Effect of Mn doping on structure, the dielectric and electric properties of BCZT ceramics

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Received: 9 January 2021 / Accepted: 3 March 2021 / Published online: 26 March 2021 © The Author(s), under exclusive licence to Springer-Verlag GmbH, DE part of Springer Nature 2021

Abstract
The synthesis of (Ba0.99Ca0.01)(Zr0.2Ti0.8)O3 (BCZT) and doped (Ba0.99Ca0.01)(Zr0.2Ti0.8-xMnx)O3 (BCZT-xMn) ceramics was successfully carried out by the solid-state method. The doping effect is followed by X-ray powder diffraction, scanning electron microscopy (SEM), and dielectric and conductivity measurements. Indeed, X-ray diffraction measurements show the crystalline structure of ceramics. SEM images indicate the doping effect on the studied perovskite microstructure. The results indicate that during doping the maximum value of the temperature (Tm) of the dielectric constant varies slightly, and there will be a considerable decrease in permittivity, dielectric losses and conductivity. Manganese ions are well integrated in the perovskite while maintaining the solid solution.

Keywords Dielectric · Ceramic · Ferroelectric · Permittivity

1 Introduction

Since the 1950s, the Pb-based ceramic perovskite compositions like Pb(Zr1-xTix)O3 (PZT) and PbMg1/3Nb2/3O3 (PMN) have been frequently used worldwide for their dielectric properties [1, 2]. This material has a very high dielectric permittivity at the Curie temperature and a coupling coefficient too. For this reason, it is found useful in various fields of applications such as transducers and sensors [3–5]. However, these lead oxides have recently been found to be toxic and seriously dangerous to the environment and human health. Much research has therefore been conducted to find its lead-free alternative with similar ferroelectric and piezoelectric effects, generally titanium-based solid solutions such as Bi0.5Na0.5TiO3 (NBT), K0.5Na0.5NbO3 (KNN), BaTiO3 (BT) and (Ba,Ca)(Ti,Zr)O3 (BCTZ) [6]. Among piezoelectric materials, we can mention the most famous one, (1-x) Ba(Zr0.2Ti0.8)O3-x(Ba0.7Ca0.3)TiO3 (BZT-xBCT), a pseudo-binary system that had a very high piezoelectric coefficient of about 600pc/N at room temperature, an amazing value that even exceeds that of the PZT perovskites [7–10].

Among the important characteristics of this pseudo-binary ferroelectric BCZT is the existence of a triple point in the previously studied BZT-BCT diagram, located at x = 0.32 where this region is considered as a separation between the rhombohedral and the tetragonal symmetry and corresponds to a high permittivity and huge electromechanical coefficients [11].

In fact, at the end of the last century, Simon et al. focused their researches on the ternary form BaTiO3-CaTiO3-BaZrO3, which led to a diagram of four zones with different structures and dielectric aspects [2, 12], as shown in Fig. 1:

Zone 1: Dielectric behavior similar to BaTiO3 in both its proximity and the Ba1-xCa_xTiO3 (BT-CT), with three anomalies corresponding to rhombohedral (R), tetragonal (T), orthorhombic (O) and cubic (C) transitions.

R-O transition temperature decreases remarkably as the substitution of Ba2+ by Ca2+ increases in perovskite A sites.

Zone 2: For solid compositions close to BaTi1-xZrxO3 with 0.1 < x < 0.27, only one dielectric anomaly is detected related to the R–C transition; the Curie temperature peak is remarkable without dispersion by frequency effect.

Zone 3: In BaTi1-xZrxO3 proximity with 0.275 < x < 0.42, there is a larger peak with higher temperature values and a frequency dispersion. At the macroscopic scale, the compositions keep their shape and polarization regardless of the temperature.
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**Zone 4**: This region separates zone II from zone III where, depending on the composition, classic ferroelectric states and relaxing states coexist.

However, the formation of the pure perovskite phase BCZT requires a very high calcinations and sintering temperature of about 1420 °C for sintering. The studies carried out by the researchers aim at reducing the temperature and improving the electrical presets of the perovskite.

The doping with various metal ions such as Ca²⁺ [13], Cu²⁺ [14], Fe³⁺ [14], Bi³⁺ [11], Mg²⁺ [14] and Mn⁴⁺ [15] either in site A or/and B can improve the properties of BCZT ceramics. As mentioned, the addition of a dopant to (BCZT) ceramics can improve densification, dielectric and ferroelectric properties. MnO₂ is an interesting additive because of its multivalence which can be a donor or acceptor dopant [16]. Research studies show that the addition of Mn can reduce dielectric losses and increase the densification of dielectric metals [5].

