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

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Abstract

Composition ($0.078 \leq x \leq 0.085$), frequency (1 KHz – 1 MHz) and temperature (30 – 600 oC) dependence of dielectric constant, loss tangent and dielectric conductivity of $[Ta_2O_5]_{1-x}$-$[TiO_2]_x$ pellets, prepared by solid state reaction method, has been presented. The x-ray diffraction patterns and dielectric constant measurements show the occurrence of high- phase. Among the prepared compositions, dielectric constant was observed maximum for the composition with x = 0.080, at all the measured frequencies and temperatures (except near transition temperature). Dielectric properties were observed dominantly driven by composition rather than the frequency or temperature, in the present system. 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; crystal growth; X-ray diffraction; dielectric properties; Phase Transition

I. INTRODUCTION

The demand for miniaturized components with enhanced performance in microelectronics applications leads to look for new materials. Dielectric constant value limits the degree of miniaturization in dynamic random access memories. Efforts have been focused on higher dielectric constant metal oxides as a replacement of low dielectric constant silicon oxy-nitrides [1-4]. Tantalum pentoxide (Ta2O5) has been proposed as one of the promising alternatives [5,6] owing to its intrinsic high dielectric constant (~35), non-narrow band gap (~4 eV), high dielectric breakdown strength [7], good chemical and thermal stability, etc. [8-10].

Dielectric constant of Ta2O5 can be enhanced further by the addition of titanium dioxide (TiO2) [11-15]. Both Ta- and Ti-oxide are compatible with the compounds as well as with the current fabrication procedures of microelectronics device fabrication.

Two phases have been reportedly observed in Ta2O5-TiO2 compositions [16-18]. The low dielectric constant phase (L-phase) is orthorhombic at room temperature (RT) [16-20]; and the higher dielectric constant phase (H- phase) is orthorhombic (pseudo- tetragonal) with a (metastable) monoclinic distortion between ~320 and 900 oC, and monoclinic or triclinic at RT [16-18,21-28]. Formation of either phase of Ta2O5 depends on the preparation conditions, e.g., fast cooling maintains H- and slow cooling results L- phase, mechanical action of crushing and grinding reverses phase (from H- to L- phase) [12,29]. TiO2 addition significantly slows the H- to L- phase reversion in Ta2O5 [23,29]. Being non-centrosymmetric at RT, H- phase [Ta2O5]1-x-[TiO2]x is a potential ferroelectric [23]. Both phase and microstructure, and also density and homogeneity, significantly affect the dielectric properties of a ceramic. The amount of TiO2 concentration and heat treatment stabilize the system in different phases [22]. Dielectric permittivity of [Ta2O5]1-x- [TiO2]x ceramics depends on fabrication process and composition (x value) [11-15].

Generally, [Ta2O5]1-x-[TiO2]x ceramics may have mixture of L- and H- phase [29], in different proportions, depending on processing conditions. Raman data [23] indicate that the stabilizing effect of TiO2 may be related to the acceptor character of Ti4+, in TiO2 added Ta2O5. The exact mechanism for enhancement of dielectric constant in TiO2- modified Ta2O5 is under

investigation, and requires better understanding of the phase transformation in pure and TiO2 stabilized H- phase Ta2O5. The present paper reports the observed dielectric properties of H- phase [Ta2O5]1-x-TiO2]x, ($0.078 \leq x \leq 0.085$). These results may be of interest for structure- property relations.

II. METHODOLOGY

In the present study [Ta2O5]1-x-[TiO2]x, ($0.078 \leq x \leq 0.085$), pellet samples were prepared by conventional solid state reaction method. Tantalum pentoxide (Ta2O5) and titanium dioxide (TiO2) 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 [Ta2O5]1-x-[TiO2]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. Room temperature x-ray diffraction (XRD) patterns of all the prepared samples were taken by Philips Analytical X- Ray Diffractometer (PW3710), using CuKα1 radiation of wavelength 1.54056Å. Surface morphology and grain size of the prepared samples were studied using the model Philips PSEM 515 (Holland). Relative densities of the prepared samples were found between 0.87 and 0.93 with respect to their theoretical density. For dielectric measurements sintered pellets were electroded, with air drying silver paste, in metal- insulator- metal (MIM) configuration [24]. Frequency, temperature and composition ($0.078 \leq x \leq 0.085$) dependence of dielectric constant (K), dissipation factor (tan δ) and dielectric conductivity (σ) of the prepared samples were measured in MIM configuration, in 1 KHz – 1 MHz frequency range, using Fluke– PM6306 RCL meter, and in the temperature range from RT to 600 oC, using a temperature controller of accuracy ±1 oC.

