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RESEARCH

Study the Effect of Potassium Doping on Piezoelectric Properties of Lead Zirconate Titanate Nanostructures Using Michelson Interferometer

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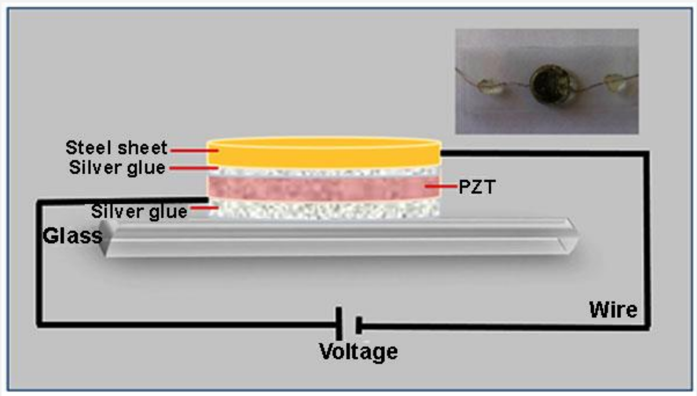
ABSTRACT

In this study, the effect of potassium atoms on the physical properties of lead zirconate titanate (PZT) nanoparticles in comparison with non-doped particles has been studied. At first, PZT and K-doped nanoparticles were synthesized in the powder phase by a well-known sol-gel method under reflux conditions. Powders are analyzed by X-ray diffraction patterns (XRD), surface electronic microscopy (SEM), dynamic light scattering (DLS), and UV-visible spectrum. Analyses showed formations of PZT nanostructures and particle sizes were compared for two samples and showed it has been increased for potassium-doped particles. Also, the indirect band gap was decreased by adding the potassium doping. Then, powders were turned into tablets under pressure and after ceramicizing them, both sides were coated by conductive layers in order to apply electric voltage. The Michelson interferometer was used to evaluate the piezoelectric properties of the tablets. Continue wave (CW) He-Ne laser beam was used as the source and the number of interference fringes was studied versus the applied voltage to the tables. By increasing the thickness of tables and changing the optical path difference, the number of the fringe was changed and obtained curves were studied which showed a meaningful increment in piezoelectric properties of potassium-doped PZT structures. This modification method can be recommended for enhancing the piezoelectricity of PZT-based devices.



Keywords: Michelson interferometer, piezoelectric, PZT nanoparticles,sol-gel method

1. Introduction

In the last decades, piezoelectric materials have been widely used as electromechanical energy converters for disks, sensors, and transformers. Compared to magnetic devices, piezoelectric devices have a simple structure with high energy density which leads to outstanding performance for small systems [1-3]. Lead zirconate titanate (PZT) exhibits ferroelectric and piezoelectric properties and has been used commercially in multi-layer capacitors. The most distinctive feature of PZT is its large piezoelectricity. PZT has a perovskite crystal structure that is eligible in structure for achieving large piezoelectric properties. Based on this property, it is also used in piezo-transducers and piezo-stages with nano and micro-movements and microphones [4-6]. Besides, researchers have focused on the synthesis of PZT nanoparticles (NPs) powders to improve the desired properties using modification of chemical structure [7-9]. The most favorite synthesized method is the sol-gel method which is usually used to prepare PZT NPs and leads to the production of powder containing nanoscale particles [10]. Controlling the size of NPs through the synthesis procedure may affect the physical and ferroelectric properties of PZT NPs [11].

The piezoelectric properties of PZT can be enhanced by optimizing the structure. Doping of different elements can drastically change the electrical and optical properties of semiconductors due to the change of band gap energy [12-

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14]. This principle has also been extended to PZT structures and doping with low-capacity (acceptor) elements improves the mechanical quality factor of PZT while high-capacity elements (donors) increase the piezoelectric constant [11]. PZT NPs doped with metal atoms modify electrical properties and have been studied in the literature [15-17]. In this way, alkali metal atoms have been used as doping in PZT structure, in few studies. Adding monovalent atoms such as sodium or lithium has been used to increase the electrical conductivity of perovskite structures and oxide films [13,14]. The effects of potassium [18] and sodium [19] ions on the mechanical losses, elastic modulus, and microstructures of PZT ceramics have been investigated.

