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Characterization and properties of lanthanide based titanium tantalate and aluminate electronic ceramic mixtures

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Abstract

The $0.9LnTiTaO_6 + 0.1Ln'AlO_3$ (Ln = Ce, Pr and Nd and Ln′ = Pr, Nd and Sm) ceramic mixtures are prepared through the solid state ceramic route. The materials are characterized using X-ray diffraction analysis, scanning electron microscopy and energy dispersive spectrometry. The dielectric properties in the radio as well as in the microwave frequencies are measured. The photoluminescence property of a representative sample is also analyzed. The materials have dielectric constant in the range 35.5–28.6, the temperature coefficient of resonant frequency in the range +35 ppm/°C to +14.1 ppm/°C and high quality factor. The measured values of ε_r and τ_f are compared with the corresponding predicted values calculated using mixture rules. Most of the compositions are useful in the field of optoelectronics and microwave communication.

Keywords: C. Dielectric properties; C. Optical properties; Ceramics; X-ray diffraction

1. Introduction

Mixture formation is one of the systematic methods to tailor the microwave dielectric properties of ceramics for various applications. This is possible if the two materials used for the mixture do not react with each other [1].

The optimum conditions for the formation of $LnTiTaO_6$ (where Ln is a lanthanide) ceramics were established by Kazantsev et al. [2]. Later Surendran et al. have reported the structure and the microwave dielectric properties of these ceramics [3]. According to the above reports the $LnTiTaO_6$ ceramics with Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy crystallize in the orthorhombic aeschynite symmetry with P*nma* space group and those with Ln = Ho, Er, Yb and Y crystallize in the orthorhombic euxenite symmetry with P*bcn* space group. The aeschynite group has high dielectric constant (ε_r) and positive temperature coefficient of resonant frequency (τ_f) while the euxenite group has low ε_r and negative τ_f.

Cho et al. [4] prepared lanthanide aluminate, $LnAlO_3$, with Ln = La, Pr, and Nd of rhombohedral symmetry and those with Ln = Sm, By, Er, Ho, and Y of orthorhombic symmetry. The microwave dielectric properties of pure and doped $LnAlO_3$ polycrystals [5,6] and single crystals [7–9] were also studied. The mixture behavior of $LaAlO_3$–$SrTiO_3$ [10] and $CaTiO_3$–$NdAlO_3$ [11] was also reported. Recently, Solomon et al. [12] and Dhwajam et al. [13] have reported the microwave dielectric and optical properties of lanthanide titanium tantalate and niobate ceramic mixtures. The $PrAlO_3$, $NdAlO_3$ and $SmAlO_3$ compositions have low ε_r and negative τ_f. Hence it is possible to develop compositions with good thermal stability and optimum ε_r by forming mixtures of lanthanide based titanium tantalates and aluminates.

An attempt is made here to check whether there is possibility for the formation of mixtures of the above mentioned systems to develop suitable specimens for practical applications. This paper reports the preparation, characterization and properties of $0.9LnTiTaO_6 + 0.1Ln'AlO_3$ (Ln = Ce, Pr and Nd and Ln′ = Pr, Nd and Sm) microwave ceramic mixtures.

2. Experimental

The polycrystalline $0.9LnTiTaO_6 + 0.1Ln'AlO_3$ (Ln = Ce, Pr and Nd and Ln′ = Pr, Nd and Sm) mixtures are prepared through the solid state ceramic route. High purity (99.9%)

