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Effects of Mg^{2+} substitution on microstructure and microwave dielectric properties of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics

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Abstract

The sintering behavior, microstructure and microwave dielectric properties of $(Zn_{1-x}Mg_x)Nb_2O_6$ ($0 < x < 1.0$) solid solution were investigated systematically by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and a network analyzer. The sintering temperature of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics increased from 1150 to 1350 °C with increasing Mg content from $x = 0$ to $x = 1.0$. The crystal structure exhibited a columbite structure for all x values. The changes of grain shape from equiaixed to rectangle were observed in sintered samples as x varied from 0 to 0.5. The dielectric properties of $(Zn_{1-x}Mg_x)Nb_2O_6$ solid solution exhibited a significantly dependence on the sintering condition, microstructure and compositions of ceramics. The dielectric constants (ε_r) of sintered samples decreased from 23.66 to 19.17 with increasing Mg content from $x = 0$ to $x = 1.0$. All quality factors ($Q \times f$) of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics were lower than those of $ZnNb_2O_6$ and $MgNb_2O_6$ and ranged from 82 220 to 31 218 GHz for sintered samples. However, the τ_f values were lower than those of $ZnNb_2O_6$ and $MgNb_2O_6$, the minimum τ_f value can be obtained at $x = 0.5$ and were −29.46 ppm/°C.

Keywords: A. Sintering; C. Dielectric properties; $(Zn_{1-x}Mg_x)Nb_2O_6$

1. Introduction

Microwave dielectric ceramics have received much attention due to its applications in mobile and satellite communication system as resonators and filters [1,2]. Dielectric materials for microwave applications should, in general, satisfy three requirements: high permittivity, low dielectric loss, and small temperature coefficient of resonant frequency. Most microwave materials with high quality for 2 GHz and higher base station application were focused on the complex perovskite compounds, such as $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Ta_{2/3})O_3$ systems [3,4]. However, the high cost of the raw materials, Ta_2O_5 is not properly for short- and long-term technical needs [5]. Therefore, researches focused on finding new composition with low cost raw materials are still active. Recently, the binary niobate compounds with general formula MNb_2O_6 (where M = Mg, Zn, Co, Ni, Cu, Mn and Ca, etc.) were investigated and found to be promising candidates for application in microwave devices [6,7]. These compounds with a columbite crystal structure, are one of the end member of the complex perovskite $A(B'_{1/3}\ B''_{2/3})O_3$, and have very low loss and high dielectric constant. Among those compounds, $ZnNb_2O_6$ and $MgNb_2O_6$ exhibit excellent dielectric properties. The dielectric properties of $ZnNb_2O_6$ and $MgNb_2O_6$ are $\varepsilon_r = 25$, $Q \times f = 83\,700$ GHz and $\varepsilon_r = 18.4$, $Q \times f = 93\,800$ Ghz, respectively [7].

More recently, many researchers have investigated the substitution of the Zn-site with Mg to form solid solutions and improve the dielectric properties of microwave materials [8–10]. For example, Thirumal et al. reported the substitution of the Zn^{2+} by Mg^{2+} in $Sr_3Zn_{1-x}Mg_xNb_2O_9$ system [8], Kim et al. investigated the dielectric properties of (Zn, Mg)TiO_3 solid solution

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[9], and Desu and O'Bryan [10] also investigated the microwave loss quality of $Ba(Zn, Mg)_{1/3}Ta_{2/3}O_3$ ceramics.

The purpose of this study is to investigate the effects of the substitution of Zn with Mg on microwave dielectric properties of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics. The sintering behavior and microstructure were also investigated in this system.

2. Experimental procedure

High-purity oxide powders (>99.99%) of Nb_2O_5, ZnO and MgO were used as starting materials. They were weighted according to the composition of $(Zn_{1-x}Mg_x)Nb_2O_6$ ($x=0$–1.0) and ball-milled in a polyethylene with zirconia beads for 6 h using a planetary mill. The products then, dried and calcined at 1000 °C for 2 h in air. The calcined powder was re-milled for 6 h. The synthesized powders were uniaxially pressed into disks with 10 mm diameter and 4–7 mm in thickness at 100 MPa. The disks were sintered at 1100–1300 °C for 2 h in air, and then cooled to room temperature.