On the other hand, the phase structures of PZT powders have been investigated in the literature [20-22]. The study of the non-elastic behavior of PZT with the help of mechanical spectroscopy showed the phenomenon of relaxation due to the interaction between wall repulsions and violation points such as oxygen vacancies [21, 22]. Adding a doping such as K^{+1} as a substitute for Pb^{+2} in the perovskite structure increases the concentration of oxygen vacancies. When oxygen ions leave their neighborhoods, the neutrality of the structure would change that leads to change in piezoelectric properties [18].

In our previous work, PZT-doped sodium nanostructure ceramics was synthesized via the sol gel method. Pure and doped powders were compared from the morphology and characterization point of view [23]. Here, the potassium-doped lead zirconate titanate (PZT:K) NPs have been synthesized and the effect of doping in comparison with non-doped particles has been studied. PZT and PZT:K NPs were synthesized in powder phase by sol-gel method and analyzed by X-ray diffraction patterns (XRD), surface electronic microscopy (SEM), dynamic light scattering (DLS), and UV-visible spectrum. The effect of potassium doping on the structure and physical properties has been studied. The powders were converted into tablets and calcined to become ceramic, and then both sides of the tablets were made conductive.

Furthermore, optical interferometers have been used widely for optical characterization of materials specially nanostructures, in the last decays. Michelson interferometer was utilized to compare the piezoelectricity of the synthesized PZT ceramics and piezoelectric properties [24]. A number of interference fringes was counted which showed a meaningful increase in piezoelectricity of potassium-doped PZT structures. Experiments indicate that doping PZT with potassium can be a favorite method to modification of PZT piezoelectric devices. Based on our researches, this study is completely new and innovative and could open new windows to the use of PZT materials.

2. Experimental

2.1. Materials and instruments

In this experiment, citric acid ($C_6H_8O_7$), nitric acid ($H_1N_1O_3$), titanium isopropoxide ($C1_2H_{28}O_4Ti$) were purchased from Sigma–Aldrich and lead nitrate ($Pb(NO_3)_2$) and zirconium nitrate ($Zr(NO_3)_4$) were prepared from Merck company. UV-Vis absorption spectroscopy was studied in the range of 200 to 800 nm by an Array Spectrophotometer (PhotonixAr 2015) and dynamic light scattering (DLS) was measured with the Malvern Zetasizer 3000. The surface morphology of PZT nanostructures was studied by scanning electron microscope (SEM) model TESCAN MIRA 3. In addition, the crystal structure was detected by XRD method with a PW1800-Phillips diffractometer with Cu Kα radiation (λ= 4 1.5418) operating at 40 KeV and 40 mA.

2.2. Synthesis of PZT nanostructures

To synthesize PZT NPs in the powder phase, the Sol-gel method was used as follows. 15 mL of 4.9 molar water solution of citric acid was prepared and 2.6 mL of nitric acid was dissolved in it. Then 2.2 mL of titanium isopropoxide was added to the resulting solution and stirred at room temperature to obtain a clear solution. 13 mL of 1.2 molar solution of Lead nitrate was prepared and warmed up to 50 ºC and added to a clear solution. Also, a solution of 5.2 gr of zirconium nitrate in 21 mL of water at 50ºC was added to the solution and placed on a heater at 120ºC for 90 minutes under reflux conditions. The obtained solution was divided into two equal parts; one was kept pure and the other was mixed with 1g of potassium hydroxide (KOH). Then, using ammonia, the pH of the first solution rose to 4.3 and the second one increased to 6. Solutions were retained at room temperature for 14 hours. After that, solutions were stirred and ammonia was added simultaneously to raise the pH of the solutions about 7. The solutions were stirred at 120ºC to evaporate the solvent and homogeneous gels were obtained. Gels were retained for 14 hours at room temperature to complete the nucleation process.

Gels were put in an oven its temperature was raised up to 400 ºC for 1 hour, and remained in this temperature for 2 hours. PZT powders were synthesized and were cooled gradually at room temperature. Pure PZT NPs are light yellow powder and PZT:K NPs are a light brown powder, as shown in **Figure 1**.

