



Synthesis and Characterization of Sol-Gel Derived Barium Calcium Zirconate Titanate ($\text{Ba}_{0.8}\text{Ca}_{0.2}$)($\text{Zr}_{0.2}\text{Ti}_{0.8}$) O_3 Powder and Ceramics

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ABSTRACT

Barium calcium zirconate titanate ($\text{Ba}_{0.8}\text{Ca}_{0.2}$)($\text{Zr}_{0.2}\text{Ti}_{0.8}$) O_3 [(Ba+Ca):(Zr+Ti) = 1:1] powder and ceramics were prepared using a sol-gel chemical route. The ceramics fabricated from the sol-gel derived powder were characterized for their structural, morphological, dielectric and ferroelectric properties. Temperature and frequency dependent dielectric properties were measured for these ceramics in the temperature range 30 to 200°C and at different frequencies of 100 Hz, 120 Hz, 1 kHz, 10 kHz, 20 kHz and 100 kHz. It was observed that ferroelectric to paraelectric transition temperature (T_c) reduced from ~120°C for pure Barium titanate (BaTiO_3) to around 20-30°C with the partial substitution of Ba^{2+} ions by calcium at A-site. Simultaneous partial substitution of Ti^{4+} ions by zirconium at B-site helped in increasing the dielectric constant at all frequencies. A well defined ferroelectric loop was observed for the ceramic. Remanent polarization (P_r) value of 0.5121 $\mu\text{C}/\text{m}^2$ was obtained for the sample at room temperature.

KEYWORDS : Barium calcium zirconate titanate, dielectric and ferroelectric properties, XRD, SEM

Introduction

ABO₃ perovskite type Barium titanate (BaTiO_3) ceramics partially substituted by calcium and zirconium at A-site and B-site respectively are promising ferroelectric material for piezoelectric applications. The material has shown promising piezoelectric properties. For instance, barium calcium zirconate titanate [($\text{Ba}_{1-x}\text{Ca}_x$)($\text{Ti}_{0.95}\text{Zr}_{0.05}$) O_3 ($x = 0.02$ to 0.20)] ceramics prepared using a solid-state reaction technique exhibited polymorphic phase transitions from orthorhombic to tetragonal phase around room temperature for $0.06 < x < 0.10$ [1]. A high piezoelectric coefficient of $d_{33} = 365$ pC/N and high planar electromechanical coupling factor of $k_p = 48.5\%$ were obtained for the sample ($x = 0.08$). With Ca^{2+} substitution, the orthorhombic-tetragonal phase transition point shifted towards room temperature while the Curie temperature (T_c) stayed around 110°C. However, grain size of ceramics strongly affects the properties of relaxor ferroelectric ceramics such as BCZT [2]. For ($\text{Ba}_{0.90}\text{Ca}_{0.10}$)($\text{Zr}_{0.25}\text{Ti}_{0.75}$) O_3 ceramics with grain sizes of 0.85, 2.5, 15, and 30 μm prepared from powders synthesized using a sol-gel process, it has been observed that as the grain size decreased, the maximum dielectric constant (ϵ'_{max}) decreased but the transition temperature increased. Hao et al. [3] reported the correlation between the microstructure and electrical properties in ($\text{Ba}_{0.85}\text{Ca}_{0.15}$)($\text{Zr}_{0.1}\text{Ti}_{0.9}$) O_3 ceramics. These ceramics were prepared using three different sintering methods: spark plasma sintering, two-step sintering, and normal sintering with grain sizes in the range of 0.4–32.2 μm . It was observed that that reducing grain size shifted the T_c to higher temperatures, and tended to enhance the relaxor behavior. For ceramics with grain sizes > 10 μm , piezoelectric properties of $k_p > 0.48$, $kt > 0.46$, $d_{33} > 470$ pC/N and $d_{33}^* > 950$ pm/V were obtained. According to Damjanovic et al. [4] the solid solution $0.5\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})_0.5\text{O}_3$ ($\text{Ba}_{0.7}\text{Ca}_{0.3}$)TiO₃ (BCZT) shows high piezoelectric coefficients that can be attributed to structural instabilities close to ambient temperature. BCZT powders have also been used as a filler in ferroelectric polymer to form composite flexible films [5]. $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Zr}_{0.15}\text{Ti}_{0.85}\text{O}_3$ ceramic particles were prepared by a conventional solid-state method and coated by dopamine. These particles were then added into a ferroelectric polymer (polyvinylidene fluoride) and composite film was prepared using solution casting method. The dielectric constant of the composite film increased with the increase of BCZT contents, however, the loss