III. RESULTS AND DISCUSSION

The observed room temperature XRD patterns of the prepared [Ta2O5]1-x-[TiO2]x, ($0.078 \leq x \leq 0.085$) pellet samples with different x values have been shown in Fig.1. The XRD patterns of the prepared samples show H- phase structure [29], and their XRD patterns are in good agreement with Joint Committee on Powder Diffraction Standards (JCPDS) (73-2323) data of monoclinic H- Ta2O5 structure, with peaks corresponding to (103), (105), (219), etc. Also these XRD patterns match with the JCPDS (21-1198) data of triclinic structure, with peaks corresponding to (013), (105), (019), etc., Fig.1 (inset). The scanning electron micrographs (SEM) of all the prepared compositions show well grown grains with elongated shapes with average length ~25 µm and breadth ~7 µm. Fig. 2 shows SEM of the prepared [Ta2O5]0.92-[TiO2]0.08 composition.

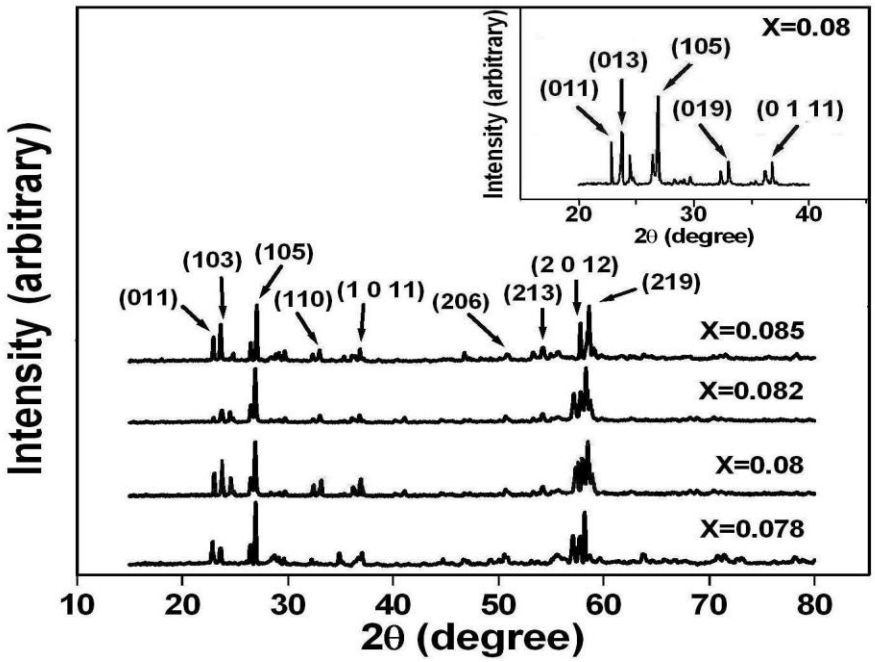

Fig. 1: XRD patterns of monoclinic $[Ta_2O_5]_{1-x}$-$[TiO_2]_x$, ($0.078 \leq x \leq 0.085$); inset shows triclinic peaks indexing, for x = 0.08.