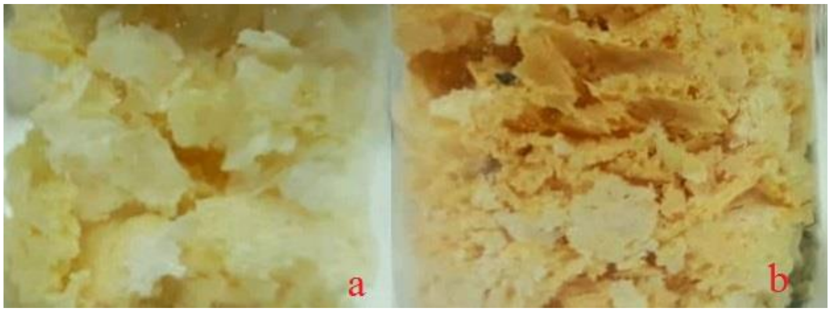

Figure 1. Synthesized PZT powders; a- pure PZT powder, and b-PZT:K powder.

2.3. Method

Since optical interferometers are common tools for measuring piezoelectric constants of materials [25], it was used in this study. The effects of potassium doping on the piezoelectricity of the prepared tablets were done using a prepared Michelson interferometer setup equipped with a He–Ne laser (λ= 632.8 nm and 5mW power). The Michelson interferometer consists of a beam splitter and two mirrors. The phase difference attributed to the path difference of two beams causes an interference pattern. **Figure 2** shows the schematic of Michelson's interferometer, in which a PZT tablet is replaced by one mirror. DC Voltage was applied to the tablets and gradually increased. After each voltage increase and relaxation of the interference pattern, the number of newly created fringes was counted.

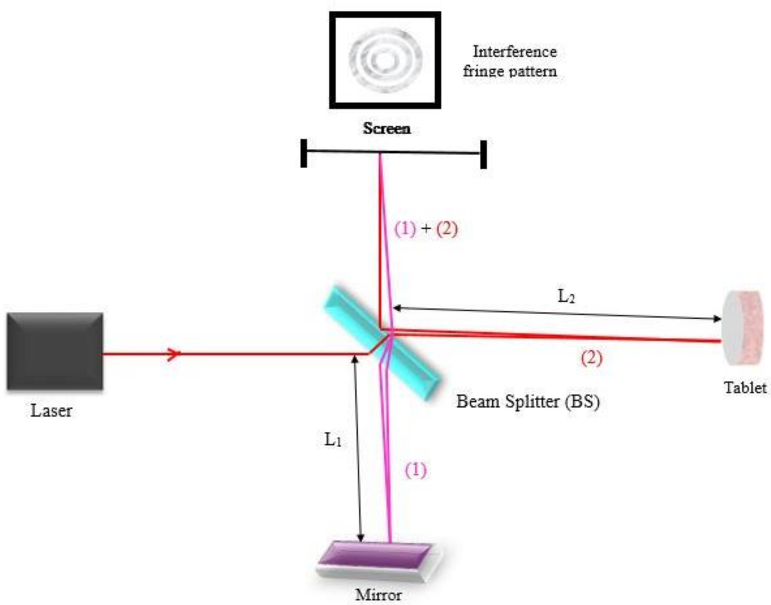

Figure 1. Schematic of the prepared setup of Michelson interferometer.

3. Results and discussion

3.1. Characterization of PZT nano-powders

As shown in **Figure 3**, for pure PZT NPs, there were diffraction peaks at 2θ =21.6, 27.7, 30.6 (main peak), 38.2, 44.1, 55, 63.8 and 73 are allocated to reflection from (002), (112), (122), (230) (004), (214), (270) and (403) planes of the $PbO.ZrO_2/PbZrO_3$ orthorhombic structure. Also, there were diffraction peaks at 2θ = 22, 31 (main peak), 38.2, 43.6, 50.3, 54.6, 64.2 and 72 corresponding to (100), (101), (111), (002), (201), (112), (022) and (103) planes, which indicates to formation of $Pb(Zr_{0.52}Ti_{0.48})O_3$ with tetragonal structure. For case of PZT:K powders, the formed phases are the same but small shift is appeared.