tangent remained constant in the frequency range of 103 to 105 Hz. Based on these results, various theoretical models were used to predict the effective dielectric constants of the composite films. For co-doped BCZT ceramics viz. $\text{Ba}_{0.9175}\text{Ca}_{0.0825}\text{Nd}_{0.0025}\text{Zr}_{0.18}\text{Ti}_{0.8175}\text{Mn}_{0.0025}\text{O}_3$ (BCZT-Y, $x = 0, 0.5, 0.75, 1.0, 1.5, 2.0$) prepared by a solid phase reaction it has been shown that Y^{3+} ion substitution can be almost incorporated into the Ti 4+ site that increased the density of BCZT-Y ceramics [6]. The Curie temperature shifted to a lower temperature. However, ϵ_{max} peak got suppressed and broadened. In a similar type of work, Zhang et al. [7] synthesized $(1-x)(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})_0.9\text{O}_3$ ($\text{BiZn}_{0.5}\text{Ti}_{0.5}$) O_3 (BCZT-NBT) ceramics for $x = 0.6$ –1.0 by the solid-state reaction method. For these ceramics it was observed that Curie temperature increased from 274°C ($x = 0.6$) to 333°C ($x = 1.0$). The maximum ϵ_r at Curie temperature was found to be 3243 at $x = 0.8$. Parjansri et al. [8] have reported the electrical properties of $(1-x)[\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3 - x](\text{BiZn}_{0.5}\text{Ti}_{0.5})_0.9\text{O}_3$ ceramics system for $x = 0.00$ –0.10 prepared using solid state reaction technique. It was observed that BZT content improved the dielectric properties of ceramic samples and a dielectric loss values lower than 0.01 (at 1 kHz) were obtained for all samples. It has also been reported that dielectric properties of doped and undoped BCZT ferroelectric ceramics depend strongly on sintering temperature. A higher sintering temperature leads to improved piezoelectric properties. For instance, Huang et al. [9] have reported that for $0.996(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})_{0.996}\text{BiY}_3$ [BCZT-BY] ceramics prepared by solid-state sintering method, and sintered at 1420°C, $d_{33} = 130$ pC/N and $k_p = 18.2\%$, were obtained. Li et al. [10] reported that BCZT ceramics doped with Ho show even better piezoelectric properties. ($\text{Ba}_{0.99}\text{Ca}_{0.01}$)($\text{Ti}_{0.98}\text{Zr}_{0.02}$) O_3 (BCZT)+xHo ($x = 0$ –0.6) ceramics prepared using solid-state reaction technique exhibited $d_{33} = 330$ pC/N and planar electromechanical coupling factor of $k_p = 40\%$ at $x = 0.2\%$. In the temperature range 20 to 100°C, Ho doped BCZT ceramics exhibited pure tetragonal phase. With the increase of Ho content, the orthorhombic-tetragonal phase transition shifted towards lower temperature, while Curie temperature (T_c) remained at about 120°C. Most of the papers found in the literature have been reported on the dielectric and piezoelectric properties of BCZT and doped BCZT ceramics prepared using solid state reaction method. Very few papers have been reported on the sol-gel synthesis of BCZT ceramics. Hence, in this paper sol-gel

synthesis and characterization of BCZT powder and ceramics is being reported.