Mn doping at B sites of the perovskite \((Ba_{0.99}Ca_{0.01})(Zr_{0.2}Ti_{0.8-x}Mn_x)O_3\) (BCZT-xMn) structure creates a variety of compositions with many properties similar to those of lead ceramics, such as cooling devices and dielectric responses enhanced by the rhombohedral (R) and tetragonal (T) phases separated by an intermediate orthorhombic (O) phase.

### 3 Results and discussions

#### 3.1 X-ray diffraction

Figure 2 depicts the X-ray diffraction of BCZT-xMn ceramics. Firstly, the diagram does not indicate the existence of other phases than the structured perovskite, which implies that the Mn⁴⁺ particles are well introduced into the unit cell of the perovskite in order to preserve the structure of the solid solution. The X-ray diagrams of the BCZT and BCZT-xMn ceramics reveal peak of diffraction at 45°, which is consistent with crystals (002) and (200), indicative of the tetragonal structure of BCZT ceramics.

In addition, the diffraction peaks are slightly shifted towards the widest angle for a higher Mn concentration indicating the decrease of the ceramic system constant (BCZT-Mn), which is linked in particular to the presence of Mn⁴⁺ occupying the B sites. In fact, the ionic radius of Mn⁴⁺ (0.54 Å) is smaller than that of Ti⁴⁺ (0.605 Å) and Zr⁴⁺ (0.72 Å).

On the other hand, the diffraction peaks of BCZT-xMn ceramics exhibit a full width at half maximum that increases with Mn content. This can be linked to the size of the ceramic grains (which decreases if the Mn content becomes higher).

The reticular planes of a crystal are defined by their Miller indices \((hkl)\), or there is an interference of planes for the triplets \((h,k,l)\) in orthorhombic structure. The interreticular distance \(d_{hkl}\) was related to the Miller indices by the following relationship [17, 18]:

\[
\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]  (1)

with \(d_{hkl}\) is calculated from the Bragg equation [17–20]:

\[
2d_{hkl} \sin \theta = n\lambda
\]  (2)
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where $n$ is the order of diffraction taken equal to one in general ($n = 1$), and $\lambda$ is the wavelength of X-ray diffraction equal to $1.5418\text{Å}$.

The calculation of the lattice parameters $a$, $b$ and $c$ is shown in Table 1. These results indicate that the addition of Mn induces a slight variation in the lattice parameters. Indeed, the ionic radius of $\text{Mn}^{4+}$ (0.54 Å) and $\text{Mn}^{3+}$ (0.645 Å) is close to the ionic radius of $\text{Ti}^{4+}$ (0.605 Å). However, the radius of $\text{Mn}^{2+}$ (0.83 Å) is larger than that of $\text{Ti}^{4+}$, and the occupation of the Ti site by Mn ions induces a weak deformation of the crystal lattice.

The calculation of the nanometric dimensions of the BCZT-xMn ceramic particles is based on the study of ray diffraction; the size of the crystallites is given by the following Scherer’s law [18, 21]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$

where $D$ is the size of the crystallites, $\lambda$ is the wavelength of the X-rays (1.5418 Å), $K$ is the Scherer constant taken equal to 0.9, $\theta$ is the diffraction peak angle, and $\beta$ is the width at mid-height of the diffraction peaks (FWHM) determined by the Match refinement.

Thus, we can follow the epsilon micro-deformation according to the law [18]:

$$\epsilon = \frac{\beta}{4 \cos \theta} \quad (4)$$

According to the figure illustrating the X-ray diffraction, the FWHM increases with the addition of Mn, which induces a remarkable decrease in the size of the nanocrystallites with the increase in the amount of dopant from 144.366 to 57.729 nm for the high intensity peak, corresponding to the Miller index (110) (Table 2).

In fact, the diffusion of manganese ions into the ceramic leads to a reduction of the grain size which is mainly related to the appearance of oxygen vacancies. These results are grouped in Table 2.

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**Table 1** Lattice parameters of BCZT-xMn (% $x = 0, 0.25$ and 1)  

| BCZT-xMn | $a$ (Å) | $b$ (Å) | $c$ (Å) | $c/a$  |
|----------|--------|--------|--------|--------|
| $x = 0\%$ | 4.0512 | 4.0447 | 4.0507 | 0.9998 |
| $x = 0.25\%$ | 4.0488 | 4.0474 | 4.0542 | 1.0013 |
| $x = 1\%$ | 4.0783 | 4.0033 | 4.0777 | 0.9998 |

**Table 2** Grain size and micro-strain of BCZT-xMn ceramics  

| BCZT-xMn | $\beta$  | $\epsilon$  | $D$ (nm)  | $\epsilon$  | $D$ (nm)  | $\epsilon$  | $D$ (nm) |
|----------|----------|-------------|-----------|-------------|-----------|-------------|-----------|
| $x = 0\%$ | 0.0998 | 0.1287 | 141.63 | 0.1929 | 94.418 | 0.1929 |
| $x = 0.25\%$ | 0.2495 | 0.1929 | 56.637 | 0.3239 | 56.637 | 0.3239 |
| $x = 1\%$ | 0.2495 | 0.1929 | 56.637 | 0.3239 | 56.637 | 0.3239 |

