

Study of dielectric and ferroelectric properties of five-layer Aurivillius oxides: $A_2Bi_4Ti_5O_{18}$ (A = Ba, Pb and Sr) synthesized by solution combustion route

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Abstract. This paper presents the ferroelectric and dielectric properties of five-layer Aurivillius oxides ($Ba_2Bi_4Ti_5O_{18}$, $Pb_2Bi_4Ti_5O_{18}$ and $Sr_2Bi_4Ti_5O_{18}$) prepared by a solution combustion route with glycine as a fuel at low calcination temperature. The phase formation of these materials with pseudo-tetragonal structure was achieved after calcination at 750°C for 3 h; as confirmed by X-ray diffraction studies. Scanning electron microscopy of the sintered ceramics shows that the grains exhibit a plate-like morphology. The ferroelectric to paraelectric transition temperature (T_c) for Ba-, Pb- and Sr-based bismuth titanate ceramics was found to be 350, 280 and 260°C , respectively. All three materials show multiple relaxation phenomena and their electrical conductivity was found to be temperature dependent. The $Pb_2Bi_4Ti_5O_{18}$ ceramic possessed the highest value of activation energy (0.68 eV) and hence shows better ferroelectric properties, as compared to barium and strontium bismuth titanates.

Keywords. Ceramics; X-ray diffraction; dielectric properties; ferroelectric properties.

1. Introduction

Bismuth layer structured ferroelectrics (BLSF) and the Aurivillius family of compounds are promising candidates for their applications in non-volatile random access memories (NVRAM), actuators, sensors, and as piezoelectric component owing to their excellent fatigue endurance property.^{1–5} These compounds are also of interest in applications such as piezoelectric sensors operating at high temperatures and frequencies. BLSF compounds are categorized as compounds with low dielectric constants, high Curie temperatures and large anisotropies in their electromechanical coupling factor as compared with lead zirconate titanate (PZT) ferroelectrics.^{6,7} These Aurivillius phases consist of perovskite-like units separated by a layer of bismuth oxide with a general formula $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$. The pseudo-perovskite blocks $(A_{m-1}B_mO_{3m+1})^{2-}$ are interleaved with a bismuth oxide layer $(Bi_2O_2)^{2+}$ along the c -axis. The cubo-octahedral A-site is occupied by mono-, di- or trivalent ions such as Na^+ , K^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} or a combination of them, the B-site is populated with ions with high valency such as Ti^{4+} , Nb^{5+} , Ta^{5+} , etc. or a combination of them and m denotes the number of perovskite layers;^{8,9} these factors are also linked to the structural stability and ferroelectric properties of the material. Almost all of these compounds possess orthorhombic symmetry at room temperature.^{10,11} Compounds with larger m -value were associated with smaller coercive field of saturated hysteresis curve.^{9,11} The value of the spontaneous polarization (P_s)

along the c -axis varies depending on whether there is an odd or even number of layers (m) in a BLSF compound. When m is an odd number, a small level of polarization was observed and when m is an even number no spontaneous polarization was observed.¹² Compounds with even number of pseudo-perovskite layers exhibit linear dielectric properties along the c -direction.¹²

As the B-site cations in BLSF do not play a major role in the polarization process of ferroelectric materials, the study of A-site substitution is more important in understanding the ferroelectric response of these materials.^{13,14} Kumar *et al*¹⁵ also highlighted the importance of the A-site substitution in determining the nature of the phase transition and ferroelectric behaviour of BLSF compounds. For example, Ba-based bismuth titanate exhibits a relaxor-type diffuse phase transition with high permittivity (ϵ) and strain over a wide temperature range, while its Sr and Ca analogs at the A-site show a normal ferroelectric to paraelectric phase transition.¹⁵

Nalini and Guru Row¹⁶ reported the synthesis of $ABi_4Ti_4O_{15}$ belonging to $m = 4$ series of the Aurivillius family by a solid-state reaction and found that the ferroelectric to paraelectric phase transition (T_c) in Ba- and Pb-based bismuth titanates is not accompanied by a structural phase transition. A similar behaviour was also observed in the $m = 2$ series of the Aurivillius family.¹⁷ Subohi *et al*³ reported that $m = 3$ series of the Aurivillius family shows low dielectric permittivity and high Curie temperature (T_c). Below T_c , they are orthorhombic and above T_c they become tetragonal.

The synthesis and the ferroelectric behaviour of $m = 5$ oxides, $A_2Bi_4Ti_5O_{18}$ where A = Sr, Ba and Pb was first reported by Aurivillius and Fang¹⁸ and Subbarao⁹ in 1962.

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There are contradictory reports regarding the existence of single phase in Ba-based bismuth titanates. Subbarao⁹

