Effect of sintering temperature on the structural properties for $CaBi_4Ti_4O_{15}$ compound

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Polycrystalline $CaBi_4Ti_4O_{15}$ (CBT) ceramics were successfully prepared by traditional ceramic technique. The X-ray diffraction spectrum of produced powder was studied at different temperatures (650 C, 850 C, and 1050C. The sintering temperature is very effective factor to obtained high crystallinity with very pure for CBT compound. The product structures analyzed using X-ray diffraction, it confirms, high purity polycrystalline phase formation revealed the existence of bismuth layered perovskite phase Aurivillius orthorhombic crystal structure at 1050^v C. The produced samples' A field emission scanning electron microscope was used to analyze the morphologies (FESEM). It shows crystallites particles in the range about 149-349 nm for the product sintered at1050^v C, it shows a dense microstructure with the presence of large orthorhombic distortion. The dielectric constant and dielectric loss were measured at room temperature as a function of frequency. The dielectric constant of CBT increases in sintering temperature. Moreover, the samples sintered at 1050 ℃ exhibits good dielectric properties and lower value of tan δ.

1. Introduction

Since the discovery of the piezoelectric effect, piezoelectric materials have been extensively researched for use as sensors, transducers, actuators, energy harvesting devices, and other applications. The orthorhombic $CaBi_4Ti_4O_{15}$ (CBT) compound, which has low electric conductivity, low dielectric loss, a relatively large piezoelectric coefficient, and is easy to fabricate using the traditional solid-state reaction method, is thought to be a promising candidate for high-temperature piezoelectric applications. [1-3]

Calcium Bismuth Titanate (CBT) gives excellent electro-optical properties. Also, ferroelectric behavior for high temperature it can be used in piezoelectric applications, memory storage, and electro-optical used because of its high Curie temperature [4].

The Aurivillius oxides family has gotten a lot of attention in the recent decade because of their excellent properties, which include unique dielectric, magnetoelectric, and ferroelectric phase transition temperatures. [5].

Basically, the crystal structure of Aurivillius alternating layers of $(Bi_2O_2)^{2+}$ and $(CaBi_2Ti_4O_{13})^{2-}$ layers, the latter is with pseudo-perovskite structure. Aurivillius family for $(Bi_2O_2)^{2+} (A_{n-1}B_nO_{3n+1})^{2-}$ general formula consist of A is a monovalent, divalent or trivalent cation located at the cub octahedral position on the corners, B metallic cations octahedral transition metal ion occupied the center, positive cations, where, the individual perovskite structure blocks consist of A and B Built. n is the number of block perovskite between successive bismuth oxide sheets. A-site cationic substitutions influence the structural characteristics of these materials.

These structures having ability to host ions at varying size in its crystalline partner, thus changing its material properties, this modifications for their gives wide application such as sensors, and in Ferroelectric Random-Access Memory (FRAM) [6], photocataliclly active [7].

Insulating materials contain polarization, but the polarization of the material changes as a result of release of charges under the influence of high temperature, which is called ferroelectric materials. As a result of changes in temperature or stress, the permanent polarization in the lattice is altered. The changes in polarization caused by temperature are characteristic of ferroelectrics [8].

When an external field is applied to ferroelectric materials, the orientation of the material changes between two or more distinct crystallographic directions, resulting in a spontaneous electric moment. Thus, ferroelectrics are characterized by the fact that their polarizations may be reversed by the suitable field application. The term 'Ferroelectricity was coined   to the close analogy to ferromagnetism/

Ferroelectric oxides in general, may be classified into two groups. The first one is Ferroelectrics in which spontaneous polarization may exist along one crystallographic axis in the non-polarized state, this group comprise potassium, tartrates etc. The second group is the materials having more than one polar axis and may further be subdivided into 4 structure types like Perovskites, Pyrochlores, Tungsten bronze materials and layer type bismuth compounds.

For many electrical applications, CBT is a suitable contender to replace lead-based materials. The problem of replacing PZT with less poisonous, more environmentally acceptable materials while maintaining performance equal to PZT is enormous. At normal temperature, $CaBi4Ti_4O_{15}$ ceramics have ferroelectric characteristics. Normal ferroelectrics, ferroelectrics with diffuse phase transition, and relaxor ferroelectrics are the three types of ferroelectric materials that can be classified based on their dielectric, polarization, and phase transition characteristics.

