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COMPARISON BETWEEN CRYSTAL STRUCTURE AND DIELECTRIC PROPERTIES ND($MG_{1/2}TI_{1/2}$)O_3 (NMT) AND ND($ZN_{1/2}TI_{1/2}$)O_3 (NZT)*

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The dielectric properties of Neodymium zinc titanium oxide (NZT) and Neodymium magnesium titanium oxide (NMT) were reviewed. The single-phase ceramic was synthesized at various temperature below 1650 ºC, at which $NdTiO_5$ phase were visible.
The result shows that value of τ_f for NZT is less than NMT, and NMT resonators have a better stability against temperature variations.
Our results are showing that rare earth materials producing a high dielectric material, despite the fact some elements are producing less negative temperature of resonant frequency (τ_f), for example Neodymium while other more negative i.e., Lanthanum. By doping a compound such as $CaTiO_3$ which has a very positive τ_f = 712 ppm/ºC and a very high relative permittivity of ε_r = 145 it is possible to tune NZT and MNT to achieve an excellent dielectric material. This work is under consideration. The results of this scientific research could be very important for modern advance applications in microelectronic miniaturization.

Keywords: Electron microscopy; dielectric properties; grain growth; single-phase; neodymium magnesium titanium oxide; Microwave dielectric ceramics.

1. Introduction

This research aim is to investigate [1,2] the structure and microwave dielectric properties of NMT and NZT. Previously, Colla *et al.*[3,4] showed a method by which he was able to tune τ_f in perovskite compounds, in this way he was able to reduce cost of devices used in

microelectronics. The structure of $BiHoCoTi_6$ which tested by Sujit Kumar shows orthorhombic structure system of dielectric materials, these result shows the contribution of grains and grains boundary significantly influence and tune the final structure of dielectric materials [5], NMT which has a monoclinic crystal structure, shows doubled unit cells is a consequence of B-site cation ordering [6,7] which reduces the available space in the A-site types of atoms. Measurement of *QL* from the resonance signal combined system of the resonant cavity, and the external load as:

$$Q_L = \frac{f_0}{\Delta_f} \qquad \textbf{(1)}$$

Wherein
QL = Loaded quality factor
f_0 = resonance frequency
Δ_f= the full width at half maximum of the resonance peak at 3 dB

The degree of octahedral tilting depends on the (τ_ε) in both strontium as well as compound materials which includes barium. Furthermore, it can be adjusted to unused any changing in relative permittivity or quality factor, by using the tolerance factor (*t*),'

$$t = (R_A + R_0)/\sqrt{2}(R_B + R_0) \qquad (2)$$

The tolerance factor value can vary between 0.93 to 1.01. In equation (2) the radii of perovskite defined by R_A, R_B, and R_O.

The consequence of the decrease in tolerance factor is the change of octahedral. Equation 3 shows the connection between τ_ε and τ_f

$$\tau_f = -\left(\frac{\tau_\varepsilon}{2} + \alpha_L\right) \qquad (3)$$

In the equation (3) α_L is equal to 10 ppm/^{o}C for perovskite crystal structure and it is called the coefficient of the linear thermal expansion for perovskites materials.

The calculated tolerance factor of the $Nd(Mg_{1/2}Ti_{1/2}O_3)$ ceramics is equal to 0.915. This value suggests an extremely tilted shape octahedral and could be for example like $FeTiO_3$ or similar structure, these kinds of materials generally produce the in-phase and the anti-phase in 1:1 type compound of perovskite material, typically the tilting of octahedra has similar properties both causing tilting of octahedra structure. Based on the tilting of oxygen octahedra, interplanetary space of A-type atoms changes in their location.

