Temperature Dependent Dielectric Properties of Monoclinic (H) - Phase $[Ta_2O_5]_{1-x} - [TiO_2]_x$, $(0.078 \leq x \leq 0.085)$

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Abstract

Observed temperature dependence of dielectric constant, loss tangent and dielectric conductivity of H- phase [Ta2O5]1-x-[TiO2]x, $(0.078 \leq x \leq 0.085)$ pellets, prepared by solid state reaction method, has been presented. Dielectric constant was observed slowly increasing with temperature showing strong transition peaks at 495, 505, 510 and 520 oC for the compositions with x = 0.078, 0.080, 0.082 and 0.085, respectively. Dielectric loss and conductivity also show anomalous increase near the transition temperature, for all the prepared compositions. Near the transition temperature, anomalous dielectric behavior may be associated with the softening of the active phonon mode.

Keywords: Ceramics, Phase Transformation, Sintering

I. INTRODUCTION

To meet out the demand for miniaturized components with enhanced performance in microelectronics applications, tantalum pentoxide (Ta_2O_5) has been proposed as one of the promising alternatives [1-6] to the low dielectric constant silicon oxy-nitrides [7-10]. Dielectric constant of Ta_2O_5 can be enhanced further [11-15] by the addition of titanium dioxide (TiO_2). Both Ta- and Ti-oxide are compatible with the compounds as well as with the current fabrication procedures of microelectronics device fabrication. Dielectric permittivity of $[Ta_2O_5]_{1-x}$- $[TiO_2]_x$ ceramics was observed significantly dependent on fabrication process and composition (x value) [16] . Depending on the composition and process conditions, $[Ta_2O_5]$1-x-$[TiO_2]_x$ ceramics may have mixture of low dielectric constant phase (L- phase) and higher dielectric constant phase (H- phase), in different proportions [16, 17] . The L- phase is orthorhombic [18-22], and the H- phase is monoclinic or triclinic [18-20, 23-30], at room temperature (RT). Appearance of H- phase (monoclinic or triclinic), and large and oriented grains may be associated with the enhanced dielectric permittivity, in TiO_2 added Ta_2O_5. Due to the structural distortion the increasing interactions of ions lead to the reinforcement of the internal electric field, and consequently to the enhanced dielectric constant. Composition dependence $(0.078 \leq x \leq 0.085)$ of dielectric constant, loss tangent and dielectric conductivity, at different frequencies has been reported in I. Dielectric constant was found increasing with x (≤ 0.080) having maximal value for x = 0.08; and for the compositions with x > 0.08 dielectric constant was observed decreasing with increasing x, in the measured composition range, for all the measured frequencies [16]. The loss tangent was observed increasing with x $(0.078 \leq x \leq 0.085)$, which may be associated with the oxygen- vacancies, other stoichiometric and impurity defects. Both phase and microstructure, and also density and homogeneity, significantly affect the dielectric properties of a ceramic. Being non-Centro symmetric at RT, H- phase $[Ta_2O_5]$1-x-[TiO2]x is a potential ferroelectric [21]. Dielectric properties of H- phase $[Ta_2O_5]$1-x- $[TiO_2]_x$, were observed dominantly driven by composition rather than the frequency or temperature [16]. In continuation to I, the present paper reports the observed temperature dependence of dielectric properties of H- phase $[Ta_2O_5]$1-x-TiO_2]x, $(0.078 \leq x \leq 0.085)$.

II. EXPERIMENTATION

In the present study $[Ta_2O_5]$1-x-$[TiO_2]$x, $(0.078 \leq x \leq 0.085)$, pellet samples were prepared by conventional solid state reaction method. Tantalum pentoxide (Ta_2O_5) and titanium dioxide (TiO_2) were used as the starting materials. Purity of starting materials was better than 99.99 %. Starting materials, dried at 200 0C for 4 hours, were weighed in stoichiometric ratio to prepare $[Ta_2O_5]$1-x-$[TiO_2]_x$, $(0.078 \leq x \leq 0.085)$. Each composition was manually dry mixed for 4 hours and with methanol for 2 hours,

