1. Introduction

Barium titanate (BaTiO₃) was the first-ever polycrystalline ceramic exhibiting ferroelectricity. During the 1950s, it was considered a potential candidate for piezoelectric transducer materials, since the phenomenological theory of domain structure of BaTiO₃ had been developed by that time [1]. Following the subsequent discovery of lead zirconate titanate (PZT), which possessed better piezoelectric properties and a higher Curie temperature (Tc), however, interest in research on BaTiO₃ diminished among members of the scientific community. For the almost five decades that followed, PZT remained a material of interest for piezoelectric applications in the research community as well as for commercial applications [2]. The health hazards of lead, coupled with its adverse impacts on the environment have long been known [3]. It was not until 2002, however, that the European Union (EU) directives regulating the use of lead and other toxic elements were introduced [4,5]. These directives resulted in the initiation of widespread research on lead-free piezoceramics. Subsequently, in 2004, Saito et al. reported the piezoelectric properties of alkaline niobate-based lead-free piezoceramics exhibiting comparable properties to those of PZT, which resulted in exponential interest in further research in the scientific community around the globe [6]. In the early years of this surge in interest in research on lead-free piezoceramics, researchers focused their attention on the alkaline niobate ceramics and alkaline bismuth titanate ceramics based on the pioneering work of Saito et al. and Takenaka et al. in these ceramic systems [7]. Until that time BaTiO₃-based piezoceramics had not been considered as potential candidates for lead-free piezoelectric applications. In 2009, however, Liu et al. demonstrated a high piezoelectric coefficient of about 620 pC/N in Ca and Zr-modified BaTiO₃ ceramics, also known as BCZT ceramics [8]. Owing to the superior piezoelectric coefficient displayed by BCZT ceramics, they soon became a ceramic system of interest among members of the research community. In the past 10 years, a huge volume of research has been carried out on BCZT ceramics pertaining to their structure, processing, microstructure, and electrical properties. It must be noted, however, that even though BCZT ceramics display superior piezoelectric properties w.r.t. PZT ceramics as well as most lead-free piezoceramics, their application has been limited by their lower Tc ~ 85°C. The same problem has persisted with respect to the host material, in this case, i.e. BaTiO₃, which exhibits a Tc of 120°C at which it undergoes a tetragonal to cubic transition, thereby becoming paraelectric. BaTiO₃-based ceramics have exhibited a maximum Tc ~ 160°C achieved through chemical modification and/or microstructural engineering [9–12]. Therefore, it is worth noting that efforts to improve the Tc of BaTiO₃ bulk ceramics have been quite limited, even though other aspects of BaTiO₃, like powder synthesis, consolidation, dielectric, ferroelectric and piezoelectric behavior have been studied in great detail [13–17]. Given the fact...
that the crystal structure and phase transitions of BaTiO$_3$ are well understood and that its synthesis and fabrication through conventional solid-state route results in high-density ceramics, efforts to improve its $T_c$ are needed, since even if BCZT ceramics exhibit superior properties w.r.t. most lead-free piezoceramics as well as PZT ceramics, as mentioned above, their applications are limited by their $T_c$. It should also be taken into account that alkali niobates which have been considered a lead-free alternative to PZT ceramics, have an environmental impact several times greater than that of PZT due to the methods used for extraction of niobium ore [18].

