Nanocomposites of Sodium Potassium Cerium Titanate at Morphotropic Phase Boundary as a Green Material for Piezoelectric Transducer and Actuator Applications

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Abstract: New lead-free piezoceramic nanocomposites of Sodium Potassium Cerium Titanate (NKCT) with general formula (1-x) K0.5 Ce0.5 TiO3 - x Na0.5 Ce0.5 TiO3), exhibiting a Morphotropic Phase Boundary (MPB), have been synthesized following hydrothermal method followed by solid state sintering. The occurrence of MPB at the composition with x=0.66, at which rhombohedral and monoclinic phases are found to coexist, has been confirmed using powder XRD. This accounts for the occurrence of large remnant polarization when the sintered ceramic pellets are subjected to electric poling at 2KV/mm. Uniform microstructure of various compositions is confirmed by SEM imaging. Dielectric and piezoelectric properties of the samples are found to be comparable to those of commercial grade PZT. At the MPB, the d33 coefficient is found to be 208 pC/N, which is close to that of commercial grade PZT, which makes NKCT a promising material to substitute lead containing PZT in the near future. The thermal properties viz thermal diffusivity, thermal effectivity, conductivity and specific heat capacity were measured using a novel indigenous technology and reported.

1. INTRODUCTION

Piezoelectric material market has witnessed a significant growth in the past few years with a Compound Annual Growth Rate (CGAR) of 6.01%, which is expected to grow even more steeply in the coming years [1]. Besides common applications like transducers, actuators, amplifiers etc., emerging applications like Piezo accelerometers, Nanogenerators, Portable and low power energy sources for applications in medical sector and structural health monitoring, Computer disk drives, Robotics etc. are on a steep increase. Accordingly, funding to this sector from both Industry and Governments is on the increase [2-6]. This has resulted in an explosive growth in piezoelectric device market during the last decade.

Because of the very attractive features like reliability and cost effectiveness there is an increasing demand for piezoelectric actuators and motors and is expected to witness a significant growth in the immediate future too. Further, piezoelectric ceramics are widely accepted by the industry since they offer high piezoelectric performance and dielectric constant, and the ease of fabricating materials into various shapes including sheets, cylinders, bars and plates [7-9]. Recently, several manufacturing companies have realized the importance of implementing automated manufacturing technology to reduce the operational cost during production and is expected to influence the growth rate positively. Another important factor that is suggested to augment the market growth is the wide variety of applications of piezoceramic materials, ranging from actuators and transducers to SONAR and motors arising from the single quality of possessing a high degree of stiffness when exposed to mechanical stress and hence to change shape. However, the rising demand for substitutes such as dielectrics and conductive polymers in manufacturing actuators is expected to hinder the growth rate.

Even though the promising thermal and electrical properties of piezoceramic materials have been known for years, surprising new effects and practical applications are being discovered with the fabrication of both existing and new materials in their nano forms [10 – 14]. Among the various fundamental properties of nanomaterials, the piezoelectric properties are prominently exploited for sensing and energy harvesting applications. For both of these applications the material need to have good piezoelectric and dielectric properties. Piezoelectric single crystals, ferroelectric ceramic materials as well as electro-active polymers have been used for pressure sensing, actuator and ultrasonic generation and detection

applications [15-19].

Cerium doped lead free piezoelectric ceramics have been widely studied in view of their possible applicability in replacing lead containing piezoelectric materials in commercial applications [20-25]. This include Cerium doped Alkali metal and Alkaline earth metal Bismuth Titanates and Niobates, Lithium, Cerium and Lanthanum doped Barium Titanate, Zinc Oxide etc. In all these cases it is reported that Cerium doping significantly improves the dielectric, ferroelectric and piezoelectric properties [25, 26] and are found to be suitable for high temperature piezoelectric applications. However, in none of these composite ceramics a Morphotropic phase boundary, which is most often exhibited by lead based piezoceramics and are reasonable for their threshold high electrical properties have been reported. However, a Morphotropic phase boundary has been reported in Ce doped (1-x) $BiScO_3$-$x$$PbTiO_3$ (BSPT) system for a composition with x =0.64 [27].

Though it seems quite usual, the most important part of the story is that, though Ce doping resulted in an improvement of dielectric constant of alkali metal, alkaline earth metal and ZNO based ceramics, the improvements in their piezoelectric properties are quite meagre, with maximum piezoelectric d_{33} coefficient reported being of the order of a few tens of pC/N. However, in the case of Ce doped BSPT ceramics the d_{33} coefficient has been reported to be 460 pC /N [27].

The present work present the hydrothermal synthesis of two novel non – hazardous Cerium based nanoceramics, namely Potassium Cerium Titanate (KCT) and Sodium Cerium Titanate (NCT) and the preparation of environment friendly piezoceramic composites of Sodium Potassium Cerium Titanates (NKCT) having Morphotropic Phase boundary with superior dielectric and piezoelectric properties compared to other Cerium doped piezoceramics. The NKCT nanoceramics are found to have properties comparable to that of BSPT ceramics and show an extraordinary enhancement of properties close to the phase boundary.

The prepared NKCT nanopowders have been characterized for their structure by X-ray diffraction and morphology by Scanning electron microscopy. The dielectric and piezoelectric properties are investigated, and are found to be superior to other Cerium doped piezoceramics. The piezoelectric coefficients and figures of merit have also been determined. It is found that the composition with x = 0.66 exhibits features that correspond to a MPB. It is also found that the dielectric and piezoelectric properties exhibit threshold maxima in their values at the composition corresponding to the above MPB. The relevant properties are compared with those of PZT so as to explore the possibilities of replacing PZT with this lead-free ceramic. It is seen that the above composition of this lead-free composite ceramic, synthesized following a relatively simple procedure, exhibits piezoelectric properties comparable to PZT type ceramics.

2. EXPERIMENTAL METHODS

Procedure followed for the synthesis of the samples and the experimental methods adopted for the characterisation and the measurement of their properties are outlined below.

2.1. Sample Preparation

For the synthesis of the NKCT composites pure nanopowders of Potassium Cerium Titanate (KCT) and Sodium Cerium Titanate (NCT) were separately synthesised following hydrothermal route. For both KCT and NCT analytical grade Cerium Chloride heptahydrate ($CeCl_3.7H_2O$, Sigma Aldrich, 99.999% pure), Titanium dioxide (TiO_2, Fisher Scientific, 98% pure) were used as the respective Cerium and Titanium precursors. For hydrothermal synthesis of phase pure nanopowders of KCT and NCT, procedure as already outlined in Chapter 2, was followed. Highly alkaline solutions of KOH and NaOH, having molarity 12M have been used as the reaction media for the synthesis of KCT and NCT respectively. For the synthesis of both KCT and NCT a stoichiometric ratio of 2:1 is maintained between Ti and Ce, in the reaction mixture.