The crystal structure of sintered samples were analyzed by X-ray diffractometry with a graphite monochromator, and CuK_α radiation with step scanning. The bulk densities of the sintered ceramics were measured by Archimedes method. The microstructure analysis was observed by a scanning electron microscopy (SEM). The microwave dielectric properties were measured using the Hakki-Coleman dielectric resonator method as modified and improved by Kobayashi and Courteny et al. by HP8720ES network analyzer in the frequency range of 6–8 Ghz [11–13].

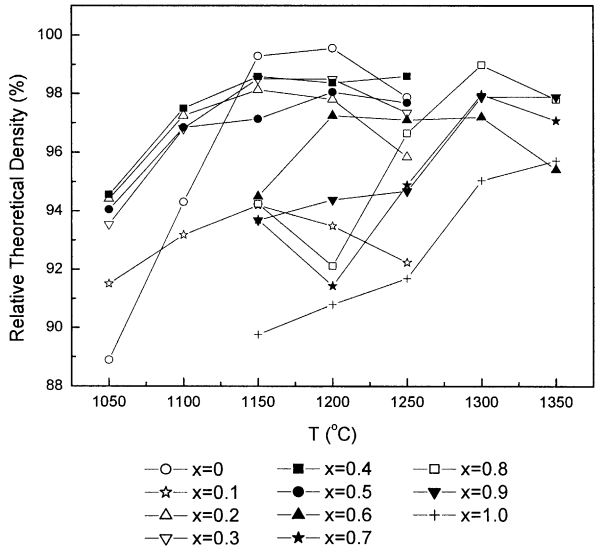

Fig. 1. The bulk densities of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics sintered at different temperature as a function of x.

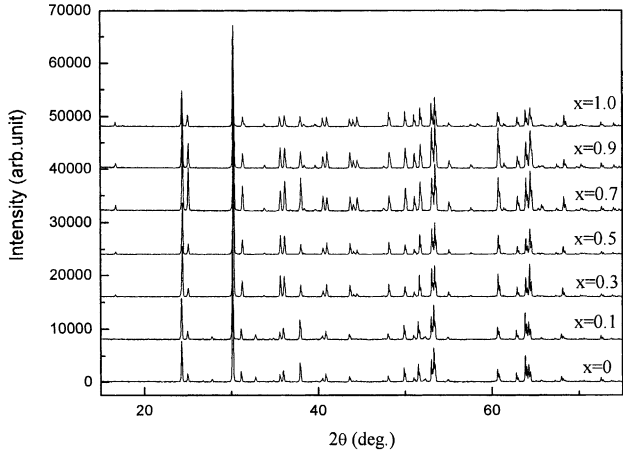

Fig. 2. The XRD patterns of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics sintered at 1200 °C for 2 h as a function of x.

3. Results and discussions

The bulk densities of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics as a function of sintering temperature were shown in Fig. 1. The bulk density of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics increased with increasing sintering temperature, and above 96% of theoretical density can be obtained for all sintered samples. The densification temperature of samples were about 1150 °C for $x=0$–0.4, 1200 °C for $x=0.5$–0.6 and 1300–1350 °C for $x=0.7$–1.0, respectively. It suggested that the