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oxides are weighed in stoichiometric ratios, mixed, ball milled and calcined. Calcination temperature is 1350 °C for aluminates and 1250 °C for tantalates. The calcined powder of tantalates and aluminates are weighed in 9:1 proportion, mixed and ground well for 2 h with acetone as the wetting medium. About 5 wt% polyvinyl alcohol is added as a binder to the dried powder, ground well and dried. The powder is then pressed at a pressure of 150 MPa using hydraulic press in the form of cylindrical pellets. The pellets are then sintered in a controlled heating schedule of 4 °C per minute up to 600 °C and soaked for an hour to expel the binder. This is followed by heating the samples at a rate of 5 °C per minute up to the sintering temperature. The sintered density of the well polished sample is then measured using Archimedes method. The sintered pellets are powdered and used for X-ray diffraction (Philips Expert Pro) studies using CuK_α radiation. Polished samples, thermally etched at 1350 °C for 30 min, are used for Scanning Electron Microscopy (SEM) (JEOL JSM 5610 LV). The dielectric constant and the quality factor of the samples are measured in the microwave frequency range using cavity resonator method using network analyzer (Agilent 8753 ET), as reported earlier [12]. The temperature coefficient of resonant frequency (τ_f) is also measured over a range of temperature 30–70 °C with the heating set up attached to the computer interfaced network analyzer. For radio frequency dielectric studies, thin pellet is made in the form of a disc capacitor with the specimen as the dielectric medium and silver coating as electrodes. The capacitance and conductance of the samples are measured using LCR meter (Hioki-3532-50) within the frequency range 1 kHz to 5 MHz. The absorption spectrum of the sample is recorded using Double beam UV-Vis spectrometer Jasco-D550 and the photoluminescence spectrum is recorded using Flurolog®-3 Spectroflurometer.

3. Results and discussion

The XRD patterns of the mixtures are given in Fig. 1(a–c). The reflections of $CeTiTaO_6$, $PrTiTaO_6$ and $NdTiTaO_6$ (here onwards denoted as CTT, PTT and NTT respectively) ceramics are indexed on the basis of the ICDD file 52-1130. Most of the reflections of the mixtures can be indexed on the basis of this file and is that of orthorhombic aeschynite symmetry with P*nma* space group. Few reflections of aluminates can also be observed in all the patterns justifying the percentage of addition. Additional peaks other than that of $LnTiTaO_6$ ceramics in the mixtures are marked as '*' in the figures. The reflections of $PrAlO_3$, $NdAlO_3$ and $SmAlO_3$ (here onwards denoted as PAL, NAL and SAL respectively) present in the patterns are indexed on the basis of the ICDD files 29-0076, 71-1596 and 52-1519 respectively.

The sintering temperature, bulk density and the measured microwave dielectric properties of the mixtures are given in Table 1. The sintering temperature of tantalates is above 1500 °C and that of aluminates is about 1650 °C [3,4]. But all the mixtures of the present study are sintered at temperature below 1450 °C.

As per the previous report [3] the ε_r and τ_f of $LnTiTaO_6$ ceramics decrease with the increase in ionic radii of the lanthanide ion. A similar variation can be observed in the present compositions also. The ε_r and τ_f of the $LnTiTaO_6$ ceramics decreased with the addition of aluminates of low ε_r and negative τ_f, as expected. Further addition of aluminates can produce more thermal stability for these materials. Thus we can develop dielectric resonators with good thermal stability, high selectivity and optimum ε_r for various applications by selecting suitable mixture concentrations. In the mixtures of present study those with SAL as one of the constituents have $\varepsilon_r > 28$, $\tau_f < 18$ ppm/ °C and good quality factor and hence suitable for practical applications.

The ε_r and τ_f of mixtures can be predicted using mixture rule models [14,15]. The expression for the predicted ε_r is

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

where V_1, ε_1, V_2, ε_2 are the volume fraction and permittivity of phases 1 and 2 respectively.

Table 1
Microwave dielectric properties of $0.9LnTiTaO_6 + 0.1Ln'AlO_3$ ceramic mixtures.