2.0 Materials and methods

1.1 Raw material and synthesis of powder and ceramic

Sol-gel synthesis of $(\text{Ba}_{0.8}\text{Ca}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ powder and ceramics

The precursors for barium, calcium, titanium and zirconium were respectively barium acetate, calcium acetate, titanium tetrabutoxide and zirconium isopropoxide. All these chemicals were procured from Sigma-Aldrich. Acetic acid [CH_3COOH >99.7%] and butyl alcohol [$\text{C}_4\text{H}_9\text{OH}$ >99.5%] were used as solvents. Barium acetate and calcium acetate were mixed in acetic acid and refluxed for 30 min using a sand bath Titanium tetrabutoxide and Zirconium isopropoxide were mixed in butyl alcohol. After cooling down to room temperature, the Ba-Ca solution was mixed with Ti-Zr solution using a magnetic blender for 30 min. A small amount of acetylacetone [$\text{CH}_3\text{COCH}_2\text{COCH}_3$] was added as a stabilizer. The sol thus obtained was hydrolysed by adding 10-15 mL of distilled water. The sol was relatively clear and stable. The sol was covered with aluminium foil and kept in a dessicator to avoid air contamination and left overnight for gelation. The sol was still transparent and clear. However, it transformed into an opaque gel upon heating. The gel was then fired in air to obtain amorphous powder. The dry gel was calcined at 900°C for 3h in a muffle furnace to obtain a poly-crystalline powder. The BCZT powder so obtained was milled and die-pressed into thick pellets under a pressure of 300 MPa. These pellets were sintered at 1350°C and 1400 °C for 1hr in a muffle furnace to obtain dense ceramics. The powder and ceramics BCZT were prepared using a procedure given in the flow chart (Fig.2.1).

2.2 Material Characterization

X-ray diffraction

Structural characterization of $(\text{Ba}_{0.8}\text{Ca}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramic sintered at 1350 °C for 1h was done using X-ray diffraction. Figure 2.2 shows a comparison of the X-ray diffractograms of BT, BCZT. The peaks show polycrystalline nature and confirm the formation of BCZT structure.

Scanning Electron Microscopy (SEM)

Morphological properties of $(\text{Ba}_{0.8}\text{Ca}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramic were studied using scanning electron microscope (SEM). The photomicrograph showing the formation of grains is shown in Fig. 2.3.

FT-IR spectroscopy

FT-IR spectrogram of BCZT powder is shown in Fig. 2.4. The peak at $\sim 595\text{cm}^{-1}$ is due to TiO6 octahedral.

Dielectric characterization

AC frequency dependent values of parallel capacitance (C_p) and loss tangent or dissipation factor ($\tan \delta$ or D) of the ceramics pellets were measured using Agilent 423B precision LCR meter. The actual thickness of samples was measured using a micrometer before electroding by application of conductive silver plate using a paint brush. Electroded samples were placed in a sample cell between two electrodes and voltage was applied. The parallel capacitance (C_p) was measured on the LCR meter. Dielectric constant was calculated using the formula:

$$(\epsilon) = C/C_0$$

where, $C_0 (= \epsilon_0 A/d)$ is the capacitance with vacuum between parallel plates and $\epsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of free space, A is the area of electrode sample, and d is the thickness of the sample. Dissipation factor (D or $\tan \delta$) was directly measured on the LCR meter. To calculate ac conductivity, parallel capacitance (C_p) and dissipation factor (D or $\tan \delta$) from 100 Hz up to 100 KHz was measured. $\sigma_{ac}(\omega)$ was calculated by using following expression:

$$\sigma_{ac}(\omega) = 2f\epsilon_0\epsilon'' = 2f\epsilon_0\epsilon'' \tan \delta$$

where $\tan \delta$ is the dissipation factor, $\omega = 2\pi f$ is the angular frequency ϵ'' is the dielectric constant ($\epsilon''/\epsilon' = \tan \delta$), and ϵ'' is the dielectric loss.