using agate mullet mortar and pestle. The ground mixtures were fired in an alumina crucible, at 950 0C for 4 hours, in ambient atmosphere. After cooling to RT, the fired mixture was further ground for 2 hours. Pellets of 8 mm diameter and about 2 mm thickness were prepared by pressing the ground fired powder, at 0.2 GPa. The pellet samples of all the compositions were placed into the furnace for sintering. The furnace was gradually heated from RT to 1400 0C, in 13 hours, and was maintained at that temperature for 16 hours, and then cooled gradually to RT, in 13 hours. The pellets were further sintered at 1450 0C, for 6 hours, excluding the fast heating (from RT to 1450 0C it reached in 3 hours) and fast cooling (from 1450 0C to RT it reached in 4 hours) duration. Dielectric constant (K), dissipation factor (tan δ) and dielectric conductivity (σ) of the prepared compositions were measured in metal- insulator- metal (MIM) configuration, at different frequencies, in the temperature range from RT to 600 oC.

III. RESULTS AND DISCUSSION

At different temperatures, the observed dielectric measurements for different prepared compositions have been shown in Fig.1. Values of all the measured dielectric parameters were observed increasing with increasing temperature. Dielectric constant, at all the measured temperatures, was found maximum for the composition with x = 0.08. Depending on the Ti concentration, formation of single donor complex 'Ti – oxygen vacancy' and electrically inactive 'Ti – oxygen vacancy – Ti' complex may be held responsible for the observed dielectric behavior of the present system.

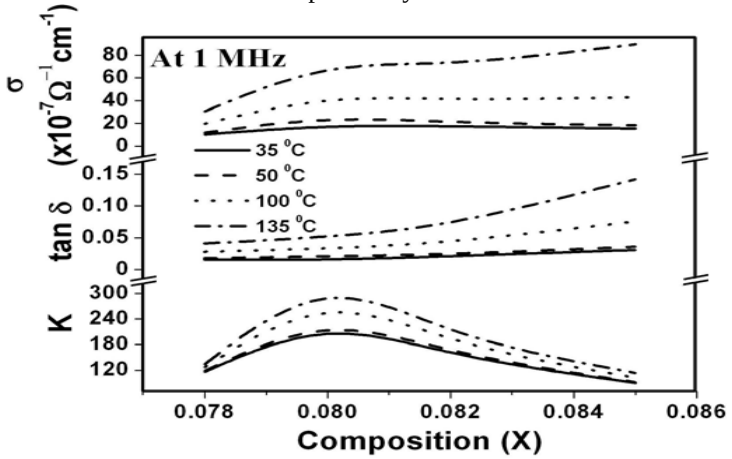

Fig. 1: Variation of (a) dielectric constant (K), (b) loss tangent (tan δ), and (c) dielectric conductivity (σ) of $[Ta_2O_5]1\text{-}x\text{-}[TiO_2]_x$, ($0.078 \leq x \leq 0.085$), with composition (x), at different temperatures.

The observed temperature dependence of dielectric constant of the prepared compositions, at 1 MHz, has been shown in Fig. 2. Dielectric constant, at all the measured temperatures (except near Tc), was found maximum for the composition with x = 0.08. Dielectric constant was found increasing with increasing temperature, showing strong anomaly at the transition temperature (Tc), for all the prepared compositions. The transition anomalies observed from dielectric constant measurements, were found at 495 (peak value 13137), 505 (peak value 15125), 510 (peak value 9876), and 520 oC (peak value 14584) for the compositions with x = 0.078, 0.080, 0.082 and 0.085, respectively, at 1 MHz, Fig. 2. These transition anomalies may be attributed to the monoclinic (or triclinic) to monoclinic (H'mon) structural change [31]. Dielectric loss and dielectric conductivity were found slowly increasing with temperature, with an anomalous rise near the transition temperature, Figs. 3 and 4, respectively, for all the prepared compositions.