A perovskite $Nd(Zn_{1/2}Ti_{1/2})O_3$ (NZT) forms in the tilted cubic perovskite system, and it's atomic and crystal system $a \neq b \neq c$ and $\alpha = \gamma = 90$ and $\beta \neq 90$ which suggest a tilted monoclinic. Its calculated (t) is equal to 0.916, based on research of Vojislav *V. Mitic et al.*[1,2], denotes tilting of octahedra. By using XRD method we were able to determine the tilting of octahedra. The superlattice reflections equivalent to the anti-phase and in-phase tilting also have been discovered. The NZT crystal structure can have $P2_1/n$ or Pbmn space groups.

There are some important properties regarding resonators which must be taken into the account: It must have minimum size, ultrathin bandwidth, and a great gain. The size of resonators (antenna)[8] can be calculated by the following equation:

$$L = \frac{\lambda}{\sqrt{\mu_r \times \varepsilon_r}} \quad (4)$$

wherein:
L = resonators size; λ = electrical size in air; μ_r = relative permeability; and ε_r = dielectric constant.

In brief**,** for a modest-size antenna, the materials with great permittivity and permeability are essential. The materials of more substandard properties create a freeloading layer that lowers the gain of the resonator[8].

2. Experimental procedure

Below, a short explanation of the material preparation for the NMT and NZT is defined. A detail information and complete description are in references nine and ten.
Powder of neodymium magnesium titanium oxide and Neodymium zinc titanium oxide were made ready using conventional mixed oxide method. Nd_2O_3, TiO_2, ZnO, and $(MgCO_3)_4Mg(OH)_{25}H_2O$ 99.9% were weighed and mixed for twenty four hours with distilled water. The compound was calcined for two hours at 1250 ^oC temperature and then mixed again for twenty hours in a ball mill zirconia. Nd_2O_3 is substance that willingly attracts water from its environments, through absorption, hence we mixed the powder with distilled water to be saturated and prevent structural changes during the process of dielectric preparation. These prepared powders were mixed with one weight precent of Dispex A40, then powder was kept in 80 ^oC for twelve hours. The mentioned fine powder was then pressed into the cylinder shape with diameter of 1 cm and height of 0.3 cm under pressure of 12.75kgf/mm^2. Samples were sintered at 1400 ^oC to 1675 in an Al_2O_3 crucible for six hours in air. To quantify the weight loss samples were measuring before and after sintering. Microwave dielectric properties of sintered sample were measured using Network analyzer to measure permittivity the post resonator method was used. An invar cavity was used to define τ_f. The silver coated cavity was several times larger than size of samples. τ_f was measured in a heat area started from -23 to 37 ^oC at a frequency 4 up to 11 GHz.
To investigate crystal structure of samples we utilized TEM, SEM, XRD and Differential scanning calorimetry and method for phase evolution as well as Rietveld refinement performed.
The phase assemblage and space group of samples checked by the following instruments: Scanning electron microscope (JSM 6300, Joel, Japan) (SEM). Siemens D5000 X-Ray Powder diffractometer. TEM laboratory contains two analytical JEOL instruments JEOL 2010 and HORIBA-Scientific Raman microscope, manufactured by HORIBA Scientific Japan. Differential Scanning Calorimeter (DSC) and Differential Thermal Analyzer (DTA) Perkin Elmer TGA7 Differential Scanning Calorimeter.

3. Results and discussions

In this study, we have explored the densities of NZT and NMT versus sintering (Figures 1 and 2) the density denoted as (ρ). The theoretical density (ρ_{th}) of NMT is quickly increased