Ferroelectric materials exhibiting diffuse phase transition (DPT) and/or relaxor features have received a lot of attention in recent decades, owing to their intriguing and still poorly understood physical properties.

The insulating materials which give a high resistance to the flow of an electric current. The most important property of dielectric materials is their ability to be polarized under the action of an externally applied field.

The term ε is referred to as a material's dielectric constant, and it is a dimensionless number that may be determined using the equation. [9].

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_\circ}$$

ε_r is called the dielectric constant or the relative permittivity of a material and is a dimensionless quantity.

Compact multilayer capacitors with high dielectric permittivity, low dispersion, and wide frequency response are used in dielectric applications.

From these measurements ε_r and tan_δ (dielectric loss factor), were made available for the evaluation of ac conductivity on prepared samples.

The value of dispersion factor or loss factor of test material by $tan\delta$. In addition, a.c conductivity were carried on for CBT samples at room temperature in the same range of the frequency, σ_{ac} measurement can be calculated by following the equation [10].

$$\sigma = 2\pi f \varepsilon_\circ \varepsilon_i$$

σ= the conductivity $(\Omega.m)^{-1}$, f = is the frequency (Hz), and ε_i= imaginary part of dielectric constant (F/m).

The goal of this study was to see if the Aurivillius orthorhombic phase could be formed using a solid-state reaction approach. Also, investigate the impact of calcination temperature on the structure and characteristics of the CBT chemical that has been created. To examine the (A.C) conductivity behavior of these materials and propose a possible mechanism for observed conductivity of these materials

2. Experimental work

Powder samples were prepared using standard ceramic technique. The reactants included $CaCO_3$, Bi_2O_3 and TiO_2 as starting materials. Stoichiometric ratio of these materials was mixed to prepare $CaBi_4Ti_4O_{15}$ compound. This method involves mixing of oxides and carbonates as stating material of the required in stoichiometric amounts with molar ratio using the following equation:

$$CaCO_3 + 2Bi_2O_3 + 4TiO_2 = CaBi_4Ti_4O_{15} + CO_2 \qquad (1)$$
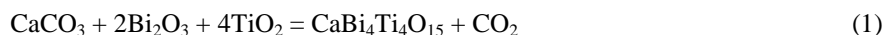
These starting materials were mixed using a gate mortar for 2 hours, then transferred to an electrical ball mill type (mixture mill 800 from American Spex instrument Inc) for 2 hours. The prepared powder was pressed into pellets using a 1 cm die at 3 tons, sample pellets where they sintered at 650° C, 850° C and 1050 °C for a period of 2 hours had been achieved. X-ray analysis using diffractometer made in Japanese Three temperature cycles were achieved with Cu-K radiation (=1.506 A) operated at voltage=40KV, current=30 mA, scanning angle (10-80), and speed=5 deg/min. A field emission scanning electron microscope (FESEM) was used to examine the microstructure (Tescana mera IIIZeiss-EM10C-100 KV).

2. Result and Discussion

The synthesis of CBT, the orthorhombic pure phases, is done by calcining precursors containing structure components, primarily oxides and carbonate, at relatively high temperatures, where the sintering temperature is extremely successful in preparing high crystallinity with pure CBT compound.

Figure (1) gives, the X-ray diffraction patterns of produced powder at various temperatures (650 C, 850 C, and 1050 C) are shown. When compared to the Aurivillius standard, the Joint Committee on Powder Diffraction Standards (JCPDS) cards are significantly less expensive. #52-1640. International Centre for Diffraction Data: ICSD-99500