The most recent exemption review of the EU regulations conducted in 2015–16 followed the objective of the EU Restriction on Hazardous Substances (RoHS) directives to restrict exemptions as far as possible. However, the piezoceramic industry stated that substitution or elimination of lead is not technically viable, since there is no single lead-free alternative to PZT piezoceramics suitable for all applications and, therefore, use of PZT has been allowed in electronic devices until the next exemption review of the EU regulations in 2021, after which the EU may not continue to allow PZT in electronic devices, and there is therefore a pressing need for the piezoceramic industry to find alternatives to PZT which are completely, or at least partially, lead free [19]. Moreover, after extensive research over the past 15 years, also the research community and piezoceramic industry have realized that there would not be an unique alternative to PZT for all applications and, thus, different piezoceramics which have been reported over the years that exhibit at least some properties equivalent or superior to those of PZT could be considered for real-time applications. Therefore, BaTiO$_3$-based materials which were the original contenders for most piezoelectric applications in the 1950s, again have become important from the perspective of the much lower toxicity level of these ceramics as compared with PZT ceramics [20,21]. Considering the fact that BaTiO$_3$ exhibits a relatively low $T_c$ of 120°C, it will indeed be necessary to shift its $T_c$ to higher temperatures to expand its applicable temperature range. Therefore, in this study, we report an increase in the $T_c$ of BaTiO$_3$ by substitution of barium with lead. Since any attempt to add lead to an otherwise lead-free piezoceramic would undoubtedly raise concerns in the research community, it should be understood that we restricted the addition of lead to 16.67 wt %, which is a relatively low percentage w.r.t. that in PZT ceramics (i.e., 63.97 wt%). It is actually quite in line with a school of thought which has demonstrated good piezoelectric properties with “reduced” use of lead [22–25]. Therefore, we report here BaTiO$_3$ with improved $T_c$ and ferroelectric and piezoelectric properties with minimum addition of lead, thereby minimizing any possible environmental impact.

2. Experimental work
Preparation of Ba$_{1-x}$Pb$_x$TiO$_3$ ($x = 0–0.20$): AR grade powders of BaCO$_3$, TiO$_2$ and PbO (all from Loba Chemie, purity >99%) were used for the sample preparation. All these powders were mixed as per the calculated molar ratios. The weighted individual compositions were homogeneously mixed for 24 h in ethanol by milling in polyethylene bottles using zirconia balls as the grinding media. The well-mixed homogeneous powders were calcined at 1150°C for 4 h in sealed alumina crucibles. The crucibles were sealed using MgO for absorption of moisture. The calcined powders were then reground for 24 h using the same procedure. After this, 2–3 drops of 3 wt% solution of polyvinyl alcohol dissolved in water were added as a binder to the powder samples and the samples were compacted into cylindrical pellets with a diameter of 12 mm & thickness of 2 mm under 60 MPa using steric acid as a lubricant. Upon drying, these pellets were again sintered at 1300°C for 4 h at a 5°C/h heating rate in a sealed crucible with a bed of powder of same composition kept at the bottom of the crucible. The crystal structure and phase identification of the powder of the sintered pellets was carried out by X-ray diffractometer (PanAlytical XPERT-PRO Diffractometer), and the refined lattice parameters (and volume) of the tetragonal perovskite unit cell were obtained using WinXCell 1.1 software [26]. The microstructure and elemental compositions were investigated using a field emission scanning electron microscope (Carl Zeiss Sigma) with an energy dispersion X-ray spectroscopy (Bruker) attached. Compositional analysis was carried out at different spots on the samples by applying an accelerating potential of 20–50 kV. The sintered pellets were polished and the flat surfaces were coated with high-purity silver paste and then dried at 300°C for 30 min, before taking dielectric measurements. Dielectric permittivity values were acquired in the frequency range of 10 Hz to 1 MHz, and measurements related to the temperature dependence of the dielectric constant were carried out in the temperature range 45°C to 200°C, wherein the samples were expected to undergo a ferroelectric to paraelectric phase transition. The loop between polarization and the electric field was plotted using data from a TF analyzer 2000. The piezoelectric coefficient values were measured using a $d_{33}$ meter.

