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Synthesis and Characterization of Lanthanum Doped $BaNd_2Ti_3O_{10}$

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***Abstract* – The high quality factor, high dielectric constant, low dielectric loss and small temperature coefficient of resonant frequency are the most desirable characteristics of the microwave dielectric materials. Considering the hazardous nature of lead based ceramics many research groups has paid great attention to the research on non-lead based perovskite ceramic. Here we synthesize the material $BaNd_{2-x}La_xTi_3O_{10}$(for x = 0.02, 0.04, 0.06 and 0.08) by choosing the method which is low cost and easy. The X- Ray Diffraction (XRD) data confirm its orthorhombic crystal structure and Scanning Electron Microscopy (SEM) picture gives grain size less than 2 μm. The dielectric measurement gives temperature independency in the range from room temperature to 523 K. The complex impedance measurement gives double hemisphere indicating separate grain and grain-boundary contributions and is well resolved at higher temperature.**

***Keywords* – Barium Neodymium Titanate, Dielectric Constant, Cole-Cole Plot, Microwave Ceramic.**

I. Introduction

The growing potential of microwave dielectric ceramics for the applications to mobile communication systems makes them very important materials [1]-[3]. The high quality factor, high dielectric constant, low dielectric loss and small temperature coefficient of resonant frequency are the most desirable characteristics of the microwave dielectric materials [4]. The dielectric resonators gives important advantages in terms of temperature stability, compactness, light weight and relatively low cost in the production of various microwave devices like band-pass filters and band-stop filters, frequency stabilization of solid state oscillators [5]. It has been reported that the compounds in Ba-Nd-Ti-O systems possess excellent dielectric properties and temperature stability; therefore they can be used in microwave devices [6]-[8].

There is large number of research publications on the hot topic of environment friendly lead free materials, especially in last decade. The European Union(EU) in 2003 included lead (Pb) in its legislature to be a hazardus substance. Similar activities and regulations are carried by many countries in the world. The literature survey made by Chinese scientist Yong-Xiang Li [9] indicates that the lead free material synthesis is the need of present for better future. At the 9th international meeting on ferroelectricity, the demand of eco materials or environment friendly materials are pointed out that ferroelectric material should comprise non-hazardous substance [9]. Since then many group has paid great attention to the research on non-lead based perovskite ceramic.

II. Experimental

To synthesize the required material we have chosen the method which is low cost and easy. Powders were weighed and mixed in stoichiometric proportion with an acetone to grind for 2 hours with agate mortar. Parent materials were $BaCO_3$, Nd_2O_5,TiO_2 and La_2O_3 (more than 99.9 % pure). After grinding the powder were presintered at 1050 ^{0}C for five hours. After presintering the material was again grinded in an agate mortar for 1 hour and used for pelletization. Polyvinyl acetate (PVA) was used as an organic binder. Five ton/cm2 pressure is applied while pelletization. The pellets were sintered in an aluminum crucible at 1150 ^{0}C for seven hours. Sintered samples are allowed to anneal at the rate of 2^{0}C/min up to 400^{0}C. Further the samples are brought to room temperature by natural rate of cooling.

The synthesized material was studied for their structural characterization through powder x-ray diffraction pattern. Miniflex-2 Goniometer was used to scan the sample from angle (2θ) 20 to 80 with step of 0.02 and CuKα as source of x-rays. Further the morphological study were made using Scanning Electron Microscopy (SEM). The samples are exposed by the SEM with x500, x5000, x10000 and x20000 with 20 KV as an excitation voltage.

Density of the synthesized material was obtained by hydrostatic weighing method and it is observed that the materials synthesized were having more than 98% dense as compared to its theoretical density. The dielectric measurements were carried out using a Precessional Impedance Analyzer (Wayne-Kerr 6500B) in the temperature range from room temperature to 523 K. The temperature variation is made by laboratory designed vertical tubular furnace. The complex impedance variation and its temperature dependence are also studied with the same setup. The electrical resistivity is measured using the Ohm’s law. The nanocurrent meter (Keithly) was used to record the current by changing the temperature of sample. Voltage source used to record the current is kept constant at 10 volt.