The XRD pattern of this card, which can be indexed by an orthorhombic lattice, was found to be in good accord with Arie et al [11], with the space group of A21 am, and it was discovered that all of the calcined samples at 1050 C are pure Aurivillius phase with no impurity phase appearances. The main peak is around 30.75$^\triangledown$.
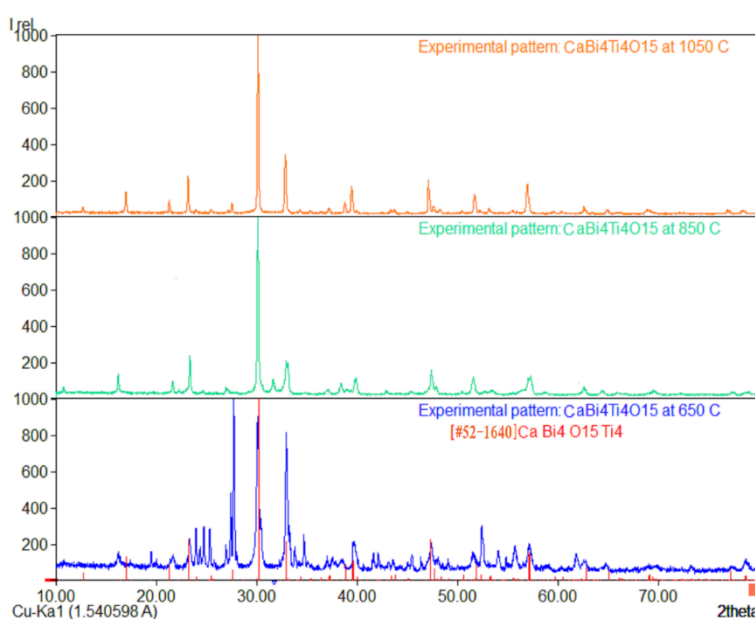

Fig. 1. XRD for CaBi₄Ti₄O₁₅ Prepared at different temperature (650˚C, 850˚C and 1050˚C).

Figure (2) shows, field emission scanning electron micrographs of the prepared compound at different calcination temperature (a) at 850°C, (b) 1050°C. The sintered powder at 850 °C consisted of fine particles in the (46-146) nm range associated with rounded-shape morphology also notice the presence of agglomerates in the same picture. The effect of heat treatment on the morphology and crystalline size is more pronounced in the samples sintered at 1050 °C as shown in figure 2(b). The grain size increase with increasing sintering temperature.

The heat treatment causes the same volatile species (e.g., bismuth oxide) to be ejected, resulting in the production of the CBT phase as the final component (here the perovskite-like phase).

After 2 hours at 1050 °C, removal of the same volatile species fractured the aggregates into fragments, which were then employed for nucleation and development of crystalline phases.

The morphologies of the crystallite particles that resulted were primarily in the 149-349 nm range.
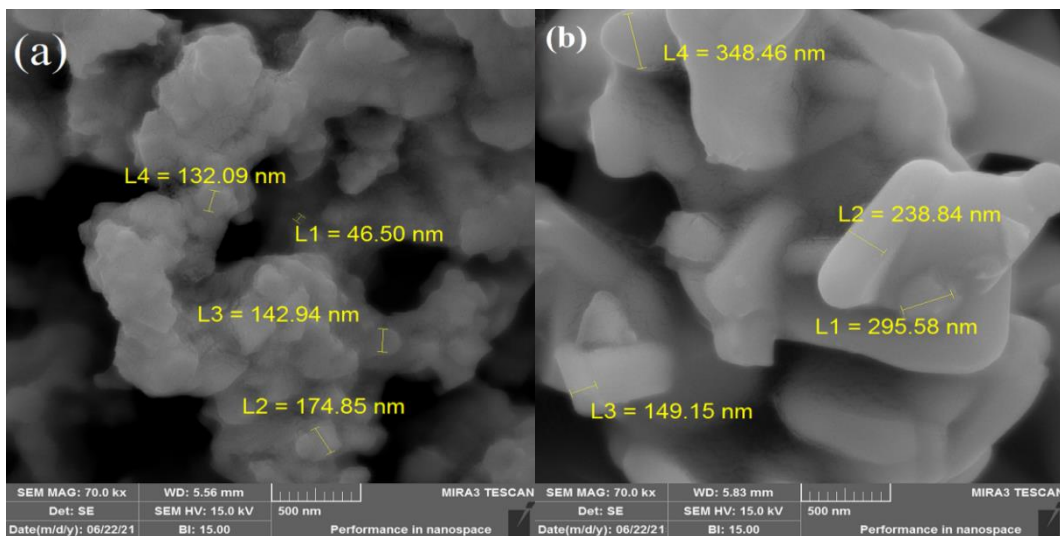

Fig. 2. Variation in sintering temperature on the grain size of prepared samples;
(a) at 850 °C, (b) at 1050 °C.

