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Influence of lead oxide addition on $LnTiTaO_6$ (Ln = Ce, Pr and Nd) microwave ceramics

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Abstract. The effect of PbO addition on the structural, processing and microwave dielectric properties of $LnTiTaO_6$ (Ln = Ce, Pr and Nd) ceramics are reported. Conventional solid state ceramic route was used for the preparation of samples. Phase pure $LnTiTaO_6$ (Ln = Ce, Pr and Nd) ceramics are prepared at a calcination temperature of 1300°C. The samples are sintered at optimized temperatures. Addition of PbO reduces the sintering temperature. The crystal structure of the materials was analysed using X-ray diffraction techniques and the surface morphology of the sintered samples was analysed using scanning electron microscopy. The dielectric constant at microwave frequency range decreases for higher PbO addition for all the samples but the quality factor improves on small PbO addition. The thermal stability of resonant frequency was also improved with PbO addition on all the systems. A number of samples with improved microwave dielectric properties were obtained on all the systems suitable for practical applications.

Keywords. Dielectrics; ceramics; sintering; microwave; dielectric resonators.

1. Introduction

Dielectric resonators are widely used in modern microwave circuits due to their compactness, thermal stability, low cost of production, high efficiency and adaptability to microwave integrated circuits (Reaney and Iddles 2006). It was first proposed in 1939, that a piece of ceramic puck can function similar to that of a cavity resonator at microwave frequencies (Richtmyer 1939) and he called them as dielectric resonators (DR). Commercial DRs must combine three desirable properties such as dielectric constant (ε_r) > 25, quality factor, Q > 2000 and temperature coefficient of resonant frequency (τ_f) < ± 20 ppm/°C (Sebastian 2008). The dielectric constant (ε_r) is related to the resonant frequency (f_0) according to the relation, $f_0 \approx c/D\varepsilon^{1/2}$, where c is the velocity of light in vacuum and D the diameter of dielectric resonator, which means that as the dielectric constant of the resonator material increases, the size of the resonator can be decreased maintaining the same resonant frequency. The quality factor, Q, is determined as the resonant frequency divided by the bandwidth, Δf_0, measured at 3dB below the maximum height at resonance, which means that Q is a measure of selectivity of a resonator at a given frequency. Q decreases with increase in frequency and $Q \times f$ is a constant for given dielectric material. The temperature coefficient of resonant frequency (τ_f) is a measure of drift of resonant frequency with temperature. So far as a number of materials with a wide range of microwave dielectric properties are reported, the search for materials with better properties for designing different microwave circuits are still active.

A special group of materials having the general formula, $A^{3+}B^{4+}C^{5+}O_6$, was reported by Kazantsev *et al* (1974). The possibility of using rare earth titanium tantalates and niobates of the above group as materials suitable for microwave applications was also reported (Maeda *et al* 1987). The microwave dielectric properties of lanthanide based titanium tantalates were reported (Surendran *et al* 2002). Various lanthanide systems of this group are reported for their good optical properties. Recently photoluminescence studies of certain polycrystalline lanthanide titanium tantalates are reported (Jacob *et al* 2007). $EuTiNbO_6$, $EuTiTaO_6$ and $Y_{0.5}Eu_{0.5}TiNbO_6$ were reported as good scintillators for gamma ray and neutron registration (Koroleva *et al* 2005). $LnTiTaO_6$ compounds with lanthanides of atomic numbers in the range 57–66 have orthorhombic aeschynite structure and those in the range 67–71 have orthorhombic euxenite structure (Kazantsev *et al* 1974). $LnTiTaO_6$ ceramics with aeschynite orthorhombic structures have positive τ_f with higher dielectric constant while those having euxenite orthorhombic structure have negative τ_f with relatively lower dielectric constant (Surendran *et al* 2002).

Tantalate based ceramics of the above family possess higher quality factor and hence gained much importance than their niobate based counterparts. Among the lanthanide