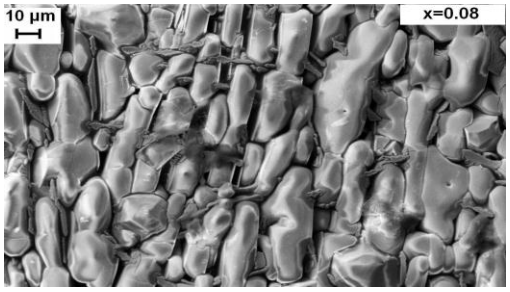

Fig. 2: SEM of $[Ta_2O_5]_{0.92}$-$[TiO_2]_{0.08}$

At RT, the observed composition dependence ($0.078 \leq x \leq 0.085$) of dielectric constant (K), loss tangent (tan δ) and dielectric conductivity (σ), at different frequencies has been given in Fig.3. Values of dielectric constant were found maximum for the composition with x = 0.08, at all the measured frequencies. Quenching effects, temperature gradient and mass transfer with directivity lead to the structural and morphological properties [21]. Either due to small quantities of additives or the preparation condition, the enhanced dielectric permittivity may be associated with the appearance of H- phase (monoclinic or triclinic), and large and oriented grains in [Ta2O5]1-x- [TiO2]x ceramics [11-15,21,30,31]. Due to the structural distortion the increasing interactions of ions would lead to the reinforcement of the internal electric field, and consequently to the enhancement of dielectric constant. In TiO2 modified Ta2O5, dielectric constant enhancement has been related with the appeared directional ordering structure [22,32]. It has been observed that the crystallization of H- phase Ta2O5 can generate a one dimensional Ta-O-Ta chain along the c- axis [21,33]. TiO2 addition modulates the chain structure and induces the stabilization of H- phase near room temperature [32]. By doping Ti atoms in Ta2O5, structure modification has been observed by XRD and Raman spectroscopy [21], high- resolution electron microscopy (HREM), and electron diffraction [22,23]. The higher density and lower porosity is beneficial to the enhancement of polarization because of the reducing of the depolarizing fields originating from defects [34].

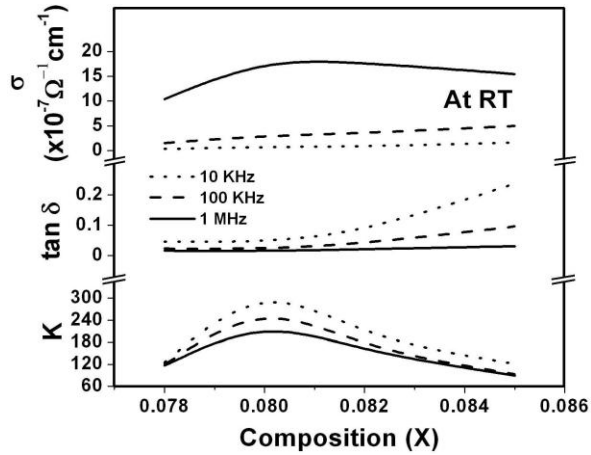

Fig. 3: Variation of (a) dielectric constant (K), (b) loss tangent (tan δ), and (c) dielectric conductivity (σ) of $[Ta_2O_5]_{1-x}$-$[TiO_2]_x$, ($0.078 \leq x \leq 0.085$), with compositions(x), at different frequencies.

Multiple lower frequency vibration modes appear after modulation, which correspond to the vibration modes between TiO6 and TaO6 octahedra [21,33]. From the density- function perturbation theory [35,36], the dielectric permittivity is obtained proportional to the inverse of the square of the active phonon mode frequency [32]. 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 [37] 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.

The loss tangent was observed increasing with x, in the measured composition range ($0.078 \leq x \leq 0.085$), at all the measured frequencies, Fig.3. Values of loss tangent were found 0.016, 0.015, 0.021 and 0.031 for the compositions with x = 0.078, 0.080, 0.082 and 0.085, respectively, at 1 MHz.

Dielectric conductivity was found increasing with x (≤ 0.080) having maximum value at x = 0.08; and for the compositions with $x > 0.08$ dielectric conductivity was observed decreasing with increasing x, in the measured composition range, for all the measured frequencies, Fig. 3. The observed conductivity behavior may be related to the defect states in Ta2O5 based systems. Like other oxides, Ta2O5 is prone to oxygen deficiency [38]. Oxygen vacancies are deep double donors [39], which make Ta2O5 a very weakly n- type large band gap semiconductor. The oxygen- vacancies, other stoichiometric and impurity defects can cause leakage current [40-44].