3. Results and discussion
XRD patterns recorded on the surface of Ba$_{1-x}$Pb$_x$TiO$_3$ ($x = 0–0.20$) pellets sintered at 1300°C reveal single
tetragonal perovskite phase formation for pure BaTiO$_3$, 5% Pb addition and 10% Pb addition as shown in Figure 1. At 15% Pb addition and above, it can be seen that splitting of (002) and (200) diffraction peaks and the corresponding intensity changes brought about by the addition of PbO indicates a symmetry change from tetragonal to orthorhombic. It is worth noting that the PbO used for introducing Pb to BaTiO$_3$ unit cells possesses an orthorhombic crystal structure. A similar change in crystal symmetry has been demonstrated by Singh et al. in the case of K$_{0.5}$Na$_{0.5}$NbO$_3$–BaTiO$_3$ ceramics [27]. However, more detailed inferences can be drawn if the XRD data is correlated with Raman spectroscopy data. With Pb$^{2+}$ substitution in place of Ba$^{2+}$, the XRD patterns revealed splitting of the peaks for most of the higher index planes, apart from a reduction in the intensity of all the peaks. This indicated an increase in the tetragonality of the lattice apart from reduction of the crystallinity of the perovskite lattice.

It is clear from Figure 2 that the c/a ratio increases from 1.009 (pure BaTiO$_3$) to 1.016 (20% Pb addition). This increase in the c/a ratio is due to the fact that substitution of Pb$^{2+}$ in Ba$^{2+}$ decreases the a-lattice parameter while increasing the c-lattice parameter. The c/a ratios conformed with the improvement in tetragonality for Pb (in place of Ba) substitution, as noted from the XRD patterns (Figure 1). The substitution of Pb$^{2+}$ for Ba$^{2+}$ was expected to stabilize the tetragonal phase by causing lattice distortions, as Pb$^{2+}$ is a Rydberg (“lone-pair”) ion [28].

It can be seen from Figure 3 that addition of PbO to BaTiO3 did result in change in the relative density of these ceramics. However, no specific trend in relative density as a function of % Pb addition was observed w.r.t. undoped BaTiO3. This can be

Figure 1. XRD pattern of sintered Ba$_{1-x}$Pb$_x$TiO$_3$ (x = 0–0.20) pellets.

Figure 2. Variation of tetragonality (c/a ratio) with lead addition.
attributed to the fact that addition of Pb resulted in liquid phase sintering whereas densification in undoped BaTiO3 proceeded via solid state sintering. Therefore, in case of addition of PbO the amount of liquid phase formed, wettability, contact angle etc. would have varied in each composition thereby resulting in either increase or decrease in relative density. However, it must be noted that in each composition was greater than 90% indicating overall satisfactory densification.

SEM photomicrographs of the surfaces of all three samples after polishing and thermal etching at 1200°C for 2 h are shown in Figure 4(a–e). The microstructures of the samples support the high density observed during actual measurements. The addition of PbO having a melting point of 888°C to BaTiO3 is moreover most likely to cause the liquid phase sintering effect [29]. The microstructure of pure BaTiO3 samples (Figure 4(a)) is fairly clean and fine grained with somewhat heterogeneous grain size distribution. For the ceramics consisting of 15 and 20 mol% Pb, however, the liquid phase sintering seems to be more pronounced and, therefore, a clean and well-developed microstructure is not seen in these compositions. This is often associated with liquid phase sintering.

\[ \text{Figure 3. Variation in relative density (expressed in } \%\text{TD, i.e., theoretical density) with Pb addition.} \]

\[ \text{Figure 4. SEM images at 10,000X magnification of (a) pure BaTiO}_3, \text{ (b) Ba}_{0.95}\text{Pb}_{0.05}\text{TiO}_3, \text{ (c) Ba}_{0.90}\text{Pb}_{0.10}\text{TiO}_3, \text{ (d) Ba}_{0.85}\text{Pb}_{0.15}\text{TiO}_3, \text{ and (e) Ba}_{0.80}\text{Pb}_{0.20}\text{TiO}_3.} \]
Sintering, as heterogeneity and coalescence of small pores into large pores are common occurrences in samples densified by a liquid phase [30, 31].

