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Behaviour of $LaAlO_3$+$LnTiTaO_6$ (Ln= Ce, Pr or Nd) dielectric ceramic mixtures

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Abstract. **The 0·1$LaAlO_3$+0·9$LnTiTaO_6$ (Ln= Ce, Pr or Nd) ceramics are prepared through solid state ceramic route. The structure of the materials is studied using X-ray diffraction analysis. The microstructure is analysed using scanning electron microscopy. The dielectric properties in the radio as well as in the microwave frequencies are measured and discussed. The photoluminescence of a representative sample is also analysed. The dielectric constant (ε_r) and temperature coefficient of resonant frequency (τ_f) are tailored without appreciable change in the quality factor. The measured values of ε_r and τ_f are compared with the corresponding predicted values. These mixtures can be made useful in optical and microwave communication.**

Keywords. **Mixture; microwave; dielectric; microstructure; resonance; optical.**

1. Introduction

The microwave dielectric properties of ceramics can be conveniently altered for various applications by forming mixture phases of materials having different dielectric constants (ε_r) and opposite temperature coefficient of resonant frequency (τ_f). Low loss materials with high ε_r and low τ_f are useful for the fabrication of devices in microwave communication (Sebastian 2008). Ceramic poly-crystals are now gaining attention in the field of optoelectronics also (Solomon 2010).

The ABO_3 (A and B are larger and smaller metal ions, respectively) simple perovskite is an important group of materials used in the electronic industry. The tolerance factor and cell parameter are two important parameters related to the symmetry of perovskites that significantly affect the dielectric properties. According to Cho *et al* (1999), $LnAlO_3$ with Ln =La, Pr and Nd have a rhombohedral symmetry and those with Ln= Sm, Dy, Er, Ho and Y have an orthorhombic symmetry. The microwave dielectric properties of $LnAlO_3$ polycrystals (Hsu and Huang 2001; Huang and Chen 2003) and single crystals (Zuccaro *et al* 1997; Mc *et al* 2001; Shimada *et al* 2005) were also studied. Among them, $LaAlO_3$ has very low dielectric loss and is a potential candidate as substrate for YBCO superconductors. The phase pure existence of $LnTiTaO_6$ (where Ln is a lanthanide) ceramics was first established by Kazantsev *et al* (1974). According to him, $CeTiTaO_6$, $PrTiTaO_6$ and $NdTiTaO_6$ ceramics possess orthorhombic aeschynite symmetry with space group, *Pnma*. The crystal structure and microwave dielectric properties (Holcombe *et al* 1974; Maeda *et al* 1987; Surendran *et al* 2002) of these materials were reported later. The doping effect of ZnO (Kumar *et al* 2007), WO_3 and MoO_3 (Kumar *et al* 2009) in $LnTiTaO_6$ ceramics were also reported. Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation. PL spectrum provides the transition energies, which can be used to determine electronic energy levels and intensity, which provides information on the quality of the surfaces and interfaces and gives a measure of relative rates of radiative and non-radiative recombination. Inorganic luminescent crystalline materials are increasingly important in the development of smaller, faster and more efficient electronic and optoelectronic devices (Qi *et al* 1996). Jacob *et al* (2007) reported the photoluminescence and low frequency dielectric properties of $LnTiTaO_6$ (Ln= Ce, Pr, Sm) ceramics. Recently, Solomon *et al* (2010) and Dhwajam *et al* (2011) reported microwave dielectric and optical properties, respectively of $PrTiTaO_6$–$YTiNbO_6$ ceramic composites. They found that ε_r and τ_f values decrease systematically with the weight percentage addition of $YTiNbO_6$ ceramics (Solomon 2010) as well as both ε_r and loss factor values decrease with radio frequencies whereas conductance values increase. UV bandgap energy was estimated as 2·85 eV and transitions causing photoluminescent properties were also identified (Dhwajam *et al* 2011). For $CeTiTaO_6$, $PrTiTaO_6$ and $NdTiTaO_6$ ceramics, the density increases with increase in ionic radii of the lanthanide ion (Surendran *et al* 2002). As they possess high ε_r in the $LnTiTaO_6$ series (Surendran *et al* 2002), an attempt has been made to fabricate a composite between them and $LaAlO_3$ having low dielectric loss. This paper reports the preparation, characterization and dielectric and optical properties of

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0.1 $LaAlO_3$+0.9 $LnTiTaO_6$ (Ln= Ce, Pr, Nd) microwave ceramic mixtures.