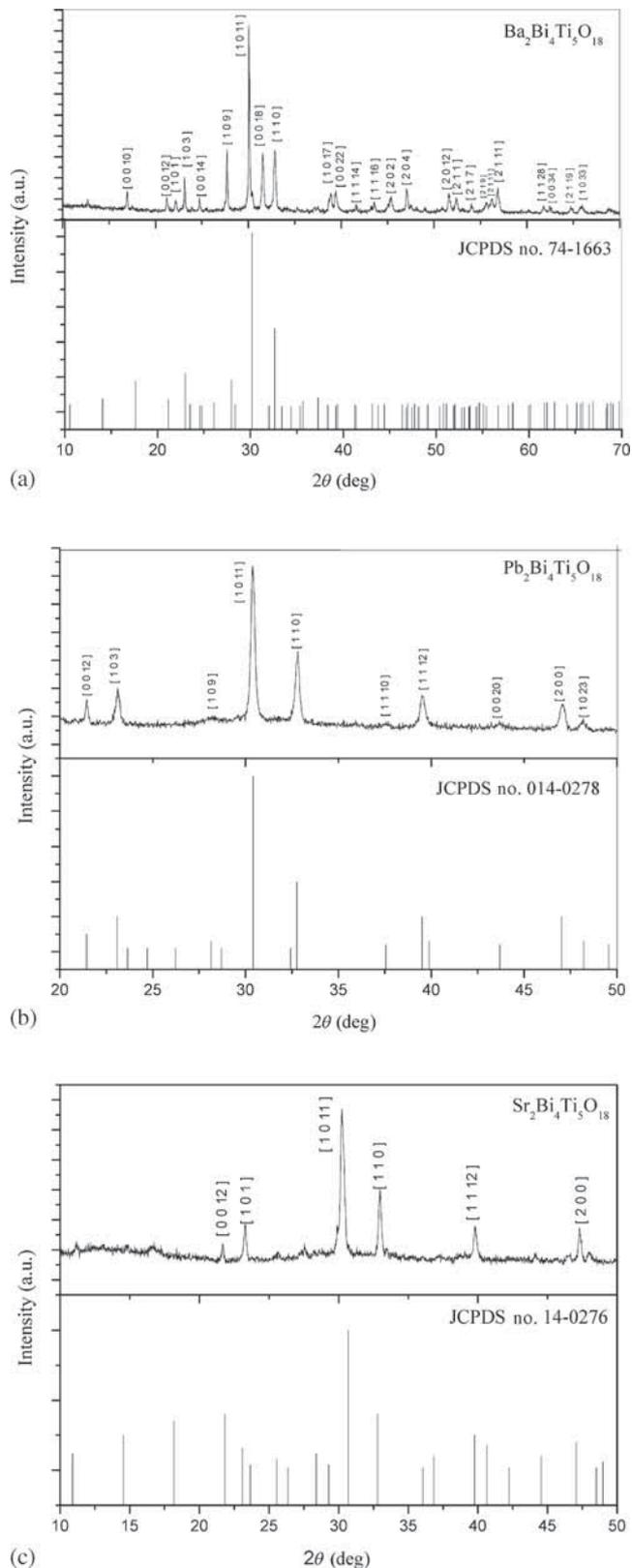


Figure 1. X-ray diffraction patterns of (a) $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, (b) $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and (c) $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ceramics.

reported that $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ exists as a mixture of a four-layer oxide $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ and BaTiO_3 , whereas, Aurivillius reported that $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ can be obtained in single phase. Irie *et al*¹⁹ indexed the patterns of Ba- and Pb-based bismuth titanate compounds in the space group B2ab. The ferroelectric properties of these compounds can also be tuned by varying the ionic radii and polarizability parameters. The substitution at the A-site with larger ionic radii and cations with a higher degree of polarization reduces the rattle space, resulting in structural displacement distortion.¹³

$\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ are five-layered ($m = 5$) members of the Aurivillius family (i.e., BLSF) which are pseudo-tetragonal at room temperature and their Curie temperatures are reported as 310–330,^{1,18} 285²⁰ and 267°C,²¹ respectively. The transition temperature of these Aurivillius family materials decreases with the increase in number of layers, which is directly related to the degree of