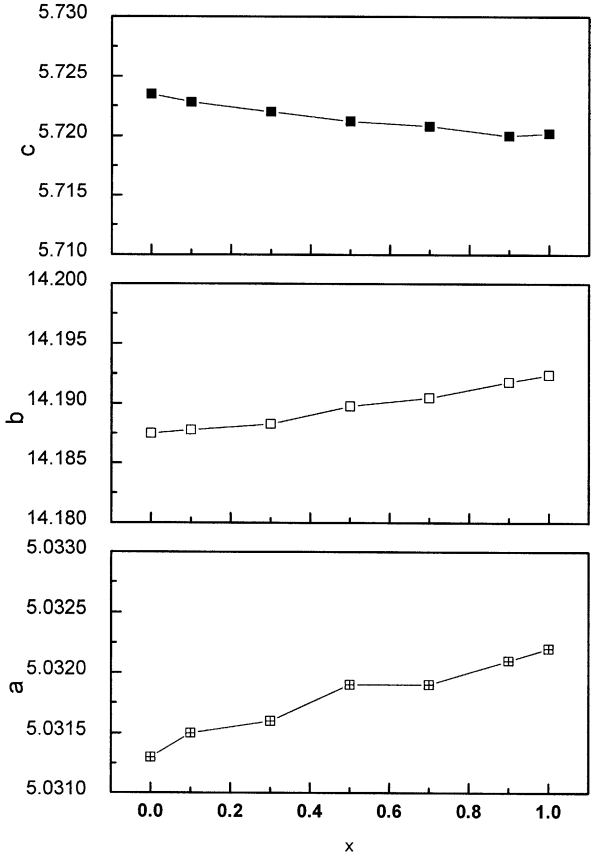

Fig. 3. Unit–cell parameters of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics sintered at 1200 °C as a function of x.

sintering temperature increase with increasing Mg content. This result was due to that the sintering temperature of $MgNb_2O_6$ is higher than that of $ZnNb_2O_6$. On the other hand, the bulk density of sintered samples decreased with increasing Mg content, which was mainly caused by the small molecular weight of Mg.

Fig. 2 shows the XRD patterns of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics sintered at 1200 °C for 2 h as a function of x. XRD patterns show that $(Zn_{1-x}Mg_x)Nb_2O_6$ solid solutions have the single columbite structure for all x values, and all the reflections could be indexed satisfactorily in the orthorhombic cell. The crystal structure of $ZnNb_2O_6$ and $MgNb_2O_6$ are orthorhombic symmetry. The lattice parameters of $ZnNb_2O_6$ and $MgNb_2O_6$ are $a = 5.0314$ Å, $b = 14.1874$ Å, $c = 5.7232$ Å and $a = 5.032$ Å, $b = 14.193$ Å, $c = 5.700$ Å, respectively. The solid solution of the zinc magnesium niobites is easily formed, because $ZnNb_2O_6$ and $MgNb_2O_6$ have the same columbite structure. In addition, a relatively smaller ionic radii of Mg^{2+} (0.66 Å) than that of Zn^{2+} (0.74 Å) tended to make it easy to substitute the zinc-site by a magnesium ion.