2. Experimental

$LaAlO_3$ and $LnTiTaO_6$ (Ln= Ce, Pr, Nd) were prepared separately through the solid state ceramic route using high purity (99·9%) oxides weighed in stoichiometric ratios. They were then mixed, ball milled and calcined. The calcination temperature of $LaAlO_3$ was 1350 °C and that of $LnTiTaO_6$ was 1200 °C. The calcined powder was weighed in the 1:9 ratio, mixed and then ground well for 2 h with acetone as the wetting medium. The specimen was again dried well and two drops of 5 wt% polyvinyl alcohol were added as a binder and again ground well and dried. The powder was then pressed at a pressure of 150 MPa using hydraulic press in the form of cylindrical pellets. The pellets were then sintered in a controlled heating schedule of 4 °C per min up to 600 °C and soaked for 1 h to expel out the binder completely, without leaving behind any voids in the pellet. This was followed by heating the samples at a rate of 5 °C per min up to the sintering temperature. The sintering temperature of $LaAlO_3$ and $LnTiTaO_6$ ceramics are about 1650 °C and 1500 °C, respectively (Cho *et al* 1999; Surendran *et al* 2002) while that of the mixtures is 1450 °C for 4 h. The sintered density of the well polished sample was then measured using Archimedes method. The sintered pellets were powdered and used for X-ray diffraction (XRD) (Philips Expert Pro) studies using CuK_α radiation. Polished samples, thermally etched at 1400 °C for 30 min, were used for scanning electron microscopy (SEM) (JEOL JSM 5610 LV) studies. The dielectric constant and quality factor of the samples were measured in the microwave frequency range using cavity resonator method with network analyser (Agilent 8753 ET). For this the specimen was placed on a quartz cylinder placed at the centre of a cylindrical invar cavity whose diameter is 3–4 times greater than the sample. The microwave signal was coupled to the specimen through loop probes and $TE_{01\delta}$ mode of resonance whose quality factor is intimately related to the dielectric loss was identified. The temperature coefficient of resonant frequency (τ_f) was also measured over a range of temperature, 30–70 °C, with the heating set up attached to the computer interfaced network analyser. For radio frequency dielectric studies, thin pellet was made in the form of a disc capacitor with the specimen as the dielectric medium. The capacitance and conductance of the representative sample were measured using an LCR meter (Hioki-3532-50) within the frequency range 1 kHz to 5 MHz. The absorption spectrum was recorded using Double beam UV-Vis spectrometer Jasco-D550 and the photoluminescence spectrum was recorded using Flurolog®-3 Spectroflurometer.

3. Results and discussion

XRD patterns of 0.1 $LaAlO_3$+0.9 $CeTiTaO_6$, 0.1 $LaAlO_3$+0.9 $PrTiTaO_6$ and 0.1 $LaAlO_3$+0.9$NdTiTaO_6$ (here onwards denoted as LCTT, LPTT and LNTT, respectively) are given in figure 1. In all the patterns, prominent phase is orthorhombic aeschynite with *Pnma* symmetry. Weak reflections other than that of this symmetry can also be observed. The prominent phase is indexed on the basis of the ICDD file 20-1361 orthorhombic $PrTiNbO_6$ and the other reflections (marked as '∗') are indexed on the basis of the ICDD file