For the synthesis of KCT nanoceramics, a 12M solution of KOH was made in the required volume by dissolving Potassium Hydroxide (KOH, Sigma Aldrich, 99.99%) in CO_2 free double distilled water. Cerium chloride heptahydrate in required weight was then added to the reaction medium kept in a beaker cleaned by ultra-sonication, under vigorous stirring. Titanium dioxide is then added to the beaker in required weight ratio so as to maintain a 2:1 stoichiometric ratio between Ti and Ce. After vigorous

stirring of the reaction mixtures for about 2 hours it turned in to a thick grey coloured homogeneous solution. An exactly similar procedure was followed for the preparation of reaction mixture for NCT, with the only difference being the replacement of the alkaline medium with NaOH having the same molarity as that of KOH used for the synthesis of KCT. After vigorous stirring of the reaction medium for about 2 hours, a pale yellow coloured reaction mixture was resulted. The concentration of Ti^{4+} and Ce^{3+} in the reaction mixture for KCT and NCT were respectively 0.5 and 1 mol/dm^3 each. The reaction mixtures were then kept in moderate stirring for another 3 hours. The mixtures were then poured in to two separate Teflon lined autoclaves and were then subjected to hydrothermal treatment at 175^{0}C and at a pressure of 1.5 bars for 48 hours. After the 48 hour long hydrothermal treatment both the reaction vessels contained fine sedimented precipitate with clear liquid content above, which was separated by pouring off. The so-obtained product was collected and the sediments were washed three times by dispersing in excess of distilled water, followed by centrifuging. The raw powder was then dried overnight at an ambient temperature of 75^{0}C. The nanopowders of NCT and KCT obtained in this manner were then calcined at around 650^{0}C for eight hours. The nanopowders after calcination were analysed for identifying their crystallinity and phase formation using Powder XRD.

2.2. Preparation of NKCT Composites

Solid state sintering method was employed for the synthesis of NKCT nanocomposites using phase pure KCT and NCT nanopowders, prepared following hydrothermal route as starting materials. In this procedure phase pure KCT and NCT were mixed in different weight ratios and ground well in a mortar, using Polyvinyl alcohol as the binder. NKCT nanocomposites with general formula (1-x) $K_{0.5}Ce_{0.5}TiO_3$ - x $Na_{0.5}Ce_{0.5}TiO_3$, where x = 0, 0.20, 0.25, 0.33, 0.50, 0.66, 0.75, 0.80, and 1.0, synthesized in this manner, were then pelletized to thin discs of 9 mm diameter and 1 mm thickness and then sintered at 50^{0}C intervals between 850^{0}C and 1000 ^{0}C for a duration of two hours each. After heat treatment of the samples, the dry weights of the pellets were measured with a balance and the bulk densities of the sintered samples were determined. Measurement of density is an important step in the processing of ceramic composites since it is a direct indicator of porosity in the material. It is inevitable to obtain composites with extremely low porosity percentage as porosity may result in false measurements with high values for dielectric and piezoelectric coefficients. The extent of porosity present in the composites could be identified in terms of their mass density.

2.3. Structure analysis using Powder XRD

The crystalline phases of the prepared composites in disc form are determined using powder XRD in the θ-2θ mode with Cu-Kα radiation of wave length 1.5406 A^0 (Bruker make, D8 Advance). The lattice parameters (*a, b* and *c*) and the unit cell volume (*V*) were calculated from the obtained XRD data using the MAUD programme. The crystallite size of the NKCT nanoceramics were determined from the Powder XRD data, and was used for the determination of the theoretical densities of the different composites. The variation of unit cell parameter with concentration of NCT indicate a change of crystallite phase and is an indication for the possible existence of a Morphotropic phase boundary in the sample.

2.4. SEM and EDX Analyses

Scanning Electron Microscopy (SEM) with Energy Dispersive X- Ray measurement (EDX) has been used to identify and characterize the matrix of various compositions. The SEM images of all the samples were recorded with a Scanning electron microscope (Jeol make, Model 6390 LV) to examine the morphology of the matrix and its homogeneity Energy Dispersive X-ray (EDX) was specifically used to obtain a qualitative information about the full elemental composition of the samples, and to detect any unknown contaminant in the matrix.

2.5. Dielectric Measurements

The NKCT ceramics were cut and polished for various physical and electrical measurements reported in this work. For the measurement of various electrical properties, an electrode plate is to be made on either faces of the pellets. This is achieved by coating a thin layer of Silver paste uniformly on either sides of the pellets. The samples were then dried in a hot air oven for about 5 minutes to dry the silver paste. Before conducting measurement of electrical properties the dipoles present in the ceramics are to be aligned in

order to enhance the properties by polarisation. This is achieved by applying an external DC field of 2 kV/mm for a duration of 20 minutes in a stirred silicone bath at an elevated temperature of 150 ^{0}C using the polling set up indigenously built in the laboratory.

The polled samples were used as the dielectric medium of a parallel plate capacitor, for the measurement of dielectric properties. The capacitance across the sample apacitor was measured using an Impedance analyser for polarising fields of different frequencies set using the Impedance analyser (Hioki make, IM 3570). From the measured values of capacitances, the corresponding dielectric constants were determined. The dielectric losses ($tan\delta$) were measured directly using the Impedance analyser. In order to analyse the temperature dependence of dielectric constant of the ceramics, the measurements were repeated at a fixed frequency of 3 KHz for the polarising field, but at different temperatures. For conducting this measurement, the sample under measurement was uniformly heated using the heating coil of a programmable PID temperature controller (Lakeshore Cryotronics, Model: DRC 82C).