Ferroelectric characterization

The ferroelectric loop of the sample was obtained using a Sawyer-Tower circuit. The loop was observed on a cathode ray oscil-

loscope. Figure 2.5a and b respectively show the photographs of ferroelectric loop obtained on BT and BCZT ceramic. Using these loops remanent polarization (P_r) as well as saturation polarization (P_s) were calculated for both BT and BCZT. For BT the P_r and P_s values were $0.0843 \mu\text{C}/\text{m}^2$ and $0.1665 \mu\text{C}/\text{m}^2$ respectively. In the case of BCZT, P_r and P_s values were $0.5121 \mu\text{C}/\text{m}^2$ and $1.0241 \mu\text{C}/\text{m}^2$ respectively.

3.1 Results and discussion

Temperature and frequency dependent dielectric behavior of $(\text{Ba}_{0.8}\text{Ca}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramics sintered at 1350°C and 1400°C are shown in Fig. 3.1. Figure 3.1a shows the temperature dependent dielectric constant of $(\text{Ba}_{0.8}\text{Ca}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramics sintered at 1400°C for 1h. It is clear from the figure that the value of dielectric constant was almost same at all temperatures at all frequencies. At T_c (almost near room temperature of 20-30°C) at 100Hz, 120 Hz and 1 kHz, a high value of dielectric constant ~ 2160 was obtained for this ceramic. However, at other higher frequencies of 10 kHz, 20 kHz and 100 kHz the ceramic exhibited an absurd behaviour for dielectric constant as well as dielectric loss. Figure 3.1b shows the temperature dependent dielectric constant of $(\text{Ba}_{0.8}\text{Ca}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramics sintered 1350°C for 1h. At T_c , at 1 kHz, a value of around 1250 was obtained for this ceramic. Thus, a slight increase in sintering temperature improved the dielectric constant of BCZT ceramic. Figure 3.1c shows the temperature dependent dielectric loss of the same ceramics. Dielectric loss was found to be below 0.1 at all frequencies close to room temperature. However, at T_c the dielectric loss was also the maximum. A comparison of the temperature dependent dielectric constant of barium titanate and BCZT ceramic measured at 1 kHz is shown in Fig 3.2. From Fig. 3.2 it is clear that the T_c of BaTiO_3 ($\sim 120^\circ\text{C}$) has shifted to the lower temperatures ($<30^\circ\text{C}$) with partial substitution of barium by calcium at A-site and titanium by zirconium ions at B-site. Furthermore, values of dielectric constant decreased sharply with increase in temperature in paraelectric phase. These trends are in accordance with the reported literature according to which the Curie temperature as well as maximum dielectric constant can be changed by partial substitution of barium and titanium ions [11,12]. Figure 3.3 show the frequency dispersion of dielectric constant (ϵ') of both the ceramics measured at room temperature (28°C). It is evident from the figure that $(\text{Ba}_{0.8}\text{Ca}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ shows highest values of dielectric constant at all frequencies.

3.2 Conclusions

Bulk ceramics of Barium calcium zirconium titanate $(\text{Ba}_{0.8}\text{Ca}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ prepared using fine powders derived from sol-gel method showed that with calcium substitution the ferroelectric-paraelectric phase transition temperature (T_c) shifted to lower temperatures. With partial substitution of Ba^{2+} by calcium ions and Ti^{4+} ions by zirconium ions, dielectric constant of barium titanate can be significantly improved ($\epsilon'_{\text{max}} > 2000$) at room temperature (25°C). The dielectric constant of BST ceramics shows no frequency dispersion at higher frequencies (1 kHz to 100 kHz).

