

1 **Electrical Fatigue Behavior of Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O₃ Ceramics Under Different Oxygen**
2 **Concentrations**

3 P. Pomyai¹, D. Munthala¹, T. Sonklin¹, R. Supruangnet², H. Nakajima², P. Janphuang², S. M.
4 Dale³, J. Glaum³, and S. Pojprapai¹

5 ¹*School of Ceramic Engineering, Suranaree University of Technology, 111 University*
6 *Avenue, Muang, Nakhon Ratchasima 30000, Thailand*

7 ²*Synchrotron Light Research Institute (Public Organization), 111 University Avenue, Muang*
8 *District, Nakhon Ratchasima 30000, Thailand*

9 ³*Department of Materials Science and Engineering, Faculty of Natural Sciences, Norwegian*
10 *University of Science and Technology, 7492 Trondheim, Norway*

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12 **Abstract:** Fatigue degradation is a significant problem in piezo/ferroelectric materials and their
13 commercial applications. The major causes of electrical fatigue degradation are a domain
14 pinning effect and physical damage such as microcracking. This work reports the fatigue
15 behavior of barium calcium zirconate titanate (Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O₃) under regular and low
16 oxygen concentration silicone oil. **LCR meter and impedance analyzer were used to determine**
17 **dielectric properties and the relationship of oxygen vacancy and activation energy were**
18 **revealed.** X-ray diffraction, synchrotron X-ray absorption spectroscopy, and scanning electron
19 microscope techniques were employed to study the local structural changes, defect
20 development, physical damage and microcracking in the ceramics. FEFF-8.4 simulations were
21 used to determine the **oxygen** vacancy creation. The study reveals the relationship **oxygen**
22 vacancy creation, domain wall pinning, microcracking and the fatigue behavior of the
23 ferroelectric ceramic. **The ferroelectric and dielectric properties of BCZT ceramics were**
24 **investigated with respect to the applied bipolar electric field.**

25 **Keywords:** BCZT, Lead-free ferroelectric; Fatigue; XANES; Oxygen defects.

26 *corresponding author: Soodkhet@g.sut.ac.th

1 **1. Introduction:**

2 The demand for piezoelectric/ferroelectric ceramic materials has been increased
3 tremendously during the past two decades. These materials are used in various industrial
4 applications such as electronic devices, actuators, transducers, and sensor applications [1-6].
5 Lead-free ceramics are trending in the market and research-oriented projects because of
6 environmental and health issues with lead (Pb) [4, 7]. Barium Calcium Zirconate Titanate
7 (BCZT) is one of the most widely studied lead-free piezoelectric material in the last decade [7,
8 8]. Among the other lead-free piezo/ferroelectric materials such as BaTiO₃ (BT) [9-11], (Bi,
9 Na)TiO₃ (BNT), and (K, Na)NbO₃ (KNN) [12-14], BCZT exhibits excellent piezoelectric
10 coefficient (550-620 pC/N) [15-17]. Degradation of ferroelectric properties under cyclic
11 electrical loading (called as “electrical fatigue”) is always a significant problem in piezoelectric
12 ceramics and causes a premature failure of the ferroelectric device [18, 19]. The main
13 contributions to fatigue behavior in piezo/ferroelectric materials are physical damage (i.e.,
14 cracks at the electrode-ceramic interface) and domain pinning due to oxygen (O) defects [20-
15 27]. Some researchers reported that fatigue behavior depends on the type of electrical loadings,
16 such as unipolar and bipolar electric fields [3, 20-23]. **However, from our knowledge there are**
17 **no research work that reveals the relationship between O vacancies and electrical fatigue**
18 **behavior on BCZT ceramics.**

19 **In this work, therefore, the effect of O vacancies on the fatigue behavior of (Ba_{0.85}Ca_{0.15}**
20 **Zr_{0.1}Ti_{0.9}O₃) ceramics was investigated. The relationship between activation energy and O**
21 **vacancies of fatigued ceramics in silicone oil with different O concentration was investigated**
22 **by using LCR meter and impedance analyzer.** X-ray diffraction (XRD), synchrotron X-ray
23 absorption spectroscopy (XAS), and scanning electron microscope (SEM) techniques were
24 also employed to investigate the crystal structure, local atomic structure, domain orientation,
25 physical damage and microcracking in the ceramics. The FEFF-8.4 simulation software
26 package was utilized to study the creation of O vacancies during the fatigue measurement. The
27 XAS experiment strongly supports that domain pinning due to O vacancies is a significant
28 contributor to the fatigue degradation of ferroelectric materials. This work also proposes the
29 qualitative and quantitative relationship between O vacancies, domain switching behavior,
30 crack propagation, and fatigue mechanisms in BCZT ceramics.