III. Result and Discussion

A) XRD: XRD results of all the synthesized samples were compared with the standard JCPD data (JCPDF No. 33-0165). From this comparison it can be concluded that the bulk powders of lanthanum doped barium neodymium titanate are of orthorhombic in nature. Most of the prominent peaks are indexed and they show good agreement with the reported data. As the doping of

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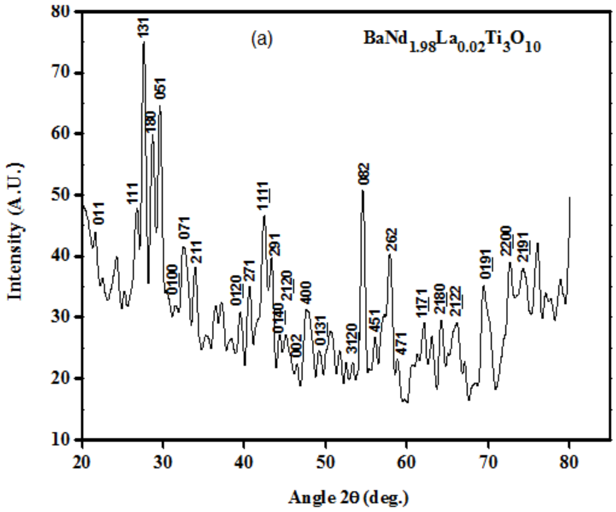
lanthanum is very small which does not give any additional peak in the X-ray diffraction pattern. The Fig.1 shown below gives the X-ray diffraction pattern of the samples for x= 0.02 and x=0.04.



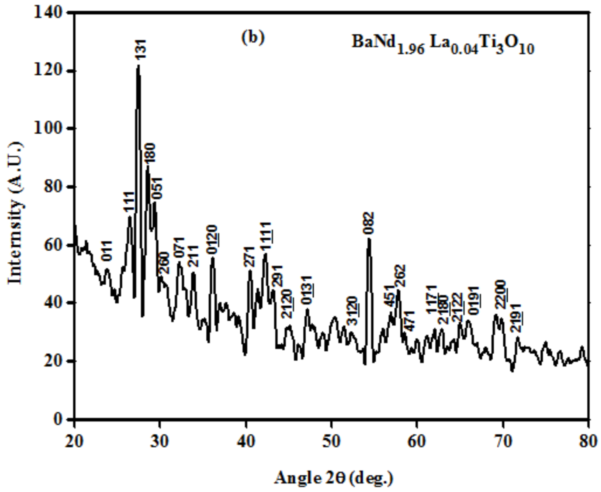
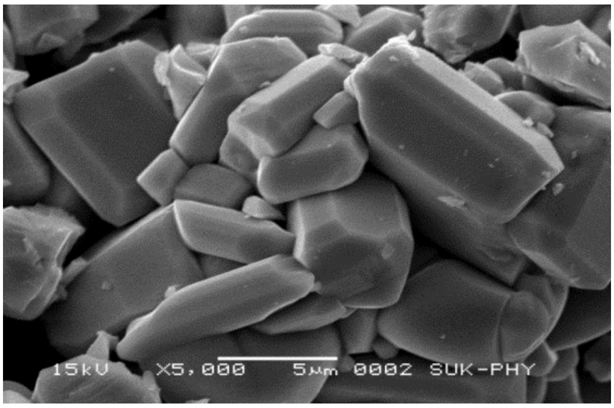
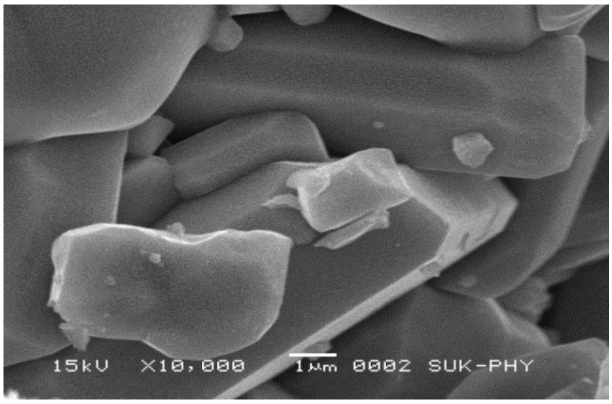