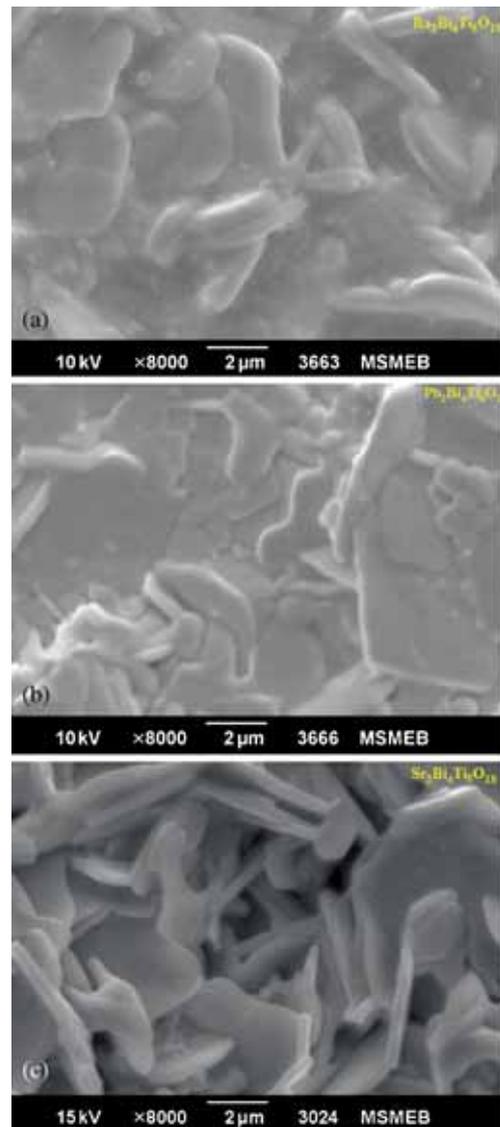
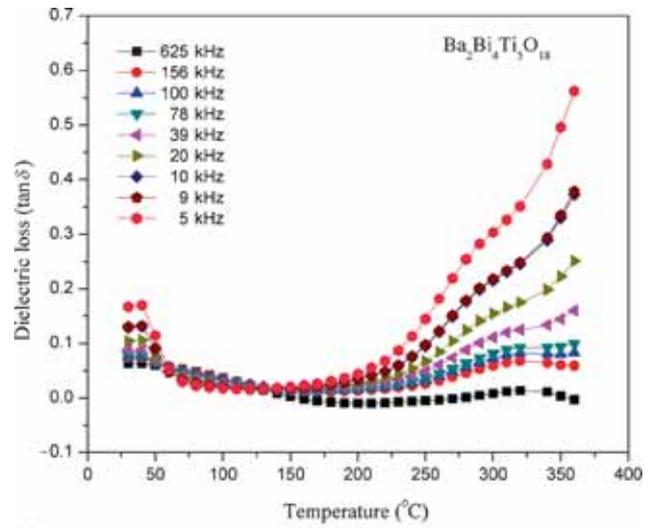
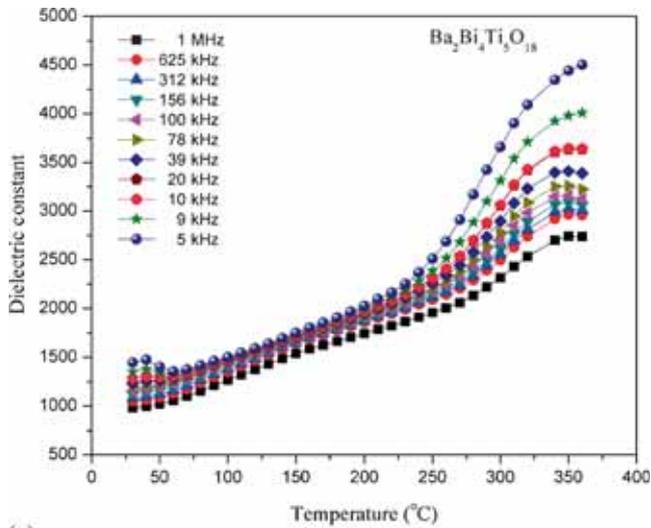
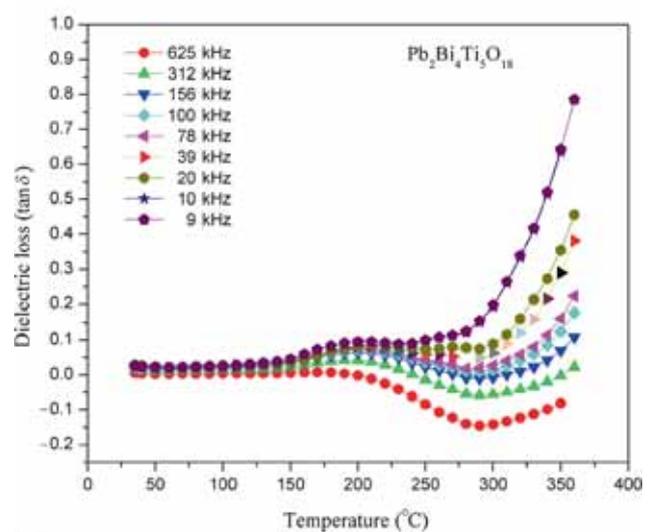
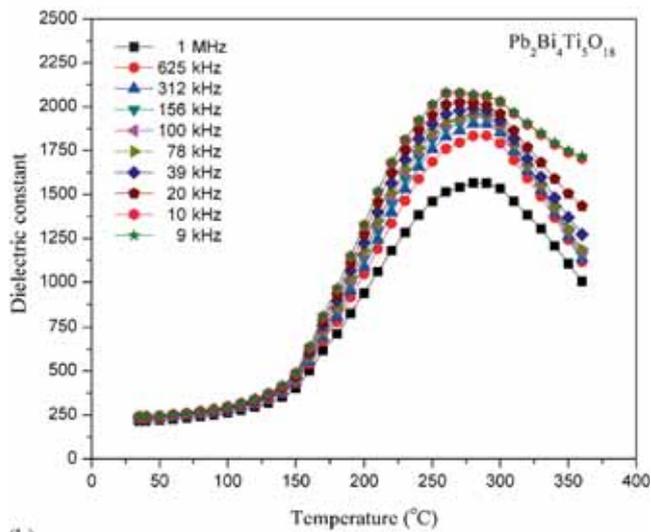


Figure 2. Surface morphology of (a) $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, (b) $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and (c) $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ceramics.



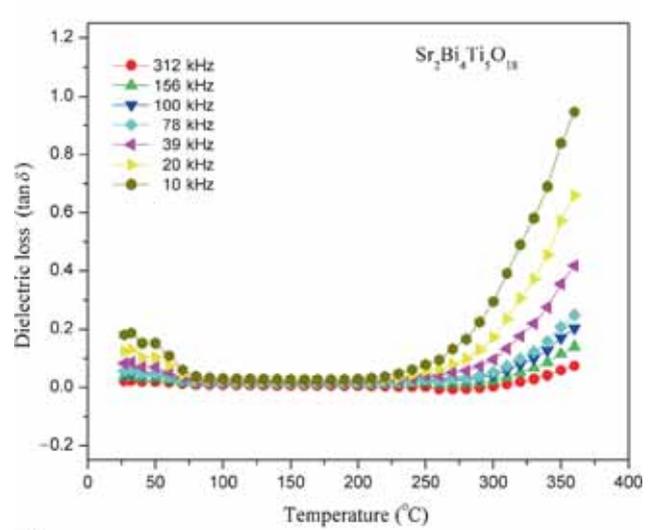
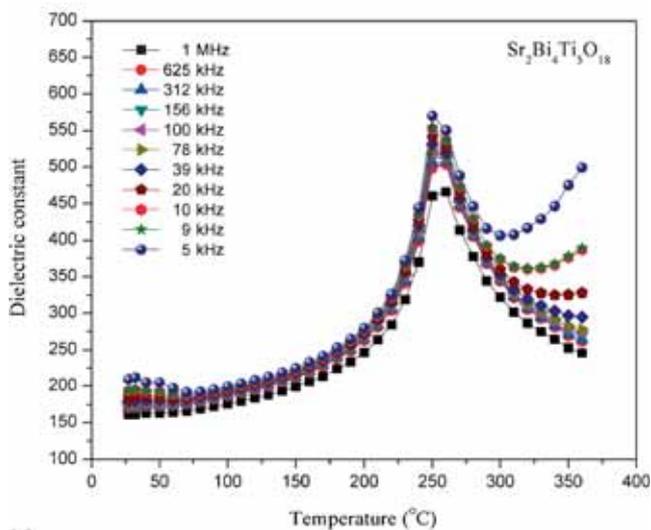
(a)

(a)



(b)

(b)



(c)

(c)

Figure 3. Dielectric constant of (a) $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, (b) $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and (c) $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ceramics as a function of temperature at different frequencies.