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Fig. 2.1: Flow chart for the preparation of BCZT powder and ceramic

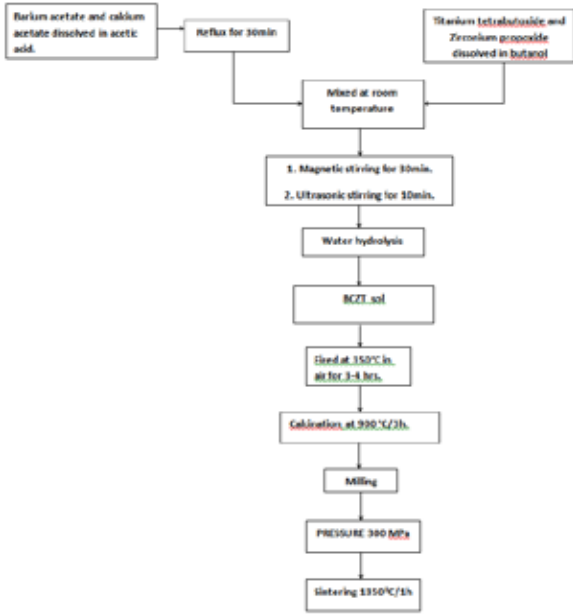


Fig. 2.2 XRD diffractograms of Barium titanate and Barium calcium zirconate titanate

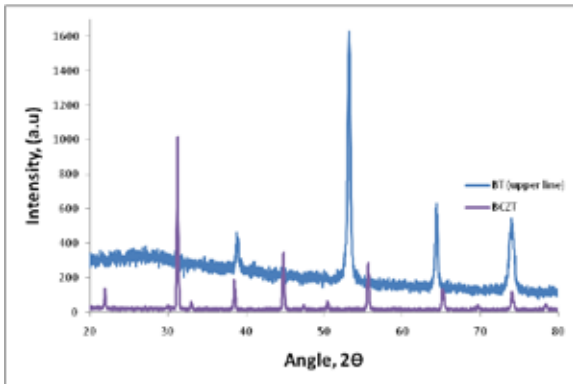


Fig. 2.3: Scanning electron micrographs at two different magnifications showing the grain formation in BCZT ceramics sintered at 1350°C for 1 hr

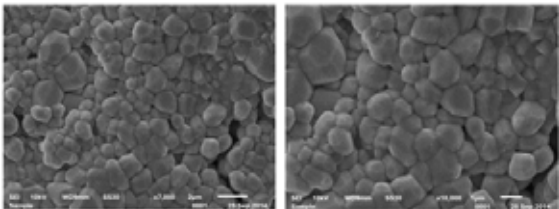


Fig. 2.4: FT-IR spectrogram of BCZT crystalline powder

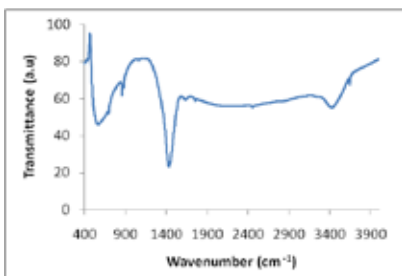


Figure 2.5a and b respectively show the photographs of ferroelectric loops obtained on BT (left) and BCZT (right) ceramics

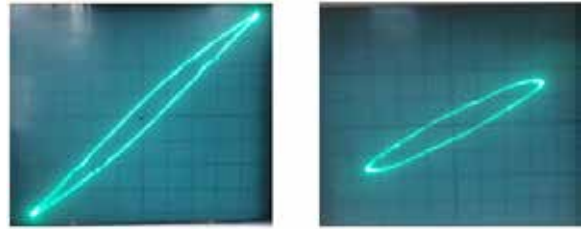


Fig.3.1a Plot of dielectric constant vs temperature for $(\text{Ba}_{0.8}\text{Ca}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramics sintered at 1400 °C for 1 hr.

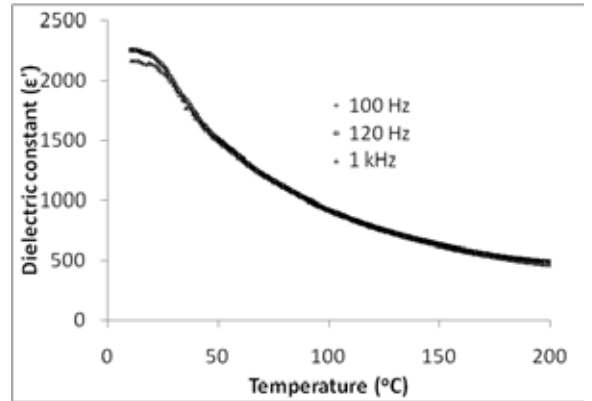


Fig.3.1c Plot of dielectric constant vs temperature for BCZT sintered at 1350 °C for 1hr.