and arrives to 89% at 1250°C then it rises to 94% of ρ_{th} at 1500°C (Figure 1). Additionally, as temperature increases, the ρ of NZT at the start increase to 6.67% of ρ_{th} and then goes to around 1450°C and finally decrease just about 1500°C. The ρ decreases at elevated heat and it is the result of ZnO volatilization which increases steadily at temperature around 1500°C and above. As shown in Figure 3, we add 50°C to every temperature from 1250°C to 1500 °C and, after four-hours sintering, each sample was investigated by X-ray diffraction. As can be seen from Figure 3, there were not any significant changes in the samples of 1250°C, 1300°C, 1350°C, 1400°C, and 1450°C. However, in the 1500°C phase, the so-called Nd_2TiO_5 appeared which indicates a significant change in the structure of NZT. These changes are result of the evaporation of ZnO which generates a vacancy in a sample and finally produces the distorted perovskite crystal structure of NZT.
Figure 1 reveals the ρ of NMT versus alternating changes of sintering by heating of samples to higher temperature. The density of NMT goes higher as heat increases and reaches 89% of ρ_{th} at 1250ºC. The ρ then increases to around 95% of the ρ_{th} at approximately 1500ºC.
Figure 2 demonstrates the ρ of NZT against temperature. At 1400ºC, it is equal to 95% of ρ_{th} and then it grows to 96.6% of theoretical density at 1450ºC.

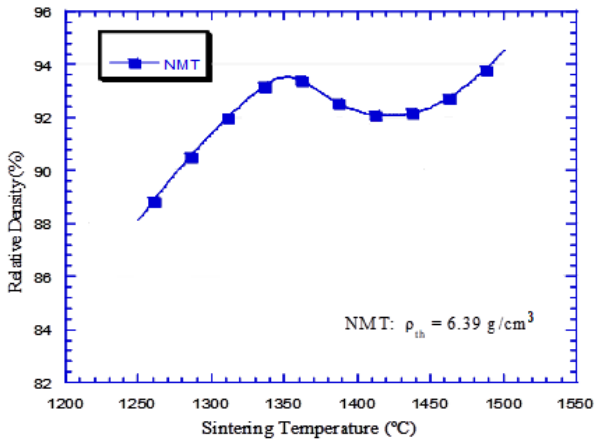

Fig. 1. The ρ_{th} of NMT samples versus sintering temperature.

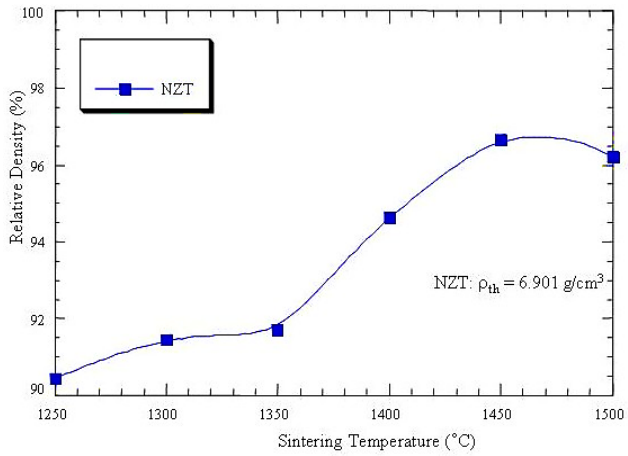

Fig. 2. The ρ_{th} of NZT samples versus sintering temperature.

All the samples show a crystal structure similar to the perovskite structure and its isomorphous materials $La(Zn_{1/2}Ti_{1/2})O_3$ [9]. A high degree of octahedral tilting crystal structure for NZT [10] was already suggested. The result of this investigation shows that, the crystal structure like the $FeTiO_3$ structure could be recommended for NZT.
The XRD diffraction of NZT is shown in Figure 3, a new phase of Nd_2TiO_5 appeared at temperature of 1500 °C, which is an unwanted phase in this research. The superlattice reflections which denoted by $\alpha$and β are presenting in Figure 3.