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1 2. Experimental procedure:

2 2.1 Electrical fatigue

3 The $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ ceramics were prepared by using a conventional solid-state
4 reaction (SSR) method [20, 28]. The density of all BCZT ceramics was calculated by using
5 Archimedes' principle (ASTM C 378–88), and the calculated density was 5.59 g/cm^3 . Different
6 SiC grits (e.g., 600, 800, 1000, and finally 1200) were used to thin down the ceramics and to
7 prepare a smooth surface. All ceramics were further annealed at $500 \text{ }^\circ\text{C}$ for 3 hrs to remove the
8 residual stress generated during the grinding process. A few nanometers of gold were deposited
9 on both sides of the ceramic(s) as a top and bottom electrode by the DC sputtering method. The
10 electrical fatigue measurement was performed when the ceramics were immersed in silicone
11 oil (to avoid electric discharge). The fatigue measurements on BCZT ceramics were divided
12 into two groups: 1) the fatigue measurement conducted in a regular silicone oil representing a
13 normal O concentration (hereafter labelled as RS-BCZT), and 2) the fatigue measurement
14 performed in a nitrogen-enriched silicone oil representing a low O concentration (hereafter
15 labelled as NS-BCZT). Low O concentration silicone oil was prepared by flowing nitrogen gas
16 into the silicone oil for 30 minutes before the fatigue measurement. The nitrogen gas flow was
17 maintained during the measurement for consistency. The amount of dissolved O in silicone oil
18 was measured by using a precision dissolved oxygen (DO-5512SD) meter. The presence of
19 dissolved O concentration in regular silicone oil was 7.7 mg/l , whereas, in low O concentration
20 silicone oil, it was in the range of $0\text{-}1 \text{ mg/l}$. Each sample was subjected to $\pm 3 \text{ kV/cm}$ of a bipolar
21 sinusoidal electrical load at 50 Hz . Up to 10^6 electrical cycles were applied to the samples using
22 a high voltage amplifier (20/20 Trek). During fatigue measurement, polarization hysteresis (P-
23 E) loops for different fatigue cycles were measured using a Sawyer-Tower circuit. **Strain-**
24 **electric field (S-E) loops of BCZT ceramics were measured by using a linear variable**
25 **differential transducer (LVDT) circuit. The dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$)**
26 **of ceramics were also measured by using the E4980A precision LCR meter with a frequency**
27 **range from 100 Hz to 1 MHz . The impedance spectroscopy of the samples was measured by**
28 **using an impedance analyzer under 100 Hz to 1 MHz of the range of frequency and $40 - 200$**
29 **$^\circ\text{C}$ of the range of the temperature.** The schematic representation of the experimental fatigue
30 setup is shown in Fig-1. Three samples were used for each testing condition to ensure the
31 reproducibility of the results. The physical damage that occurred during electrical loadings was
32 investigated using cross-sectional micrographs of the fatigued samples observed by SEM

1 (JEOL, JSM-6010LV). The crystal structure and domain orientation of BCZT ceramics were
2 determined using an XRD (Bruker Phaser DII).

3 2.2 Synchrotron X-ray absorption spectroscopy

4 Synchrotron soft X-ray absorption spectroscopy (XAS) measurement was performed
5 on pristine and fatigued ceramics at the beamline-3.2Ua (BL-3.2Ua), Siam Photon Laboratory,
6 Synchrotron Light Research Institute (SLRI), Thailand. To determine the local structure and O
7 vacancies that are generated during fatigue, O K-edge X-ray absorption near-edge structure
8 (XANES) was performed on these ceramics. The electron beam specifications were 1.2 GeV
9 in energy and 60 – 150 mA in the current of the storage ring. XAS measurements were
10 performed in total-fluorescence-yield (TFY) using a varied line spacing plane grating
11 monochromator (220-1040 eV). XANES spectra were recorded at O K-edge energy range
12 between 520-555 eV with an energy step of 0.1 eV. The ATHENA (version 0.9.26) software
13 package was used to normalize and analyze the recorded spectrums. The ATOM software
14 (version 2.50) and *ab-initio* FEFF (version 8.4) software were used to simulate the XANES
15 spectra to analyze the experimental result. During the FEFF8.4 simulation, full multiple
16 scattering (FMS) was 4.5, and the self-consistent field (SCF) was more than 183 atoms
17 considered.