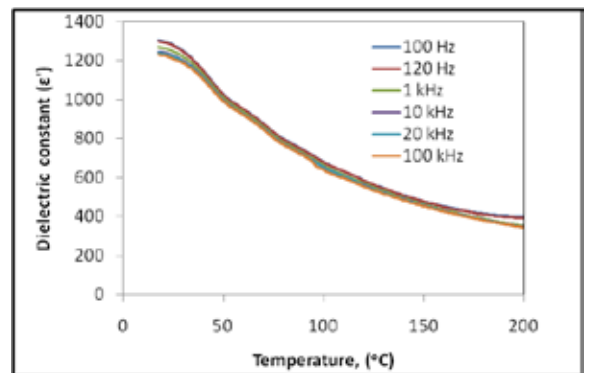


Fig.3.1d Plot of dielectric loss vs temperature for BCZT sintered at 1350 °C for 1hr.

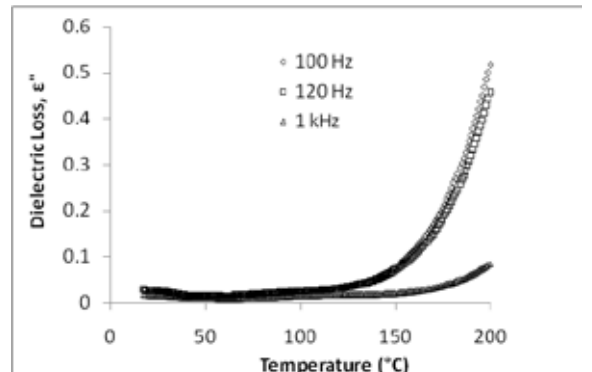


Fig. 3.2: A comparison of the temperature dependent dielectric constant of barium titanate and barium calcium zirconate titanate ceramics measured at 1 kHz

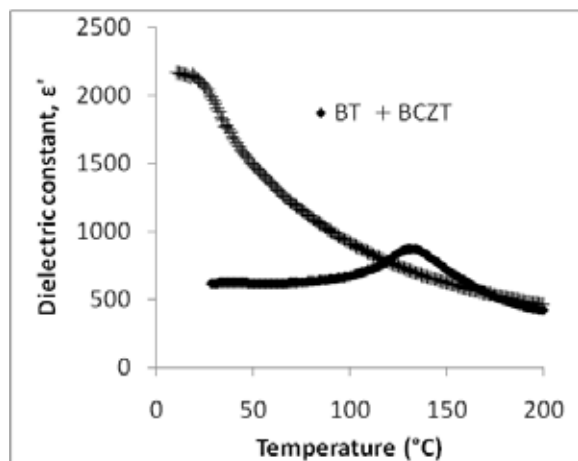
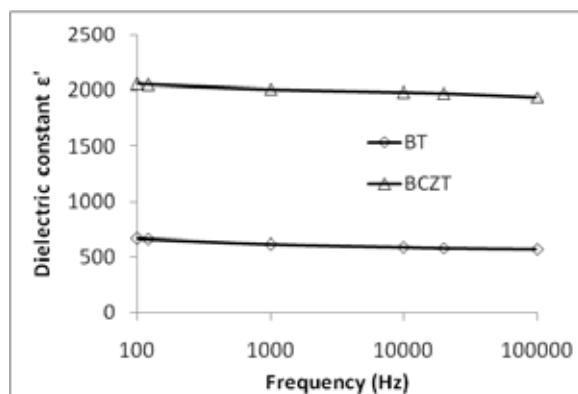


Fig.3.3: Dielectric constant of barium titanate (BT) and Barium calcium zirconate titanate (BCZT) ceramics measured at different frequencies at room temperature (28oC)



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