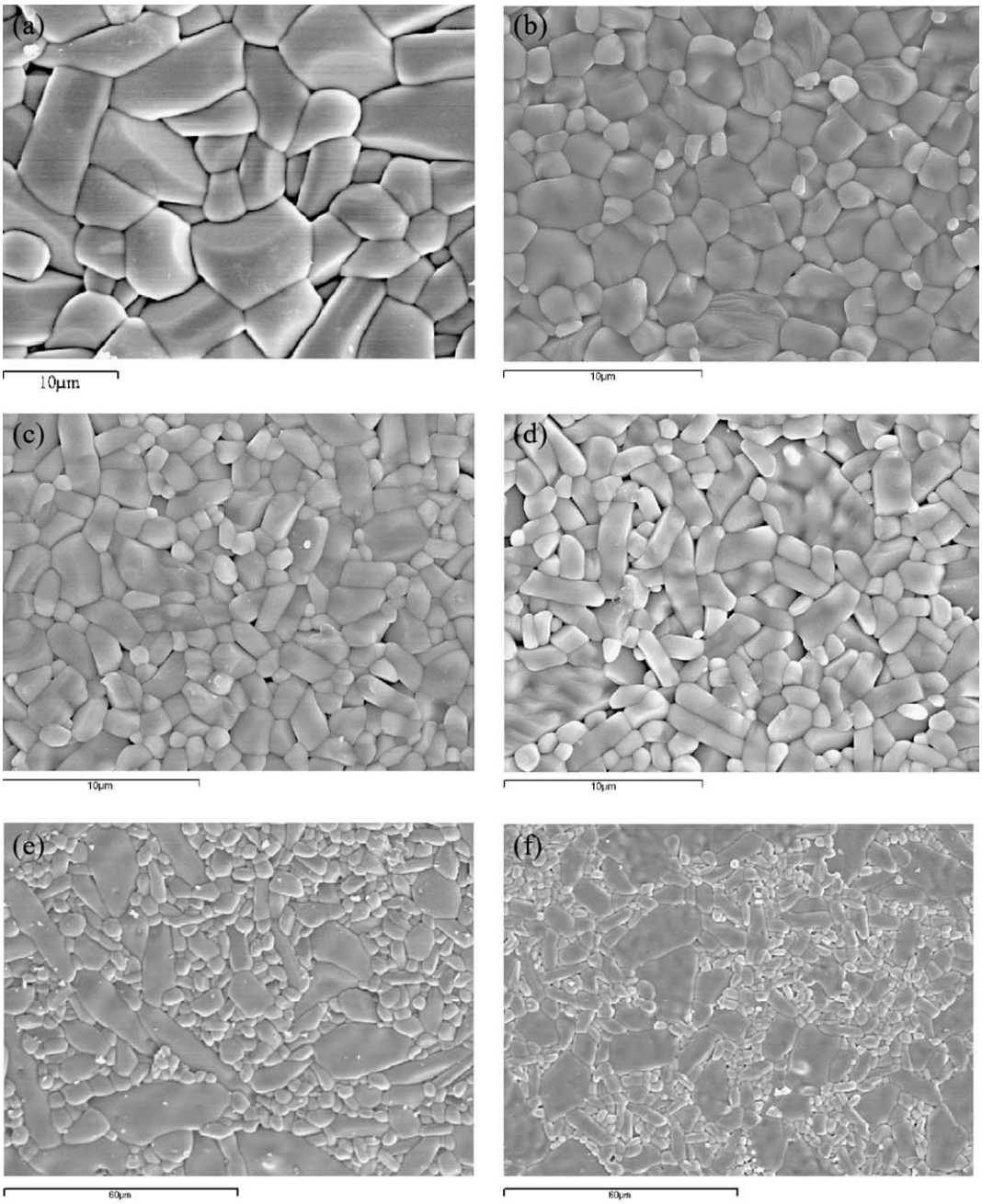

Fig. 4. SEM micrographs of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics sintered at different temperature: (a) $x = 0$, 1150 °C (b) $x = 0.1$, 1150 °C (c) $x = 0.3$, 1150 °C (d) $x = 0.5$, 1150 °C (e) $x = 0.7$, 1300 °C (f) $x = 0.9$, 1300 °C.

Unit–cell parameters were investigated to determine the effect of the substitution of zinc ions by Mg ions on the crystal structure of $(Zn_{1-x}Mg_x)Nb_2O_6$ solid solution (Fig. 3). The *a*-axis and *b*-axis parameters of $(Zn_{1-x}Mg_x)Nb_2O_6$ linearly increased as the amount of Magnesium increased, and *c*-axis parameters decreased as x increased. Those phenomena obey the general known Vegard's law, and can be explained by the difference in the ionic radii of Zn^{2+} and Mg^{2+}.

The typical microstructure of the as-sintered surfaces of $(Zn_{1-x}Mg_x)Nb_2O_6$ (x=0-1.0) ceramics were shown in Fig. 4. The homogeneous and uniform microstructure were observed for all x values. The grains exhibit two different size ranges, the fraction of large grain is greater than that of small grains. EDS analyses show that the compositions of samples are homogeneous in $(Zn_{1-x}Mg_x)Nb_2O_6$ solid solution (not shown here). However, the changes in grain shape of sintered samples were observed. The grain shape of samples changed from equiaixed to rectangle as x varied from 0 to 0.5 [Fig. 4(a–d)]. And the abnormal grain growth was also observed in some samples as $x>0.5$ [Fig. 4(e, f)]. Those phenomona might be related to the oriented growth of grain caused by the formation of solid solution.