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Fig. 2 X-ray diffraction pattern of the Mn (0%, 0.25% and 1%) doped BCZT
3.2 Surface morphology

Figure 3 displays the micrographs of the BCZT and BCZT-xMn ceramics using the SEM analysis. The images taken of the different samples clearly depict a non-homogeneous particle size distribution. The addition of a small amount of Mn in doped ceramics leads to a larger grain size than in BCZT ceramics. Such addition promotes the growth of the ceramic grains, and therefore, a substitution of the B-site with Mn$^{3+}$ and Mn$^{4+}$ ions will occur, leading to the creation of oxygen vacancies and an improved mass and energy transfer.

3.3 Dielectric study

To monitor the effect of Mn doping on the dielectric permittivity and dielectric losses of BCZT-xMn ceramics, measurements will be made for BCZT ceramics and both doped, and recorded in Fig. 2 for a frequency range from 1 to 1 MHz.

Figure 4 shows that:
(i) Maximum dielectric permittivity decreases with frequency.
(ii) For the BCZT ceramics (Fig. 4a), the maximum temperature is close to room temperature and there is a slight dispersion at maximum.
(iii) Both curves correspond to Mn-doped ceramics (Fig. 4b and c); the peak widens as soon as the amount of Mn increases and the dielectric maximum decreases with a temperature shift associated with the maximum permittivity. It is also noted that there is a slight dispersion of the permittivity for $T \leq T_m$ and the dielectric losses decrease with temperature for all samples.

Indeed, Ti$^{4+}$ ions are less chemically stable and are reduced to Ti$^{3+}$ ions according to Eq. (5):

$$Ti^{4+} + \frac{1}{2} O^o_o \rightarrow Ti^{3+} + \frac{1}{2} V^-_o$$  \hspace{1cm} (5)

When the Mn$^{4+}$ ions diffuse into the BCZT ceramic, they are substituted with the Ti$^{3+}$ ions according to the reaction (6):

$$Mn^{4+} + Ti^{3+} \rightarrow Mn^{3+} + Ti^{4+}$$  \hspace{1cm} (6)

This is notably linked to Mn additions, which limit the concentration of vacant oxygen positions and causes the decrease of the permittivity [22].

The dielectric permittivity in the paraelectric zone for a normal ferroelectric is given by the following Curie Weiss formula (7):

$$\varepsilon'_r(T) = \frac{C}{T - T_m}$$  \hspace{1cm} (7)

where $C$ and $T_0$ are the Curie constant and Curie temperature, respectively. The deviation from the Curie law is due to the assembly of short-range nanopolar domains [23].

Uchino and Nomura proposed another form for the previous law of Curie–Weiss given by Eq. (8) [23, 24]:

$$\varepsilon'_r(T) = \frac{C}{T - T_m^2}$$  \hspace{1cm} (8)
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\[ \frac{1}{\varepsilon_r'} - \frac{1}{\varepsilon_{r_{\text{max}}}} = \frac{(T - T_m)'}{C} \]  

(8)

where \( \varepsilon_{r_{\text{max}}} \) is the maximum permittivity of ceramics, and C is a multiplicative constant.

\( \gamma \) is a constant corresponding to the degree of diffuseness [22, 25, 26], and it gives information on the phase transition in perovskite determined by the linear fit of the experimental data.

A plot of \( \ln \left( \frac{1}{\varepsilon_r'} - \frac{1}{\varepsilon_{r_{\text{max}}}} \right) = f \left( \ln T - T_m \right) \) drawn for \( T > T_c \) for a frequency of 1 kHz allows us to obtain the value of \( \gamma \) (Table 3).

The relaxation behavior is described by the quantity \( \Delta T_{\text{relax}} \) defined by:

\[ \Delta T_{\text{relax}} = T_m(100 \text{kHz}) - T_m(1 \text{ kHz}) \]  

(9)

This relaxation parameter increases from 1 to 2 with the growth of the quantity of Mn added (Table 3).