The synthesis is carried out by sintering precursors containing the structural components, primarily oxides and carbonates, at quite high temperatures. This approach requires solid ceramics with a sufficient grain size. The sintered samples at 1050 °C had a dense microstructure with orthorhombic structures present.

$CaBi_4Ti_4O_{15}$ (CBT) ferroelectric were prepared using traditional ceramic technique at different temperatures. Higher sintering temperatures result in crystalline CBT. The dielectric constant of CBT increases in sintering temperature. Where the samples sintered at 1050 ℃ exhibits good dielectric properties as shown in figure 3. The dielectric constant was enhanced from 116 to 162 at room temperature by increasing the sintering temperature from 850 to 1050 °C. The polarization of defect dipoles is mostly responsible for the dielectric loss in the frequency range of 10^3–10^4 Hz. The dielectric constant dispersion is high at lower frequencies, but it is small beyond the prescribed frequency.
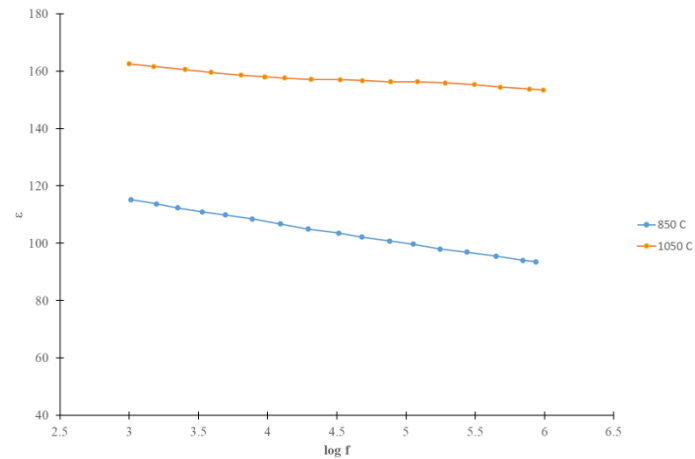
Fig. 3. Variation in dielectric constant measured at different frequency at room temperature for CBT compound.

The loss (tanδ) of all CBT ceramics was found in figure 4 to be the lowest value of tanδ at all frequencies at a sintering temperature of 850 ℃ and1050 ℃, indicating that high-quality ceramics are manufactured.
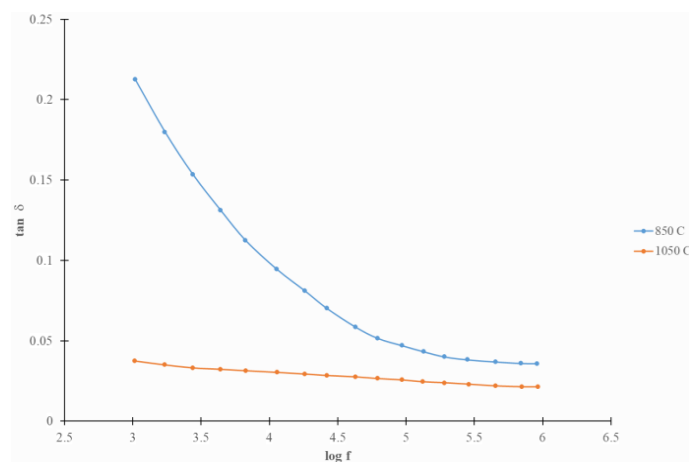

Fig. 4. Variation in tangent loss measured at different frequencies and room temperature for CBT compound.