Fig.1. XRD patterns of (a) $BaNd_{1.98}$ $La_{0.02}$ Ti_3 O_{10} and (b)$BaNd_{1.96}$ $La_{0.04}$ Ti_3 $O_{10.}$

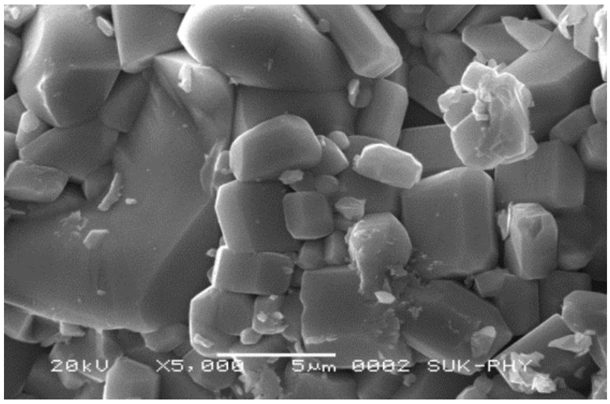
B) SEM: As the scanning electron microscopy reveals the information of surface morphology, it gives the confirmation of dense material. The grain size observed from the SEM micrographs varies from 4-5 µm to 400 nm. Average grain size is about 2µm. The microstructure observed for these ceramic materials are confirmation of single phase material synthesis. Fig.2 gives the SEM micrographs 0f $BaNd_{1.98}La_{0.02}Ti_3O_{10}$ and $BaNd_{1.96}La_{0.04}Ti_3O_{10.}$



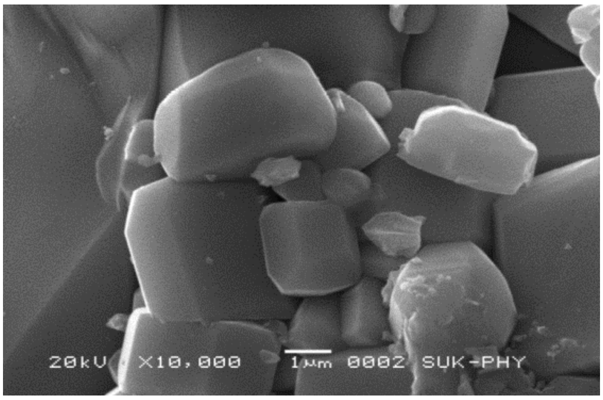
(a)



(b)



(c)



(d)

Fig.2. SEM micrographs of (a and b) $BaNd_{1.98}La_{0.02}Ti_3O_{10}$ (c and d) $BaNd_{1.96}$ $La_{0.04}$ $Ti_3O_{10.}$

C) Dielectric constant: The temperature dependence of dielectric constant of the synthesized samples is shown in Fig.3. It was found that the dielectric constant of all the samples did not significantly depend on the temperature variation [1]. However beyond the temperature range of 450 K the dielectric constant slightly increases. The temperature variation was made from room temperature to 523 K. The table-I shows the dielectric constant at room temperature and it is observed that the room temperature dielectric constant is more than 100. However the earlier report shows that the dielectric constant is less than 100. The level of substitution gives an appreciable rise in the room temperature dielectric constant, which leads to nearly 500 for x=0.08. This value of doping concentration and the dielectric constant suggest that one may tailor the doping concentration still further to achieve the larger dielectric constant by keeping the low dielectric loss. This is an optimistic result towards its microwave dielectric constants. The values ofloss factor are also promising and it remains below unity. The variation of loss factor with temperature gives goodcoordination with the dielectric constant. Fig.3 shows the loss factor variation with temperature.