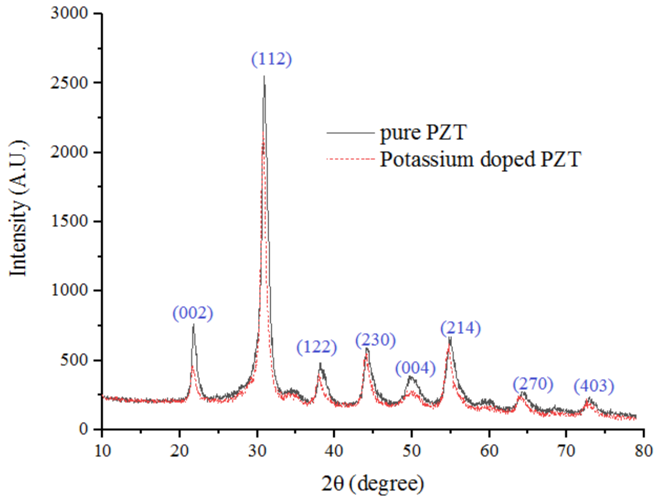

Figure 3. XRD diffraction patterns of pure PZT and PZT:K powders.

The morphology of the powders has been studied using SEM images. **Figure 4** indicates formation of nano-scale islands. Inserting potassium atoms in the PZT structure leads to the formation of more recognizable particles, but in the pure PZT powder, islands are more interconnected and indiscernible.

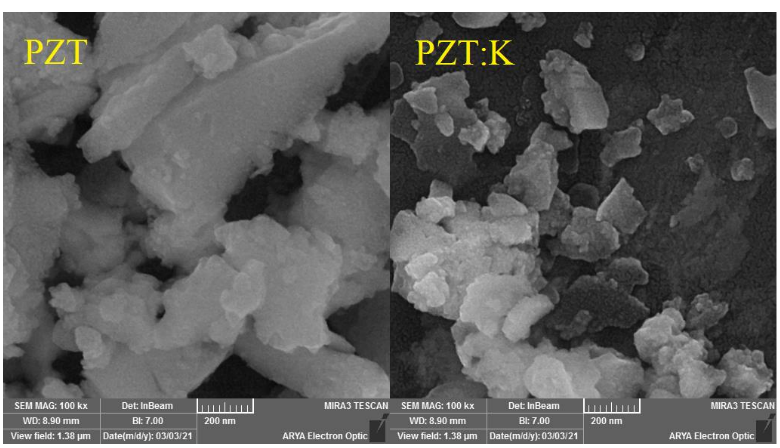

Figure 4. SEM images of pure PZT and PZT:K powders.

Absorption spectrum of PZT and PZT:K were plotted in **Figure 5**. To obtain a smooth curve, powders were dispersed in a solution of water and ethanol using sonication. Then the solutions were centrifuged at 500 rpm for 10 min, to remove submicron particles that contribute to light scattering. This procedure leads to a pure absorption spectrum without any light scattering noises and gives more accurate bandgap energy. Tauc plots of the NPs shown in **Figure 5** indicates a little decrease for indirect bandgap by adding potassium doping. Eq.1 was used to calculate the indirect band gaps of the NPs [23,26]:

$$(\alpha h\nu)^{0.5} = A(h\nu - Eg) \quad \textbf{(1)}$$

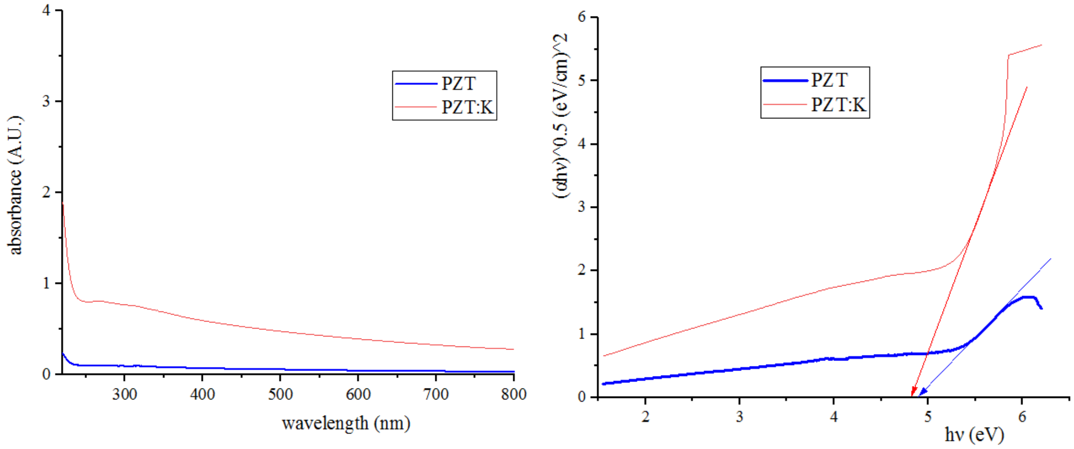

Figure 5. UV-visible absorption spectrum and Tauc plots of PZT and PZT: K NPs. The bandgap of the structures were obtained 4.9eV and 4.8eV, respectively.