18 3. Result and Discussion

19 3.1 Degradation of ferroelectric properties

20 The P-E hysteresis loops, remnant polarization (P_r) and coercive field (E_c) of BCZT
21 ceramics at different applied cyclic electrical loadings are shown in Fig-2. P-E curves measured
22 at 1, 10^3 , 10^4 , 10^5 , and 10^6 fatigue cycles are shown in Fig-2a (RS-BCZT ceramics) and 2b
23 (NS-BCZT ceramics). P_r and E_c values are extracted from P-E loops at different fatigue cycles,
24 as shown in Fig- 2c and 2d. The characteristics of the P-E hysteresis loops depend on both the
25 number of electrical cycles as well as the condition of the utilized silicone oil. In the initial
26 state (1st cycle), P_r values of RS-BCZT and NS-BCZT ceramics are ± 2.48 and ± 1.65 $\mu\text{C}/\text{cm}^2$,
27 respectively. These P_r value gradually decreased from ± 2.48 to ± 1.57 $\mu\text{C}/\text{cm}^2$, and from ± 1.65
28 to ± 1.14 $\mu\text{C}/\text{cm}^2$ with an increasing number of electrical loadings up to 10^6 cycles. The P_r value
29 of RS-BCZT and NS-BCZT ceramics dropped to 36% and 31% at the end of 10^6 cycles,
30 respectively. Similarly, at the initial condition (1st cycle), the E_c values of RS-BCZT and NS-
31 BCZT ceramics were ± 1.51 and ± 1.43 kV/cm, and they decreased gradually to ± 1.46 kV/cm
32 and ± 1.38 kV/cm up to 5×10^3 cycles, respectively. Afterward, the E_c value increased sharply

1 to ± 1.82 kV/cm at 5×10^4 cycles for RS-BCZT ceramics, and to ± 1.78 kV/cm at 10^5 cycles for
 2 NS-BCZT ceramics. Further electrical cycling (up to 10^6 cycles), led to an abrupt decrease of
 3 the E_c value of RS-BCZT and NS-BCZT to ± 1.23 kV/cm and ± 1.19 kV/cm, respectively. The
 4 variation of P_r , E_c values, and their corresponding percentage changes are listed in Table-1.

5 The S-E loops of pristine, RS-BCZT, NS-BCZT ceramics were performed before and
 6 after 10^6 cycles, as shown in Fig-3. The maximum strain (S_{max}) values and piezoelectric strain
 7 coefficient (d_{33}^*) values were extracted from the measured S-E loops. It can be seen that the
 8 S_{max} values of pristine, RS-BCZT and NS-BCZT ceramics are 0.127%, 0.131%, 0.149%, and
 9 d_{33}^* values are 1,036, 1,067, 1,124 pm/V, respectively. After 10^6 cycles, S_{max} increased by
 10 0.4% for RS-BCZT ceramic and 2.2% for NS-BCZT ceramic compared to unfatigued ceramic.
 11 Similarly, d_{33}^* value increased 2.9% for RS-BCZT ceramic and 8.5% for NS-BCZT ceramic
 12 compared to the unfatigued ceramic. The frequency-dependent dielectric constant (ϵ_r) and
 13 dielectric loss ($\tan \delta$) values were measured and shown in Fig-4. The ϵ_r and $\tan \delta$ of all samples
 14 decreased with an increase of frequency [29]. These results, decrease of ϵ_r , an increase of \tan
 15 δ and d_{33}^* values indicate that the significant increase of defect concentration via “wake up”
 16 field effect [30]. In general, the lower O vacancy concentration of the material relates to higher
 17 activation energy (E_a), which further confirms that the O vacancy conduction mechanism of
 18 BCZT ceramics at grain boundaries [31]. The activation energy of ceramics was calculated by
 19 using the Arrhenius formula [32, 33]:

$$\sigma = \sigma_0 \exp(-E_a/K_B T) \quad (1)$$

20 where σ represents the electrical conductivity, σ_0 represents the pre-exponential term, E_a
 21 represents the activation energy, and K_B represents the Boltzmann constant. E_a can be
 22 calculated from the slope of $\ln \sigma$ and $1000/T$ plot (as shown in Fig. 5(a-c)). The highest
 23 activation energy is needed in case of the lowest oxygen vacancy concentration [31, 33]. The
 24 activation energy of the pristine, RS-BCZT ceramics and NS-BCZT ceramics are 2.15, 1.57
 25 and 1.10 eV, respectively. The results indicate that NS-BCZT ceramics has the lowest
 26 activation energy, indicating the oxygen vacancies are superior. Moreover, the highest
 27 activation energy of the pristine BCZT ceramic suggests that it has the lowest O vacancy
 28 concentration and the lowest activation energy of NS-BCZT ceramic confirms the highest O
 29 vacancy concentration.
 30

1 3.2 Microstructure of the Near-Electrode Regions

2 Besides the changes in ferroelectric properties, the interface microstructure of the
3 BCZT ceramics was examined before and after fatigues using cross-sectional SEM (Fig-6).
4 The pristine sample shows that there is no visible physical damage or microcracking in the
5 interface between electrode and ceramic as well as in the bulk of the material (Fig-6a).
6 However, some porosity (pore size around 1 μm) in bulk can be seen. After fatigue with 10^6
7 bipolar cycles, there is visible damage such as cracks and microcracks at the interface (Fig-6b
8 and Fig-6c) in both RS-BCZT and NS-BCZT ceramics. The average damage widths of the
9 cracks are 45 μm and 107 μm for RS-BCZT and NS-BCZT, respectively. It can be noticed
10 that the damage width in the NS-BCZT ceramics is twice that in the RS-BCZT ceramics. Some
11 researchers reported that the width of the damage near the electrode region in PZT ceramics
12 extended up to 100 μm [19]. It is well-known that bipolar cycling seriously affects domain
13 mobility due to a domain pinning effect induced by O vacancies/charged defects. At the
14 beginning of the fatigue test, O vacancies/charged defects may not have enough time to migrate
15 and accumulate when the number of cycles increased from 1 to 5×10^3 . In this period, the
16 migrated defect concentration at the domain walls is low. The gradual decrease of P_r and E_c
17 values could be due to a weak domain wall pinning effect [5, 6, 19]. Further, an increase in
18 fatigue cycles from 5×10^3 to 5×10^4 , defects agglomeration at domain walls increased, and this
19 leads to a stronger domain wall pinning effect. The rise of the E_c value after 5×10^3 cycles could
20 be due to the field screening effect because of physical damages near electrode regions [19,
21 35]. At this period, domain switching under a local electric field resulted in a domain wall
22 moving over a certain distance. When the load dropped during a cycle, some domain walls
23 travel backward while some cannot revert to the original position because of the pinning effect.
24 At the local domain switching zone near the microcrack tip, this movement of domain walls
25 may enhance high local strain and induce crack opening and propagation [5, 19, 36-37]. The
26 abrupt decrease of E_c value after 5×10^4 cycles could be due to increased local conduction
27 through the walls induced heat recovery of pinned domains [19]. Interestingly, it is observed
28 that the sharp rise of E_c value of RS-BCZT ceramics peaked at 5×10^4 cycles while that of NS-
29 BCZT ceramics peaked at 10^5 cycles. The possible reason for this behavior (difference in
30 peaked E_c value) could be attributed to the different heat recovery rates of pinned domains in
31 RS-BCZT and NS-BCZT ceramics. Considering the surface morphology, P_r and E_c (Fig-2 and
32 6), the effect of the O concentration on polarization and crack propagation can be seen clearly.
33 In the case of NS-BCZT ceramics (representing a low O concentration system), the polarization
34 decay is faster, and crack propagation per cycle is greater than the case of RS-BCZT ceramic

(depicting a normal O concentration system). As mentioned above, these relationships could be attributed to domain switchability, which is the driving force of polarization degradation and cracks propagation under cyclic loading. Therefore, XRD measurements were performed on the ceramics before and after fatigue tests to investigate the domain switchability.