2.6. Measurement of Thermal Properties

The thermal properties of NKCT ceramics are measured using the modified photo – pyroelectric (PPE) technique in which the sample, the pyroelectric detector and the backing medium are kept in a thermally thick regime. The sample in thermally thick region is periodically heated via optical absorption of light from an intensity modulated laser beam, which give raise to periodic temperature variations in the sample that ultimately result in thermal wave generation which are detected by a thin (28μm) PVDF film with Ni – Cr coating on both sides being used as a pyroelectric detector. In this experiment, a He – Cd laser having 120 mW power and 442 nm wave length is used as the optical heating source and the intensity modulation is achieved with the help of a mechanical chopper (Stanford Research Systems, Model SR 540). The amplitude and phase of the thermal wave are measured using a Dual phase lock-in amplifier (Stanford Research Systems, Model SR 830). The thermal thickness of all the NKCT ceramic composites is verified by plotting the variation of PPE amplitude and phase with modulation frequency at room temperature. Since all the NKCT ceramics used in the measurement are pale yellow ceramic pellets with low optical absorption an extremely thin coating of carbon black is provided on the front surface of the sample under illumination, which improves the optical absorption and consequent thermal wave generation, considerably.

Before conducting the measurement of thermal parameters using PPE technique, the experimental set up is calibrated by measuring the thermal properties of the detector from the measured amplitude and phase of the thermal wave at the detector. Further, during measurements the temperature of the specimen is kept constant to ascertain that the sample gets sufficient time to reach thermal equilibrium.

2.7. Measurement of Piezoelectric coefficients

The polled samples after dielectric measurements were directly used for the measurement of piezoelectric measurements at room temperature. The measurements are carried out using a conventional Berlin court Piezo D33 Test System (Piezotest make, PM300). From the measured values of piezoelectric strain constants d_{33} the piezoelectric figures of merit viz. piezoelectric voltage coefficient (g_{33}) and electro-mechanical coupling coefficients (k^2) were determined using equations (3.2) and (3.3). Piezo D33 Test System PM 300 also offers the additional feature of measuring the dielectric constant and dielectric loss and could be used for a comparison with the measurement already made.

The Piezo-measurement system PM 300 works by clamping the sample and subjecting it to a low frequency force. Comparison of electrical signals from the sample with a built in reference give the set up a determination of the piezoelectric strain constant of the sample.

3. RESULTS

Results of material characterisation and measurement of various properties of NKCT ceramics are discussed below. In order to make a clear analysis of the variations of various thermal and electrical properties with NCT concentration, the expected values of these parameters under the effective medium theory have been calculated [33, 34]. An agreement between theoretical and experimental values of properties are found only in the case of material densities and the dielectric, piezoelectric and thermal properties never follow the

mean field approximation.

3.1. Bulk density of Samples and their Porosity

The theoretical density of pure KCT and NCT nanoceramics were determined from XRD analysis and were found to be 6.561 g /cc and 5.752 g/cc respectively. The experimental density of all NKCT samples have been determined using Archimedes method. In this method the densities of the samples are directly determined as the ratio of mass of the sample and the volume of a liquid that the sample displaces when immersed in it. As expected the density of various NKCT composites show a mean field type variation. This is clearly evident from Fig.1, which represents the variation of bulk densities of NCT with change in composition. With an increase in concentration of lighter NCT, it can be seen that the density of composites decreases and is minimum for pure NCT. Further, from the figure it can also be seen that the theoretical and experimental densities are in agreement. This is further confirmed by analysing the variation of percentage porosity of various NKCT samples with an increasing concentration of NCT. This is shown in Fig.2. It can be seen that the change in percentage porosity of various samples is quite small, of the order of 0.5%.

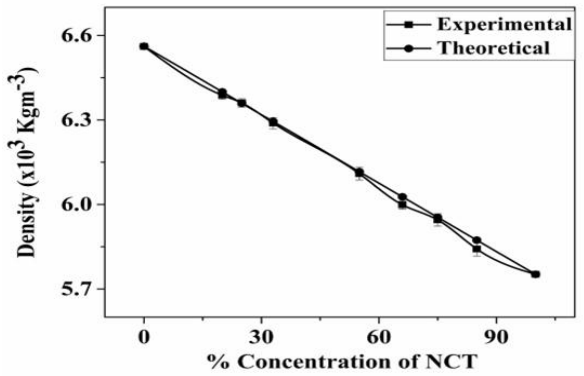

Fig.1: Variations of mass density (theoretical and experimental) with concentration of NCT in NKCT ceramics

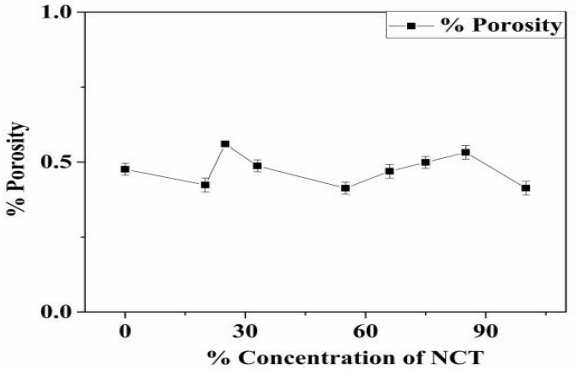

Fig. 2: Variation of porosity with concentration of NCT in NKCT ceramics

3.2. Structure and Morphology

The powder XRD patterns of pure KCT, NCT and all the NKCT composites are shown in Fig. 3. The X – ray diffraction patterns indicate perovskite structure formation in pure NCT, KCT and all the NKCT composites. The crystallite size of all the composites that are sintered at a temperature of 1000 ^{0}C are found to be in the range from 40 to 60 nm. The rhombohedral crystal phase of NKCT is characterised by a (003) peak at about 39.8^0 and a (200) peak at about 43.2^0 [35]. Whereas the monoclinic phase of NKCT is characterised by a single (202) peak at around 47^0 and a (122) peak at around 58^0 [36]. From the figure it can be observed that, with an increase in concentration of NCT all the (003), (200), (202) and (122) peaks shift towards the higher angle region, which is an indication for monoclinic phase formation, which might have resulted from the replacement of K^+ by Na^+ at the cube corners of the perovskite. The (003) and (200) peaks corresponding to rhombohedral phase are found to persist in composition with x up to 0.66 and these peaks are found to be considerably intense for the composition with x=0.66. At the same time, the (202) and (122) peaks corresponding to monoclinic phase are also visible in the composition with x=0.66, though shifted to the higher angle region. Additional peaks corresponding to monoclinic phase are visible for compositions with $x > 0.66$ whereas those corresponding to rhombohedral phase can be seen in composites with $x < 0.66$. In composition with x=0.66, the peaks corresponding to rhombohedral and monoclinic phases exist simultaneously with considerable intensity. This indicates that in the composites, rhombohedral and monoclinic phases of NKCT coexist and this is supposed to be maximum in the case of the composition with x= 0.66. Further, on the basis of the intensities of the relevant peaks it can be suggested from the XRD patterns that the NKCT composites are predominantly rhombohedral in compositions with $x < 0.66$ and are monoclinic in composition with $x > 0.66$.

