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Comparison between Lithium Substitution and Doping on the Physical and Piezoelectric Properties of Lead-Free BCZT Ceramics

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ABSTRACT

Defects generation in ceramics by element substitution or doping may improve their properties. However, different results will be obtained even though the same element is involved due to different mechanisms. Ceramics $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ (BCZT) is one of the potential candidates to replace lead-based material PZT. However, the conventional method requires high-temperature calcination and sintering process to synthesize this material. Thus, Lithium (Li) can act as the sintering aid to lower the temperature at the same time, the properties of piezoelectric can be enhanced. In this paper, the structural, physical, and piezoelectric performance of lead-free $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ (BCZT) ceramics with Lithium Li substitution and doping, synthesized by the solid-state reaction method were studied. The substitution of Li increases the density, ρ and piezoelectric coefficient, d_{33} of BCZT which are 4.075 g/cm^3 and 304.6 pC/N, respectively. These results demonstrate that Li substitution is more beneficial to the piezoelectric properties than doping because it produces higher grain boundary resistance and activation energy and has lower conductivity than doping. This can provide a definite strategy during the chemical composition design and manufacture of BCZT ceramics.

1. Introduction

Since 1990 lead-free piezoelectric materials have been intensively studied due to the material's ability as an energy resource. On top of that, they can be used as an initiative to replace the most popular lead-based piezoelectric material, Lead Zirconate Titanate (PZT), which has dominated the current piezoelectric ceramics field since the 1950s. PZT is an ABO_3 perovskite structure material with good performance of piezoelectric coefficient (d_{33}, d_{31} ~ 370 pC/N), electromechanical coupling factor (kp, kt ~ 60%), ferroelectric properties and dielectric properties [1–3]. However, the high-level toxicity (> 60 wt%) produced by this lead-based material during the preparation process (fabrication,

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calcination and sintering) causes environmental problems and climate change. These phenomena have been subjects of environmental concern since 19th century and can lead to the greenhouse effect and also global warming. This problems to the human health resulting in sickness and fatalities [4–9]. Piezoelectricity is the ability of certain materials to generate an electrical current when applied with mechanical stress or vice versa [10]. Piezoelectric materials have been used in various applications, such as in communication systems, medical instruments, and electronic devices like buzzers, actuators, transducers, resonators, microphones and optoelectronics [11–13].

Lead-free Barium Calcium Zirconate Titanate (BCZT) is one of the most promising candidates that has drawn attention since the past decade due to its good performance of electrical properties. BCZT is a Barium Titanate (BT) based ceramic with Calcium (Ca) ion and Zirconium ion (Zr) substitution at the A-site and B-site, respectively [14]. This material exhibits a high piezoelectric coefficient (d_{33} ~ 300 - 650 pC/N) due to the shifting of the orthorhombic-tetragonal (TO-T) temperature towards ambient temperature that is called the polymorphic phase transition (PPT) [15–18]. It also has good electromechanical coupling coefficient, kP, dielectric constant and ferroelectric properties with large remnant polarization, Pr and low coercive field. However, its low Curie temperature (Tc ~ 83-100 °C) is the drawback for this material [18–21].

Some researchers reported that the properties of BCZT can be improved by doping it with a specific compound. Adding a suitable amount of low-temperature melting additives such as Lithium (LiF and $LiCO_3$) could lower the sintering temperature [22]. This sintering aids not only reduces the sintering temperature but could also enhance the crystallization of material even in low calcination temperatures [23, 24]. However, in some cases, the piezoelectric properties may be decreased due to the existence of a secondary phase due to the addition of these sintering aids [22]. Thus, this study will use the Li element to substitute at the Ca site in the BCZT ceramics materials. The structural, physical, and electrical properties will be determined and compared with the Li-doped BCZT ceramics results.

