Dielectric properties of nano crystalline LnTiNbO$_6$ (Ln = Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb) ceramics

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Abstract. Nano ceramics are potential candidates for various technological applications. Nano sized LnTiNbO$_6$ ceramics are prepared using solution combustion technique. The properties of the nano ceramics are compared with that of micro ceramics. XRD shows that nano crystalline LnTiNbO$_6$ (Ln= Ce, Pr, Nd, Sm) have aeschynite orthorhombic structure and Ln= Gd, Dy, Er, Yb have euxenite orthorhombic structure. The structure is confirmed by FTIR. From the TEM study, it is clear that polycrystalline powder is nano sized. The sintering temperature and sintering time of nano ceramics get lowered as compared to micro ceramics. The SEM image shows the surface morphology of the sintered sample. The variations of dielectric constant ($\varepsilon_r$), conductance (G) and loss factor (tan $\delta$) of the samples are studied in the radio frequency range. The nano ceramics show enhanced dielectric properties than that of micro ceramics.

1. Introduction
Synthesis of nano material is one of the major challenges in material producing technology. Nano materials are the suitable for various technological applications, because they exhibit enhanced properties than bulk materials. Nano crystalline materials have better sinterability, high surface to volume ratio, superior phase homogeneity, greater chemical activity, etc. For the communication and satellite broadcasting, microwave dielectric resonators (DR) are essential component. Nano ceramics are potential candidate for developing DR’s due to their improved electrical and dielectric properties than micro ceramics. Sebastian et al [1] reported microwave dielectric properties of LnTiNbO$_6$ micro ceramics. Here we reports the enhanced properties of nano sized LnTiNbO$_6$ ceramics.

2. Experimental
LnTiNbO$_6$ (Ln= Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb) is prepared by solution combustion technique [2] using the corresponding metal nitrate (oxidizing agent) and suitable fuel (reducing agent) [3]. Calculations are based on the principles used in propellant chemistry, keeping fuel to oxidant ratio unity in order to produce maximum energy. In this synthesis, high-purity Niobium pentachloride, Titanium isopropoxide and the respective rare earth oxides are used as cation sources and oxidant agents, and urea is used as fuel reagent. Citric acid is used as complexing agent to get precursor complex. Stoichiometric amount of oxidizing agents and reducing agent in a minimum volume of deionized water to obtain transparent aqueous solutions in a glass beaker is heated using a hot plate at 250 °C to forms a viscous gel. The gel thus formed undergoes dehydration on further heating and self-ignites with the evolution of huge quantity of gases. Hence the residual ash that is formed after combustion has a fluffy nature. This ash is further heated up to 600 °C to get the pure phase nano powder. The prepared powder is mixed with one drop of 1 wt% solution of polyvinyl alcohol and
uniaxially pressed at room temperature for 1 min at the pressure 190 MPa. The sintering of the pressed pellet is done with the help of furnace.

3. Characterization

The XRD (Model: Philips PW1710 diffractometer) is used to determine the formation of the desired phase, for the powder. The particle size of the prepared powders is also analyzed by the TEM (Model: TM-300, Philips). The Fourier Transform infrared (FTIR) spectra of the samples are recorded in the range 400-4000 cm\(^{-1}\) on a Thermo-Nicolet Avatar 370 Fourier Transform Infrared Spectrometer using KBr pellet method. The density of the sintered pellets are measured. The microstructures of the sintered samples are analyzed by SEM (Mode: JEOL JSM-5800) taken on the polished surfaces. The dielectric constant (\(\varepsilon_r\)), ac conductance (G) and the tangent loss (\(\tan \delta\)) measurements are done at radio frequency range on the polished pellet samples as a function of frequency using LCR meter (HIOKI, model 3532, Japan). Here after we denote LnTiNbO\(_6\) (Ln= Ce, Pr, Nd, Sm, Gd, Dy, Er and Yb) as CTN, PTN, NTN, STN, GTN, DTN, ETN and YbTN respectively.

4. Result and discussions

The XRD patterns of nano LnTiNbO\(_6\) ceramics are shown in figure 1. The patterns are indexed according to the ICDD files (File nos. 15-0864, 20-1361, 52-1130, 27-0221, 20-1434 and 20-1216). The XRD patterns of Ln= Ce, Pr, Nd, Sm are similar and have aestchynite orthorhombic structure with space group Pnma and that of Ln= Gd, Dy, Er, Yb have euxenite orthorhombic structure with space group Pbcn. The XRD pattern is closely agreement with the result that reported by sebastain et al [1]. The peaks are broad as compared to micro ceramics, which indicates that the particle size gets lowed. This is due to the nano size and micro strain in the crystallites. The particle size calculated using scherrer formula [4] from the main peak of XRD patterns are tabulated in the table 1.

