Dielectric behavior of the Aurivillius compound $Bi_{3.6}La_{0.4}Ti_3O_{12}$ prepared by hybrid process

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ABSTRACT: The component of $Bi_{3.6}La_{0.4}Ti_3O_{12}$ was prepared by hybrid process (sol-gel hydrothermal) at low temperature 400 °C. Bismuth acetate, lanthanum acetate and titanium isopropoxide were used as metallic source. By X-ray diffraction, the $Bi_{3.6}La_{0.4}Ti_3O_{12}$ ceramic has single $Bi_4Ti_3O_{12}$ phase of Aurivillius type. The assignment of the infrared transmittance bands, especially in the region 400– 1000 cm^{-2}. Dielectric properties of the obtained material at different frequencies 100 Hz, 1 kHz and 10 kHz as a function of temperature were investigated.

KEYWORDS: Sol-gel, hydrothermal, X-ray diffraction, infrared, dielectric proprieties.

1 INTRODUCTION

$(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ is a general formal of Aurivillius phases, where A is a mono-, di- or trivalent element (or combination) with cub octahedral coordination, B is a transition element suitable to octahedral coordination and m (1<m<6) is the number of octahedral layers in the perovskite slab.[1].

$Bi_4Ti_3O_{12}$ belongs to the Aurivillius family [2]. It has great applications in optical devices and ferroelectric memories [3]. Many authors has been studied La-doped [4, 5], it has a high Curie temperature (TC = 675 °C), is best candidate material for FeRAM devices. However, the fatigue-free behavior of lanthanum-substituted bismuth titanate $Bi_{4-x}La_xTi_3O_{12}$ (BLT) received increasing attention [6], wish it is easy to substitute selectively bismuth in layered perovskite by lanthanum. BLT has many attractive properties, such as low processing temperature and large values of remnant polarization.

The compounds of La-doped bismuth titanate (BLT) were prepared by various methods, where require more or less higher temperatures to achieve. By solid state, BLT ceramics were sintered using the conventional sintering method at 1150 °C.

According to Guo Dong-Yun et al. [7], The $Bi_4Ti_3O_{12}$ and $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films were prepared on the $Pt/Ti/SiO_2/Si$ substrate using the sol–gel method annealed at different temperatures (550–750 °C). A sol–gel process was used to prepare BLT powders synthesized by sol–gel method and calcinated at 900 °C [8], other authors may have prepared the BLT at 650°C and 750°C by sol-gel and co-precipitation respectively. However, there is scarcities information of $Bi_{4-x}La_xTi_3O_{12}$ prepared by hydrothermal method.

The sol–gel-hydrothermal processing represents an alternative to the calcinations for the crystallization of an objective compound under mild temperatures [9]. To our knowledge, the sol-gel hydrothermal method as called hybrid process could be a novel technique to prepare $Bi_{3.6}La_{0.4}Ti_3O_{12}$ powder. Our challenge is to form sufficient large pure powder at low temperature by combing hydrothermal and sol-gel process.

2 EXPERIMENTAL

The first step is to prepare the powder by a sol-gel, in this respect the process of the preparation is reported in Figure 1. The used precursors are acetate bismuth, acetate lanthanum and titanium isopropoxide. The temperature of colloidal sol was kept at about 60–80 °C. Then the xerogel was gained.

The second step involves the hydrothermal method; the fine powder was kept under stirring in a solution of KOH (1 M) for 1 h, and then put into an autoclave (Filling ratio superior to 80%) and heated at 180 °C during 12. After filtration and drying, the powder was calcend at 400 during 24 h. The calcined fine powder was pressed into cylindrical pellet of 6 mm in diameter and 1 mm in thickness using a uniaxial press with a pressure of 5 MPa. This pellet was sintered at 450°C for 4 h, which was obtained on silver electrode sample in plane capacitor configuration.