2. Methodology

A conventional solid-state reaction method was used to prepare $Ba_{0.85}Ca_{0.15-x}Li_xZr_{0.1}Ti_{0.9}O_3$ with x = 0.00 and 0.06. The starting raw materials were barium carbonate, $BaCO_3$, calcium carbonate, $CaCO_3$, titanium oxide, TiO_2, zirconium oxide, ZrO_2 and lithium carbonate, $LiCO_3$. The sample preparation by using solid-state reaction is shown in Figure 1. The raw powder materials were weighed according to stoichiometry and ball milled using zirconia balls for 24 hours at 250 rpm in ethanol. Then the mixture was dried for 2 hours at 150 °C and calcined at 1000 °C for 4 hours. Afterwards, the powder was ground manually using mortar before being compacted into pellets using a hydraulic press. All samples were sintered at 1350 °C for 2 hours. The phase and structure of the ceramics was determined using an X-ray diffractometer, XRD (Bruker D8 Advance), with CuKα radiation in 2θ range from 20° to 80°. The samples' morphology and microstructure were observed using field emission scanning electron microscope (FESEM, Zeiss Supra 55VP). The density of the materials was measured in silicon oil using Archimedes' principle. For the electrical properties study, the flat surfaces of the pellets were polished and coated with silver electrodes. The samples were poled at 60 °C in silicon oil by applying an electric field of 2.5 kV/mm for 10 minutes for the piezoelectric properties determination.

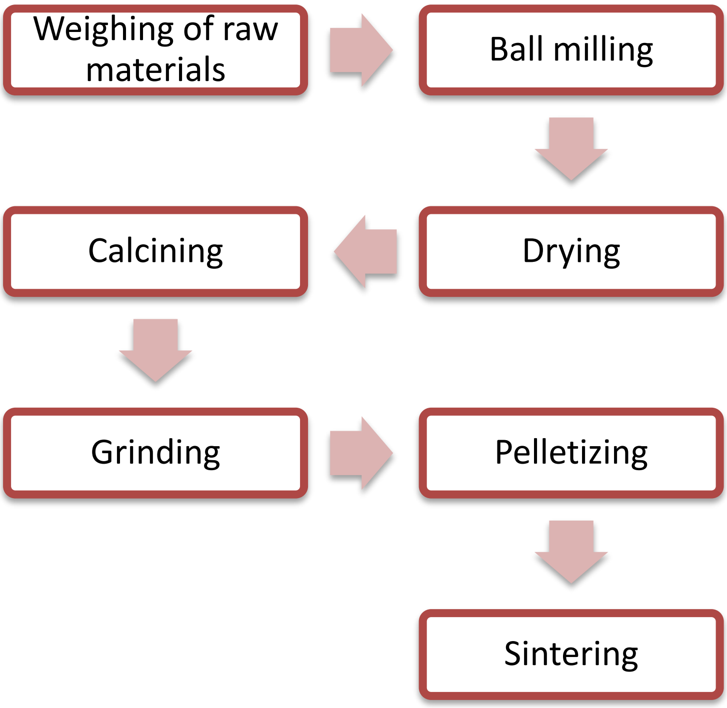
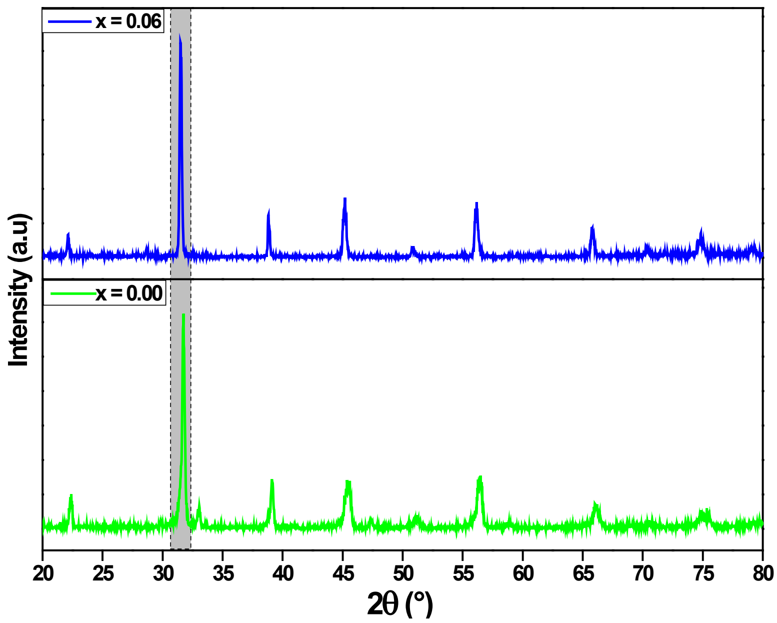