Figure 4. Variation of dielectric loss with temperature at different frequencies for (a) $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, (b) $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and (c) $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ceramics.

distortion of the perovskite structure. As the transition temperature decreases, structural distortion decreases and the tolerance factor (t) increases.²² These compounds exhibit good ferroelectric properties such as low coercive field ($E_c = 10\text{--}90\text{ kV cm}^{-1}$), improved remanent polarization ($P_r = 0.6\text{--}2\text{ }\mu\text{C cm}^{-2}$),^{12,23,24} this is due to the increased number of perovskite layers.^{1,2} Small values of remanent polarization (P_r) are possible because of the accumulation of defects, such as oxygen vacancies near the domain walls. A lower remanent polarization (P_r) limits their application in high-density FeRAMs.²⁵ Watanabe and Funakubo¹⁰ and Qiang *et al*²⁶ reported that in order to obtain large P_r , the control of defects in the perovskite layers is required.

Very little is known about the $m = 5$ (five layered) group in comparison to the lower orders such as $m = 2, 3$ group. The methods used to synthesize these materials are solid-state reaction,^{21,27} mechano-chemical activation²⁸ and sol-gel synthesis.² These synthesis routes require high processing temperatures, long processing times, and achieving the desired product with a high-purity phase can be difficult.^{22,28} The solution combustion (SC) technique can produce fine particle size powders from nanometre to submicron scale and requires a low calcination temperature that can minimize the volatilization of Bi. Furthermore, the SC technique requires relatively simple equipment, is low cost and offers better control over the stoichiometry.^{29,30} The SC technique involves a self-sustained redox reaction in a homogeneous solution of oxidizer (e.g., metal nitrate) and fuels (urea and glycine), which are also reducing agents. This process yields nano-sized oxide material and allows uniform grain formation in single step.³¹ Glycine is used as a fuel in place of conventional fuels such as urea and citric acid because it decreases the combustion temperature due to its complexing ability and zwitter ionic nature which forms a temporary complex and decomposes without forming hypergolic mixture of gases. In addition, glycine has a high number of carbon atoms which decreases the flame temperature due to the zero value of their enthalpy of formation. Further, the crystalline phase formation and microstructure are significantly affected by the combustion temperature.³² The synthesis of these five-layered members ($\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$) of the Aurivillius family by the SC route is yet to be reported in the literature.

In the present work Ba-, Pb- and Sr-based bismuth titanate ceramics were synthesized using the SC technique with glycine as fuel and their phase formation, morphology, ferroelectric, dielectric and electrical properties were investigated.

2. Experimental

2.1 Synthesis

Barium nitrate $\text{Ba}(\text{NO}_3)_2$, lead nitrate $\text{Pb}(\text{NO}_3)_2$, strontium nitrate $\text{Sr}(\text{NO}_3)_2$, bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) (Merck), and titanium isopropoxide $\text{TiC}_{12}\text{H}_{28}\text{O}_4$

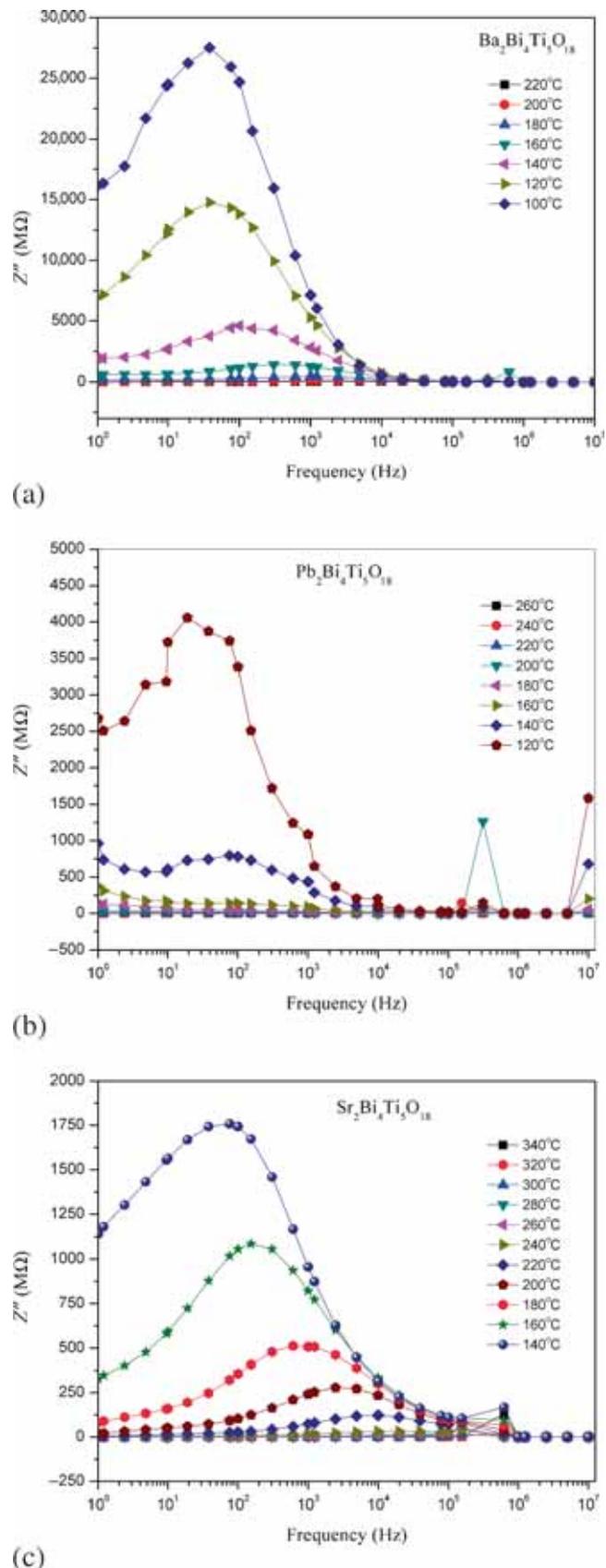
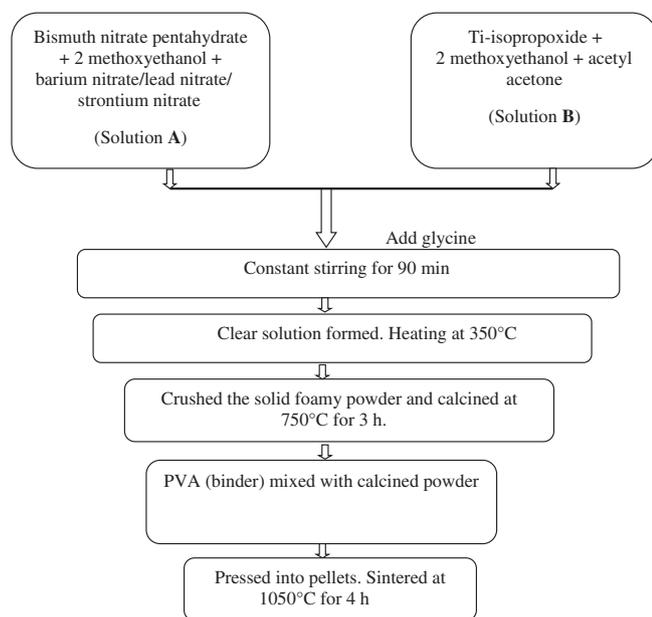