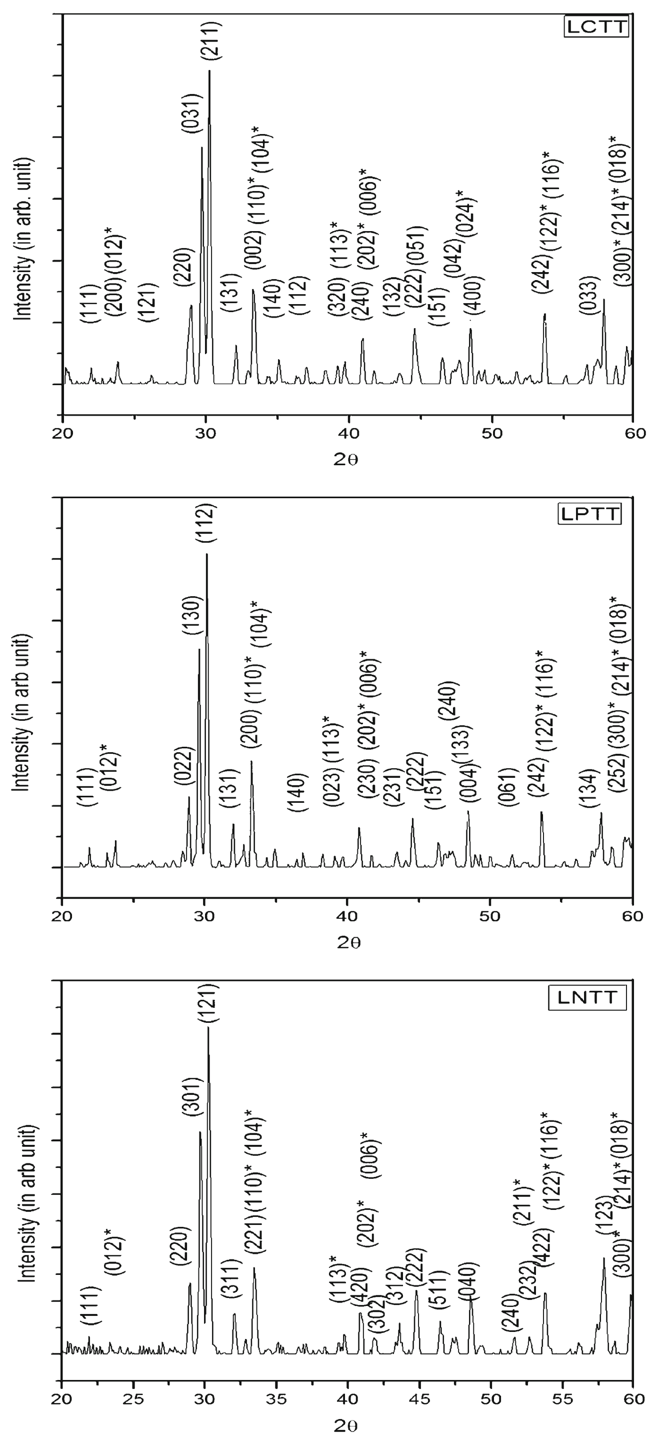

Figure 1. XRD patterns of LCTT, LPTT and LNTT ceramics.

82-0478 of $LaAlO_3$. It can be concluded from the patterns that there is coexistence of orthorhombic $LnTiTaO_6$ and rhombohedral $LaAlO_3$ phases, though the latter is present in trivial quantity.