The polarization of defect dipoles is mostly responsible for the dielectric loss in the frequency range of 10^3–10^4 Hz, the dielectric loss of each sample rapidly falls as the frequency rises, then only minimally decreases as the frequency rises further.
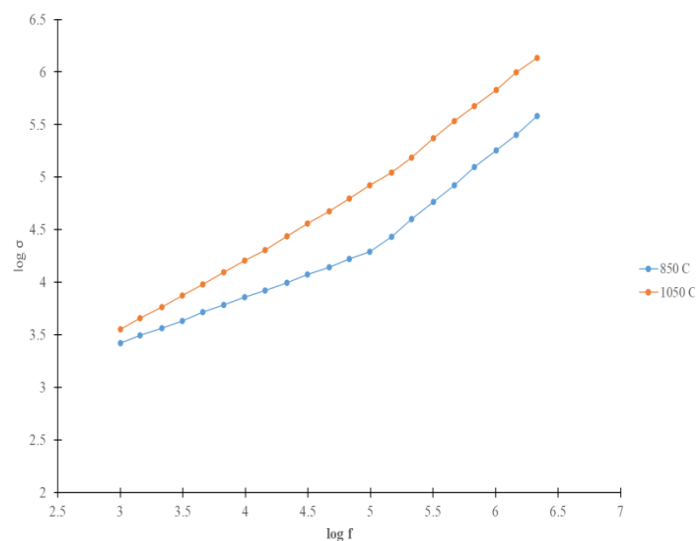
Fig. 5. The fluctuation in ac conductivity measured at room temperature with different frequencies for CBT samples with varied sintering temperatures.

The conductivity shows strong frequency scattering as shown in Figure (5). The conductivity increases with an increasing frequency. It clear that the measured ac conductivity shows an abrupt increase value.

4. Conclusions

Aurivillius $CaBi_4Ti_4O_{15}$ ceramic compound were successfully synthesized standard ceramic technique, crystal structure with the A21 am space group. Crystalline structures of the as-fabricated samples were investigated by X-ray diffraction. The effect of sintering temperature on the properties such as crystal structure, and dielectric properties was also investigated, where the samples sintered at 1050 ℃ exhibits good dielectric field emission scanning electron microscope, it's clear that effect of heat treatment on the morphology and crystalline size is more pronounced in the samples sintered at 1050 °C, the microstructure of the sintered samples at this temperature is dense.

The dielectric constant increases as the sintering temperature increasing it have acceptable dielectric characteristics, and the dielectric loss of each sample rapidly falls as the frequency rises.

References

[1] Mengdi Fan, Guangda Wu, Fapeng Yu, Lili Li, Yanlu Li, Xiufeng Cheng, Xian Zhao, Crystals, 10, 698, 2020; https://doi.org/10.3390/cryst10080698

[2] B. J. Kennedya, Y. Kubotab , B.A. Hunterc , Ismunandard, K. Kato, Solid State Communications 126, 653-658, (2003); https://doi.org/10.1016/S0038-1098(03)00332-6

[3] J.-B. Li, a Y. P. Huang, G. H. Rao, G. Y. Liu, J. Luo, J. R. Chen, and J. K. Liang, Applied Physics Letters 96, 222903 (2010).

[4] T. Badapanda, R. Harichandan, T. B. Kumar, S. R. Mishra, S. Anwar, Journal of Materials Science: Materials in Electronics volume 28, pages 2775-2787 (2017); https://doi.org/10.1007/s10854-016-5858-6

[5] C.L. Diaoa, H.W.Zhenga, Y.Z.Gua, W.F.Zhanga, L.Fangb, Ceramics International, 40, Issue 4, May, Pages 5765-5769,2014; https://doi.org/10.1016/j.ceramint.2013.11.015

[6] K.Yao, Sh.Chen, S. Ch. Lai, Y. M. Yousry, Advanced Science, Wiley-VCH GmbH, 2021

[7] M. Kudo, S. Tsuzuki, K.-I. Katsumata, A. Yasumori, and Y. Sugahara, Chem. Phys. Lett., 393, pp. 12-16 (2004); https://doi.org/10.1016/j.cplett.2004.06.010

[8] A.P.Levanyuk, B.A.Strukov, Encyclopedia of Condensed Matter Physics, Pages 192-201,2005; https://doi.org/10.1016/B0-12-369401-9/00435-6

[9] C. Kittel, Introduction to Solid State Physics, 8th Edition, Wiley, 2004.

[10] M. Sucher, and J. Fox; Handbook of Microwave Measurements", third Edition, Printed by the Science Press, Inc. (1963).

[11] H. Irie, M. Miyayama, T. Kudo, Structure dependence of ferroelectric properties of bismuth layer structured ferroelectric single crystals, J. Appl. Phys., vol. 90, no 8, pp 4089-4094 (2001); https://doi.org/10.1063/1.1389476