Figure 5. Variation of imaginary part of the impedance (Z'') with frequency at different temperatures of (a) $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, (b) $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and (c) $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ceramics.

(Sigma Aldrich) have been used as precursors. Glycine (Rankem) was used as fuel, 2 methoxyethanol (Rankem) as a solvent, and acetylacetone (Merck) as a chelating agent. Solution **A** was prepared by dissolving $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 2 methoxyethanol. $\text{Ba}(\text{NO}_3)_2/\text{Pb}(\text{NO}_3)_2/\text{Sr}(\text{NO}_3)_2$ was also dissolved in solution **A**. Solution **B** was prepared with Ti-isopropoxide, 2 methoxyethanol and acetylacetone. Solution **B** was then added to solution **A** drop-wise along with constant stirring and finally glycine was added to the final solution. This final solution was then stirred for 90 min at room temperature until a clear solution was formed, then it was heated at 350°C in a muffle furnace leading to evaporation and then followed by combustion. The resultant solid product was foamy, consisting of light homogeneous flakes. The solid was subsequently crushed to give a fine powder. The obtained powder was calcined at 750°C for 3 h. The calcined powder was mixed with a binder polyvinyl alcohol (PVA) and then compacted into discs of diameter 10 mm using a hydraulic press at a pressure of 140 MPa. These pellets were heated at 500°C for 30 min to achieve binder burnout followed by sintering at 1050°C for 4 h.

Flow diagram for the synthesis of Ba, Pb, Sr bismuth titanates.



2.2 Characterization

An X-ray diffractometer (Rigaku-Miniflex II) equipped with $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation was used to analyse the presence of phases in the sintered ceramics. Scanning electron microscope (JEOL-JSM6390) was used for observing the surface morphology of ceramics. For ohmic contacts, a silver electrode coating was applied on both the surfaces of the sintered pellets. Ferroelectric properties of the synthesized ceramics were determined using an automatic P - E loop tracer (Marine India Pvt. Ltd). Dielectric measurements were carried out as a function of temperature from room temperature to 400°C over the frequency range 1 Hz–1 MHz using an impedance analyzer (Nova controls, Alpha A).

3. Results and discussion

3.1 X-ray diffraction (XRD) analysis

XRD patterns of $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ceramics are shown in figure 1. The sharp peaks in XRD pattern confirm that the material has reached complete crystallinity by sintering at 1050°C for 4 h. It was observed that the pellets sintered at temperatures less than 1050°C were brittle, probably due to incomplete grain formation which results in lower density. Decomposition of these ceramics was observed at temperatures of approximately 1100°C . The crystallite size of the ceramics was determined using the Scherrer equation.³³ The crystallite sizes of $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ were found to be 57, 24.3 and 31.5 nm, respectively. It is also observed that peaks match well with the respective JCPDS files and the prepared samples possess pseudo-tetragonal (orthorhombic) symmetry with space group of B2cb .^{18,22} The highest intensity diffraction peak in the XRD pattern is the reflection from $(1\ 0\ \underline{1})$ plane of all the three compounds, which is the characteristic peak of bismuth layer structured ceramics belonging to $m = 5$ group.

3.2 Scanning electron microscopy (SEM)

The surface morphology of the prepared ceramics belonging to the five-layered Aurivillius family is shown in figure 2. A random orientation of isomeric grain growth of the

Table 1. Values of frequency corresponding to Z''_{max} at different temperatures for Ba-, Pb- and Sr-based bismuth titanate ceramics.