D) Complex Impedance Measurement: The electrical properties of electronic ceramics are a result of different contributions of various components and processes present in the materials. In general the overall dielectric properties arise due to intra-grain, inter-grain and electrode processes. The motion of charges could take place in any fashion viz. charge displacement, dipole reorientation, space charges formation etc. [10] in order to achieve reproducibility and to have control over the properties, these so called grain, grain-boundary and electrode contributions must be separated out.

For separating out these contributions, the method of complex impedance analysis [10] has emerged as very powerful tool. In this method the imaginary part Z" of the total complex impedance (Z"=Z'-jz") 0f the sample is plotted as function of the corresponding real part, Z' at different frequencies. This plot shows different features depending upon various relative contributions. For example for an electronic ceramic having well separated relaxation times for grain-grain boundary and electrode contributions, three distinct semicircular arcs are obtained and for two contributions, two arcs are obtained [10]-[13]. The analysis is carried out further by representing and visualizing these contributions processes by simple components are determined by finding the intercepts on the Z axis [10] or by using the method of complex non-linear squares [10]-[14]. A general problem encountered here is the choice of a simple circuit that could represent the experimental data best. Before receiving at any particular systematic to fit the complex impedance curves, we shall define a few preliminary concepts and parameters.

The ac response of material can be expressed in any of four basic formalisms [10].These are conventionally expressed as complex impedance (Y*), complex permittivity (E*) and complex modulus M*= (E*) – 1. The interrelationship among these can be explained with the help of lossy dielectric, which can be expressed as a RC circuit. The four functions broadly called emmittance functions [10] are given by

$$Z^* = Z' - jZ''$$

$$Y^* = (Z^*) - 1 = Y' + jY''$$

$$E^* = (j\omega C_O Z^*) - 1 = E' - jE''$$

$$M^* = (E^*) - 1 + j\omega C_O Z^* = M' + jM''$$

Where ω is the frequency of the ac excitation and Co the capacitance of the empty cell used to house the material and it depends on the geometry. The study of E* as a function of frequency has been widely used since the pioneering work of Cole and Cole [15] and it is mostly suited for dielectric materials having very low or vanishing conductivity [10]. Being a very low loss as observed in all the samples (>1) and very high resistivity (<20 MΩ), the above method of analyzing the complex impedance is best suitable tool. The complex impedance curves are observed to be composed of two hemispheres indicating separate contribution for the grain and grain boundaries. These contributions of grain and grain boundaries are not properly resolved at room temperature.

To resolve these contributions and to arrive at any systematic variation of the grain and grain boundary contributions, the complex impedance studies are extended over the temperature. The complex impedance curves are observed to be well resolved as the temperature is increased and shown in Fig. 4.

IV. Conclusion

The discussion above indicates that the synthesized material is a good candidate for microwave dielectric resonator; however the detailed curve fitting of Cole-Cole plot and measurement at microwave region is further necessary requirement.