The size distribution of centrifuged PZT NPs was studied by DLS by calculating the hydrodynamic diameter of the particles. As shown in **Figure 6**, the average size is obtained below 30 nm and the size of doped NPs is rather bigger.

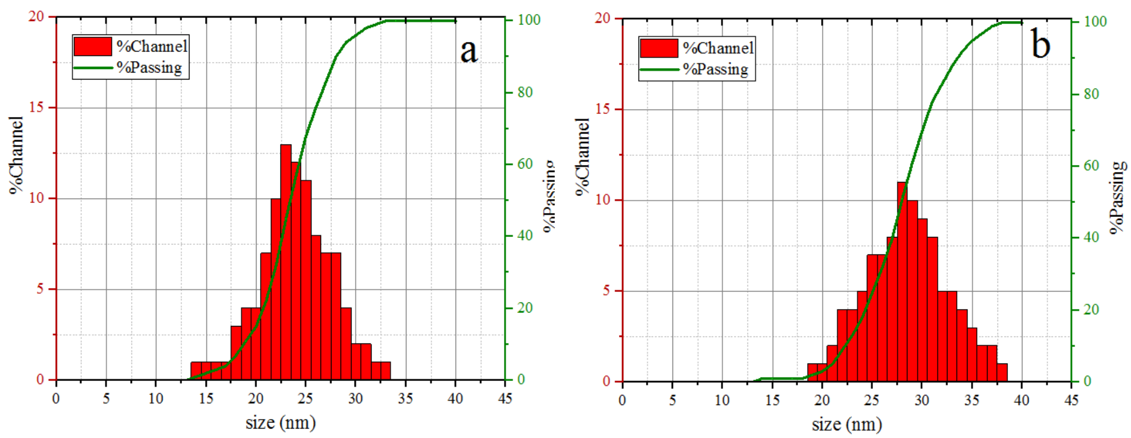

Figure 6. DLS diagrams of a- PZT and b-PZT: K NPs.

3.2. Preparation of tablets

Two powder samples PZT and PZT: K were made into tablets with a thickness of 1.2 mm using a tablet maker machine (tablet press), under a pressure of 20 bar. Then each of the tablets was glued on a glass plate with silver glue. Tablets were again covered with silver glue and a sheet of stainless steel was put on it. Finally two cupper wires were connected to the steel sheet and silver glue, due to electrical connections. **Figure 7** shows a schematic of prepared PZT Tablets which placed on a glass plate and the electrical connections attached to it.

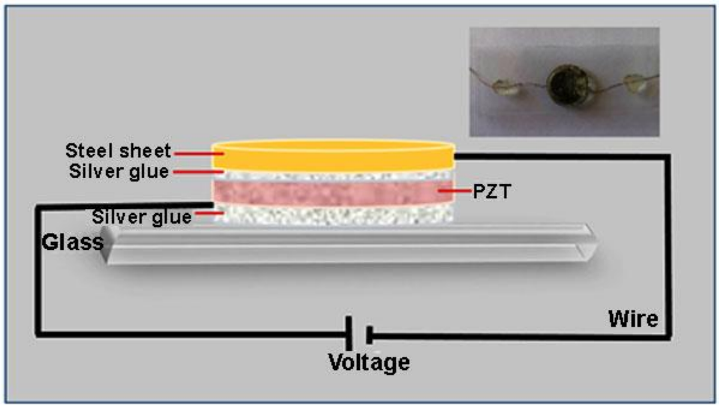

Figure 7. The Schematic of the PZT Tablet is placed on a glass plate and the electrical connections are attached to it.

3.3. Measuring piezoelectric properties using Michelson interferometer

Prepared PZT tablets were used as a mirror in one arms of Michelson interferometer, as shown in **Figure 1**. A He-Ne laser beam with 632.8nm wavelength and 5mW output power was used for this setup. Using the copper wires which are soldered to the silver-plated surface of the tablets, different electrical voltages were applied to the tablets and micrometer expansion was happened due to their piezoelectricity. Increasing the thickness of tablets can be measured using the change in the number of interference fringes. The fringe pattern on a vertical white screen was observed and the number of rings was counted. Through about 80 s after each voltage increase, the fringes pattern was stabilized and calmed down and the number of fringes change was counted. Number of created fringes versus the applied voltage is offered in **Table 1**.