Temperature ($^\circ\text{C}$)	$\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$		$\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$		$\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$	
	Frequency (Hz)	Z''_{max} (M Ω)	Frequency (Hz)	Z''_{max} (M Ω)	Frequency (Hz)	Z''_{max} (M Ω)
140	106	4721	75	800	73	1757
160	409	1426	100	173	160	1079
180	1053	499	109	45	916	516
200	3317	170	113	20	2835	277

Aurivillius family is confirmed by the SEM images. The size of the grains in $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ is approximately $0.5 \mu\text{m}$ and length is $3 \mu\text{m}$. Platelets or pockets of small grains of diameter $4 \mu\text{m}$ are present in $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$. $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ possesses plate-like grains having $0.25 \mu\text{m}$ thickness and $4 \mu\text{m}$ length. The SEM images of $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ceramics show a compact grain formation with almost no pores between the grains, whereas in $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ the grains appear to be loosely formed.

3.3 Dielectric properties

The dielectric constant (permittivity) as a function of temperature (RT to 350°C) and frequency (1 Hz–1 MHz) is shown in figure 3. $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ shows a sharp peak at the transition temperature indicating that it is a normal ferroelectric. However, the other two members of the group $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ exhibit a diffuse phase transition and the transition temperature of these compounds shift towards a lower temperature with the decrease in frequency, thus demonstrating relaxor ferroelectric behaviour. In $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, the broadened peaks of dielectric constant around T_c , rather than a sharp peak, indicates the characteristics of a disordered perovskite structure with a diffuse phase transition.³⁴ The broadening of the peak may be attributed to substitutional disordering in the arrangement of cations at one or more crystallographic sites in the structure. This results in microscopic or nanoscopic heterogeneities in the compounds, with different local Curie points.³⁵ The ferroelectric to paraelectric transition temperature (T_c) of $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ is found to be 350 , 280 and 260°C , respectively, which are similar to the values reported in the literature.^{18–20}

The values of dielectric constant for all the three compounds are relatively high and no anomalous peaks below T_c are observed. The absence of these anomalous peaks indicates a decrease in the oxygen vacancies and defects formed due to volatilization of bismuth ions at lower sintering temperature (1050°C as compared with 1195°C).^{36,37}

The variation of dielectric loss with temperature at different frequencies is shown in figure 4. The dielectric loss is almost constant and is ~ 0.1 , below transition temperature in all the three samples. A sudden rise in loss tangent is observed around T_c which may be because of the increase in conduction of residual current and absorption current in the sample. It is also observed that, as the frequency increases from 4 kHz to 600 kHz , $\tan \delta$ decreases drastically. This can be termed as frequency dispersive behaviour of these compounds and it is indicative of the fact that these compounds show stable dielectric properties.³⁵

3.4 Electrical properties

The variation of imaginary part of the impedance (Z'') with frequency at different temperatures is shown in figure 5. A peak is observed in the impedance vs. frequency curve

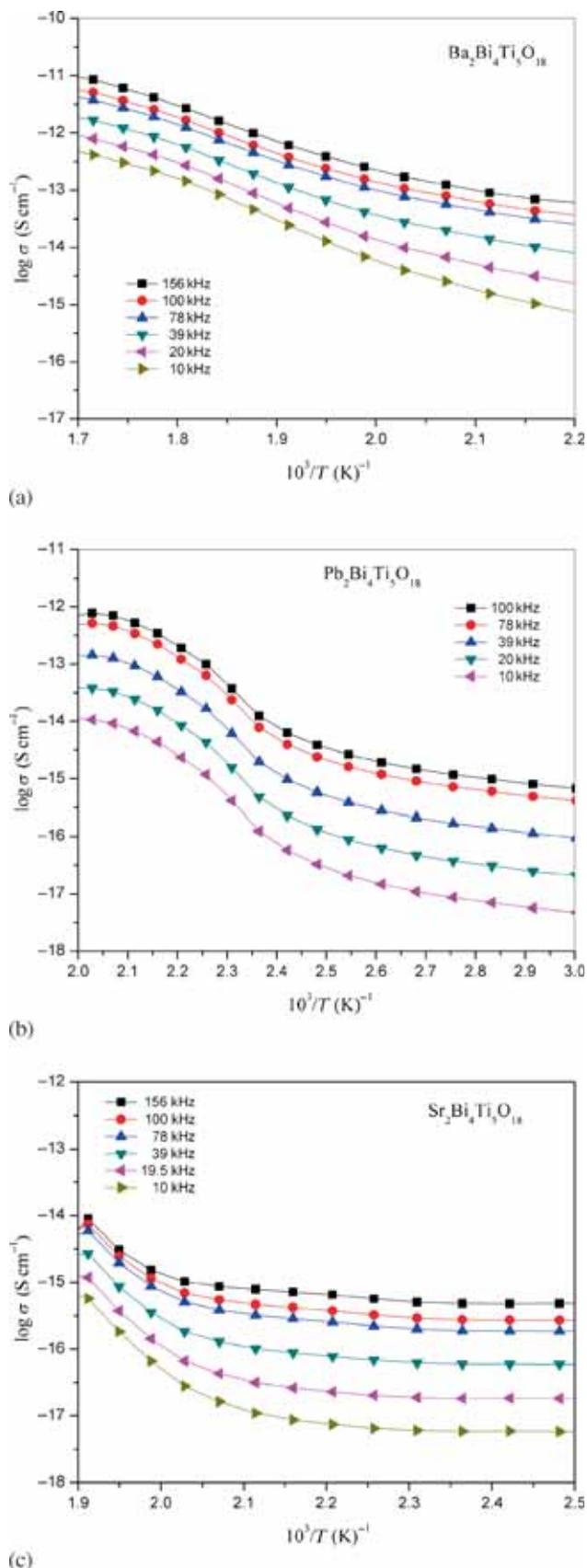


Figure 6. Variation of ac conductivity with inverse of temperature (Arrhenius plots) at different frequencies of (a) $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, (b) $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and (c) $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ceramics.

