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The effect of Ta$_2$O$_5$- and ZnO-doping on the Curie temperature of BaTiO$_3$

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Abstract The phase, microstructure and Curie temperature of Ba$_{1-2x}$Ta$_{2x}$Ti$_{1-x}$Zn$_x$O$_3$ (0.005 ≤ x ≤ 0.1) have been investigated in an attempt to widen its temperature stable region. The compositions formed dense, single-phase, fine-grained BaTiO$_3$ ceramics at x ≤ 0.01 and multiphase ceramics at x ≥ 0.015. The dielectric constant decreased with an increase in the dopant concentration due to second phase formation. The Curie temperature increased from ~123°C at x = 0.005 to ~148°C at x = 0.1 and the optimum sintering temperature decreased from ~1430°C at x = 0.005 to 1276°C at x = 0.1.

1. Introduction
A number of ABO$_3$-type compounds have excellent electrical properties making them suitable for industrial applications e.g. multilayer ceramic capacitors (MLCCs), transducers, sensors and resonators. To expand the temperature range of their applications, the effect of various dopants on the A and/or B site of the perovskite structure have been tried and investigated [1-3]. Barium meta-titanate (BaTiO$_3$), with ABO$_3$ type perovskite structure, is one of the most widely used dielectric materials, e.g. as a dielectric in MLCCs due to its high permittivity and low losses, and in electro-optic devices and thermistors because of its good dielectric characteristics [1,2]. BaTiO$_3$ has five isomorphs namely, hexagonal >1430°C, cubic >120°C, tetragonal below 120°C to 5°C, orthorhombic below 5°C to -90°C and rhombohedral below -90°C. Its cubic form is paraelectric while in the other forms its behavior is ferroelectric [4,5]. The low Curie temperature ‘$T_c$’ (~120°C) of BaTiO$_3$ limits its temperature stable region for applications like MLCCs. Various dopants have been tried on the A and/or B sites of BaTiO$_3$ in an attempt to overcome this disadvantage. Doping of Ce$^{3+}$ or Y$^{3+}$ on the Ba$^{2+}$ site and Ce$^{4+}$ on Ti$^{4+}$ sites is known to lower $T_c$ [6,7]. Co-doping of BaTiO$_3$ with rare earth ions of relatively smaller radii has been reported to shift $T_c$ towards higher values with increased tetragonality [8,9]. Of all the single element dopants, only Pb doping on the A-site of BaTiO$_3$ could increase $T_c$ to ~490°C but Pb is avoided due to its toxic nature. Recently, Kumada et al [10] reported a rise in $T_c$ of BaTiO$_3$ up to 140°C as a result of co-doping with Bi and Cu. Here we report our findings regarding the effect of Ta and Zn co-doping on the phase, microstructure and Curie temperature of BaTiO$_3$. 

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2. Experimental

BaTiO$_3$ samples were prepared by solid state mix-oxide route using laboratory reagent grade BaCO$_3$, TiO$_2$, Ta$_2$O$_5$, and ZnO. Batches of Ba$_{1-2x}$Ta$_{2x}$Ti$_{1-x}$Zn$_x$O$_3$ (0.005 ≤ x ≤ 0.1) were mix-milled for 24h in a horizontal ball mill with Y-toughend ZrO$_2$ balls as milling media and 2-propanol as lubricant. The resulting slurries were dried overnight and sieved. Powder samples were calcined at 1210°C for 15h, with a cooling/heating rate of 10°C/min. The calcined powders were re-milled for 30 min to dissociate agglomerates, dried, sieved and pressed into 2-3 mm high 13 mm diameter pellets at ~100 MPa. The pellets were sintered for 2h at temperatures ranging from 1276°C to 1430°C for different compositions at 5°C/min. Density of sintered pellets was measured using a MD-300S Electronic densitometer. A Philips 1700 series X-ray diffractometer (CuK$_\alpha$ radiations with $\lambda$ ~1.54Å) operating at 40 kV and 30 mA was used for phase analysis. Microstructural characterization of thermally etched gold-coated samples was performed using a JEOL JSM-5910 SEM operating at 15-20 kV. Electrical properties were measured using a HP 4287A LCR meter from RT-200°C at 1 kHz to 1 MHz.