$0.9LnTiTaO_6 + 0.1Ln'AlO_3$		Sintering temperature (°C)	Bulk density (g/cm^3)	Resonant frequency (GHz)	ε_r	τ_f (ppm/°C)	$Q_u \times f$ (GHz)
Ln	Ln′						
Ce	Pr	1400	6.57	4.850	35.5	35.1	15,700
Ce	Nd	1400	6.53	4.960	34.6	23.9	15,400
Ce	Sm	1400	6.46	4.951	33.2	17.7	15,300
Pr	Pr	1440	6.60	4.990	34.6	32.0	15,850
Pr	Nd	1440	6.61	4.961	33.4	22.2	16,800
Pr	Sm	1440	6.70	4.952	32.0	15.8	15,350
Nd	Pr	1430	6.71	5.191	30.2	21.8	18,800
Nd	Nd	1430	6.68	5.489	29.0	15.0	20,150
Nd	Sm	1430	6.73	5.312	28.6	14.1	18,350

This rule considers the interactive effects between the fields of neighboring spheres.

The expression for τ_f as per mixture rule is

$$\tau_{fc} = V_1\tau_{f1} + V_2\tau_{f2} \quad (2)$$

where τ_{f1} and τ_{f2} are the temperature coefficients of resonant frequencies of phase 1 and phase 2 respectively [16,17].