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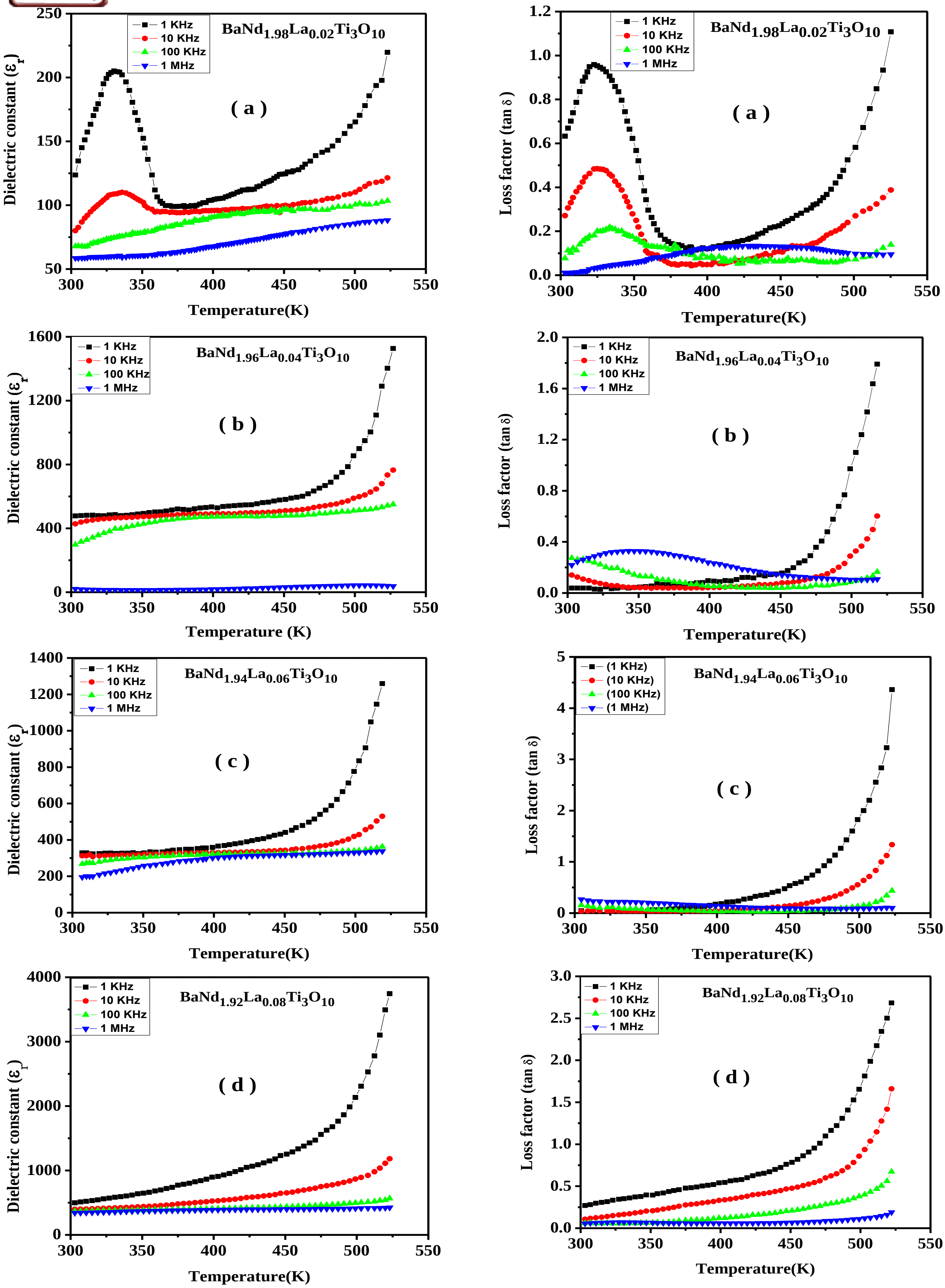

Fig.3. Variation of Dielectric constant (ε_r) and Loss factor(tanδ) with Temperature for (a) $BaNd_{1.98}La_{0.02}Ti_3O_{10}$ (b) $BaNd_{1.96}La_{0.04}Ti_3O_{10}$ (c) $BaNd_{1.94}La_{0.06}Ti_3O_{10}$ (d) $BaNd_{1.92}La_{0.08}Ti_3O_{10}$.