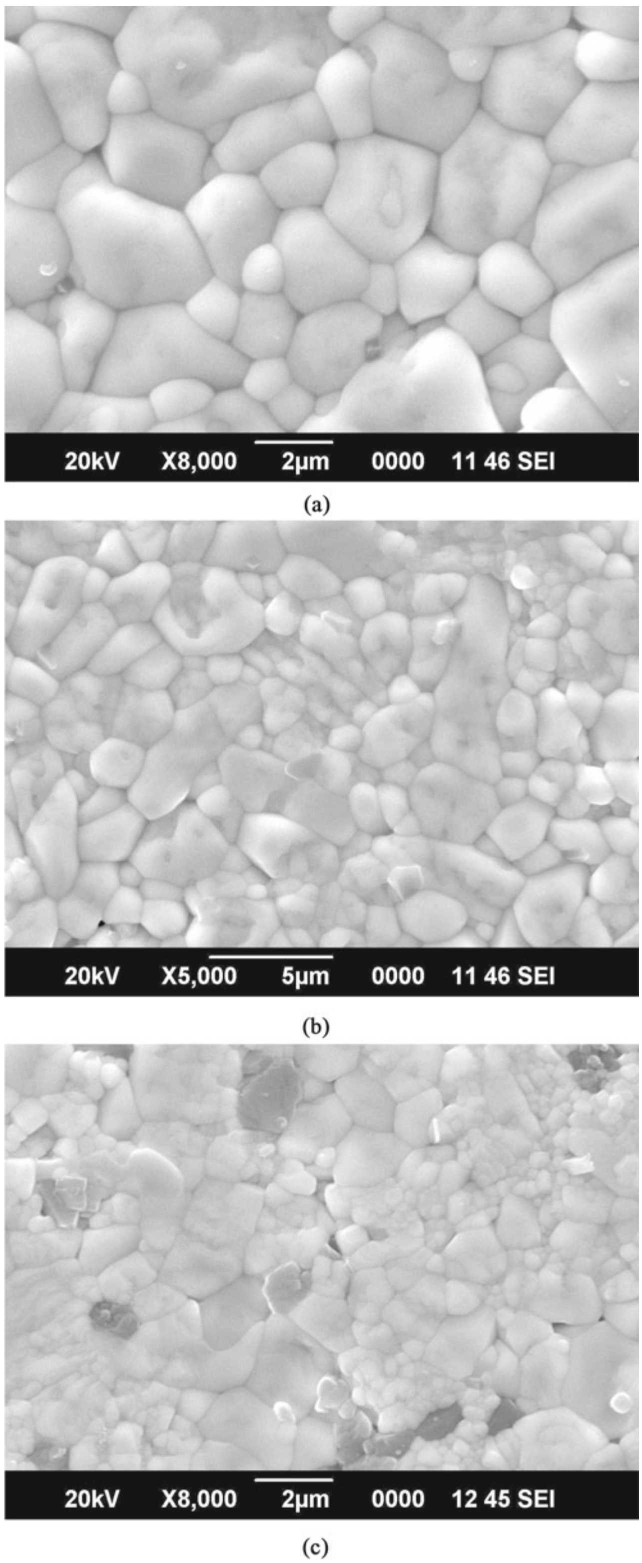

Figure 2. SEM images of LCTT, LPTT and LNTT ceramics.

Table 1. Microwave dielectric properties of LCTT, LPTT and LNTT ceramics.

Compound	Density (g/cc)	Resonant frequency (GHz)	ε_r	τ_f (ppm/K)	$Q_u x f$ (GHz)
LCTT	6·69	4·760	37·1	25·8	15650
LPTT	6·87	4·890	35·7	24·2	12300
LNTT	6·90	5·148	31·3	20·5	19820

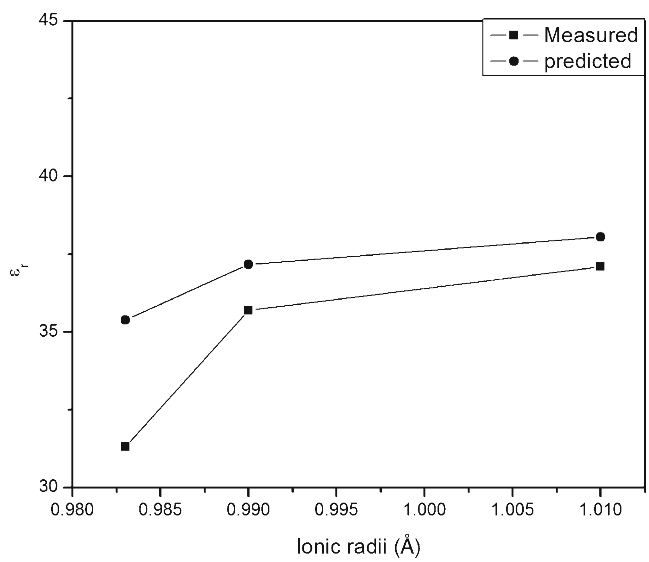

Figure 3. Variation of measured and predicted values of ε_r of mixtures with ionic radii of Ce, Pr and Nd.

SEM images of the sintered and thermally etched pellets are given in figure 2. It is clear from the images that the samples are well sintered with minimum porosity. Most of the grains are flatter and brighter and will be that of the prominent orthorhombic phase. The average sizes of these grains are about 1·6 μm, 1·2 μm and 0·9 μm for LCTT, LPTT and LNTT, respectively. Few darker and smaller grains can also be observed in the images. These grains with an average size $<$0·1 μm may be that of $LaAlO_3$.

The density and measured microwave dielectric properties of the mixtures are given in table 1. For $LnTiTaO_6$ ceramics the density increases with the increase in ionic radii of the lanthanide ion (Surendran *et al* 2002). Similar variation can be observed in the case of mixtures also. They have more than 92% of the average theoretical density of the constituents.