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based titanium tantalates, Ce, Pr and Nd-based ceramics possess higher dielectric constant. But tantalate based ceramics requires higher processing temperatures (of the order of >1500°C). In order to optimize the dielectric properties of microwave ceramics, the commonly used methods include doping with suitable materials or by preparing solid solutions and composites of different materials (Reaney and Iddles 2006). Additives are generally used in ceramic processing to alter the properties of ceramics to the desired values and for lowering the processing temperature (Choi *et al* 2000; Puller *et al* 2003; Zhang *et al* 2003; Bijumon and Sebastian 2005; Huang *et al* 2006). In spite of that, additives can change the physical properties of ceramics which make them suitable for practical applications in the various fields of applied sciences. Generally, elements with valency and ionic radii different from that of the compositional elements of the host material and having a low melting point are used as dopants. ZnO, WO_3 and MoO_3 are reported as good additives for $LnTiNbO_6$ and $LnTiTaO_6$ ceramics (Solomon *et al* 2006; Kumar *et al* 2007, 2009). PbO is a material with low melting point of about 890°C and hence, can be used as dopant to reduce the sintering temperature of ceramics. Also it can be used as a dopant to alter the dielectric properties of ceramics since it has a valency of 2^+ which is different from that of the elements present in $LnTiTaO_6$ ceramics. In the present paper, we report the effect of PbO addition on the processing and microwave dielectric properties of lanthanide titanium tantalates.

2. Experimental

Polycrystalline samples of $LnTiTaO_6$ (Ln = Pr, Sm and Dy) ceramic materials were prepared through the conventional solid state ceramic route. The samples were calcined at 1300°C for 5 h in electrically heated furnace. A definite mass of calcined powder was mixed with different weight percent of PbO and 5% polyvinyl alcohol was added to this powder as a binder. The powder was then pressed in the form of cylindrical pellets at a pressure of 100 MPa using hydraulic press and then sintered at optimized temperatures in a controlled heating schedule. Samples were then furnace cooled to room temperature.

The sintered densities of well polished samples were measured using Archimedes method. Powdered samples were used for X-ray diffraction (Philips Expert Pro) studies using $Cu-K_\alpha$ radiation. Polished samples were thermally etched at 50°C below the sintering temperature and analysed by scanning electron microscopy (SEM) (JEOL JSM 5610 LV). The dielectric properties of the samples were measured in the microwave frequency range using cavity resonator method (Krupka *et al* 1998). The specimen was placed on a quartz cylinder placed at the centre of a cylindrical brass cavity whose size is 3–4 times greater than the specimen. 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 dielectric constant (ε_r) and the unloaded quality factor (Q_u) were then calculated using the computer interfaced network analyser (Agilent 8753 ET). The temperature coefficient of resonant frequency (τ_f) was also measured over a range of temperature 30–70°C with the help of Keithley 2000 multimeter attached with a Keithley 2001 model TC scanner connected to the experimental set up.

3. Results and discussion

Figures 1a–c show the XRD patterns of pure and doped $LnTiTaO_6$ (Ln = Ce, Pr and Nd) ceramics. No peaks other

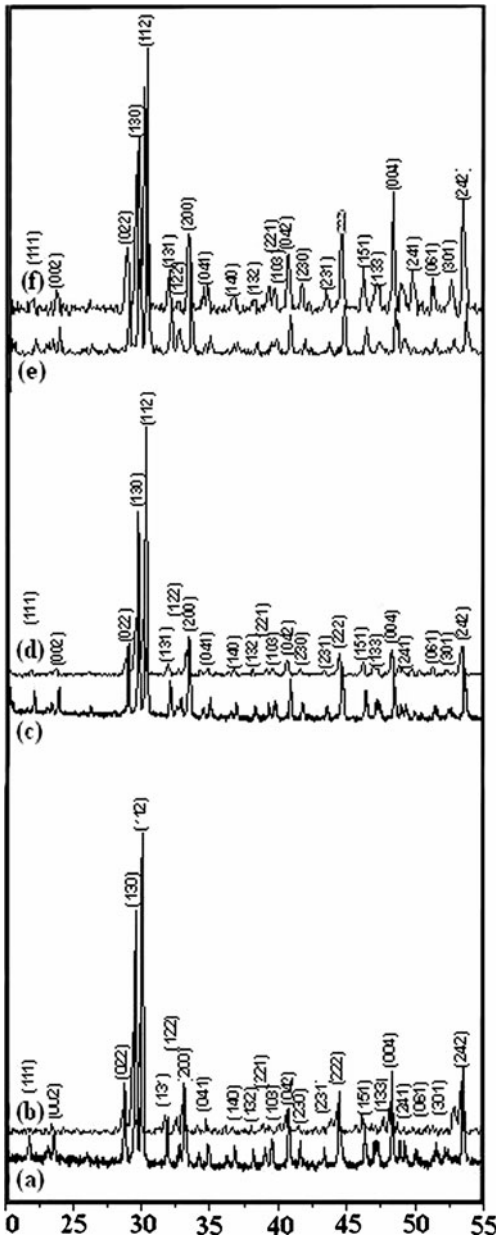

Figure 1. XRD patterns of (a) pure $CeTiTaO_6$, (b) 2% PbO added $CeTiTaO_6$, (c) pure $PrTiTaO_6$, (d) 2% PbO added $PrTiTaO_6$, (e) pure $NdTiTaO_6$ and (f) 2% PbO added $NdTiTaO_6$.

than the aeschynite orthorhombic structured $LnTiTaO_6$ ceramics are found in the doped ceramics, which means that the structures of the samples are not altered. The maximum doping concentration of PbO is up to 2% which is relatively a very low doping concentration and may be the reason for the absence of additional phases.