Figure 5 illustrates the variations of permittivity as a function of temperature for \( f = 1 \text{ kHz} \); it allows us to go back to the values of maximum temperature \( T_m \) relative to the maximum of dielectric permittivity, critical temperature \( T_0 \) and temperature \( T_d \) from which the dielectric constant starts to deviate from Curie’s law Figure 6. For this purpose, the degree of deviation from the Curie–Weiss law can be described by means of parameters \( \Delta T_m \) defined as follows:

\[ \Delta T_m = T_d - T_m \]  

(10)

The values of this parameter increase if Mn concentration increases which suggests that Mn doping induces a diffusion of the ceramic phase transition BCZT, where the diffuseness character of the phase transition is described by the following empiric parameter:

\[ \Delta T_{\text{diff}} = T_{0.9\varepsilon_r_{\text{max}}}(1 \text{ kHz}) - T_{r_{\text{max}}}(1 \text{ kHz}) \]  

(11)

The value of this parameter indicates the effect of doping ceramics BCZT-xMn. The main values extracted from the study on the ceramic dielectric of BCZT doped Mn are summarized in Table 3.

Figure 7 describes the variations of dielectric permittivity and dielectric losses as a function of frequency for \( T = T_m \) for a range from 1 to 1000 kHz. In this range, the dielectric constant is reduced as the frequency increases.

![Fig. 4 Temperature dependence of dielectric constant and loss for BCZT-xMn ceramics](image)

### Table 3 Dielectric properties of BCZT-xMn ceramics

| % x | \( T_m \) (K) | \( \varepsilon_m \) at 1 kHz | \( \Delta T_{\text{diff}} \) (K) | \( \Delta T_m \) (K) | \( \Delta T_{\text{relax}} \) (K) | \( \gamma \) |
|-----|---------------|-----------------|----------------|-----------------|----------------|-----|
| 0   | 302           | 3570.91         | 11.75         | 33.89           | 1.045          | 1.29|
| 0.25| 304           | 1570.32         | 28.3          | 57.65           | 1.568          | 1.89|
| 1   | 317           | 850.29          | 51.58         | 59.8            | 2.091          | 1.92|
and decreases with Mn content due to the reduction in particle size with MnO$_2$ doping. The dielectric losses vary slightly with frequency, and a minimum value of around 0.01 can be recorded.

Figure 8 shows the conductivity measured at the critical temperature $T_m$ as a function of the frequency of the BCZT ceramic. It is defined according to the following relationship:

$$\sigma_{ac} = \omega \varepsilon_0 \varepsilon_1 \tan \varepsilon_1$$  \hspace{1cm} (12)

where $\omega$ is the angular frequency, both $\varepsilon_0$ and $\varepsilon_1$ are the dielectric constants of vacuum and the relative dielectric
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The conductivity is highly frequency dependent and follows a linear variation. It increases with frequency, which implies a decrease in resistance according to the law:

\[ R = \frac{l}{\sigma S} \]  

(13)

The conductivity also reduces with Mn doping as a result of the presence of defects or impurities in the ceramic.

4 Conclusion

BCZT and BCZT-xMn-doped ceramics are successfully prepared by the solid–solid method. The DRX spectra highlight the presence of the pure phase of the material, indicating that the Mn$^{4+}$ ions are well integrated in the perovskite while maintaining the solid solution.

The addition of Mn reduces the permittivity of doped ceramics and reduces dielectric losses. In fact, the addition of manganese oxide reduces the concentration of vacant oxygen by occupying the perovskite site B while substituting with Ti$^{4+}$ ions and also reduces the size of the grains.

![Fig. 7 Dielectric constant and dielectric loss as functions of frequency for BCZT-xMn ceramics at T = T_m](image)

![Fig. 8 AC conductivity as function of frequency for Mn doped for BCZT-xMn (x=0, 0.25 and 1) at T_m](image)
In fact, DRX shows that the Mn doping decreases the granular size, in accordance with the values of the crystallite size which evolves from 144.36 nm for the parent compound up to 57.729 nm for an addition of 1% of Mn for the main peak (110). The low deformation of the perovskite is given by constant epsilon called micro-deformation. The calculation of the mesh parameters indicates an orthorhombic structure of the ceramics.

SEM characterization allows us to trace the microstructure of ceramic compounds. The study of the dielectric part as a function of temperature for a frequency range from 1 kHz to 1 MHz indicates that the maximum relative permittivity (at temperature $T_m$ for 1 kHz) decreases by adding Mn of 3570.91 for $x=0\%$, 1570.32 for $x=0.25\%$ to 850.29 for $x=1\%$. The curve $\ln(1/\varepsilon-1/\varepsilon_m) = f(\ln(T-T_m))$ allows us to know the nature of the phase transition by following the values of the diffusion coefficient which varies between 1 and 2. As well as the degree of deviation and the character of diffusion are, respectively, given by $\Delta T_{\text{diff}}$ and $\Delta T_d$ at the frequency 1 kHz. The decrease in permittivity and dielectric losses as a function of frequency at maximum temperature can also be marked for each composition.

A study of the conductivity shows that it varies linearly as a function of the frequency at temperature $T_m$ for each proportion of Mn.

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