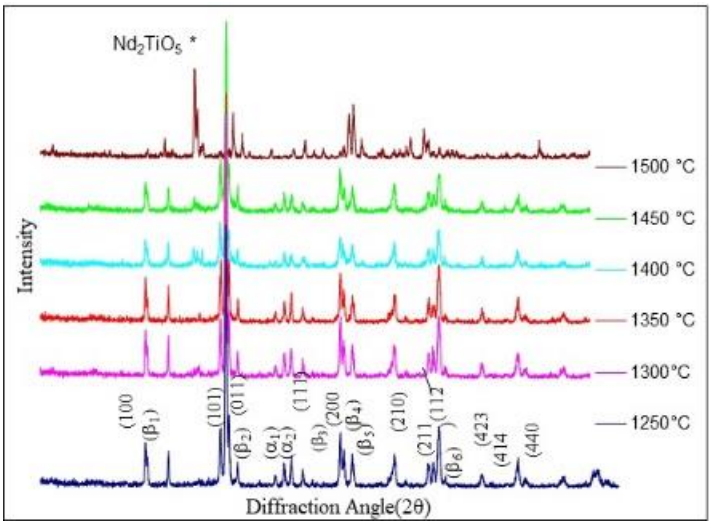

Fig. 3. The XRD diffraction of NZT at 1250-1500ºC. The $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are presenting superlattice reflections.

The X-ray diffraction results of NMT tests from 1400 ºC to 1675ºC is shown in Figure 4. These samples indexed using pseudocubic lattice parameter a=3939 nm. The results show a slight shift and broadening in the position of the peaks, which indicates building block of a monoclinic crystal.

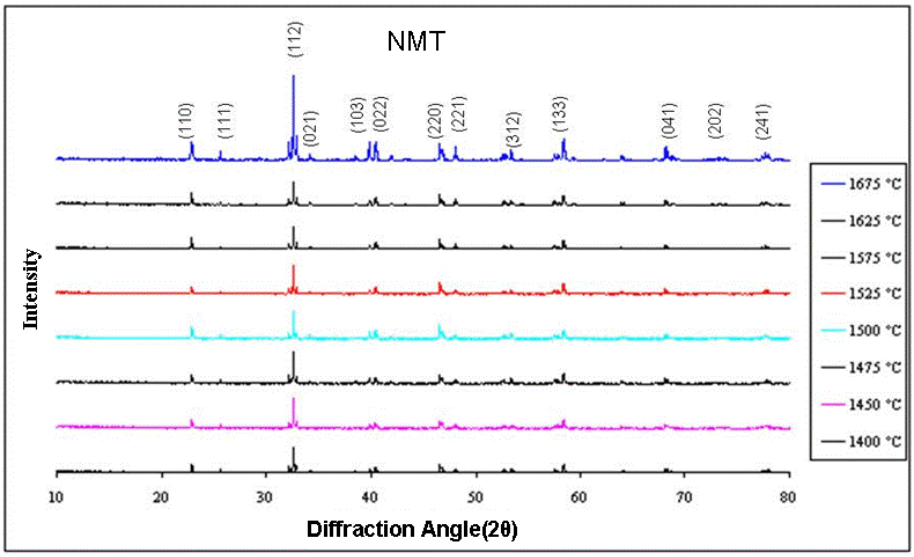

Fig. 4. The XRD diffraction of the NMT powder from 1400°C to 1675°C. The X-ray diffraction shows similar spectrum, as illustrated there was not find any impurities.

The relative permittivity of two ceramics samples, the NMT and the NZT, were calculated. As a result, the NMT sample shows a better stability at higher temperatures because Zinc oxide (ZnO) in the NZT structure evaporates at higher temperatures and causes octahedral tilting in the perovskite structure. Nevertheless, in the crystal structure of NMT, Magnesium oxide (MgO) is stable even at higher temperatures which indicates that NMT has a better dielectric constant.

The result of our $Q\times f$ measurements for NZT and NMT shows that NMT has better quality factors and a narrower bandwidth while NZT has better dielectric constant (ε_r = 36) in comparison to NMT (ε_r= 25) but a lower bandwidth, respectively. The τ_f is better in NZT, and it has better dielectric properties than NMT. It can be used at lower temperatures. NMT can be used in both higher and lower temperatures, but it has a lower dielectric constant which affects the size of resonators.