The formation and quality of powder were verified with X-ray diffraction (XRD). FTIR used to identify types of chemical bonds (functional groups). The dielectric constant (ε) and loss tangent (tanδ) of the compound were measured using a HP 4284A with a home-made furnace.
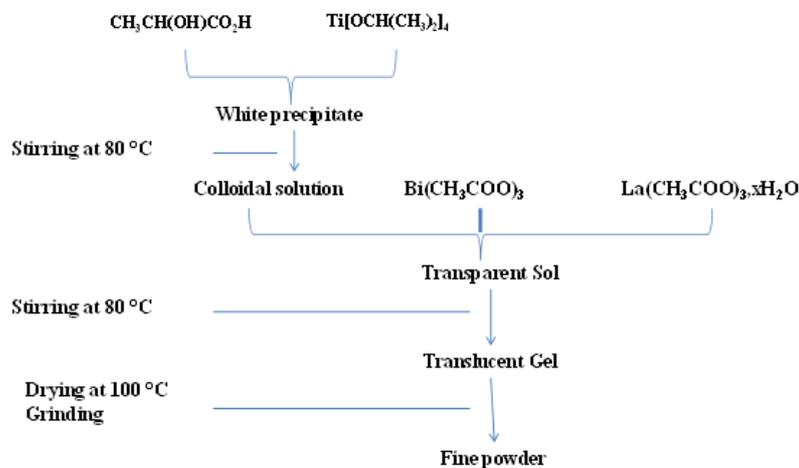

Fig 1. Flowchart for preparation of powder by sol-gel

3 RESULTS AND DISCUSSION

The powder X-Ray diffraction pattern (Figure. 2) confirms the layered perovskite structure, simulated with the reference pattern number JCPDS 00-035-0795 for $Bi_4Ti_3O_{12}$. The unit cell structure was found to be orthorhombic in accordance with matched reference pattern; a=5,424 Å; b=5,436 Å and c=32,824 Å. According to the Scherrer's formula [10, 11, 12], the crystallite size is found to be 81 nm.
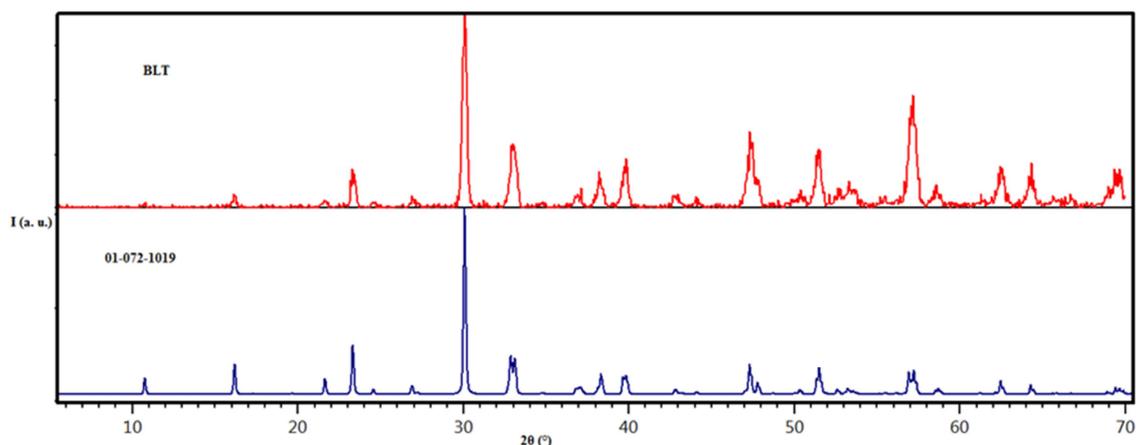