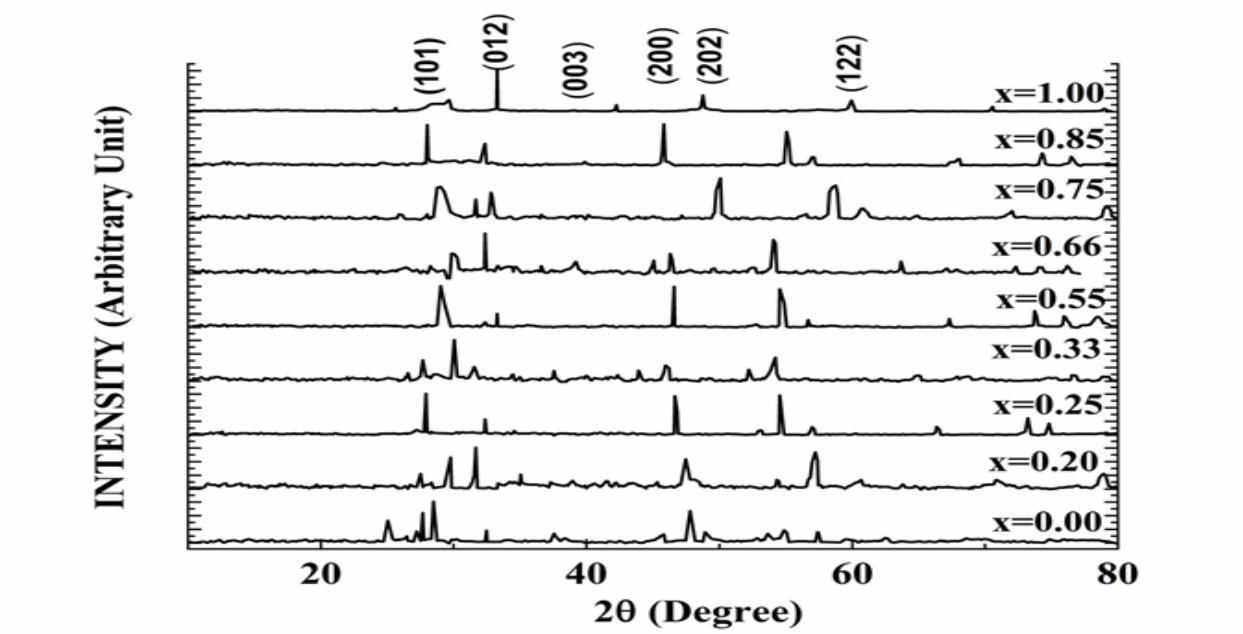

Fig. 3: XRD patterns of hydrothermally synthesized Sodium Potassium Cerium Titanates, *(1-x) K0.5Ce0.5TiO3 - x Na0.5Ce0.5TiO3,* where x = 0 (pure KCT), 0.20, 0.25, 0.33, 0.50, 0.66, 0.75, 0.80, and 1.0 (pure NCT), all sintered between 850 and 1000^0C for three hours.

The SEM micrographs of pure KCT, NCT and all the NKCT composites are shown in Fig.4. Since the particles are in the nanostructure regime a complete prevention of agglomeration is not possible and this agglomeration is visible in the composites.

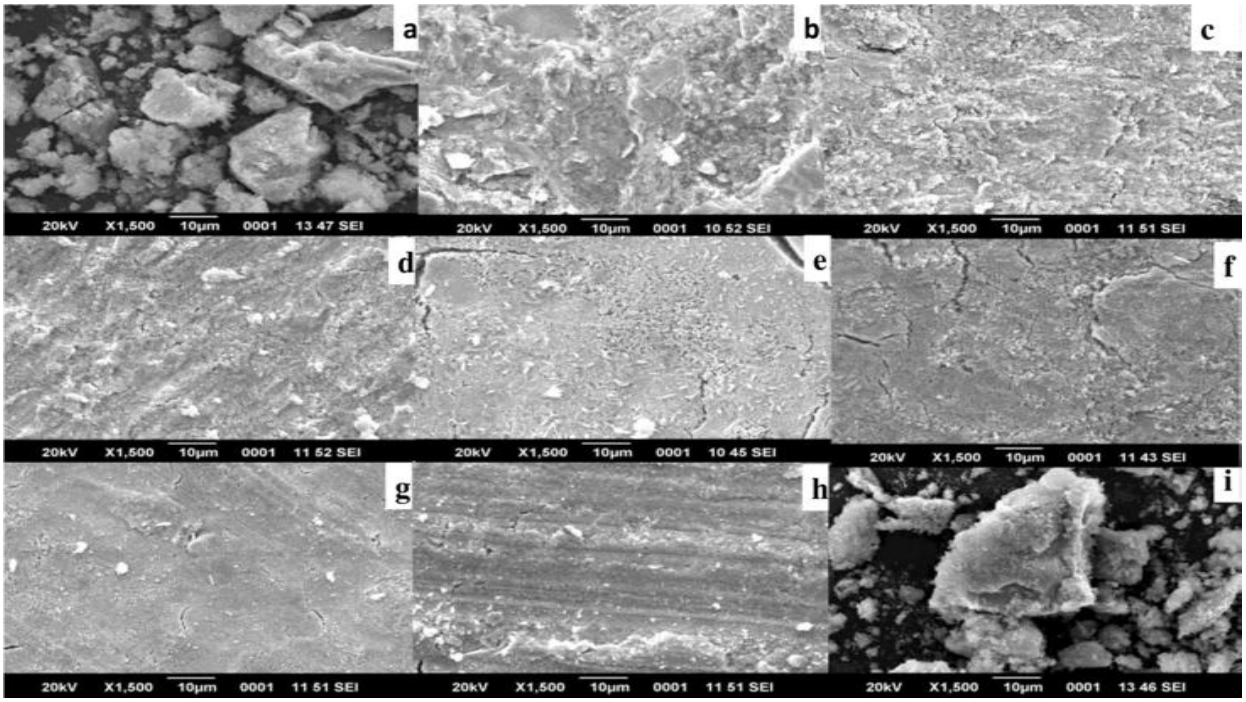

Fig. 4: SEM images of hydrothermally synthesized Sodium Potassium Cerium Titanates*, (1-x) K0.5Ce0.5TiO3 - x Na0.5Ce0.5TiO3,* where x = 0 (pure KCT), 0.20, 0.25, 0.33, 0.50, 0.66, 0.75, 0.80, and 1.0 (pure NCT), all sintered between 850 ^{0}C and 1000^0C for three hours.

