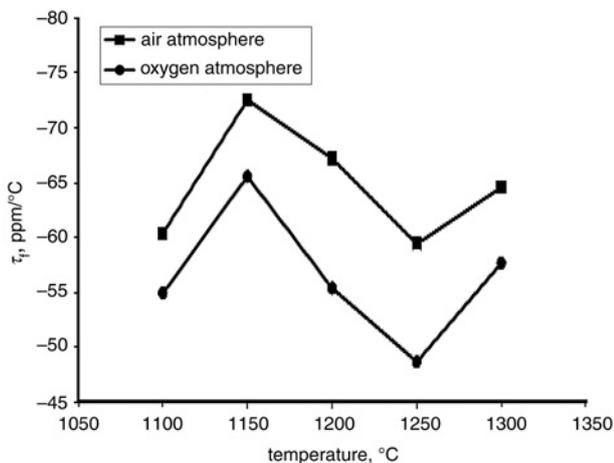


Fig. 8 Variation of τ_f with sintering temperature for ZN ceramics sintered in air and oxygen atmospheres

(Fig. 7). For these ceramics the changes of $Q \times f$ with sintering temperature can be related to the variation of density (Fig. 2). The dependence of $Q \times f$ on density for samples sintered in oxygen atmosphere can be explained by the fact that for these ceramics grain size values are much higher than those for the samples sintered in air (Fig. 5); therefore, the detrimental effect of grain boundaries on quality factor is mainly eliminated and density plays an important role, whereas for samples sintered in air high level of losses due to lower values of grain size dictates loss properties.

The variation of τ_f with sintering temperature for samples sintered in air and oxygen atmospheres is presented in Fig. 8. As can be seen similar trends are observed for both sintering atmospheres; however, for any sintering temperature samples sintered in oxygen atmosphere exhibit better values of τ_f . It is not possible to interpret these results using microstructural features because factors affecting τ_f are not fully known and require further research [19, 20]. The best values of τ_f for air and oxygen sintering atmospheres which both occur at 1250°C are -59.4 and -48.6 ppm/°C, respectively.

4. Conclusion: The effect of sintering in air and oxygen atmospheres on microstructural and microwave dielectric properties of ZN ceramics has been investigated and compared. No second phases were observed for samples sintered at different temperatures under either atmosphere. Lower ZnO losses under oxygen atmosphere resulted in higher density for most cases. The highest densities obtained for samples sintered in air and oxygen atmospheres were 93.6 and 95.2% of the theoretical value, respectively. The variation in the density values with temperature for samples sintered in air and oxygen atmospheres dictated the variation of relative permittivity. The highest values for relative permittivity (ϵ_r) for samples sintered in air and oxygen atmospheres were 22.6 and 23.5, respectively. Sintering in oxygen atmosphere resulted in a considerable improvement in $Q \times f$. When sintering was performed in oxygen the highest $Q \times f$ value (81,204 GHz) was observed at a lower sintering temperature of 1150°C, whereas for samples sintered in air the maximum $Q \times f$ (82,688 GHz) occurs at 1300°C. For samples sintered in air at different temperatures, changes in $Q \times f$ values follows the changes in grain size, whereas for samples sintered in oxygen the changes in $Q \times f$ values are influenced by density values. Samples sintered in oxygen atmosphere exhibited better τ_f values compared with those sintered in air. The best values of τ_f for air and oxygen sintering atmospheres are -59.4 and -48.6 ppm/°C, respectively.

The results of this Letter indicate that the sample sintered at 1150°C for 2 h in oxygen atmosphere exhibits good density and promising relative permittivity and quality factor values which makes it suitable for use in practical applications; however, further research is needed to achieve τ_f values close to zero for this sample.

5 References

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