Table 2. Calculated values of activation energy of Ba₂Bi₄Ti₅O₁₈, Pb₂Bi₄Ti₅O₁₈ and Sr₂Bi₄Ti₅O₁₈ at 100 kHz.

Material	Activation energy at 100 kHz (eV)
Ba ₂ Bi ₄ Ti ₅ O ₁₈	0.36
Pb ₂ Bi ₄ Ti ₅ O ₁₈	0.68
Sr ₂ Bi ₄ Ti ₅ O ₁₈	0.37

and the values of frequency corresponding to maximum impedance (Z''_{\max}) are given in table 1. These peaks tend to broaden and shift towards a higher frequency with the increase in temperature. This can be attributed to multiple relaxations in the material which occur due to the change in the structure as a result of random occupation of bismuth at certain sites.⁶ The maximum value of Z'' decreases with the increase in temperature which shows an increase in capacitance and a decrease in resistance of the material, indicating an increase in conductivity. The curves for all temperature merge into one another in the higher frequency region. This may be due to the release of space charge because of reduction in the barrier properties of materials at higher temperature, which enhances the ac conductivity at higher frequencies.³⁸

The variation of ac conductivity with inverse of temperature (Arrhenius plots) at different frequencies for all the three samples is shown in figure 6. It is observed that the conductivity increases with increase in temperature. This may be due to the loss of oxygen during sintering of the ceramic at higher temperatures.³⁹ It is also observed that the variation of conductivity with temperature is linear in the higher temperature range and in the lower temperature range it remains almost constant, this may be ascribed to the Mott's hopping phenomenon.⁴⁰ This type of behaviour is attributed to the ordering of the defect dipoles.⁴⁰

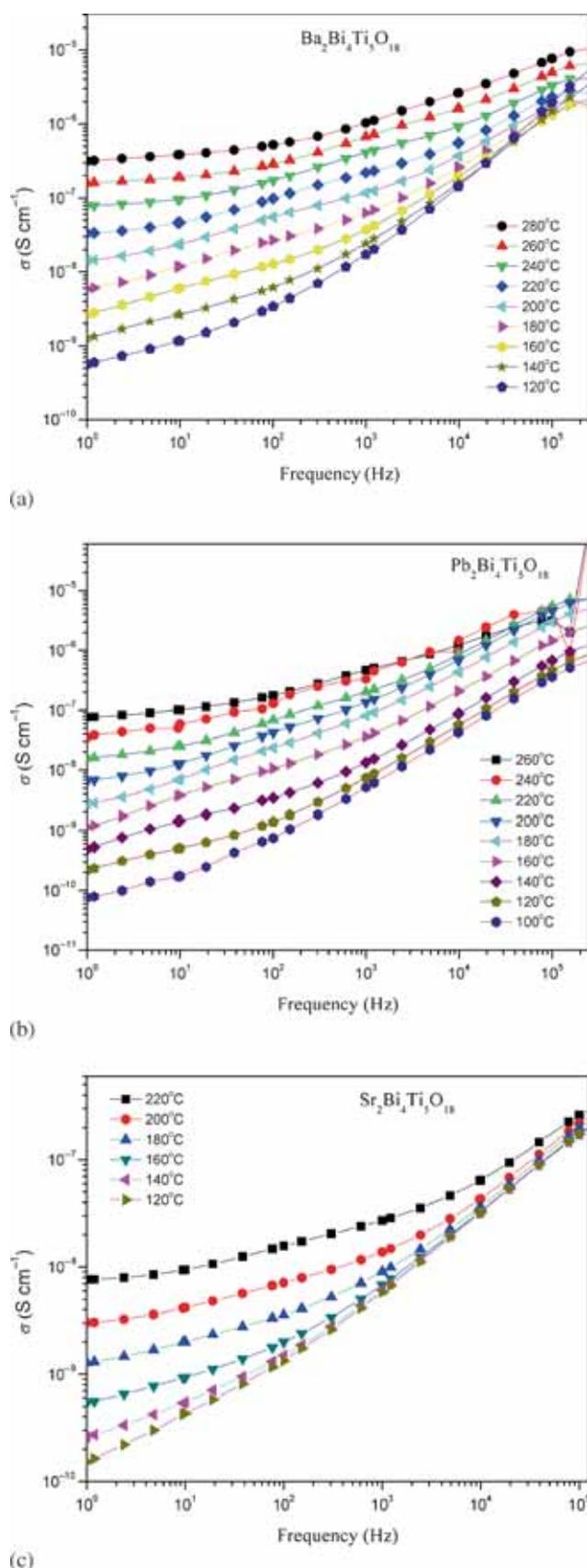
The activation energy is calculated using the Arrhenius equation

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right), \quad (1)$$

where σ is the conductivity of the sample, σ_0 the pre-exponential constant, k the Boltzmann constant, T the absolute temperature and E_a the activation energy.

The calculated values of activation energy for the three samples are given in table 2 which indicates that the activation energy of Ba- and Sr-based bismuth titanates is less as compared to Pb bismuth titanates. This may be due to the influence of electronic contribution to the conductivity of Ba- and Sr-based bismuth titanate ceramics.^{36,41} The higher activation energy of Pb₂Bi₄Ti₅O₁₈ is believed to be due to the higher polarizability of Pb²⁺ ions.

The variation of electrical conductivity with frequency at different temperatures is shown in figure 7. The plots show that the conductivity increases with temperature. Conductivity is almost constant with frequency in the lower frequency region. The dispersion region is observed in higher

**Figure 7.** Variation of electrical conductivity with frequency at different temperatures of (a) Ba₂Bi₄Ti₅O₁₈, (b) Pb₂Bi₄Ti₅O₁₈ and (c) Sr₂Bi₄Ti₅O₁₈ ceramics.