3. Results and Discussion

XRD revealed the presence of tetragonal BaTiO$_3$ (PDF# 5-626) only in the samples calcined at 1210°C and sintered at 1430°C and 1400°C at low (x≤0.01) doping concentrations (figure 1); however, with an increase in the amount of dopant >0.01, additional XRD peaks due to secondary hexagonal Ba$_3$Ta$_5$Ti$_5$O$_{21}$ (PDF# 83-2318) phase emerged (figure 1). A few more low intensity peaks (labeled as ‘?’) were also present on the XRD patterns from x≥0.015 samples which could not be identified.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** XRD patterns of Ba$_{1-2x}$Ta$_{2x}$Ti$_{1-x}$Zn$_x$O$_3$ sintered at a) 1250°C at x = 0, b) 1430°C at x = 0.005, c) 1400°C at x = 0.01, d) 1320°C at x = 0.015 and e) 1276°C at x = 0.1 showing almost single phase BaTiO$_3$ at x≤0.01 and multi-phase ceramics at x>0.015.

SEM revealed the presence of somewhat hexagonal-shaped BaTiO$_3$ grains of size ~0.3x0.3μm$^2$ to <1x1μm$^2$ in the sintered microstructure of Ba$_{1-3x}$Ta$_x$Ti$_{1-x}$Zn$_x$O$_3$ (x=0.005) (figure 2a) and the grain size decreased up to ~0.2x0.2μm$^2$ to 0.5x0.5μm$^2$ with an increase in x to 0.01 (figure 2b). At x = 0.015, the
general morphology of the grains appeared unchanged; however, a few relatively larger grains labeled as ‘S’ containing ~67wt% BaCO$_3$, 25wt% TiO$_2$, and 8wt% Ta$_2$O$_5$, indicative of second phase formation could be seen (figure 2c). The microstructure of the samples with $x = 0.1$ (figure 2d) demonstrated a multiphase microstructure with elongated grains labeled as ‘R’ containing ~51wt% BaCO$_3$, 41wt% TiO$_2$, 6.5wt% Ta$_2$O$_5$, and 1.5 wt% ZnO and deformed irregular-shaped massive grains labeled as ‘M’ containing ~34wt% BaCO$_3$, 20wt% TiO$_2$, and 46wt% Ta$_2$O$_5$ in a fine grained matrix of composition close to BaTiO$_3$. BF-TEM images and corresponding SADPs from sintered Ba$_{1-2x}$Ta$_{2x}$Ti$_{1-x}$Zn$_x$O$_3$ samples showed single-phase compound iso-structural with tetragonal BaTiO$_3$ at $x=0.005$ (figure 3a) and an additional Ba$_{3}$Ta$_{3.2}$Ti$_{5}$O$_{21}$ phase at $x=0.1$ (figure 3b) consistent with XRD results.

**Figure 2.** SEIs from Ba$_{1-2x}$Ta$_{2x}$Ti$_{1-x}$Zn$_x$O$_3$ samples showing a-b) visibly fine-grained, single phase microstructure at $x \leq 0.01$ and multiphase microstructure at $x \geq 0.015$.

**Figure 3.** BF-TEM images and relevant SADPs from Ba$_{1-2x}$Ta$_{2x}$Ti$_{1-x}$Zn$_x$O$_3$ samples showing a) single-phase compound iso-structural with tetragonal BaTiO$_3$ at $x=0.005$ and b) Ba$_{3}$Ta$_{3.2}$Ti$_{5}$O$_{21}$ at $x=0.1$. 


The maximum $\varepsilon_r \sim 3000$ at 10 kHz to 1 MHz (figure 3a) measured in the present study corresponded to the ~95% dense sample with minimum dopants concentration ($x = 0.005$). The relative density slightly increased from 95% to 97% with an increase in dopant concentration from $x=0.005$ to 0.1; however, $\varepsilon_r$ decreased (figure 4a-b) probably due to second phase formation. Keeping in view the very small variation in density with increase in $x$ from 0.005 to 0.1, the observed increase in Curie temperature from $\sim 123^\circ$C to $148^\circ$C may be due to the increase in dopant concentration (figure 4a-b). This indicates that Ta and Zn are more effective dopants at low concentrations than Bi and Cu [10] and can be used to widen the temperature stable region of $\text{BaTiO}_3$.

4. Conclusions

$\text{Ba}_{1-x}\text{Ta}_x\text{Ti}_{1-x}\text{Zn}_x\text{O}_3$ sintered to single phase dense ceramics with $\varepsilon_r \sim 3000$ at $x \leq 0.01$. The highest $T_c$ ($\sim 148^\circ$C) was achieved for the composition with $x=0.1$ but with decrease in $\varepsilon_r$ due to second phase formation at $x \geq 0.015$. The optimum sintering temperature decreased from $\sim 1430$ to $1276^\circ$C with increase in $x$ from 0.005 to 0.1.

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References