3.3 Domain switchability investigation by X-ray diffraction

The XRD patterns of BCZT ceramics before and after fatigue measurements are presented in Fig-7. Initial observation shows that there is an overall intensity variation between pristine and fatigued ceramics. All ceramics exhibited a pure perovskite, morphotropic phase boundary (MPB) structure. The peak around $2\theta = 45.5^\circ$ indicates the presence of multiple phases in the perovskite structure. The details of these various phases can be revealed by the deconvolution of this peak, as illustrated in Fig-7b, which indicates the existence of both tetragonal and rhombohedral phases. The deconvoluted peak positions at 44.87° and 45.09° of 2θ belong to the $(002)_T$ and $(200)_T$ of the tetragonal phase, while the peak position at 45.33° of 2θ belongs to the $(202)_R$ of rhombohedral phase. The above crystallographic planes are well matching with ICDD files 00-063-0612 and 00-065-0109, respectively. After the ceramics were subjected to electrical loading, the $(002)_T$ peak intensity increased while the $(200)_T$ peak intensity decreased. The change in relative intensity of the $(002)_T$ and $(200)_T$ peaks gives the qualitative information of tetragonally-distorted perovskite structure [38-40]. On the other hand, the change of the $(202)_R$ peak intensity before and after the fatigue tests is very small. Theoretically, the domain switchability of BCZT ceramics before and after the fatigue tests can be estimated by the change of XRD peak intensities. Especially the domain-switching behavior of tetragonally distorted perovskite ceramics is characterized by the changes in $(002)_T$ and $(200)_T$ peak intensities. This represents the in-plane (parallel to the electrode surface) and out-of-plane (perpendicular to the electrode surface) domains. The preferential orientation of the domains in an electric field direction can be explained in the concept of multiples of random distribution (MRD) [41, 42]. The following formula is used to calculate the MRD:

$$\text{MRD}_{002} = 3 \times \frac{(I_{002}/I_{002}^R)}{(I_{002}/I_{002}^R)+2 \times (I_{200}/I_{200}^R)} \quad (2)$$

where I_{002} and I_{200} are the integrated intensities of the $(002)_T$ and $(200)_T$ peaks of a fatigued sample. I_{002}^R and I_{200}^R are the integrated intensities of the 002 and 200 peaks from the sample with random domain orientation. Theoretically, $\text{MRD} = 1$ represents random domain orientation, and $\text{MRD} = 3$ represents perfectly aligned domains in the poling or the applied electric field direction (i.e., in this case, the field direction is perpendicular to the electrode surface) as illustrated in Fig-8. After the fatigue test, the calculated MRD values of RS-BCZT

1 and NS-BCZT ceramics are 1.41 and 1.38, respectively. It means that domains in RS-BCZT
2 ceramics are more likely oriented parallel to the field direction (MRD value is higher) than in
3 the NS-BCZT ceramics. Therefore, the domain switchability of RS-BCZT ceramics is greater
4 than that of NS-BCZT ceramics. This implies that the degree of domain wall pinning in NS-
5 BCZT ceramic is more substantial than in RS-BCZT, which agrees with the degradation of
6 polarization as a function loading cycle number, as shown in Fig-2c.

7 Based on the ferroelectric (P - E , P_r , E_c), dielectric (ϵ_r and $\tan \delta$), structural (XRD), and
8 microstructural (SEM) properties, the possible correlation is represented in a schematic
9 diagram, as shown in Fig-9. This model is based on the relationship between the domain
10 pinning and mechanical damage mechanisms. Oxygen related defects and their diffusion
11 during fatigue are the considerable primary cause for all the observed effects [19, 43-44]. The
12 Ba-O bonding is known to be more stable than that of Ti-O in the BaTiO₃ system [45].
13 Therefore, O vacancies/defects are highly possible from the Ti-O bonds at domain walls during
14 the domain wall motion. In early cycles, the polarization of domains is more easily switched
15 by the applied field with a weak domain pinning effect (due to the low level of O defects). As
16 the number of cycles progressing, the increase of O defects causes the strong domain pinning
17 effect. Severely affected domain walls could act as a current-conducting channel, and those
18 electrical conduction may increase the lattice temperature abruptly. Consequently, this could
19 indirectly cause the release of pinned domains (e.g. the heat recovery of pinned domains, as
20 mentioned in the previous section). **The ferroelectric and dielectric properties of ceramics could**
21 **be associated with the number of the defects/defect dipoles, adsorption and desorption of O in**
22 **the ceramic.** To support the proposed model, the XANES results can give the local structure
23 related to O bonding and O atoms in BCZT ceramics.