The deep double donor oxygen vacancies are capable of producing two free electrons. When the relatively small quantity of Ti is added, the 'Ti – oxygen vacancy' forms a single donor complex capable of producing a single electron [42,43]. A single donor is shallower than a double donor. When there is sufficient number of Ti ions, it is possible for two Ti single acceptors to complex

with oxygen vacancy to form an electrically inactive 'Ti – oxygen vacancy – Ti' complex. When the concentration of Ti is relatively low, the 'Ti – oxygen vacancy' single donors are more likely to form than the electrically inactive complexes, resulting increasing conductivity with increasing x, up to x = 0.080. For sufficiently added quantity of Ti electrically inactive complexes may be formed, and leakage current reduces with further increase of x (> 0.080).

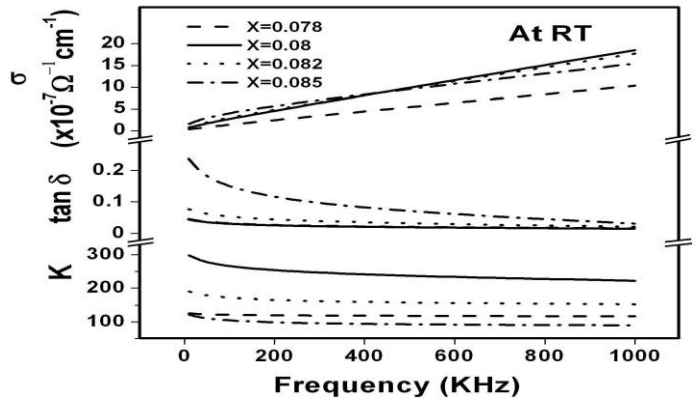

Fig. 4: Variation of (a) dielectric constant (K), (b) loss tangent (tan δ), and (c) dielectric conductivity (σ) of $[Ta_2O_5]1\text{-}x\text{-}[TiO_2]x$, ($0.078 \leq x \leq 0.085$), with frequency, for different compositions.

The observed frequency variation of K, tan δ and σ, for different compositions is shown in Fig. 4. Generally, dielectric constant and loss tangent were observed decreasing and dielectric conductivity increasing with increasing frequency. These observations are in good agreement with the reported results for other oxides [23, 45-48]. The damping out of successive polarization modes may be held responsible for the observed frequency dispersion of dielectric properties [45]. The observed decreasing loss with increasing frequency can be understood by an equivalent parallel resistor- capacitor circuit for a lossy dielectric [46]. At higher frequency, capacitor provides low reactance path to the sinusoidal signal and thus conduction losses in the resistor reduce, which results decreasing loss with increasing frequency, in the dielectric.

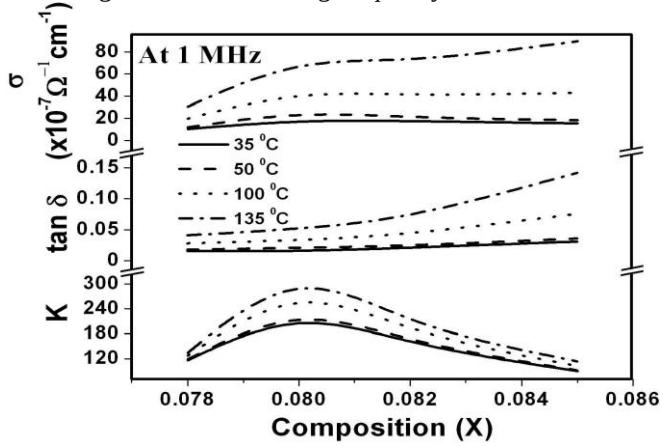

Fig. 5: Variation of (a) dielectric constant (K), (b) loss tangent (tan δ), and (c) dielectric conductivity (σ) of $[Ta_2O_5]1\text{-}x\text{-}[TiO_2]x$, ($0.078 \leq x \leq 0.085$), with composition (x), at different temperatures.