Fig 2. XRD pattern of SBLT powder

The FTIR spectrum is shown in Figure 2. The bands around 582 and 823 cm^{-1} (red line) related to the crystallization of the phase $Bi_4Ti_3O_{12}$ [13]. According Zhiwu Chen et al. [14], the bands around 814 and 600 cm^{-1} corresponded to the stretching vibrations of Bi-O and Ti-O, respectively, further indicating formation of well crystallized $Bi_4Ti_3O_{12}$. La-O bond was assigned to the presence of the absorption band at around 415–423 cm^{-1} [16]. The C–O vibration, at 1064 cm^{-1}, persists because of the residual carbon, wish not decomposed at 400 °C [17]. The bands around 3434 and 1630 cm^{-1} are attributed to the O-H groups of the water adsorbed at the powder surface when the sample was in contact with the environment. It noted that the absence of a C=O vibration around 1450 cm^{-1}, indication that the powders are free of carbonates [18].
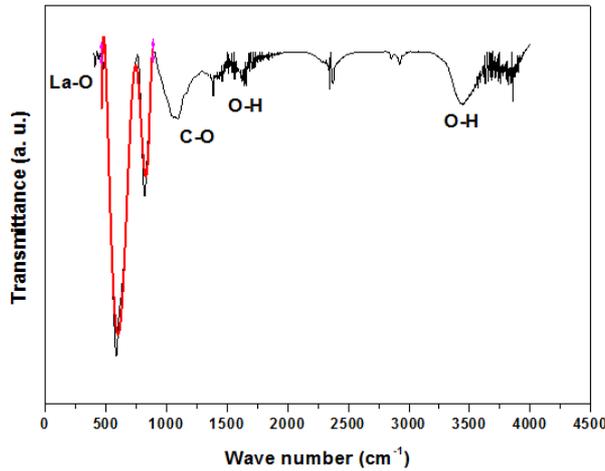

Fig 3. Characterization of powder by FTIR

Figure 3, shows the variation of dielectric (a) constant and (b) tangent loss with frequency at different temperatures. The ε' and tanδ increase with temperature and decrease with increasing frequency. It's observed to be high at lower frequency. Well, Below 370 °C, the variation in dielectric constant is much less frequency dependent, above 370 °C the increment in dielectric constant is stronger and much more frequency dependent, may due to the space charge polarization and inter face effect, or this is due to lattice expansion, polarizability of the constituent ions due to increase of atomic polarizability [19]. Another explanation suggests that these observations may be due to the fact that the dipoles cannot follow the fast variation of the applied field [20, 21].
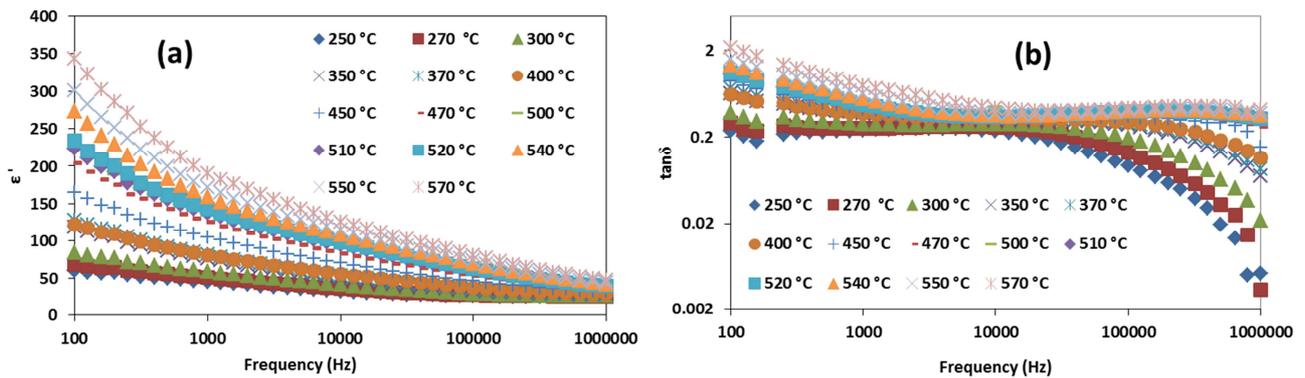

Fig 4. Variation of (a) dielectric constant and (b) tangent loss as a function of frequency at different temperatures