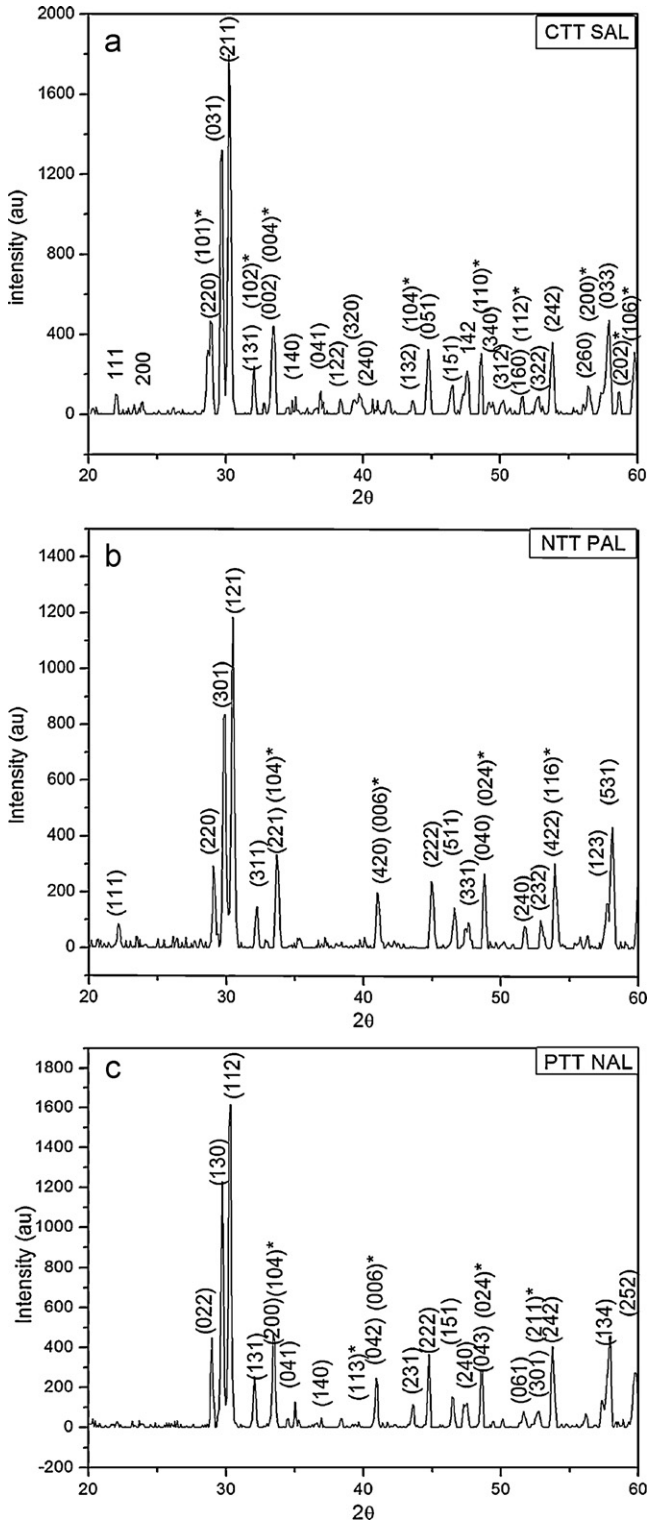

Fig. 1. XRD patterns of mixtures.

The CTT, PTT and NTT ceramics have ε_r values 40, 39 and 37 and τ_f values +41, +33 and +30 ppm/ °C respectively [2,18]. As per the report by Cho et al. [4] the PAL, NAL and SAL ceramics have ε_r of 23, 22.3 and 22 and τ_f of −25, −33 and

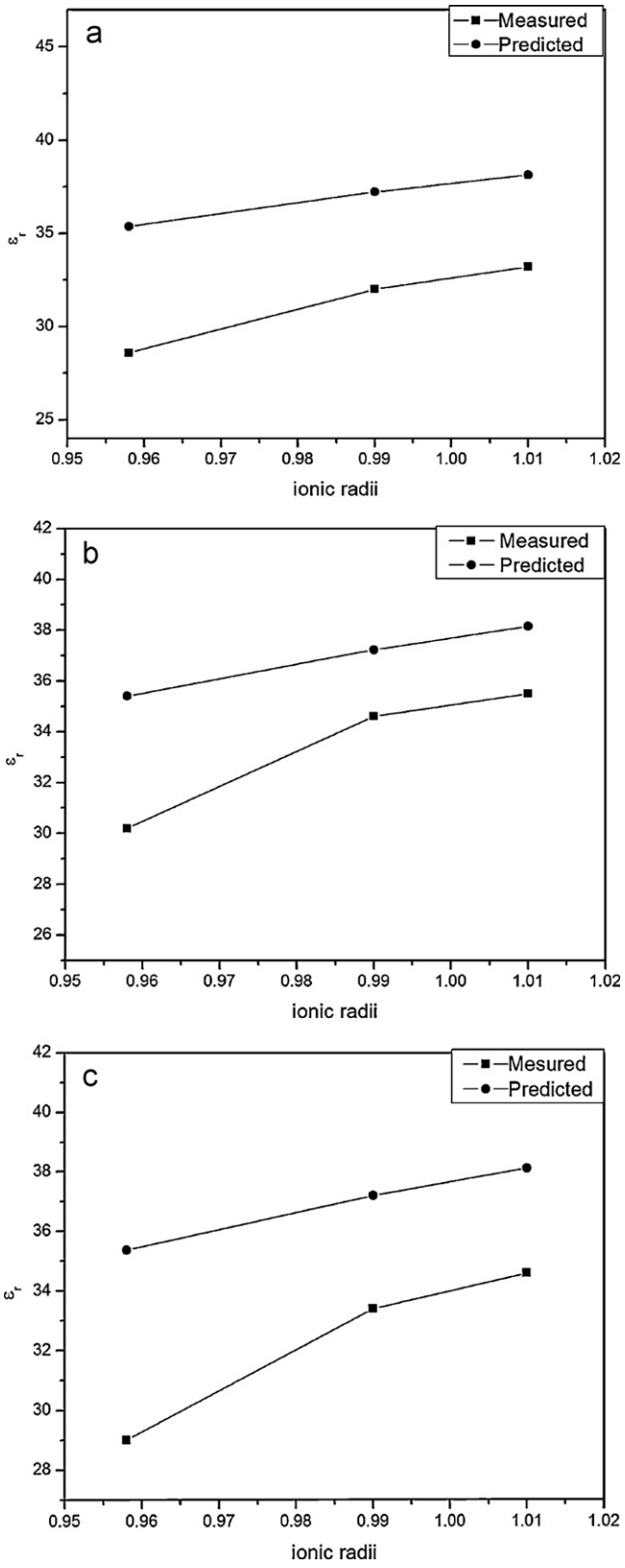

Fig. 2. Variation of measured and predicted values of ε_r.