Figure 2 shows the variation of sintering temperature of $LnTiTaO_6$ (Ln = Ce, Pr and Nd) ceramics with respect to PbO addition. Addition of PbO reduces the sintering temperature of $LnTiTaO_6$ (Ln = Ce, Pr and Nd) ceramics significantly. All the Ce, Pr and Nd based compounds are sintered to a density >95% of the theoretical density.

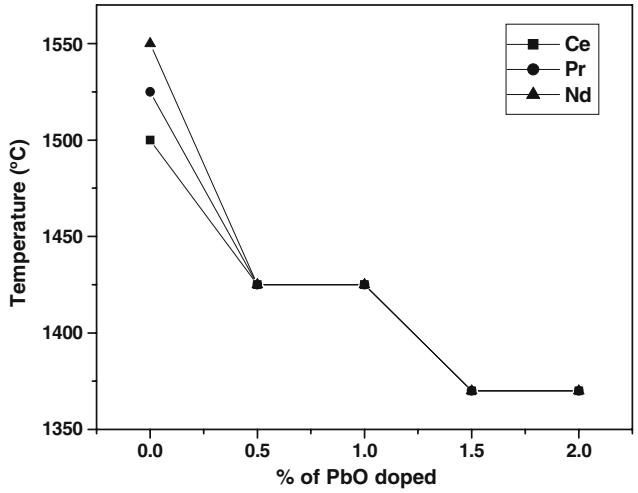

Figure 2. Variation of sintering temperature of $LnTiTaO_6$ ceramics with % of PbO addition.

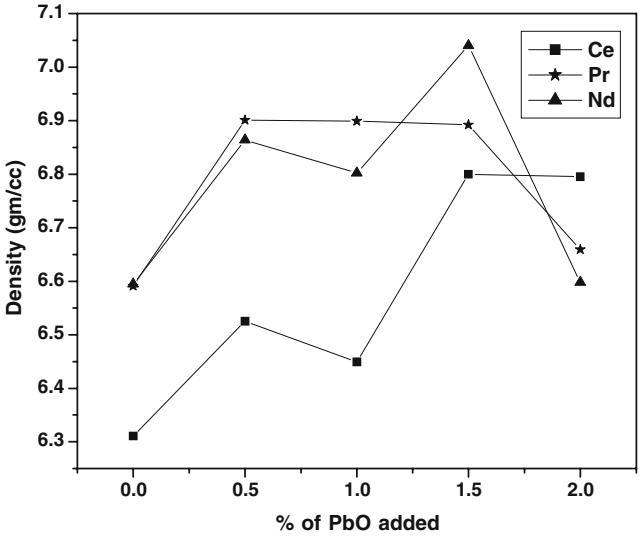

Figure 3. Variation of sintered density with respect to % of PbO addition.

Figure 3 shows the variation of sintered density with respect to the percentage of PbO addition. The density increases with the increase in the PbO concentration but decreases above 1·5 wt percentage of PbO addition. The slight variation in density may be due to the evaporation of