24 3.4 Fatigue induced defects investigated by XANES

25 Fig-10 shows the normalized O K-edge XANES spectra of the BCZT ceramics. O K-
26 edge XANES spectra can reveal information about the covalent mixing of metal and O states.
27 Overall, the peak intensity decreased after fatigue treatment. The XANES spectra peak
28 intensities and their corresponding changes are listed in Table-2. Peaks A and B are attributed
29 to electron transition from O 1s orbital to O 2p-Ti 3d derived orbital (t_{2g} and e_g) states [46-48].
30 Peak C1 and C2 are attributed to electron transition from O 1s orbital to O2p-Ca 3d/Ba 5d
31 derived hybrid states [49]. Peak D1 and D2 are attributed to the influence of the empty Ba-5f
32 band on O-2p states [45]. Finally, peak E is assigned mainly to the hybridization of O 2p with
33 Ti 2p and Ca 4f [50]. All the peak intensities and corresponding percentage changes are listed

1 in Table-2. After the fatigue test, peak A and B intensities, as well as the intensity ratio (A/B),
2 dropped significantly. Peak A and B are related to the anti-bonding of type t_{2g} and e_g M(Ti)-O
3 (oxygen) transitions [46-48]. The dissociation or perturbation in Ti-O bondings can influence
4 peak A and B intensities. The decrease of peak intensity ratio (A/B) can be attributed to either
5 reduction of the Ti oxidation state, reduction of the unit cell dimension (c/a ratio), or can be
6 related to O defects, sometimes, the effects mentioned above are mutually dependent.
7 Similarly, Peak C1 and C2 associated with the hybridization states (type t_{2g} and e_g) between O
8 and Ca/Ba, and corresponding peak intensity ratio (C1/C2) dropped after the 1st cycle and then
9 increased again after 10^6 cycles. The reduction of O in Ti-O bonding also influences the
10 bonding of Ca/Ba-O and their corresponding transitions. The reduction in A/B peak ratio and
11 increment in the C1/C2 ratio at 10^6 cycles could be related to the creation of O vacancies.
12 During electrical loading, O vacancies that form at the domain walls near the interface of the
13 electrode increase. With an increasing number of cycles, this defect density may increase and
14 finally pin the domains. Considering the above result (as shown in Fig-10 and Table-2), the
15 decrease of A/B peak intensity ratio is more significant in NS-BCZT ceramics than in RS-
16 BCZT ceramics. This can imply that the level of O vacancy concentration in NS-BCZT
17 ceramics is higher than that in RS-BCZT and, consequently, the domain wall pinning effect
18 and degree of fatigue degradation in NS-BCZT is stronger. To understand and support the
19 features observed in the O K-edge XANES spectra of BCZT samples, XANES spectra with
20 various virtual O vacancies were simulated using *ab-initio* FEFF8.4 simulation. Here, for the
21 sake of simplicity, the tetragonal $BaTiO_3$ structure was considered for simulation to represent
22 the tetragonally distorted BCZT ceramics [51], and the same simulation plots are shown in Fig-
23 11. XANES simulations indicated that the intensity of peak A decreased when the number of
24 O vacancies increased. From Fig-11, it can be seen that peak A intensity of a $BaTiO_3-V_O$ (single
25 O vacancy per unit cell) and a $BaTiO_3-V_O-V_O$ (double O vacancy per unit cell) crystal dropped
26 by 8%, and 39%, respectively, compared to a $BaTiO_3$ crystal. Simulated peak intensities and
27 their corresponding percentage changes are listed in Table-3. Overall, the simulated data of
28 $BaTiO_3$ with O vacancies can be used to support the experiment results, which showed the
29 change of XANES peak intensity reflecting the change of O vacancy concentration in NS-
30 BCZT and RS-BCZT ceramics before and after fatigue measurements.