3.3. Dielectric Properties

Before conducting dielectric measurements, the samples are poled following corona poling procedure at an elevated temperature of 140^0 C. In this poling procedure a strong DC electric field is applied to the sample using a thin electrode placed a few mm above the sample. Generally poling will be done at elevated temperatures which will increase the mobility of the molecules allowing an easy rotation of ferroelectric domains. Variations of dielectric constant and dielectric loss with frequency for all the NKCT composites are measured and reported. These are shown in Fig.5 and Fig.6 respectively. Variations for only representative samples are displayed in the figures, though these have been recorded for all the samples. As expected, the dielectric constants of all samples show a normal variation generally observed in the case of ceramic samples. In the frequency range of a few KHz, the composite NKCT materials exhibit values for dielectric constant close to 1000.

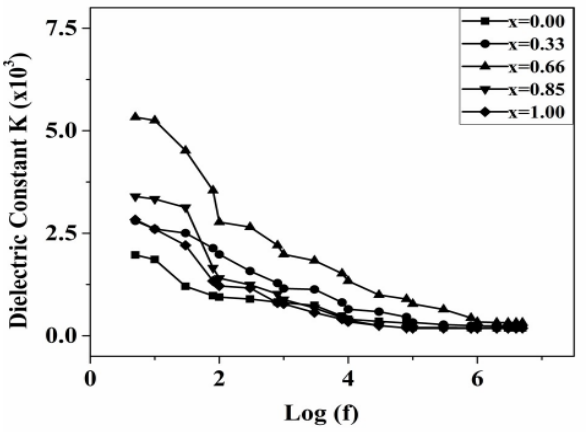

Fig. 5: Variations of Dielectric constant with frequency for different selected samples, listed in the inset.

NKCT composites with low concentration of NCT or KCT more or less follow a mean field approximation, however, they show deviation from mean field approximation for a value of x = 0.33 onwards. For value of x > 0.33, there occurs an extraordinary raise in dielectric constant with increase in concentration of NCT. The dielectric constant is found to be maximum in the case of composition with x = 0.66 and exceed that of all the other composites at all frequencies. Further, at all frequencies the dielectric constant of this NKCT composite largely exceeds the value of dielectric constant predicted by the mean field theory. This can be explained on the basis of the formation of a Morphotropic phase boundary existing in this composition, where there occurs the coexistence of rhombohedral and monoclinic phases resulting in an inherent constraint to the sample enabling it to be highly susceptible to polarisation, particularly under the effect of an external field or mechanical stress [37].

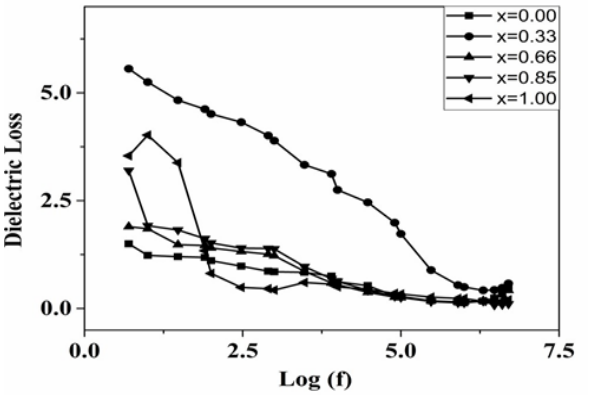

Fig.6: Variations of dielectric loss with frequency for different selected samples, listed in the inset.

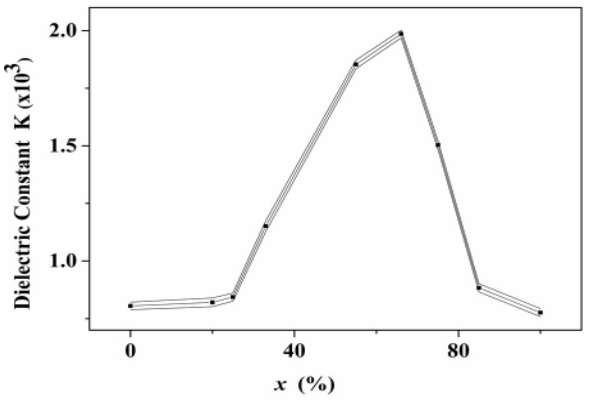

Fig.7: Variations of Dielectric constant with percentage concentration of *NCT (x)* at 3 kHz.

The variations of dielectric constant of the composites at an input frequency of the polarising field, 3 KHz, with increasing concentration of NCT is shown in Fig.7. As can be seen from the figure, with an increase in concentration of NCT the dielectric constant increases and is found to be maximum for the composition with x = 0.66. For lower concentrations of NCT (x= 0.20, 0.25 etc.,) the dielectric constants almost follow the mean field approximation where the dielectric constant is almost equal to the weighted average of dielectric constant of the individual phases. However, from x=0.33 onwards the dielectric constant

shows a sharp increase which persist for composition with x = 0.66, after which it falls. It can also be noticed that, compared to composites having small concentrations of NCT and KCT the increase in dielectric constant is almost ten times and the compositions close to MPB also offer promising dielectric properties permitting them to be used as good electrical energy storage materials. The dielectric loss of all the NKCT samples are low as found in the case of ceramic materials. However, with increase in concentration of NCT the dielectric loss is found to decrease slightly.

3.4. Piezoelectric Coefficients

The piezoelectric strain constant d_{33} of all NKCT composites were measured using a Berlin Court piezoelectric d_{33} meter, Piezotest PM 300. The d_{33} coefficient of pure KCT and NCT samples were found to be respectively 125 pC/N and 131 pC/N respectively. With the addition of NCT to pure KCT matrix, the material is found to be more susceptible to spontaneous polarisation. As a consequence of this the d_{33} coefficient found to increase with an increase in concentration of NCT. From the analysis of XRD data using MAUD programme it is found that the monoclinic strain factors are maximum for the composition with x=0.66 leading the material to be under an inherent stress making it highly susceptible to the influence of mechanical stress. This is important from the view point that piezoelectric effect is a combined electro – mechanical effect.