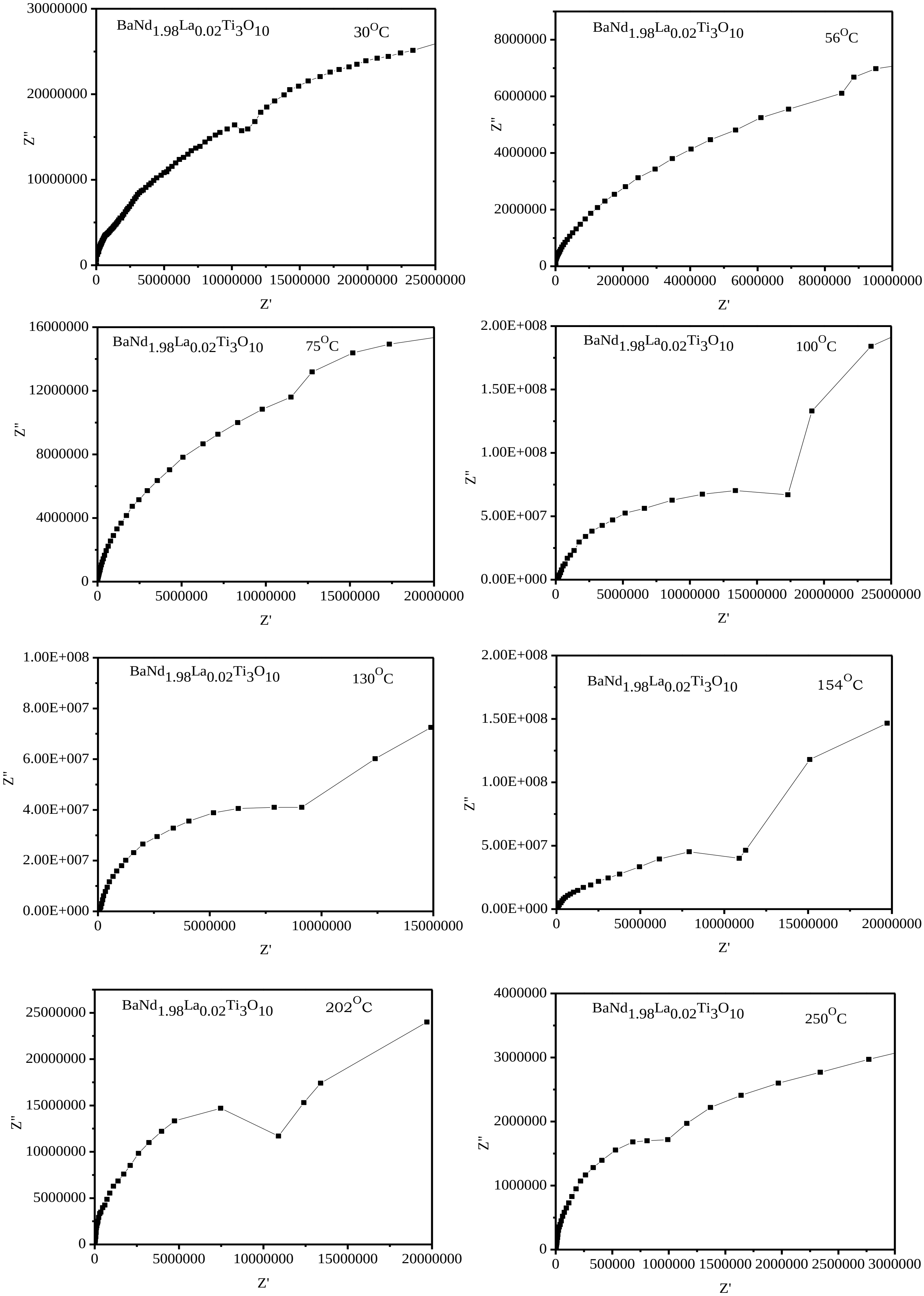

Fig.4. Temperature dependence of grain and grain boundary contribution of complex Impedance of $BaNd_{1.98}La_{0.02}Ti_3O_{10}$