The dielectric constants of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics as a function of sintering temperature were shown in Fig. 5. The relationship between ε_r values and sintering temperature was as the same as that between the bulk density and sintering temperature. Those phenomena were attributed to the increase of relative density which depends on the sintering temperature. The maximum ε_r values of sintered samples decreased from 23 to 19 as x varied from 0 to 1.0. In this work, the dielectric constant of $ZnNb_2O_6$ and $MgNb_2O_6$ are 23.66 and 19.17, respectively. Therefore, it suggested that the ε_r values have a significant dependence on the composition of $(Zn_{1-x}Mg_x)Nb_2O_6$ solid solution system.

Fig. 6 shows the quality factors of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics as a function of sintering temperature. The $Q\times f$ values of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics increased with increasing the sintering temperature, after reached the maximum value at a certain temperature, then decreased. It is expected that the $Q\times f$ values of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics system vary linearly between $ZnNb_2O_6$ and $MgNb_2O_6$. But all $Q\times f$ values were lower than those of $ZnNb_2O_6$ and $MgNb_2O_6$, and ranged non-linearly in the region from $x=0$ to $x=1.0$. The $Q\times f$ values of sintered samples firstly decreased with increasing Mg content from $x=0$ to $x=0.5$, the minimum $Q\times f$ value were observed at $x=0.5$ and were 33 112 Ghz, then, the $Q\times f$ values increased from 33 112–68805 Ghz as x varied from 0.5 to 1.0. The maximum $Q\times f$ values obtained at sintering temperature for $x=0.1$, 0.3, 0.5, 0.7, and 0.9 were 47 889, 37 097, 33112, 49 807, and 68 805 Ghz, respectively. In general, microwave dielectric loss could be divided into two fields: the intrinsic loss and extrinsic loss. The intrinsic loss was mainly caused by lattice variation modes while the extrinsic loss was mainly dominated by secondary phase, oxygen vacancies, grains sizes and densification [14]. The $Q\times f$ values were independent of the density or the porosity when the relative density is greater than 95% of theoretical density. In this study, it can be considered that the effects of the relative density can be ignored since the densities of the samples were higher than 95% TDs. Grain size and grain distribution might be suggested to affect the $Q\times f$ values of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics due to large grains resulted in less grain boundary, which meant less lattice mismatch and lower dielectric loss. The $ZnNb_2O_6$ ceramics

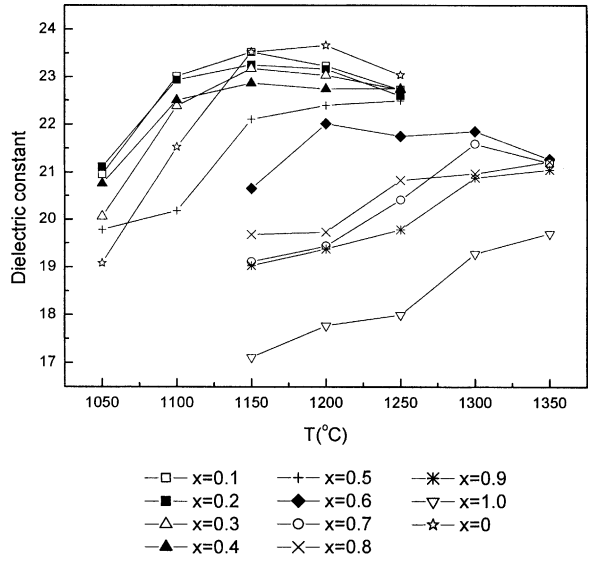

Fig. 5. The dielectric constants of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics sintered at different temperature as a function of x.