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1 **4. Conclusion:**

2 In summary, this work investigates the ferroelectric, dielectric, structural, and
3 microstructural properties of BCZT ceramics under electrical fatigue measurements in regular
4 silicone oil (RS-BCZT ceramics) and low oxygen concentrated silicone oil (NS-BCZT
5 ceramics). The gradual decrease of P_r and E_c values during the initial cycles could be attributed
6 to a weak domain pinning effect, whereas the sharp increase of E_c value around 10^5 cycles
7 could be associated with the field screening effect. The abrupt decrease of the E_c values after
8 10^5 cycles could be caused by the increase of local current conduction through domain walls,
9 which induced by heat recovery of pinned domains. **The activation energy of each sample was**
10 **determined. The higher activation energy is needed in case of RS-BCZT ceramics which has**
11 **the lower oxygen vacancy concentration while the lower activation energy is required for NS-**
12 **BCZT ceramics which has higher oxygen vacancy concentration.** The concept of MRD was
13 utilized to explain the domain switchability and domain pinning effect. After the fatigue
14 treatment, the MRD value of RS-BCZT ceramics is greater than that of NS-BCZT ceramics,
15 which implies that the mobility of domain walls in RS-BCZT is greater than that of NS-BCZT.
16 Both experimental and simulation results of O K-edge XANES supported the assumption of O
17 vacancies created during the fatigue measurement. It has been observed that the created O
18 vacancies in NS-BCZT ceramics are greater than the number of O vacancies in RS-BCZT
19 ceramics. That reflects the domain pinning effect is more pronounced in NS-BCZT ceramic;
20 therefore, fatigue degradation of NS-BCZT ceramic is more severe than that of RS-BCZT
21 ceramic.

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6 Tables

7 **Table-1** Remnant polarization (P_r) and coercive field (E_c) values of RS-BCZT and NS-BCZT
8 ceramics under different cyclic electrical loading.

9 **Table-2:** O K-edge XANES spectra peak intensities and their percentage changes for RS-
10 BCZT and NS-BCZT ceramics.

11 **Table-3:** Simulated O K-edge XANES spectra (for single and double O defects) peak
12 intensities and their percentage changes in the BaTiO₃ system.
13

14 Figures

15
16 **Fig-1:** The drawing of the experimental setup of fatigue measurement.

17 **Fig-2:** The P–E hysteresis loops and fatigue behavior of BCZT ceramics at 1, 10³, 10⁴, 10⁵ and
18 10⁶ cycles: (a) P–E loops for RS-BCZT ceramics, (b) P–E loops for NS-BCZT ceramics, (c)
19 remanent polarization and (d)coercive field for 10⁶ fatigue cycles.

20 **Fig-3:** Strain electric field (S-E) loops of BCZT ceramics.

21 **Fig-4:** (a) dielectric constant (ϵ_r) and (b) dielectric loss ($\tan \delta$) behavior of BCZT ceramics at
22 1, 10³, 10⁴, 10⁵ and 10⁶ cycles.

23 **Fig-5:** Arrhenius plots and the fitted activation energy (E_a) values of the samples (a) pristine,
24 (b) RS-BCZT ceramic, and (c) NS-BCZT ceramic.

25 **Fig-6:** Cross-sectional SEM micrographs of the BCZT ceramics: a) pristine, b) RS-BCZT
26 ceramics, c) NS-BCZT ceramics and enlarged view of d) RS-BCZT and e) NS-BCZT ceramics.
27 Red arrows indicate crack and microcrack positions.

28 **Fig-7:** (a) XRD patterns of both pristine and fatigued BCZT ceramics, (b) deconvolution
29 profile of the XRD peak around 45° of 2 θ .

30 **Fig-8:** Schematic representation of domain orientation in terms MRD equal to 0, 1, and 3.

- 1 **Fig-9:** Schematic diagram of defect creation, domain wall pinning and crack propagation
- 2 between the electrode and bulk ceramics.
- 3 **Fig-10:** O K-edge XANES spectra of BCZT ceramics spectra of BCZT ceramics before and
- 4 after fatigue measurements.
- 5 **Fig-11:** Simulation of O K-edge XANES spectra for BaTiO₃ using FEFF8.4 simulation.