In order to understand the local elemental compositions of these ceramics, energy dispersive spectroscopy (EDS) was conducted on a few samples, especially samples with a higher lead content. Table 1 shows the theoretical and actual elemental compositions of ceramics containing 15 and 20 mol% Pb at the Ba site. It can be seen that, except for Ti, there is a deviation in the actual amount present for each element w.r.t. the theoretical composition. This deviation can be attributed to the fact that these ceramics were prepared using the solid-state method, for which such a local chemical inhomogeneity has been reported earlier as well. The elemental composition was studied using EDS, moreover, which is a more qualitative tool without which accurate measurement of each of these elements would not have been possible. Nevertheless, it is to be noted that the presence of Pb in a very small quantity of 3 and 4 atom% was detected in these compositions in both the ceramics, albeit with a lesser concentration. The EDS spectra for both the compositions are shown in Figure 5.

It is noted from Figure 6 that the value of the dielectric constant in the case of pure BaTiO$_3$ shows a continuous decrease with increase in frequency, whereas, it remains almost constant for Pb-substitution over the entire tested frequency range (1–10$^6$ Hz). The drop noted in the case of pure BaTiO$_3$ samples, especially is attributed to the inability of the dipoles to follow the field variation at higher frequencies. The value of the dielectric constant noted was close to 2880 for pure BaTiO$_3$, which was reduced to

| Composition | Theoretical atom% | Experimental atom% |
|-------------|-------------------|--------------------|
| Ba Pb Ti O  | Ba Pb Ti O        |
| Ba$_{0.85}$Pb$_{0.15}$TiO$_3$ | 17 3 20 60 | 12.93 1.25 20.97 64.85 |
| Ba$_{0.80}$Pb$_{0.20}$TiO$_3$ | 16 4 20 60 | 10.5 1.38 19.1 69.01 |

Figure 5. EDS spectra for (a) Ba$_{0.85}$Pb$_{0.15}$TiO$_3$, (b) Ba$_{0.80}$Pb$_{0.20}$TiO$_3$. 

Table 1. Comparison of the elemental composition of Ba$_{0.85}$Pb$_{0.15}$TiO$_3$ and Ba$_{0.80}$Pb$_{0.20}$TiO$_3$ ceramics detected through EDS with the theoretical composition.
1050, 850, 680 and 400 for 5 at%, 10 at%, 15 at% and 20 at% Pb substitution (at 1 KHz frequency), respectively. This reduction in the values of the dielectric constant is due to the formation of PbTiO$_3$, as the dielectric constant of PbTiO$_3$ is lower than the dielectric constant of BaTiO$_3$ [32].

The data given in Figure 7 have shown very interesting results related to the Curie temperature and the values of the dielectric constant noted. The Curie temperature associated with the phase transition from a low-temperature tetragonal perovskite phase to a high-temperature cubic perovskite phase in the case of BaTiO$_3$ is located where the maximum dielectric constant is observed. A notable increase was observed in the value of the dielectric constant at the Curie temperature from a value of 5500 for pure BaTiO$_3$ to 8000 and 7500 at 5 at% and 10 at% Pb substitution, respectively. This was attributed to an increase in the tetragonality ($c/a$ ratio) of the Pb substituted samples [27]. The decrease in the value of the dielectric constant upon further addition of Pb is due to porosity present in the samples. Apart from this, a substantial shift in the value of $T_c$ from 120°C for pure BaTiO$_3$ to 170°C for Ba$_{0.80}$Pb$_{0.20}$TiO$_3$ was also noted, which was more than that seen with any other dopant used [29, 33–41] (refer to Table 2).

While plotting the variations in the dielectric loss with frequency for Ba$_{1-x}$Pb$_x$TiO$_3$, ($x=0$–0.20) as shown in Figure 8, another interesting observation was made. While the dielectric loss tangent ($\tan \delta$) values were showing an increasing trend with increase in frequency for pure BaTiO$_3$, these demonstrated a decreasing trend for Ba$_{1-x}$Pb$_x$TiO$_3$ samples. Both the Pb-substituted samples demonstrated a substantial decrease in $\tan \delta$ values.

The physical significance of $\tan \delta$ is the energy dissipation in the dielectric system, which is proportional to the imaginary portion ($\varepsilon''$) of the dielectric constant. The lower the $\tan \delta$ value, the better the performance a dielectric is expected to show during actual working. The trend noted is as per expectations, moreover, as the dielectric constant and dielectric loss values usually show an opposite behavior. The lower and upper ends
of the frequency range of testing were neglected while noting the variations of tan δ with frequency at room temperature. This was because they were likely due to limitations of the instrument, since there was no other likely cause for their occurrence.