−74 ppm/ °C respectively. These values of ε_r and τ_f are substituted in Eqs. (1) and (2) to obtain the corresponding predicted values. Figs. 2 and 3 show the variation in the measured and predicted ε_r and τ_f respectively, with respect to the ionic radii of Ln. From the graphs it is clear that both the parameters decrease with the increase in ionic radii, similar to the previous report [4]. The measured and predicted values are closer, justifying the proper formation of mixtures. The quality factor does not follow any mixture rule.

The variation in ε_r and conductance of with respect to the logarithm of frequency ($\log f$) of NTTSAL, in the radio frequency region is given in Fig. 4. The ε_r decreases slightly with the increase in $\log f$. This small variation confirms the

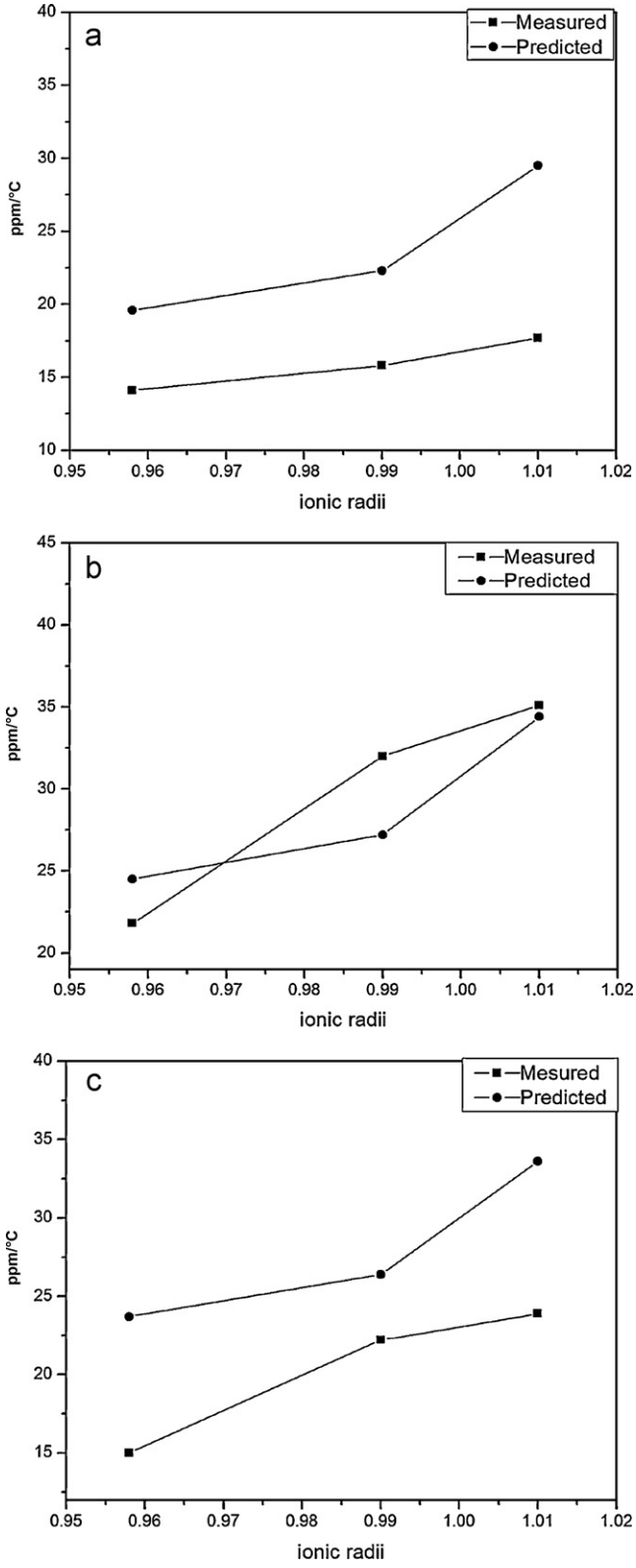

Fig. 3. Variation of measured and predicted values of τ_f.