Table 1. Number of created fringes by Michelson interference at different voltages.

Applied voltage (V)	Count(PZT)	Count(PZT:K)
1.02	0	1
2.3	1	2
4.1	2	4
5	3	4
5.9	4	5
8.9	4	5
9	4	6
15	5	6
17.9	5	7
21	6	7
24.1	6	7
31	7	8

Results are plotted in **Figure 8**. By increasing voltage, the number of fringes formed on the screen has also increased. Using a simple curve fitting with logarithm function, the relation between the number of fringes (Δm) and the applied voltage was obtained as:

$$\Delta m = 1.864 Ln(V) - 0.0372 \quad (2)$$

for pure PZT tablet and also:

$$\Delta m = 1.8885 Ln(V) + 1.2779 \quad (3)$$

for pure PZT:K tablet. Using the following equation [27]:

$$\Delta d = \lambda\Delta m / 2 \quad (4)$$

One could obtain the displacement of the tablets against the voltages. It was proved that when the PZT crystal structure is doped with an alkali metal such as potassium, the piezoelectricity and correspondingly, the number of counted fringes obtained from the Michelson interferometer increases [23]. Results are comparable with Na-doped PZT tables, reported in our previous study [23]. It can be concluded that doping with alkali metals can improve the piezoelectricity of PZT devices.

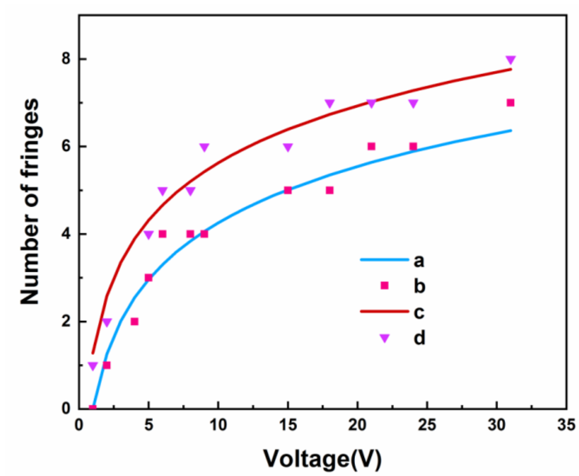

Figure 8. Number of created fringes versus applied voltage obtained by Michelson Interferometer for pure PZT tablets and potassium-doped tablets. (**a**) Numerical curve of PZT (**b**) Experimental data of PZT (**c**) Numerical curve PZT: K (**d**) Experimental data PZT: K.

4. Conclusion

In summary, the effect of potassium doping on the structure and piezoelectricity of lead zirconate titanate (PZT) NPs has been studied. Results were compared with non-doped PZT NPs. At first, PZT NPs were synthesized in powder phase by sol-gel method and analyzed by XRD, SEM, DLS and UV-visible spectrum. Analyses showed formations of PZT nanostructures and particles sizes were compared for two samples. The particle size was increased and the indirect band gap decreased by adding the potassium doping. Then, the powders were turned into tablets under 20bar pressure and both sides of them coated by conductive layers in order to apply electric voltage. The Michelson interferometer was used to evaluate the piezoelectric properties of the tablets and the number of interference fringes was studied versus the voltage and diagrams were obtained and studied which showed meaningful increment in piezoelectric properties of potassium doped PZT structures. In this research, what has been seen is that due to the increase in voltage, we have more interference frequencies, which indicates an increase in the path difference. In this way, it expresses the increase in the piezoelectric property of the material doped with potassium, so you can have a stronger piezoelectric PZT than pure PZT with potassium doping.

Authors' contributions

All authors contributed to the study conception and design. Material preparation, data collection and experiments were performed by A.K., E.K., F.M.M. and M.M.P. The first draft of the manuscript was written by M.R.R., E.K., F.M.M. and J.B. and all authors commented on previous versions of the manuscript. Finally, all authors read and approved the final manuscript.

Declaration of competing interest

The authors declare no competing interest.

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Data availability

Data will be made available on request.

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