Composition dependence of K, tan δ and σ, at different temperatures has been shown in Fig. 5. Values of all these parameters were observed increasing with increasing temperature. Dielectric constant, at all the measured temperatures, was found maximum for the composition with x = 0.08. Figs 4 and 5 indicate that the dielectric properties of H- phase [Ta2O5]1-x- [TiO2]x are dominantly driven by composition rather than the frequency or temperature, in the observed composition range.

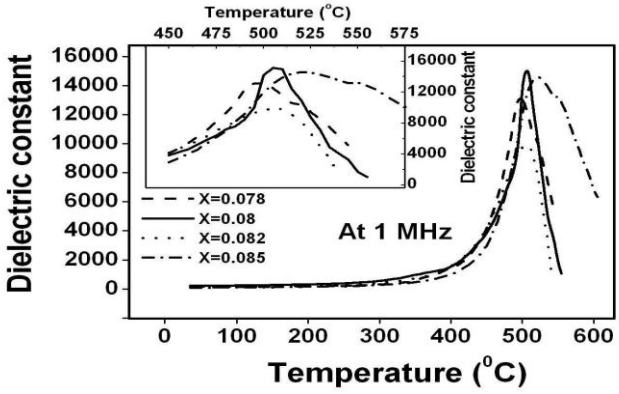

Fig. 6: Temperature dependence of dielectric constant (K) of $[Ta_2O_5]_{1-x}\text{-}[TiO_2]_x$,

$(0.078 \leq x \leq 0.085)$, at 1 MHz.

The observed temperature dependence of dielectric constant of the prepared compositions, at 1 MHz, has been shown in Fig. 6. 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. 6. These transition anomalies may be attributed to the monoclinic (or triclinic) to monoclinic (H'mon) structural change [49]. Dielectric loss and dielectric conductivity were found slowly increasing with temperature, with an anomalous rise near the transition temperature, Figs. 7 and 8, respectively, for all the prepared compositions.

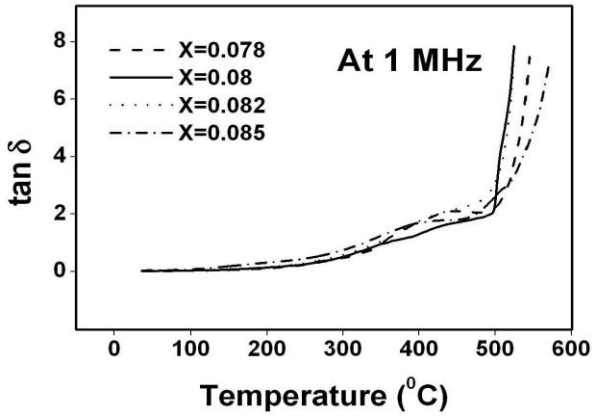

Fig. 7: Temperature dependence of loss tangent (tan δ) of $[Ta_2O_5]1\text{-}x\text{-}[TiO_2]x$, $(0.078 \leq x \leq 0.085)$, at 1 MHz.

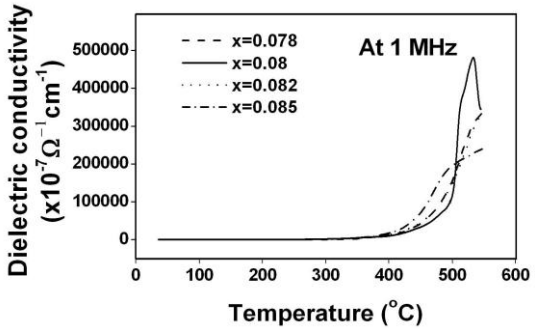

Fig. 8: Temperature dependence of dielectric conductivity (σ) of $[Ta_2O_5]1\text{-}x\text{-}[TiO_2]x$, $(0.078 \leq x \leq 0.085)$, at 1 MHz.

Frequency of the active mode decreases with increasing temperature, which results increase in the dielectric constant with temperature [32]. 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 [49-53]. 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 [18], and temperature dependent Raman data [49]. 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, 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 [50-54].

The observed dielectric constant values are significantly greater than those for silicon oxy-nitrides currently used in microelectronics industry, and are useful when memory densities higher than those obtained by using Ta2O5 are required. By reducing the leakage current further applications may include gate dielectrics for miniaturization of integrated circuitry.

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