The results of our measuring illustrate that NMT has a better-quality factors $Q\times f$ = 60000 at 9.76 GHz and it has a dielectric constant equal to 25 and τ_f= -72 ppm /ºC. It has narrower bandwidth, while NZT has quality factor of $Q\times f$ = 42000 at 4.24 GHz and higher relative permittivity $\varepsilon_r = 36$ but a lower bandwidth, respectively. The temperature coefficient of resonant frequency of NZT is τ_f= -48 ppm/^{0}C, these results shows that NZT has better τ_f

and dielectric properties than NMT. As mentioned, It can be used at lower temperatures. NMT can be used in both higher and lower temperatures, but it has a lower dielectric constant which affects the size of resonators.

3.1. Structure of NZT

The XRD of the NZT samples were illustrated in Figure 3. Our calculated lattice constants are equal to a =7787 nm, b=7564 nm, and c=8049 nm. The reflections marked α_1 and α_2 in Figure 3 are connected to the anti-phase tilting of oxygen octahedral for more information regarding the antiphase tilting of octahedra please look at reference [11]. The A-site cation Nd^{+3} shows antiparallel displacement and defined by β peaks.
The Raman spectrum of NZT shows a disorder perovskite crystal structure of NZT [10] because tolerance factor of NZT is far away from perovskite it is equal to 0.916.

The secondary electron images of NZT sintered at 1600°C for six hours is shown in Figure 5 The contrast of figure indicated each sample is single-phase and relatively dense, with the grain size of approximately 2-6 μm. It is important to noticed that for microwave we need the structure of materials to be as close as possible to perovskite structures. It means our material must have $\tau_{f=0}$ and $Q\times f$ must be as high as possible.

The energy dispersive spectroscopy (EDS) analysis applied for qualitative investigation and the chemical characterization of NZT sample (Figure 6), it shows that there is not existing any impurity or other phase in the sample, it also illustrates that Nd element is dominating peak and proves the existence of titanium and Zinc in the sample.

Our results show that the NMT crystal structure is more stable because MgO is not evaporated during temperature treatments. Consequently, there are no significant changes of NMT in every temperature from 1400ºC to 1600ºC as shown previously in Figure 4.
Though, at higher temperature ZnO, which exist in NZT evaporates and this phenomenon causes significant changes in the crystal structure of NZT while the structure of NMT remains stable.

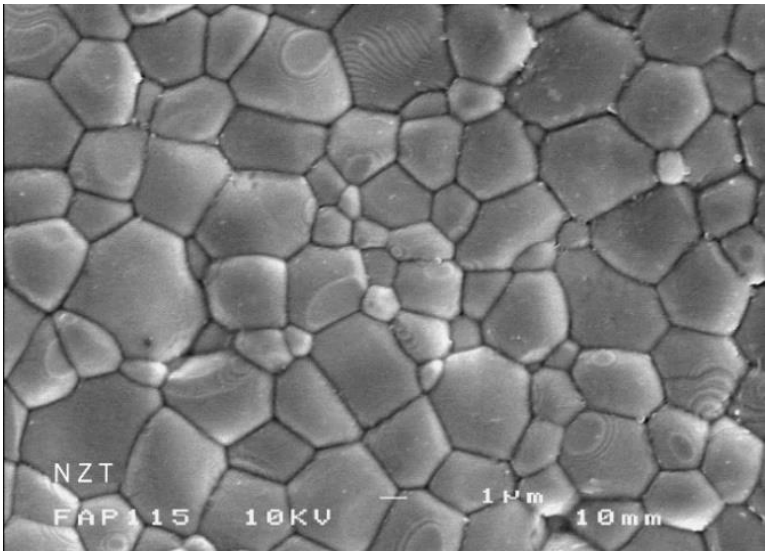

Fig.5. The SEM sample of NZT sintered at 1400ºC. There is not any changes in image contrast of sample.