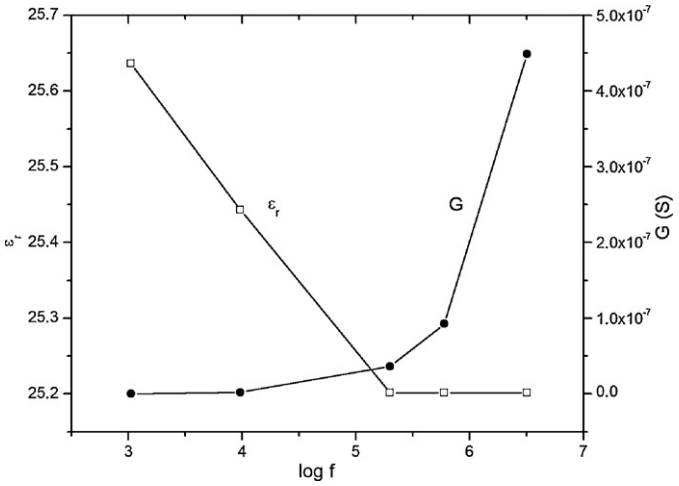

Fig. 4. Variation in ε_r and conductance of NTTSAL.

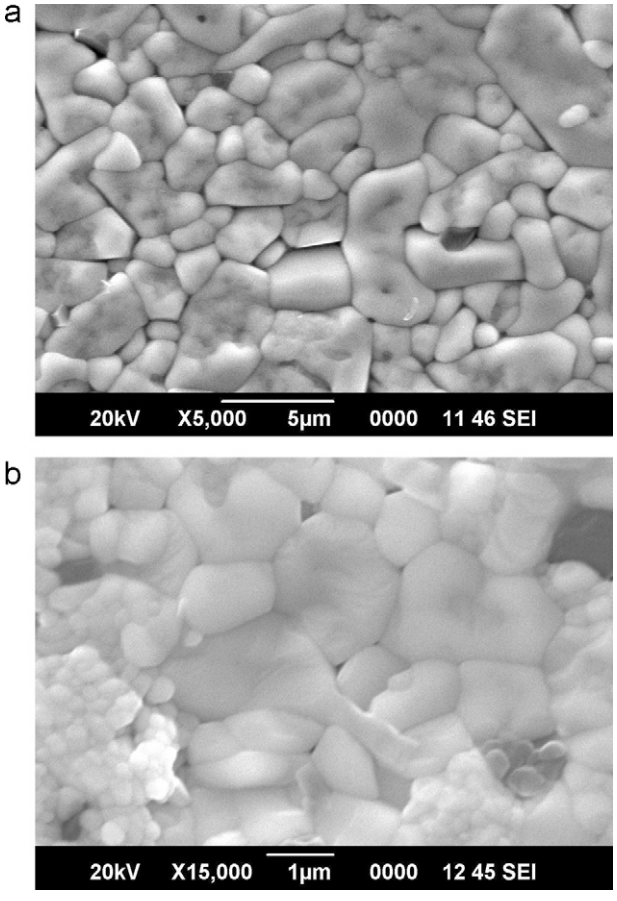

Fig. 5. SEM images of mixtures.