Fig. 1. The solid-state reaction process of $Ba_{0.85}Ca_{0.15-x}Li_xZr_{0.1}Ti_{0.9}O_3$ material

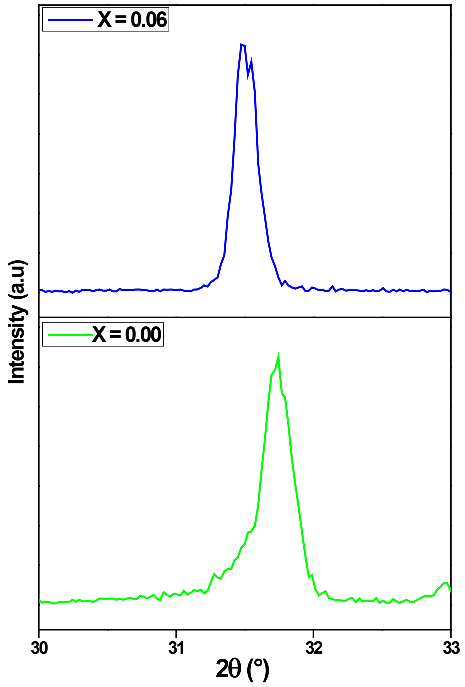
3. Results and Discussion

3.1 Structure and Phase

The X-ray diffraction (XRD) patterns of $Ba_{0.85}Ca_{0.15-x}Li_xZr_{0.1}Ti_{0.9}O_3$ (x = 0.00 and x = 0.06) ceramics in Figure 2 exhibit perovskite structure based on the International Centre for Diffraction Data (ICDD). Based on Figure 2 (b), the peak position moved to the lower angle diffraction with Li substitution, showing the lattice parameter increment. The Li substituted sample (x = 0.06) also shows no secondary phase formed, as shown in BCZT with x = 0.00.



(a)

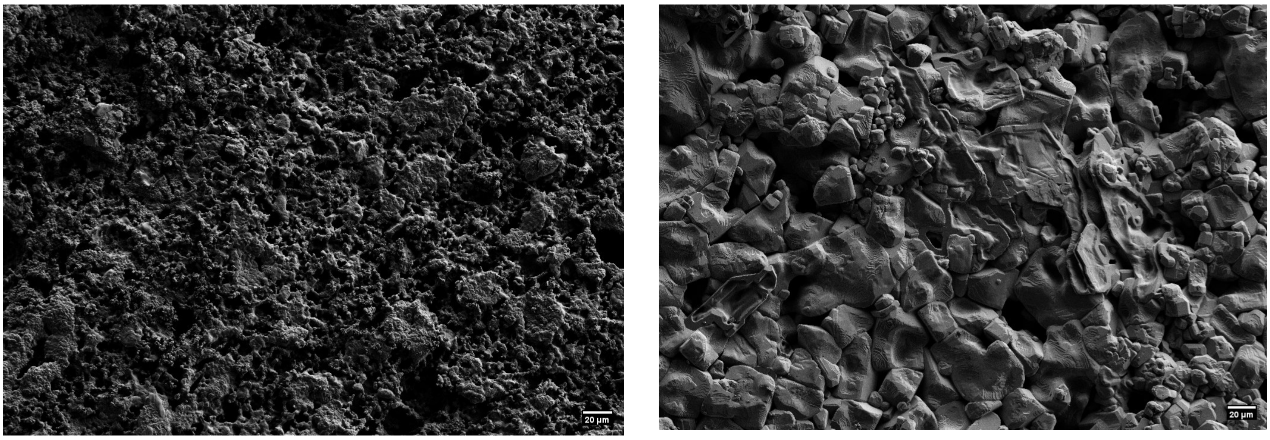


(b)

Fig. 2. The XRD patterns of (a) $Ba_{0.85}Ca_{0.15-x}Li_{2x}Zr_{0.1}Ti_{0.9}O_3$ for x = 0.00 and x = 0.06 and (b) enlarged region at 2θ between 44.5° and 46°

3.2 Morphology

Figure 3 shows the morphology images of $Ba_{0.85}Ca_{0.15-x}Li_xZr_{0.1}Ti_{0.9}O_3$ when x = 0.00 and x = 0.06. BCZT, when x = 0.06, looks denser than without the substitution of Li (x = 0.00). Fewer pores existed, and the grain size was larger than when x = 0.00. This is due to the formation of a liquid phase during sintering, which helped the grain growth.