The ε_r of a mixture can be predicted using mixture rule models (Jayasundere and Smith 1993; Poon and Shin 2004) given by the equation

$$\varepsilon_c = \varepsilon_1 \frac{V_1 + \varepsilon_2 V_2 \left[3\varepsilon_1/(\varepsilon_2 + 2\varepsilon_1)\right]\left[1 + 3V_2(\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + 2\varepsilon_1)\right]}{V_1 + V_2 \left[3\varepsilon_1/(\varepsilon_2 + 2\varepsilon_1)\right]\left[1 + 3V_2(\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + 2\varepsilon_1)\right]}, \quad (1)$$

where V_1 and V_2 and ε_1 and ε_2 are the volume fraction and permittivity of phases 1 and 2, respectively. The ratio of wt% of $LaAlO_3$ and its density is divided by the sum of the ratios of wt% of component compounds and their densities to obtain V_1. The same procedure is repeated for V_2 with wt% of $LnTiTaO_6$. This rule considers the interactive effects between the fields of neighbouring spheres. The pure $LnTiTaO_6$ (Ln= Ce, Pr, Nd) ceramics have ε_r values of 40, 39 and 37, respectively and pure $LaAlO_3$ has $\varepsilon_r = 23$. These values of ε_r are substituted in (1) to get the predicted values of ε_r. Figure 3 shows variation of measured and predicted values of ε_r with the ionic radii of Ce, Pr and Nd.

The τ_f of mixtures can also be predicted using the equation,

$$t_{fc} = V_1 t_{f1} + V_2 t_{f2}, \tag{2}$$

where τ_{f1} and τ_{f2} are the temperature coefficients of resonant frequencies of phases 1 and 2, respectively (Fukuda *et al* 1993; Kim *et al* 2000). The τ_f of $LnTiTaO_6$ (Ln= Ce, Pr, Nd) ceramics are +41, +33 and +30 ppm/K, respectively and that of $LaAlO_3$ is −44 ppm/K. The values of predicted τ_f of mixtures calculated using (2) are compared with the measured values in figure 4. From figures 3 and 4 it is evident that the measured values of ε_r and τ_f decrease with the increase in ionic radii and are in good agreement with the predicted values. By 10% addition of $LaAlO_3$, ε_r and τ_f of the $LnTiTaO_6$ ceramics decreased without much variation in the quality factor. Hence by changing the percentage of the mixture compositions in these systems, materials with any desired ε_r and τ_f can be developed as per the requirements in microwave communication.

The variation in ε_r and conductance of the representative sample (LNTT) with respect to logarithm of frequency (log f), in the radio frequency region, is given in figure 5. The ε_r decreases slightly with the increase in log f. This small

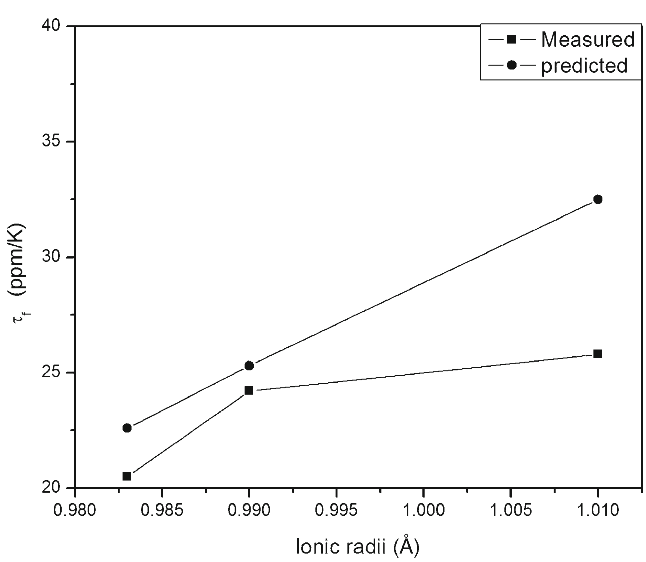

Figure 4. Variation of measured and predicted values of τ_f of mixtures with ionic radii of Ce, Pr and Nd.