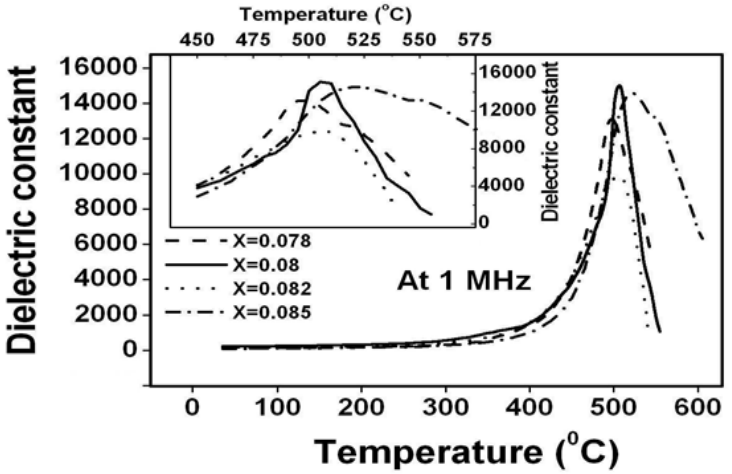

Fig. 2: Temperature dependence of dielectric constant (K) of $[Ta_2O_5]1\text{-}x\text{-}[TiO_2]_x$, ($0.078 \leq x \leq 0.085$), at 1 MHz.

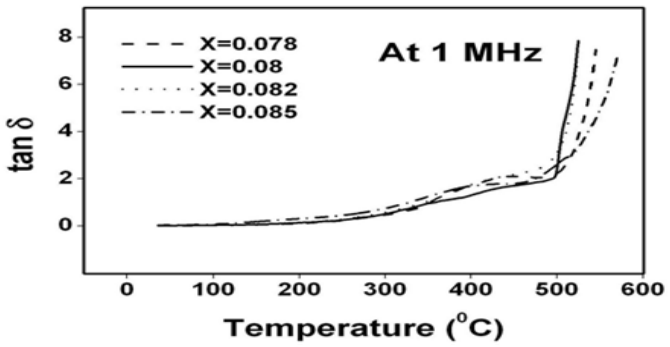

Fig. 3: Temperature dependence of loss tangent (tan δ) of [Ta2O5]1-x- [TiO2]x, (0.078 ≤ x ≤ 0.085), at 1 MHz.

Multiple lower frequency vibration modes appear after modulation, which correspond to the vibration modes between TiO6 and TaO6 octahedra [31]. The dielectric permittivity is obtained proportional to the inverse of the square of the active phonon mode frequency [31] on the basis of density- function perturbation theory [17]. When Ta is substituted by Ti atoms, due to the modification of bond length, covalence, ionic charge and radii, cell parameters, etc., change in the force constant results shift in the active phonon mode frequency. Meng et al [32] have observed that the intensity of the phonon modes under consideration becomes maximum for x = 0.08 composition, which matches best for the reported [11-15] and presently observed highest dielectric constant measurements.

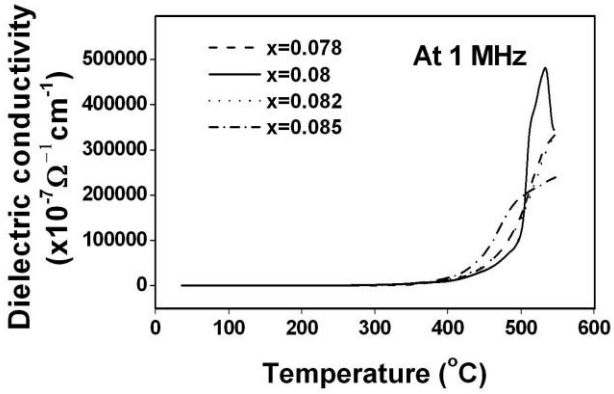

Fig. 4: Temperature dependence of dielectric conductivity (σ) of $[Ta_2O_5]_{1-x-}$ $[TiO2]_x$, (0.078 ≤ x ≤ 0.085), at 1 MHz.

Frequency of the active mode decreases with increasing temperature, which results increase in the dielectric constant with temperature [31]. With increasing temperature frequency of the active phonon mode softens and ceases abruptly at Tc and the lattice displacement associated with it becomes unstable, leading to the phase transition [31]. A ceasing soft mode, at Tc, gives rise to large value of dielectric constant, loss and dielectric conductivity, and also to the anomalies measured in the thermal strain versus temperature data [14], high temperature x-ray diffraction data [20], and temperature dependent Raman data [31]. For the composition with x = 0.08, a dielectric conductivity peak was observed at 530 oC, which is higher than the transition temperature determined from the dielectric constant measurements. The competition among active phonon mode softening [31] activation energy of surface terms and the grain boundary potential barrier heights may be held responsible for the shifting of the conductivity peak from the transition temperature observed from the dielectric constant measurements. These results may be of interest for structure- property relations.

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