The variation of piezoelectric strain constant d_{33}, voltage coefficient g_{33} and the electro-mechanical coupling coefficient are shown in Fig.6. It can be seen that an increase in concentration of NCT causes an increase in the piezoelectric coefficient for NKCT initially, till the composition with x=0.66 is reached, where it rises to a maximum value of 208 pC/N. With a further increase of NCT concentration, the value of strain constant falls. It is also identified that for smaller weight fractions of NCT and KCT, the increase in the value of the coefficient is rather smaller, however, for compositions closer to MPB, the d_{33} coefficient increases rapidly. The piezoelectric voltage coefficient, g_{33}, also increases with an increase in concentration of NCT, however, unlike the strain constant, the value of g_{33} is not maximum for the MPB composition and is due to the extraordinary large value of dielectric constant for the MPB composition. The electro-mechanical coupling coefficients of the NKCT compositions are comparatively lesser and is found to be maximum in the case of the MPB composition with a value higher by 38%. Almost all of the NKCT compositions offer an electro- mechanical coupling in this range which is lesser compared to lead free ceramics, but are comparable to those of traditional lead based ceramics like PZT [38,39].

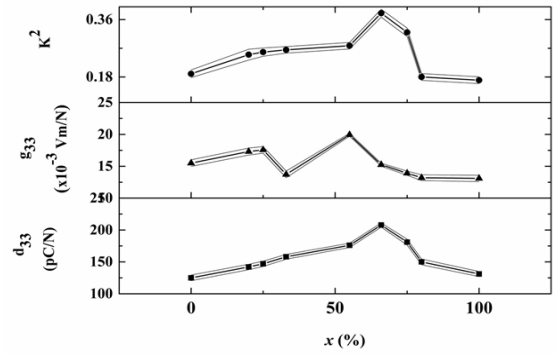

Fig.8: Variations of Piezoelectric figures of merit with percentage concentration of NCT (x)

3.5. Thermal Properties

Thermal properties, particularly the thermal conductivity and specific heat capacity of solids change drastically when they are synthesized in the nanometer range and also when there are lattice distortions. An analysis of the variation of these thermal properties with change in composition of NCT may bring light to the new effects that these nanomaterials possess and also the effects of lattice distortions and lattice vibrations do have on thermal properties of solids. This was the motivation for the measurement and analysis of thermal properties of NKCT nanocomposites. Modified PPE detection method, used for the measurement of thermal properties, provide accurate determination of thermal properties since it employs controlled heating of the sample via light absorption from an intense laser source which is modulated using an external chopper. The experimental set up also has the facilities to reduce or even avoid any possible noise generation within experimental limits. The amplitude and phase of the thermal wave are measured in the PPE setup using a lock-in amplifier from which the thermal diffusivity and effusivity are determined directly. From the measured values of diffusivity and effusivity, thermal conductivity and specific heat capacity are determined.

The variations of PPE amplitude and phase with modulation frequency for pure NCT, KCT and some selected NKCT composites are shown in Figures 9 and 10 respectively. With an increase in modulation frequency, the PPE amplitude increases till the critical frequency is reached at which the sample reaches a thermally thick region, and afterwards it falls gradually, whereas the PPE phase shows a regular decrease with increase in modulation frequency. Thermal conductivity and specific heat capacity are two important properties as long as the possible application of the NKCT samples as piezoelectric transducer is concerned. A low value of thermal conductivity and specific heat capacity are often desirable for a piezoelectric transducer. All the NKCT samples are found to accomplish this requirement. The variation of various thermal parameters of NKCT composites are shown in Fig.11. With an increase in concentration of NCT the thermal properties are found to increase slightly till the MPB composition, with the MPB composition having a thermal conductivity and specific heat capacity values 9760 $Wm^{-1}K^{-1}$ and 1932 $JKg^{-1}K^{-1}$ respectively.

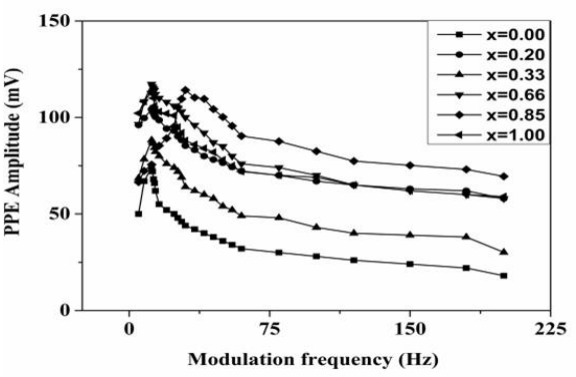

Fig.9: Frequency dependence of Photopyroelectric amplitudes with modulation frequency at room temperature for the Samples shown in the inset.

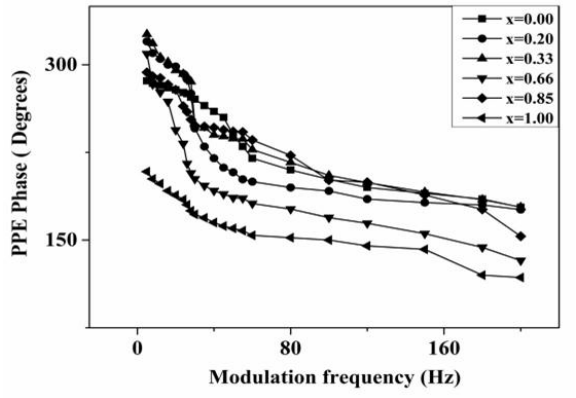

Fig.10: Frequency dependence of Photopyroelectric phases with modulation frequency at room temperature for the Samples shown in the inset.

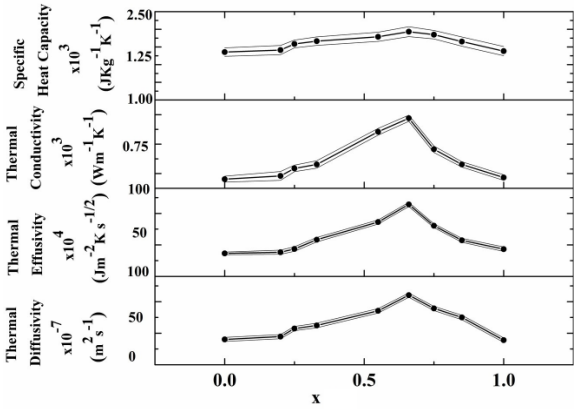

Fig.11: Variations of thermal diffusivity, thermal effusivity, thermal conductivity and specific heat capacity for NKCT samples with percentage composition of NCT (x)

4. DISCUSSION OF RESULTS

Generally, the properties of composites follow a mean field approximation where the properties of composite materials are often the weighted averages of the properties of its components. With this background, a comparison of the experimental properties with the result of mean field approximation has been done. It is found that the NKCT composite follow more or less a mean field approximation only at low concentrations of NCT or KCT. However, this calculation is completely contradicted at higher concentration of NCT or KCT.