![Figure 1. XRD patterns of the nano ceramics LnTiNbO\(_6\).](image)

In FTIR spectra, very strong and broad absorption bands ranging from 400 to 800 cm\(^{-1}\) are observed in figure 2. In figure 2(a) the symmetric stretching vibrations of Nb/TiO\(_6\) octahedra give rise to \(\nu_1\)A\(_{1g}\) mode is observed at 814 cm\(^{-1}\). The \(\nu_2\)E\(_g\) mode of Ln= Ce, Pr, Nd, Sm is observed at 661 cm\(^{-1}\) and Ln= Gd, Dy, Er, Yb at 655 cm\(^{-1}\) confirm that figure 2(a) has the aestchynite and figure 2(b) has euxenite structure. In the range of 3000–3500 cm\(^{-1}\) a band corresponding to O-H bond [5].This is due to the contact of sample with atmospheric oxygen and water vapour.

![Figure 2. FTIR spectra of the nano ceramics LnTiNbO\(_6\).](image)
The particle size is confirmed from TEM image of NTN ceramic is shown in figure 3. The average particle diameters lay in the range of 23 nm for NTN nano powder, which is in close agreement with the crystallite size obtained from XRD. The corresponding selected area electron diffraction (SAED) pattern of the sample NTN showed more “spotty” patterns of an assembly of nano crystallites shown as inset. This indicates the polycrystalline nature of the crystallite.

Figure 3. TEM image and SAED pattern of NTN ceramic

Due to fine nature of Nano-sized ceramics, it has high surface area and surface energy which leads to its excellent sintering characteristics. They are sintered below 1300 °C only for 2 hrs which is relatively shorter time and temperature as compared to the conventional micro ceramics. Sebastain et al [1] have reported that micro sized LnTiNbO$_6$ ceramics sintered around 1370 °C for 4 hrs. The sizes of the particles also affect the duration and temperature of sintering. Percentages of densification obtained for all samples are higher than micro ceramics. Table 1 compares the sintering temperature and density attained.

The scanning electron micrographs (SEM) of the sintered samples of STN and GTN are shown in figure 4(a) and 4(b). STN has elongated uniform grains and GTN has equiaxed grains and are appeared to be size less than 4 µm. It is evident from the SEM picture that the samples have achieved high densification with minimum porosity.

Figure 4. Surface morphology of (a) STN and (b) GTN

Figure 5 shows variation of $\varepsilon_r$, G and tan $\delta$ with frequency range 100 Hz to 5 MHz at room temperature. Dielectric constant decreases initially with the increase in frequency and it reached a constant value at higher frequency range are given in the table 1. This is due to Maxwell-Wagner interfacial polarization [6]. The decrease in dielectric constant is due to the delay in polarization with the application of the electric field because of inertia. Dielectric constant of group I decreases from Ce to Sm depending on its ionic radii and that of group II get low values.

Variation of loss shows that it reached a minimum value and almost constant as frequency increases for all ceramics in accordance with Koops phenomenological model [7]. It means that, material has low loss in radio frequency range because of the relaxation frequency of the sample is out of this frequency range. Therefore, dissipation of electrical energy is low at this range. Loss-factor can be attributed to the presence of impurities like voids in the material and to the electrode effects.
Figure 5. Variation of (a) $\varepsilon_r$ (b) $G$ (c) tan $\delta$ with radio frequency (I. aeschynite II. euxinite structure)

Table 1. Particle size and dielectric properties of LnTiNbO$_6$ nano ceramics

| Ceramic | Particle size (nm) | Sintering temperature ($^\circ$C) | Density attained (g/cm$^3$) | $\varepsilon_r$ |
|---------|--------------------|-----------------------------------|-----------------------------|----------------|
| CTN     | 25                 | 1200                              | 5.4                         | 55             |
| PTN     | 27                 | 1230                              | 5.3                         | 53             |
| NTN     | 23                 | 1260                              | 5.7                         | 51             |
| STN     | 32                 | 1250                              | 5.6                         | 45             |
| GTN     | 22                 | 1290                              | 5.7                         | 25             |
| DTN     | 34                 | 1290                              | 5.9                         | 23             |
| ETN     | 28                 | 1280                              | 5.8                         | 15             |
| YbTN    | 29                 | 1280                              | 6.1                         | 13             |

And at low frequency range the variation of $G$ is very less and almost constant up to 1MHz, and then increases according to the increase in frequency. Thus this material can be useful for capacitive applications in MW communication systems.

5. Conclusion
The Nano LnTiNbO$_6$ ceramics have been prepared using solution combustion technique. The particle sizes calculated from XRD are in the range of 20-35 nm which is agreement with TEM. XRD and FTIR studies shows that ceramics (Ln= Ce, Pr, Nd, Sm) possess aeschynite orthorhombic structure and ceramic (Ln= Gd, Dy, Er, Yb) possess euxenite orthorhombic structure. SEM image clarifies the high densification of nano ceramics. Dielectric constant is in the range 30 to 35. The variation of ac conductivity, dielectric loss gave the evidence that samples can be used as DR application in communication systems. From this study it can be concluded that solution combustion is a potential technique for the preparation of highly sinter-active, phase pure, nano powders of lanthanide oxide ceramics. And also the nano ceramics show enhanced dielectric properties than that of micro ceramics prepared by solid state ceramic route.
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