Ferroelectric hysteresis measurements were carried out on sintered samples primarily to study their polarization behavior. Figure 9 shows a P–E hysteresis loop recorded at room temperature for the Ba$_{1-x}$Pb$_x$TiO$_3$ (x = 0–0.10) samples. It is clear from these curves that the value of maximum polarization as well as the shape of the hysteresis loops depends strongly on the Pb substitution made. With increases in the amount of Pb substitution, associated increases in the saturation polarization, coercive electric field, and energy loss (see Table 1) is also seen. The latter makes the ceramics behave as hard ferroelectrics. Furthermore, the P–E loop swells out for increases in Pb substitution. With increases in Pb substitution, the P–E loop becomes nearly square. The ferroelectric parameters of Ba$_{1-x}$Pb$_x$TiO$_3$ ceramics are listed in Table 3.

Though there appears to be a cyclical opening of P–E loops in all the samples, this opening is clearly visible only in Ba$_{0.95}$Pb$_{0.05}$TiO$_3$ samples. This effect may be attributed to both the retention characteristics of the samples and their limited resistivity, which causes leakage of charges due to conduction [8]. The saturation polarization of the 10 at% Pb-substituted samples has increased by one-and-a-half times to ~18 µC/cm$^2$ from ~12 for pure

Table 2. Effect of various dopants/substitution on dielectric properties of BaTiO$_3$ ceramics fabricated by solid-state reaction route.

| S. No. | Substitution/doping Qty. | Curie temp. ($^\circ$C) $T_c$ | Dielectric constant $\varepsilon_r$ (100 kHz) | Remanant polarization $P_r$ (µC/cm$^2$) | Coercive field $E_c$ (KV/cm) | Piezo-electric coeff, $d_{33}$ (pC/N) | Dielectric loss (tan δ) |
|-------|--------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1     | Fe 1.50 at%              | 95              | 1200            | 0.31            | −0.66           | x               | x               |
|       | 1%                       | 102             | 1200            | 0.3             | −0.2            | x               | x               |
| 2     | Cu 0.01 at%              | 125             | 600             | x               | x               | 0.09            | [27]            |
|       | 0.02                     | 120             | 650             | x               | 0.06            |                 |                 |
|       | 0.03                     | 115             | 666             | x               | 0.03            |                 |                 |
| 3     | Ni 0.05 at%              | x               | x               | 12              | 8               | x               | x               |
|       | 0.1                      | x               | x               | 6.5             | 13              | x               | x               |
|       | 0.15                     |                |                | 3.5             | 16              | x               |                 |
| 4     | W 0.15 at%               | 85              | 800             | 3               | 5               | x               | x               |
| 5     | La 0.0005 at%            | 153             | 9766            | 3.1             | 3.8             | 0.025           | [31]            |
|       | 0.001                    | 143             | 10055           | 3.5             | 4.95            | 0.02            |                 |
|       | 0.003                    | 133             | 13606           | 5.9             | 3.73            | 0.02            |                 |
| 6     | Al 0.01 at%              | 113             | 2000            | x               | x               | 135             | x               |
| 7     | Li$_2$O 0.5 mol%         | 123             | 2000            | 2               | 8               | 200             | x               |
|       | 0.7                      | 125             | 1300            | x               | 183             | x               |                 |
| 8     | Co 0.75 at%              | 115             | x               | x               | 190             | 1.8             | [34]            |
|       | Co &Nb                   | 114             | x               | x               | 200             | 0.4             |                 |
| 9     | Zr 2.4 at%               | 74              |                | x               | x               | 0.025           | [39]            |

(x – denotes values not reported).