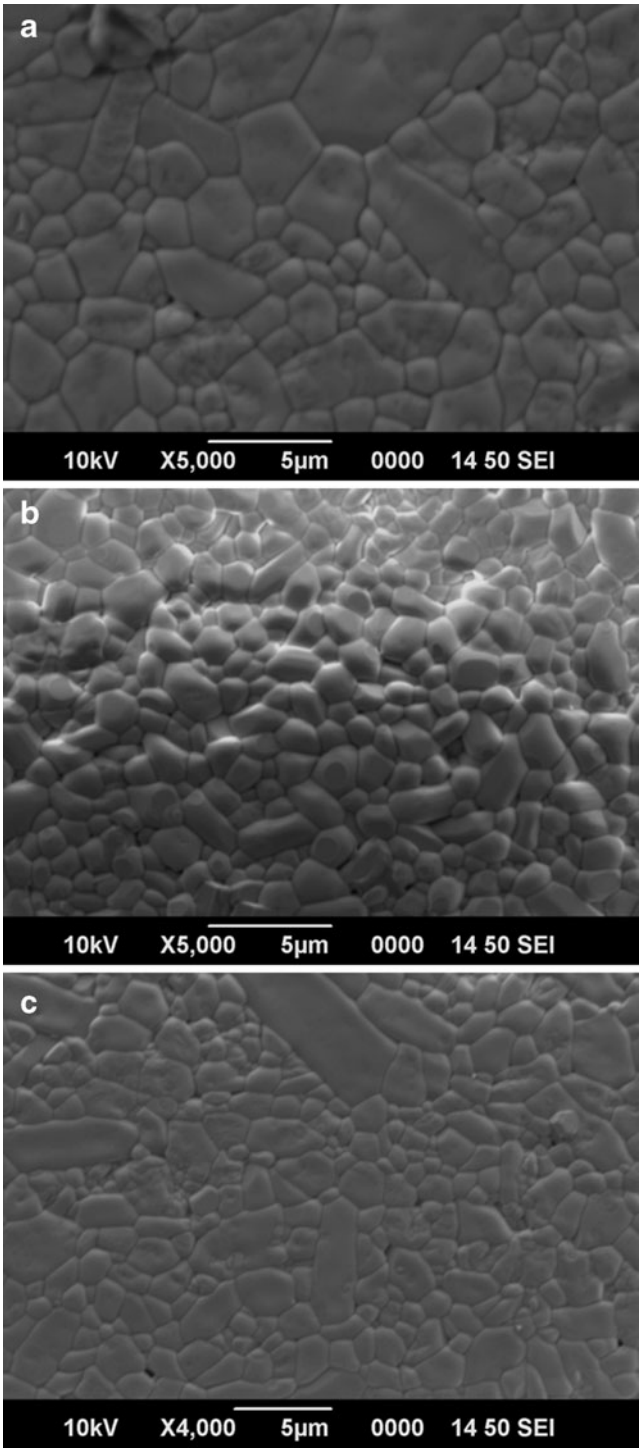

Figure 4. SEM images of 1 wt% PbO added **a.** $CeTiTaO_6$ ceramic, **b.** $PrTiTaO_6$ ceramic and **c.** $NdTiTaO_6$ ceramic.

Table 1. Microwave dielectric properties of PbO added $LnTiTaO_6$ ceramics.

Material					
Lanthanide	% of PbO addition	ε_r	Frequency (GHz)	$Q_u \times f$ (GHz)	τ_f (ppm/°C)
Ce	0	39·50	4·688	11500	+60
	0·5	39·43	3·891	13300	+59·1
	1	39·30	3·896	11700	+50·8
	1·5	38·07	4·060	8000	+39·1
	2	38·55	4·021	6800	+38·7
Pr	0	39·64	4·8039	13000	+56
	0·5	39·2	3·991	13500	+42·5
	1	39·0	3·976	12300	+58·4
	1·5	38·8	4·001	8500	+47·5
	2	37·8	4·091	7500	+50·1
Nd	0	37	3·960	11300	+54
	0·5	37·6	4·070	19700	+35
	1	37·18	4·066	26000	+48
	1·5	36·8	4·112	6851	+34·9
	2	35·5	4·124	7200	+34·8

lead oxide and the variation in porosity from sample to sample. Figures 4a–c show the SEM images of 1 wt % PbO added $LnTiTaO_6$ ceramics. All the samples are found to be well sintered with minimum porosity. It was reported that aeschynite structured $LnTiTaO_6$ ceramics possess elongated grain morphology (Solomon *et al* 2001; Oishi *et al* 2005). The grain morphologies of all the samples are found to be similar to that of the grains of aeschynite structured ceramics. The grains are found to have almost uniform grain size especially for Pr and Nd based systems which may be one of the reasons for the improved quality factor of these samples.

The microwave dielectric properties of PbO added $LnTiTaO_6$ ceramics are given in table 1. The dielectric constant decreases with increase in the concentration of PbO. This is in agreement with the variation in the experimental density. Addition of PbO decreases the sintering temperature to about 200°C with much improvement in the thermal stability and quality factor.

4. Conclusions

Addition of PbO reduced the sintering temperature to about 200°C. No considerable change in crystal structure was observed in X-ray diffraction studies. The SEM images show that the samples are well sintered with grain morphology similar to that of aeschynite structured lanthanide titanium tantalates. The dielectric constant was found to decrease on higher PbO addition and the temperature coefficient of resonant frequency also was found to be decreased. For all the systems, a number of materials with increased quality factor are obtained and they can be used for practical applications.

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