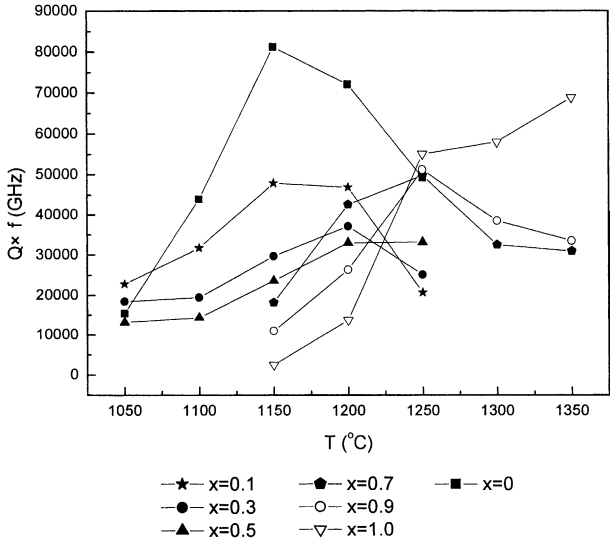

Fig. 6. The quality factors of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics sintering at different temperature as a function of x.

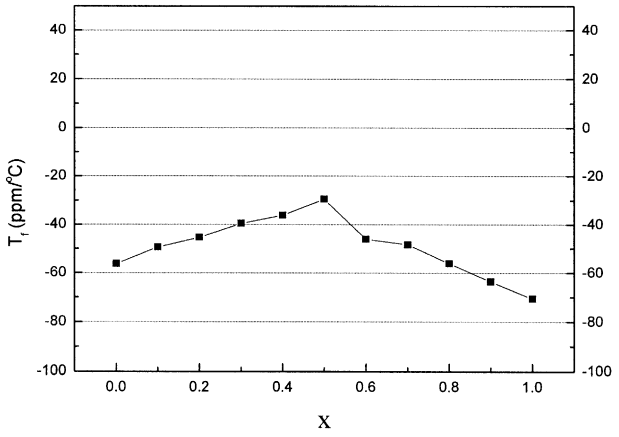

Fig. 7. The temperature coefficients of resonant frequency of sintered $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics as a function of x.

have the highest $Q\times f$ value among $(Zn_{1-x}Mg_x)Nb_2O_6$ solid solutions due to its homogeneous microstructure with equiaxied grains. However, the appearance of small grains and abnormal grain growth observed in samples for $x=0.1$–1.0 seriously affected the $Q\times f$ values of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics.

The temperature coefficient of resonant frequency as a function of x was shown in Fig. 7. The temperature coefficient of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics firstly increased with increasing Mg content from $x=0$ to $x=0.5$, then, decreased as x value varied from 0.6 to 1.0. The minimum τ_f value was observed for $x=0.5$ and was -29.46 ppm/°C. In general, τ_f value is known to be related with the temperature coefficient of dielectric constant (τ_ε) and the thermal expansion coefficient (α_l) of which the value is approximately 10 ppm/°C in the microwave dielectric ceramics. Colla et al. suggested that the anomalous variation in τ_ε of the solid solution between $Ba(Zn_{1/3}Nb_{2/3})O_3$ and $Sr(Zn_{1/3}Nb_{2/3})O_3$ is strongly correlated to the tilting of MO_6-octahedra with increasing Sr content [15]. Therefore, in the case of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics, the presence of minimum τ_f value might be influenced by the difference in tilting of MO_6-octahedra caused by the substitution of Zn^{2+} with Mg^{2+}.

4. Conclusions

Dielectric ceramics comprised of $(Zn_{1-x}Mg_x)Nb_2O_6$ $(x=0$–$1)$ with promising microwave properties were prepared by solid ceramic route. The sintering behavior, microstructure and microwave dielectric properties of $(Zn_{1-x}Mg_x)Nb_2O_6$ were investigated systematically in this study. The sintering temperature of $(Zn_{1-x}Mg_x)Nb_2O_6$ ceramics increased from 1150 to 1350 °C with increasing Mg content from $x=0$ to $x=1.0$. The crystal structure exhibits a columbite structure for all x values. The grain shape of samples changed from equiaixed to rectangle as x varied from 0 to 0.5. $(Zn_{1-x}Mg_x)Nb_2O_6$ system has excellent dielectric properties, the ε_r values ranged from 23.66 to 19.17, the $Q\times f$ values ranged between 81 220 and 33 112 Ghz, the τ_f ranged from -70.56 to -29.46 ppm/°C. However, the τ_f values of this system are needed to further study and adjust to zero for practical application in microwave devices.

Acknowledgements

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