Figure 8. Variation of dielectric loss with frequency for Ba$_{1-x}$Pb$_x$TiO$_3$ (x = 0–0.20) ceramics.
BaTiO$_3$ samples (see Table 1). The increase in tetragonality with Pb-substitution, introduced because of the difference between the ionic radii of Pb$^{2+}$ (1.49 Å) and Ba$^{2+}$ (1.61 Å) ions apart from the difference between the electronegativity values of Pb (1.87 Paulings) and Ba (0.89 Paulings), has most likely contributed to this enhancement. When ferroelectric hysteresis measurements were conducted for Ba$_{1-x}$Pb$_x$TiO$_3$, ($x=0.15–0.20$), no hysteresis loop could be obtained. The samples showed conductive behavior resulting from their large porosity.

An increase in the remnant polarization noted from the P-E loop suggested a likely enhancement of $d_{33}$ values due to Pb-substitutions. Variations in $d_{33}$ as a function of the percentage of Pb substituted at the Ba site are shown in Figure 10. These are reflected in the actual measurements conducted. The value of 95 pC/N noted for the basic BaTiO$_3$ samples almost matched those obtained by other researchers following a solid-state reaction route [16, 33] similar to that we used. A monotonic increase in the $d_{33}$ value from 95 pC/N for pure BaTiO$_3$ samples to 220 pC/N for 15 at% Pb-substituted samples was seen. This increase in the $d_{33}$ value was due to an increase in the tetragonality (c/a ratio) of the sample with increases in the lead percentage in the sample. This increase was by almost one-and-a-half times. A 15 at% lead addition is followed by a decrease in the $d_{33}$ value (which is still higher than that of pure BaTiO$_3$) due to the porosity present in the sample. This was attributed to an increase in the tetragonality character with Pb-substitution. Further refinement of the density and

Figure 9. PE loop for Ba$_{1-x}$Pb$_x$TiO$_3$, ($x=0–0.10$) ceramics (at 1 kHz).

| Sample     | $P_s$ (µC/cm$^2$) | $P_r$ (µC/cm$^2$) | $-P_r$ (µC/cm$^2$) | $E_c$ (V/cm) | $-E_c$ (V/cm) | Energy Loss (µJ/cm$^2$) |
|------------|------------------|------------------|-------------------|-------------|-------------|------------------------|
| Undoped    | 12.36            | 1.8014           | 1.8472            | 2383.8      | 2472.008    | 22891.9                |
| 5% Pb      | 16.12            | 7.8100           | 7.6313            | 4783.54     | 4137.64     | 37121.4                |
| 10% Pb     | 17.8             | 12.2711          | 12.7292           | 8211.37     | 6426.74     | 35320.3                |

Figure 10. $d_{33}$ values for Ba$_{1-x}$Pb$_x$TiO$_3$, ($x=0–0.20$) ceramics as a function of atom% Pb$^{2+}$ at the Ba$^{2+}$ site.
4. Conclusions

Dense Ba$_{1-x}$Pb$_x$TiO$_3$ ($x = 0–0.20$) samples (>90% TD) were fabricated by a solid-state reaction route followed by sintering at 1300°C for 4 h. All the samples revealed a tetragonal perovskite crystal structure. The tetragonality grew monotonically with increases in the substitution of Pb. The SEM revealed the transformation of the grain shape from non-uniformly distributed equiaxed grains into prismatic grains for higher Pb addition, indicative of the occurrence of liquid phase sintering. Measurements of the dielectric constant showed a drop to 400 for 20 at% Pb substitution from an initial value of 3000 for un-substituted (pure) samples, whereas the dielectric loss was reduced by almost 50% vis-a-vis pure BaTiO$_3$ samples for 10 at% Pb substitution. A substantial increase in the Curie temperature from ~120°C to 170°C associated with a substantial increase in the dielectric constant (with the value becoming almost 8000 at the Curie temperature) for the Pb-substitutions was the main achievement of this study. Both the saturation and remnant polarization were increased by almost one-and-a-half times and six times, respectively, for the Pb-substitutions made. The $d_{33}$ values also showed an increase from 95 pC/N the pure BaTiO$_3$ samples to 220 pC/N for 15 at% Pb-substituted samples.

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Disclosure statement

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