The bulk density of NKCT composites measured experimentally following Archimedes method and theoretically calculated following mean field approximation are in good agreement. However, there are a few compositions (x= 0.25, 0.50, 0.80) for which there are a slight fall from the expected value of bulk density. This necessitated the determination of the % porosity of the composites as a test of agreement between theoretical and experimental values. It was found that the % porosity of the composites are very small and the required density for the samples have been attained following the sintering procedure. Further it is confirmed from the analysis of XRD data that the unit cell volume of the composites with this contradiction shows a slightly larger values due to the lattice distortion suffered by them due to the

interaction of the different component phases in them. The coexistence of rhombohedral and monoclinic phases as evident from the XRD is further analysed by evaluating the lattice parameters and unit cell volumes of all the NKCT composites. The variations of lattice constants with increase in concentration of NCT is shown in Fig.12. For those compositions with very low and very high concentration of NCT the lattice parameters *a* and *b* are nearly equal and all the three lattice parameters of pure NCT and KCT are in agreement. This comparable values of lattice parameters of NCT and KCT account for a miscibility of the two perovskite structured compounds during composite formation. The lattice parameters, unit cell volume and the various unit cell strain constants evaluated from XRD data using MAUD programme are shown in Table 1. It can be seen from the table that with an increase in NCT contribution both the lattice parameters *a* and *b* show a regular gradation, though small, along with a steep increase of lattice constant *c*, transforming the composite to a monoclinic phase from a rhombohedral one at both the extremities. In order to confirm this result further the rhombohedral strain constant *b/a* and the monoclinic strain constants *c/a* and *c/b* were determined. The rhombohedral strain constants *b/a* are 1 only for the compositions with very low concentration of NCT and KCT. For *x*=0.25 onwards there occur deviation of rhombohedral strain constant from 1 and correspondingly the monoclinic strain constants *b/a* and *c/a* increase. For the MPB composition *c/a* increases to 2.28 whereas *c/b* to 1.88. Further, it is found that the deviation from the rhombohedral structure is very small in compositions with x up to 0.25 and beyond 0.75; however, it is steeper at compositions closer to MPB. This further implies that the composites retain rhombohedral symmetry for small concentration of NCT or KCT and is dominantly monoclinic for NKCT composites with considerable concentration of both NCT and KCT and for the composition with x=0.66 the monoclinicity factor is maximum indicating a change of phase around this composition. This accounts for a change of phase resulting from a change of composition around x=0.66 in NKCT composites and hence the Morphotropic phase boundary occurring around this composition. From the analysis it is also evident that for the NKCT compositions closer to MPB the rhombohedral and monoclinic phases coexist at different extents with the maximum adjustment of this coexistence being observable for the composition with x=0.66. The phase coexistence and the resultant competition of the two ferroelectric phases have a number of consequences on the dielectric, thermal and mechanical properties of the material as this may create crystal defects and account for a greater number of ferroelectric domain orientations. The inherent strain of the crystal at this composition may lead it to possess highly susceptible spontaneous polarisation, low polarisation anisotropy, high elastic softening etc. [38].

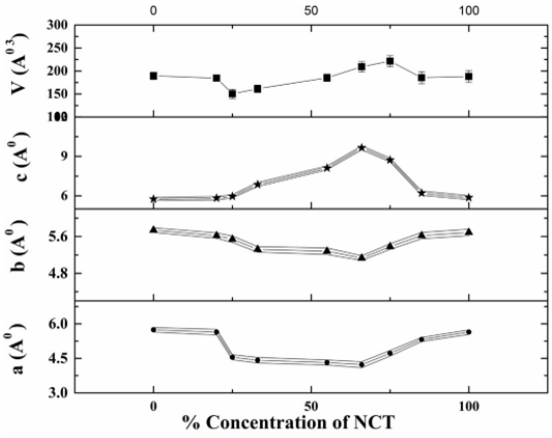

Fig.12. Variation of lattice parameters and unit cell volumes of NKCT composites with percentage concentration of NCT.

In a system involving rhombohedral - monoclinic phase coexistence, the number of ferroelectric domains per unit cell rises to 15 from a total of eight or five for a material with phase pure rhombohedral or monoclinic structures. In a ferroelectric material not all domains are easily polarisable though there are a number of domains. Ferroelectric domains are assemblies of spontaneously polarised unit cells capable of forming regions of same polarisation so that each domain has a macroscopic electric polarisation. The directions of polarisation of adjacent domains make definite angle with one another such that at a domain interface they maintain electrical neutrality so as to have minimum free energy for the crystal. In a real crystal external factors, crystal temperatures, growth conditions, polarising field during poling etc., may disturb uniformity of domain structure [39]. Compared to a phase pure material, material with phase coexistence offer more number of polarisable domains with this being maximum in the case of composition corresponding to MPB as in PZT [40]. Due to the original strain to which the MPB

composition is subjected to, a large number of domains out of the coexisting 15 R – M ferroelectric domains of NKCT are easily polarisable leading the composite with MPB, to large spontaneous polarisation.

Table 1: Lattice parameters of NKCT composites for different concentrations of NCT

x (%)	Lattice Parameters						
	a (A^0)	*b* (A^0)	*c* (A^0)	*V* ($A^{0\,3}$)	*b/a*	*c/b*	*c/a*
0	5.742±0.004	5.742±0.015	5.752±0.013	189.65	1.000	1.001	1.002
20	5.643±0.004	5.622±0.005	5.822±0.013	184.71	0.996	1.036	1.032
25	4.549±0.003	5.542±0.002	5.961±0.011	150.28	1.218	1.076	1.310
33	4.423±0.005	5.321±0.004	6.862±0.003	161.49	1.203	1.289	1.551
55	4.325±0.002	5.282±0.005	8.122±0.011	185.54	1.221	1.538	1.878
66	4.225±0.006	5.132±0.005	9.65±0.011	209.24	1.215	1.880	2.284
75	4.723±0.005	5.382±0.005	8.721±0.004	221.68	1.139	1.620	1.846
80	5.321±0.005	5.622±0.007	6.225±0.012	186.22	1.057	1.107	1.169
100	5.642±0.007	5.692±0.005	5.856±0.013	188.06	1.008	1.029	1.038