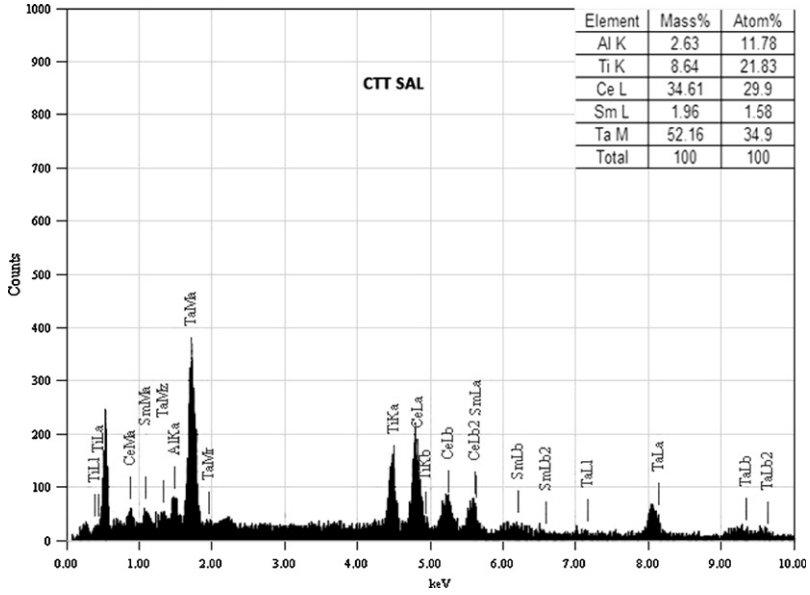

Fig. 6. EDS of representative mixture.

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

The SEM images of some selected samples are given in Fig. 5. From these micrograms it is evident that the samples are well sintered with minimum porosity. Among the two types of grains, the majority larger and brighter grains may be that of $LnTiTaO_6$ ceramics and few smaller and darker grains may be that of $Ln'AlO_3$ ceramics. The average size of the larger grains is about 1.5 μm and that of the smaller grains is about 0.5 μm. Fig. 6 shows the EDS of the ceramic mixtures. These spectra substantiate the presence of the stoichiometric concentrations of constituent elements.

Lanthanides normally absorb photons in the UV and visible regions. The transitions responsible for this absorption appear to involve the various energy levels of 4f electrons [13]. These inner orbitals are largely screened from external influences by electrons occupying orbitals with higher quantum numbers. As a consequence, their spectra consist of narrow and well defined characteristic peaks. Fig. 7 shows the absorption spectrum of the PTTNAL ceramic. The material has strong absorption in the visible region. A graph (Fig. 8) is plotted between $(\alpha h\nu)^2$ and $h\nu$, where α is the absorption coefficient. The value of the band gap can be estimated by extrapolating the steep portion of the graph to zero absorbance. This tangential line coincides with the X axis at 2.57 eV. The photoluminescence spectrum of the above mixture when excited by radiation of wave length 400 nm is given in Fig. 9. The sample has 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 [19]. The lanthanides Nd and Pr present in the mixture have emission around 442 nm.

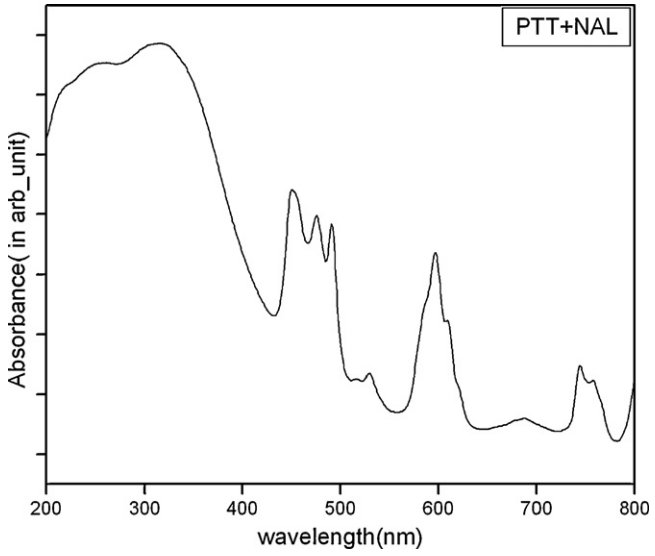

Fig. 7. Absorption spectrum of PTTNAL.