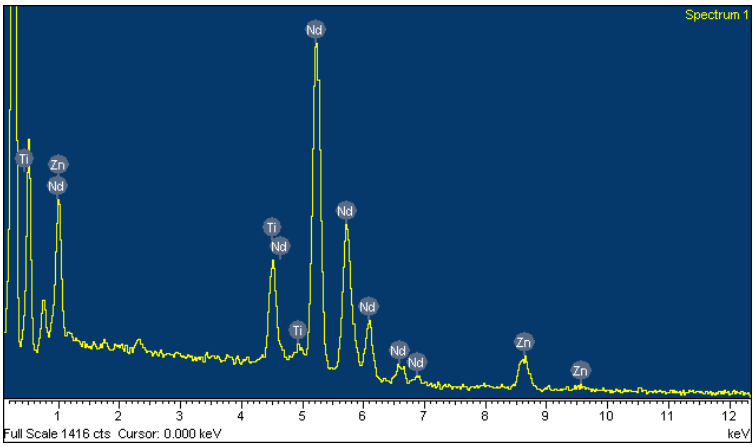

Fig. 6. The EDS analysis of NZT shows no other phases or impurities.

There was not much information about NZT, the structure is not yet exactly defined. Therefore, by using TEM, we applied a selected area diffraction pattern (SADP) to be able to index and practically to observe the spot pattern of NZT sample. The pseudocubic of 0.39449 nm which is a basically used for perovskite selected to be able to apply the SADP. As Figure 7 shows, the γ reflection equal to in phase tilting of octahedra is absent. α equal to anti-phase tilting of octahedra and β equal to anti parallel cation displacement. The spot pattern in the direction of [100] and [110] shows a regular and ordered shape.

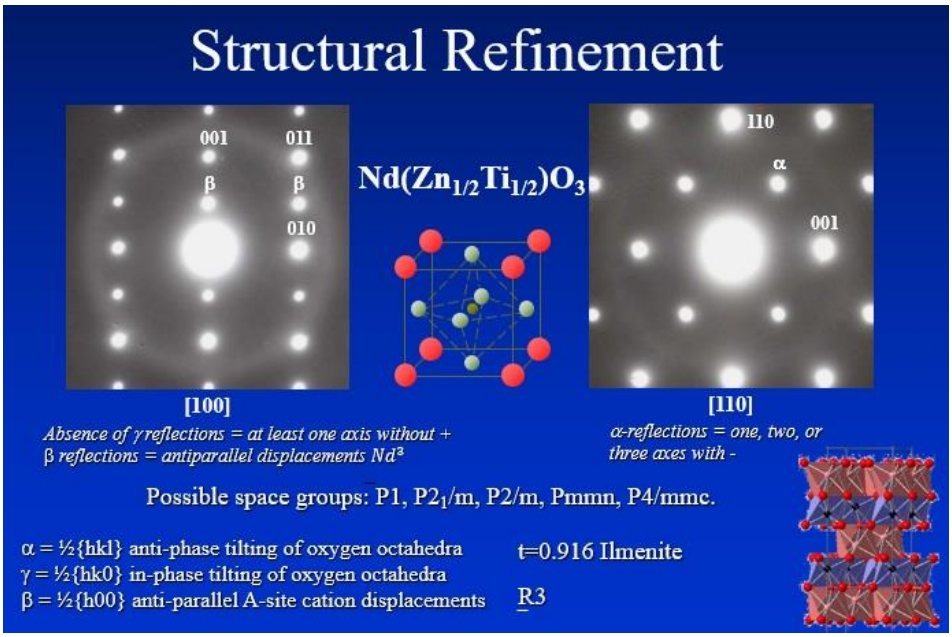

Fig. 7. Selected are diffraction Pattern of Neodymium zinc titanium oxide in direction of [100] and [110]. The sample ion milling by instrument model 600, Gatan CA, USA and for testing the sample Transmission electron microscopy (JEM, Jeol 2010, Japan) used to identify the structure.