In a system involving rhombohedral - monoclinic phase coexistence, the number of ferroelectric domains per unit cell rises to 15 from a total of eight or five for a material with phase pure rhombohedral or monoclinic structures. In a ferroelectric material not all domains are easily polarisable though there are a number of domains. Ferroelectric domains are assemblies of spontaneously polarised unit cells capable of forming regions of same polarisation so that each domain has a macroscopic electric polarisation. The directions of polarisation of adjacent domains make definite angle with one another such that at a domain interface they maintain electrical neutrality so as to have minimum free energy for the crystal. In a real crystal external factors, crystal temperatures, growth conditions, polarising field during poling etc., may disturb uniformity of domain structure [39]. Compared to a phase pure material, material with phase coexistence offer more number of polarisable domains with this being maximum in the case of composition corresponding to MPB as in PZT [40]. Due to the original strain to which the MPB composition is subjected to, a large number of domains out of the coexisting 15 R – M ferroelectric domains of NKCT are easily polarisable leading the composite with MPB, to large spontaneous polarisation.

Spontaneous polarisation of a dielectric material directly affects the overall electrical properties of a material. In NKCT composites polarisation is mainly due to ionic and orientation polarisation. In the former the ionic bonds in the composites are elastically deformed by the applied field due to the displacement of cations and anions along and opposite to the direction of the applied field respectively, whereas the latter is mainly due to the displacement of the octahedrally co – ordinated Ti^{4+} ions from its ideal symmetric position, as in $BaTiO_3$, allowing it to move back and forth between the two positions permissible to it under an alternating field [41,42].

The variation of dielectric constant with polarisation is governed by the equation [43],

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N\alpha}{3\varepsilon_0} \quad \text{---------- (1)}$$

where ε_r is the relative permittivity, N is the number of dipoles per unit volume and α is the polarisabilty. Clearly an increase of N or α or both will lead to a proportionate increase in the permittivity.

Similar to the dielectric properties, the piezoelectric properties of NKCT composites also have direct dependence on polarisation in the material since the piezoelectric strain constant used characterize the material itself is a measure of the charge induced due to polarisation per unit applied stress. Further, the phase change occurring as a consequence of compositional change tends to make the material more susceptible to mechanical stress induced polarisation. Phase coexistence, restrictions on free energy surface and elastic instabilities in the material, especially close to MPB, etc. contribute to this in a positive manner. This is responsible for the peaking of piezoelectric strain constant for the composite at MPB. Piezoelectric voltage coefficient is a measure of the induced voltage per unit applied stress and is measured as the ratio of the strain constant and dielectric permittivity so that for

a better voltage coefficient a material with proper agreement between d_{33} and permittivity is to be selected.

From Fig. 11, showing the variation of thermal diffusivity (α), effusivity (*e),* thermal conductivity (*k*) and specific heat capacity ($_{Cp}$) with concentration of NCT, it can be seen that these properties show an anomalous variation. With an increase in concentration of NCT all except specific heat capacity increase rapidly the till MPB composition is reached and falls afterwards. So these parameters are peaking to a maximum value for the MPB composition. In the case of specific heat capacity, though there is a regular rise till the MPB composition and falls afterwards the variation is rather gradual and the specific heat capacity of the composite ceramics are nearly the same. Further, it can also be seen that there occurs an overall enhancement of thermal properties up on composite formation and further with MPB formation. An increase in thermal conductivity always reflects a corresponding increase in thermal diffusivity and effusivity as the latter quantities are directly proportional to the square root of the former. An increase in thermal conductivity with MPB formation in NKCT is due to a proportionate increase in mean free path of phonons due to a fall in collision rate with MPB formation.

Phonons govern the thermal properties in semiconductors and insulators. Similar to the case with conduction electrons in metals, density of states of phonons in semiconductors and insulators are affected by the dimensionality of the material. Since the NKCT composites are synthesised as nanostructures there often occur dimensional confinement of phonons which will inevitably alter phonon - phonon interactions. Further, dimensional confinement of phonon imposes restrictions in the phase space of phonon wave vectors resulting in a restriction on carrier –phonon interaction in nanostructures. Both these effects are found to increase the mean free path [44]. Specific heat capacity, which is specifically the amount of heat required to rise the temperature of unit mass by unity and major contribution of this heat is the amount that excites lattice vibrations, which also depend on the phonon density of states. The observed variation of specific heat of NKCT composites can be explained on the basis of the softening of phonon modes with compositional change.

From the above discussion we see that NKCT composites with varying compositions of NCT and KCT show superior dielectric and thermal properties compared to their phase pure counterparts and there occurs a coexistence of rhombohedral and monoclinic phases in the NKCT composite with x = 0.66, resulting in a Morphotropic phase boundary. Because of the phase coexistence the number ferroelectric domains for this composition increases largely with most of them being electrically polarisable. This increase of spontaneous polarisation account for the large increase of dielectric and piezoelectric properties of NKCT composition with MPB. Further, it is found that compositions close to MPB also have larger number of polarisable ferroelectric domains compared to phase pure NCT and KCT. The anomalous behaviour of the thermal properties are attributed to the phonon confinement in nanostructured NKCT ceramics and the subsequent reduction in phonon – phonon, phonon – impurity and phonon – crystal boundary collision rates, ultimately leading to the softening of phonon mode and an increase in phonon mean free path.

5. CONCLUSIONS

1) Novel lead- free nanoceramics of Sodium Cerium Titanate (NCT) and Potassium Cerium Titanate (KCT) have been synthesized following hydrothermal route.
2) Various nanocomposites of Sodium Potassium Cerium Titanate are successfully synthesised by sintering NCT - KCT nanopowder mixtures in desired weight ratios, at elevated temperatures. NKCT nanocomposites with crystallite size around 50 – 60 nm are synthesized.
3) Based on the analysis of XRD data, a phase coexistence between rhombohedral and monoclinic phases is found with compositional change and this is found to be maximum for the composition with an NCT contribution of 0.66. This account for a Morphotropic phase boundary for this composition.
4) Dielectric and piezoelectric properties of phase pure NCT, KCT and NKCT composites are determined and reported. Both these properties were found to increase with an increase in concentration of NCT and the properties are found to be threshold maximum for the composition with MPB.

5) The thermal properties of NKCT composites are reported and discussed.
6) This work report relevant information about possible applicability of a novel lead-free material for piezoelectric transducer application.

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