(a) (b)

Fig. 3. The SEM images of The XRD patterns of (a) $Ba_{0.85}Ca_{0.15-x}Li_{2x}Zr_{0.1}Ti_{0.9}O_3$ when (a) x = 0.00 and (b) x = 0.06

3.3 Density

Archimedes' principle was used to obtain the density of the samples in pellet form. Table 1 below shows the density value when Li is substituted or doped into BCZT materials. In this research, the substitution of Li with x = 0.06 shows a higher density than BCZT with x = 0.00 due to increasing grain size that lessens the pore size. Even though the density value of the samples synthesized using the substitution method is lower than other research using the doping method, it shows that the density can be increased and potentially give a higher value by a particular method.

Table 1
The density of Li substitution on $Ba_{0.85}Ca_{0.15-x}Li_{2x}Zr_{0.1}Ti_{0.9}O_3$ and Li doped on $Ba_{0.85}Ca_{0.15-x}Zr_{0.1}Ti_{0.9}O_3$

Materials	Substitution/doping (preparation method)	Density, ρ (g/cm^3)	References
$Ba_{0.85}Ca_{0.15-x}Li_{2x}Zr_{0.1}Ti_{0.9}O_3$ (x = 0.00)	Without substitution	2.624	This research
$Ba_{0.85}Ca_{0.15-x}Li_{2x}Zr_{0.1}Ti_{0.9}O_3$ (x = 0.06)	Substitution (SSR)	4.075	This research
$Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BCZT) – 0.5 wt% $LiCO_3$	Doping (Sol-gel)	5.8651	[25]
Ba0.85Ca0.15Zr0.1Ti0.9O3 (BCZT) – 1 wt% LiCO3	Doping (Citrate method)	5.7957	[26]

3.4 Piezoelectric Properties, d_{33}

Piezoelectric coefficient, d_{33} is the charge generated in the direction of the z-axis when mechanical stress was applied in the same direction, which is z-axis. Table 2 below shows the result of d_{33} in different methods of the substitution/doping of Li into BCZT materials. In this research, the substitution of Li with x = 0.06 shows the increment of the piezoelectric coefficient, d_{33}. This may be affected by the increasing density of the sample.

Table 2
The d_{33} of Li substitution on $Ba_{0.85}Ca_{0.15-x}Li_{2x}Zr_{0.1}Ti_{0.9}O_3$ and Li doped on $Ba_{0.85}Ca_{0.15-}Zr_{0.1}Ti_{0.9}O_3$

Materials	Substitution/doping (preparation method)	Piezoelectric coefficient, d_{33} (pC/N)	References
$Ba_{0.85}Ca_{0.15-x}Li_xZr_{0.1}Ti_{0.9}O_3$ (x = 0.00)	Without substitution	122	This research
$Ba_{0.85}Ca_{0.15-x}Li_xZr_{0.1}Ti_{0.9}O_3$ (x = 0.06)	Substitution (SSR)	304	This research
$Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BCZT) – 0.5 wt% $LiCO_3$	Doping (Sol-gel)	447	[25]
$Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BCZT) – 1 wt% $LiCO_3$	Doping (Citrate method)	336	[27]
$Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ + 0.3 wt.% Li_2CO_3	Doping (SSR)	512	[28]

4. Conclusions

This research studied the substitution of Lithium in $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ materials on the structure, morphology, density, and piezoelectric properties, d_{33}. The substitution of Lithium can improve the physical and electrical properties of ρ = 4.075 g/cm^3 and d_{33} = 304.6 pC/N compared to Li dopant in lead-free BCZT ceramic materials.

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