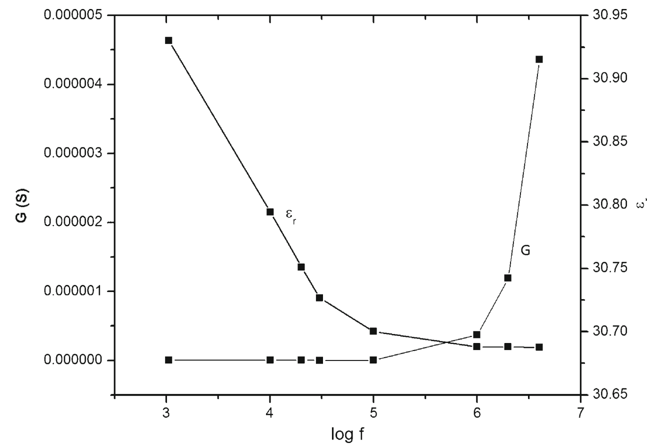

Figure 5. Variation in ε_r and conductance of LNTT ceramic with respect to logarithm of frequency (log f), in the radio frequency region.

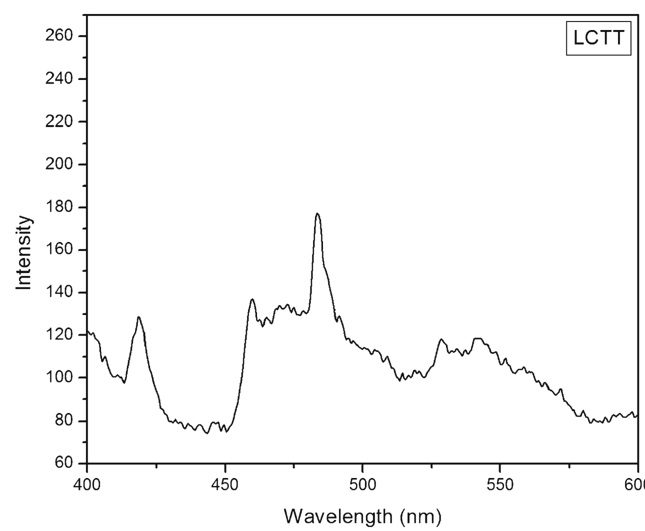

Figure 6. Photoluminescence spectrum of LCTT ceramic.

variation confirms the highly sintered nature of the ceramic samples. The variation of conductance is complimentary to the variation in ε_r.

As per the report (Jacob *et al* 2007), the $LnTiTaO_6$ ceramics have emission lines in the visible region. Figure 6 gives photoluminescence spectrum of LCTT when excited by radiation of wavelength, 350 nm. The samples have intense emission lines in the visible region. The transitions of the constituent elements of the compounds causing emission are identified on the basis of the data book by Payling and Larkins (2000). The emission line at 419 nm can be assigned to ${}^4P_{0\cdot5} - {}^6D^0_{0\cdot5}$ and ${}^2D_{2\cdot5} - {}^0A^0_{1\cdot5}$ transitions of Ta and La, respectively. The peak around 461 nm may be due to the transitions ${}^2G_{3\cdot5} - {}^0A^0_{2\cdot5}$ and ${}^1G_{3\cdot5} - {}^1G^0_4$ of La and Ce, respectively. The very intense peak at 483·5 nm can be assigned to the transitions ${}^6S_{2\cdot5} - {}^6D^0_{1\cdot5}$ and ${}^2P_{1\cdot5} - {}^4D^0_{1\cdot5}$ of Ta and La, respectively.

4. Conclusions

The $0{\cdot}1LaAlO_3+0{\cdot}9LnTiTaO_6$ (Ln= Ce, Pr, Nd) mixtures are prepared through the solid state ceramic route. The characterization is done using X-ray diffraction analysis and scanning electron microscopy. $LaAlO_3$ has rhombohedral symmetry while $LnTiTaO_6$ ceramics have orthorhombic aeschynite symmetry. The composite has most of the reflections similar to that of the orthorhombic structure. The dielectric properties in the microwave frequencies are measured and are comparable with the predicted values. The ε_r is almost constant in the measured radio frequency region. The conductance varies between 5×10^{-7} to 5×10^{-6} S. The photoluminescence property and the corresponding transitions are also analysed. Thermal stability is achieved by the addition of $LaAlO_3$ without much variation in other microwave dielectric properties. Hence it is possible to develop materials with any desired ε_r and τ_f by changing the percentage of the mixture compositions in these systems for various applications in the field of communication. Further work using other lanthanide aluminates is in progress.

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