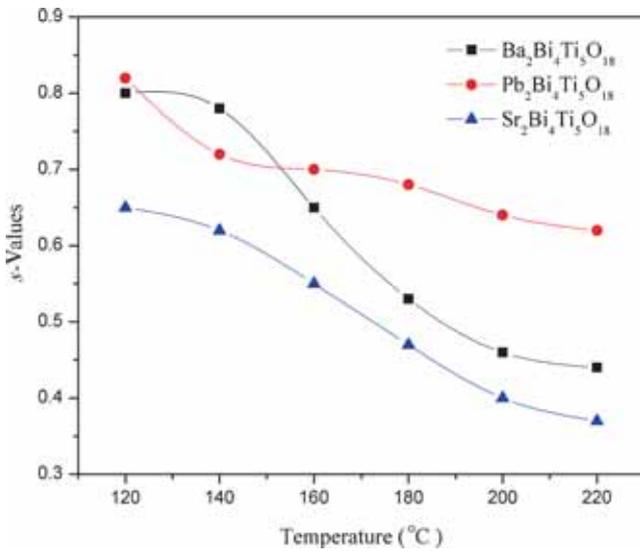


Figure 8. Variation of s -values with temperature for $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$.

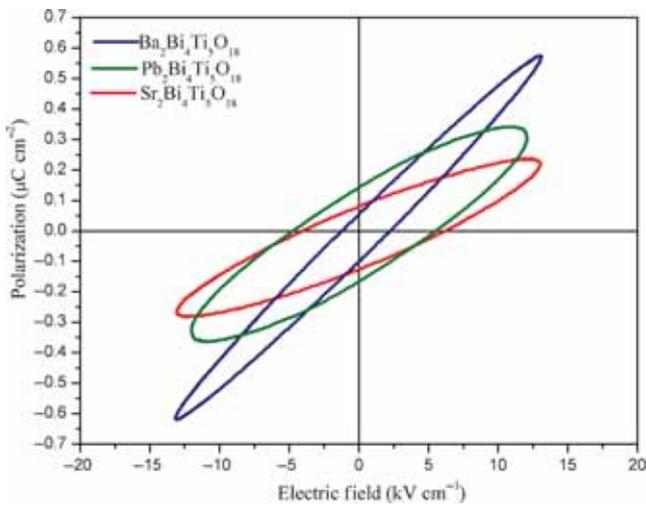


Figure 9. P - E hysteresis loop of $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ taken at room temperature.

frequency regime where the conductivity is sensitive to frequency. The frequency at which the conductivity becomes frequency dependent is called as hopping frequency. The hopping frequency shifts toward higher frequency side with an increase in temperature. In high frequency region the increase in the conductivity is caused due to the hopping of charge carriers in finite clusters.^{42,43}

The variation in conductivity with frequency follows Jonsher's power law⁴⁴ given by equation

$$\sigma = \sigma_{\text{dc}} + A\omega^s \quad (2)$$

The frequency-independent part of the curve is represented by the first term σ_{dc} and the frequency-dependent part is given by the second term $A\omega^s$, where A and s are temperature-dependent parameters, s is being calculated

Table 3. Remanent polarization and coercive field of $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ measured at room temperature.

Material	Remanent polarization ($2P_r$) ($\mu\text{C cm}^{-2}$)	Coercive field ($2E_c$) (kV cm^{-1})
$\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$	0.159	3.37
$\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$	0.318	10.24
$\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$	0.208	9.66

from slope of σ - f plots in the higher frequency region. From figure 8 it is observed that s decreases with the increase in temperature, indicating the conductivity in these samples is a temperature-dependent phenomena.⁴⁴

3.5 Ferroelectric property

The P - E hysteresis loop of the samples of $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ taken at room temperature at an applied field of 20 kV cm^{-1} are shown in figure 9. The values of remanent polarization and their coercive field for the samples $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ are given in table 3. The remanent polarization of these samples is somewhat smaller which is typical of a layered structure. A low remanent polarization may be attributed to higher conductivity of the sample due to the movement of oxygen vacancies which are created during the sintering process.³ The other reasons for lower values of P_r could be, (i) the electric field needed to fully switch the polarization of the c -axis epitaxial of samples are very high, i.e., higher than the breakdown field of the sample and (ii) the ferroelectricity along the c -axis is weak.⁴⁵ Pb being a polarizable cation, it plays an important role in influencing the ferroelectric properties. Hence $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ possesses higher remanent polarization than other members of this group.

4. Conclusions

Ba-, Pb- and Sr-based bismuth titanate ceramics belonging to the five-layered Aurivillius family have been successfully prepared by the solution combustion technique with glycine as a fuel. SC decreases the synthesis temperature and the reaction time to a small fraction ($\sim 20\%$) as compared to the solid-state reaction. Glycine decreases the combustion temperature which improves the pseudo-tetragonal crystalline phase formation and morphology of Ba-, Pb- and Sr-based bismuth titanate ceramics. XRD study confirms the single phase formation of these compounds possessing pseudo-tetragonal symmetry. SEM analysis reveals a plate-like morphology of these ceramics. The $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ceramic shows normal ferroelectric behaviour, whereas $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ceramic exhibit relaxor nature. These samples possess multiple relaxations and the conductivity is a temperature-dependent phenomenon in these five-layered compounds belonging to the Aurivillius family.

$\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ possesses higher value of remanent polarization and activation energy as compared with $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ and $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ due to lower conductivity in this Pb-based titanates. The higher value of remanent polarization and activation energy in Pb-based bismuth titanates is possibly due to the higher polarizable nature of Pb^{2+} .

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