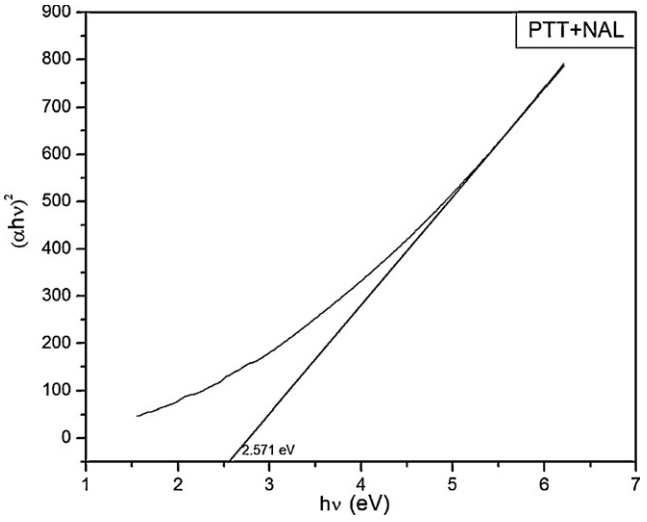

Fig. 8. Graph for the calculation of band gap energy of PTTNAL.

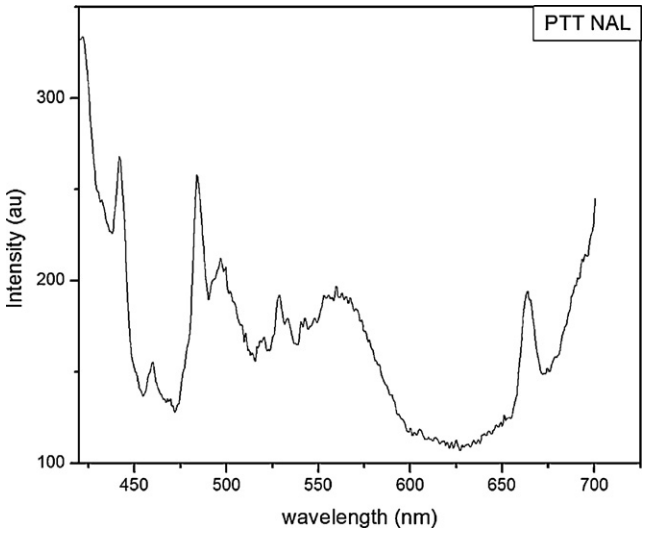

Fig. 9. Photoluminescence spectrum of PTTNAL.

The strong emission line around 460 nm may be due to the combined emission of Pr and Ta. The emission line around 664 nm may be due to the transitions occurring in Ti and Pr.

4. Conclusions

The preparation, structure, dielectric properties and optical characterization of $0.9LnTiTaO_6 + 0.1Ln'AlO_3$ (Ln = Ce, Pr and Nd and Ln′ = Pr, Nd and Sm) ceramic mixtures are discussed. The sintering temperature, ε_r and τ_f are decreased by the addition of $Ln'AlO_3$ in $LnTiTaO_6$ ceramics. The variation in the measured and predicted ε_r and τ_f with respect to the ionic radii of Ln are comparable, justifying the proper formation of mixtures. The results obtained indicate that the ε_r and τ_f of these mixtures can be tuned to any desired value by suitably changing the proportion of the constituents. The materials have good absorption and emission in the visible region. The $SmAlO_3$ added mixtures of this study have $\varepsilon_r > 28$, $\tau_f < 18$ ppm/ °C and good quality factor and hence suitable for dielectric resonator applications.

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