3.2. Structure of NMT

The high-resolution X-ray diffraction pattern of NMT at different temperatures from 1500°C to 1600°C, previously illustrated in Figure 4. These results are comparable to the results which testified by Hyun Yoon [12] and *Ferreira et al.* [13] the lattice vibrational characteristic and dielectric properties of similar materials also was inspected by *Jae Beam et al.*[14] to determine the crystal structure. Recently, LMT and NMT were examined by *Mitic et al.*[15] indicates most of these materials have monoclinic structures.
Our calculated lattice parameter are as follows: a = 546610 nm, b = 559050 nm, c = 776800 nm, a= 90°, β=90.01° and γ = 90°. Additional NMT described by Mitic et al.[15], shows irregular perovskite structure. A single-phase monoclinic crystal structure can be recommended for NMT.

For NMT, the calcination temperature was 1400°C while the density was 6.02 g/cm^3. The volatilization of Zn^{+2} in the crystal structure of NZT causes dramatic changes in structure while Mg^{+2} in the structure of NMT remains even at high temperatures. Therefore, the tolerance factor of NMT will be equal to 0.920 and, in the case of NZT, it will be 0.916 which is lower. Consequently, the position of peaks is shifted to lower angles with respect to NMT. Figure 8 shows the scanning electron microscopy image of NMT with the grain size of approximately 1-6 μm. This result shows that there is not any changes in image contrast which is other evidence to proof it is a single-phase material and applicable for microwave purposes.

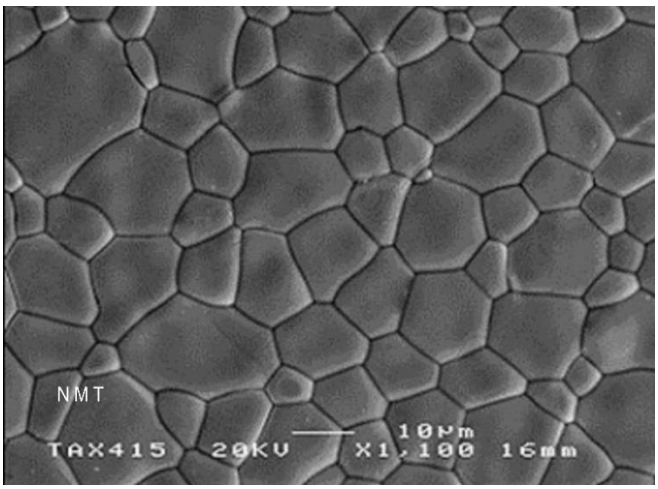

Fig.8. The SEM sample of NMT sintered at 1600ºC. There is not any changes in image contrast of sample.

In the perspective future research, we plan to continue with additional characterization by fractal nature analysis, what is important from thin layers in contact interface. For further investigation in electronic structure of materials we are planning to apply Density Function Theory (DFT) for modeling method.

4. Conclusion

The crystal structure of NMT is monoclinic and NZT has a disorder monoclinic atomic structure. The evaporation of ZnO creates a disorder atomic structure of NZT. It is better to use NZT at temperatures between1400-1500ºC. When temperature is very high, NMT can be used. As a result, both the NZT and the NMT composition show a promising dielectric property. The crystal structure of NMT is monoclinic and NZT has a disorder monoclinic atomic structure, because of the evaporation of ZnO. When temperature is higher NMT can be more stable. As a result, both the NZT and the NMT compositions have an outstanding dielectric property. The NZT has $\varepsilon_r = 36$, Q×f = 42000 at 4.33 GHZ and τ_f= -48 ppm/ºC; Despite the fact NMT has $\varepsilon_r = 25$, Q×f = 60000 at 10 GHz and

τ_f = -72 ppm/^{o}C. These materials have exceptional potential and can be used as a filter in the field of mobile microwave telecommunications.
In the next step of our research, we will open the frontiers for new approach in microelectronics, what is the key demand especially for mobile communications.

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