Figure 4, shows frequency dependence of dielectric constant at different temperatures. The pattern shows peaks around 600 °C for all frequencies which describes the normal ferroelectric phenomenon in the material. From literature the T_C was found to be around 630°C [22]. The dielectric constant peaks are 325, 155 and 100 for 100 Hz, 1 kHz and 10 kHz respectively. On the other hand, Figure 5 illustrates the variation of loss tangent (tan δ) as a function of temperature at 10 kHz. The tanδ

increases with increasing temperature. A kink appears around 590 °C; the value of tangent loss kink is 0.4. This bow observed may be due to the ferroelectric–paraelectric transition.
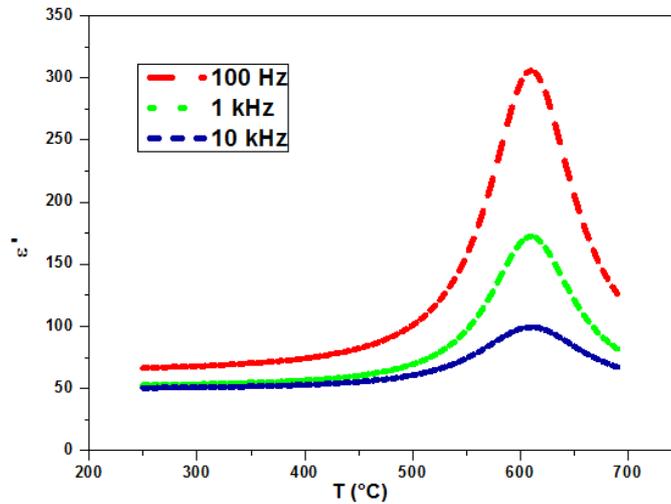

Fig 4. Variation of dielectric constant with temperature at different frequencies
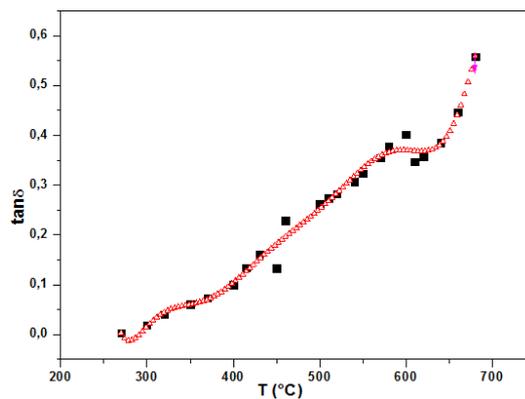

Fig 5. Dielectric loss as a function of temperature at 10 kHz

For a normal ferroelectric, should follow the Curie-Weiss law when the temperature exceeds the Curie temperature [23, 24]. The plot of the inverse dielectric constant as a function of temperature at 10 kHz is shown in Figure 7. When one extends the linear paraelctric portion of this curve back across the temperature axis, it intersects at the Curie-Weiss temperature (T$_{CW}$ = 595 °C), wish is close to T$_C$. Its shows feature characteristic of a second order phase transition.
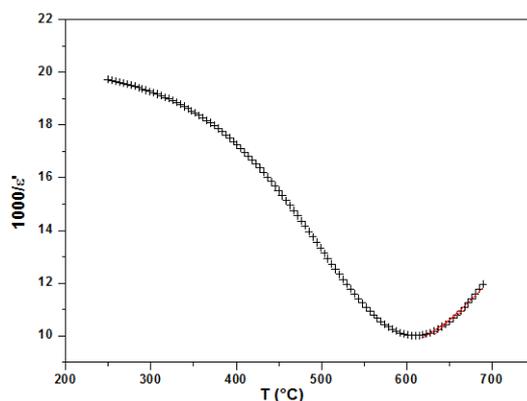
Fig 5. Inverse dielectric constant vs temperature at 10 kHz

4   CONCLUSION

The paper talks the low-temperature synthesis of $Bi_{3.6}La_{0.4}Ti_3O_{12}$ powder by the sol–gel-hydrothermal method. XRD pattern shows orthorhombic structure. The FT-IR spectra conforms result obtained from XRD. Dielectric measurements have shown T_C is at higher temperature and dielectric behavior is frequency dependent as well as temperature dependent. The microstructure is now examined in the future work under the name structural and dielectric properties of SBLT prepared by sol gel hydrothermal process.

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