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Enhanced electrocaloric response and high energy-storage properties in lead-free (1-x) $(K_{0.5}Na_{0.5})NbO_3$ - $xSrZrO_3$ nanocrystalline ceramics

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ABSTRACT

Recently electrocaloric effect in lead-free environmental friendly ferroelectrics is in its peak research. The feasible and existed electrocaloric response in lead-free (1-x) $(K_{0.5}Na_{0.5})NbO_3$ - $xSrZrO_3$ (KNN-xSZ) nanocrystalline ceramics is demonstrated using Maxwell's thermodynamic approach. The maximum electrocaloric response of 1.19 K at 367 K was observed under the electric field of 35 kV/cm, and the corresponding electrocaloric responsivity value was found to be 3.40×10^{-7} K m/V at 367 K for x = 0.10. A significant coefficient of performance (COP) and electrical energy storage density (W_{rec}) were calculated to be 0.62 and 0.20 J/cm^3, respectively. The atomistic mechanism of the electrocaloric effect is discussed. The results indicate that KNN-xSZ is a favourable material in the cooling system applications and energy-storage for electronic devices. The material allows electrocaloric cooling mode with versatile properties for the cooling operation by an external electric field and operating temperature.

1. Introduction

The low cost, high-efficiency and environmental-friendly electrocaloric refrigeration have received reasonable attention as an emerging alternating technology for refrigeration and power generation for micro-electromechanical and micro-electronic systems [1–4]. The electrocaloric (EC) cooling is based on the EC effect which is the temperature/entropy change ($\Delta T/\Delta S$) under the adiabatic condition of a ferroelectric material by the external electric field [5,6]. The electrocaloric effect (ECE) describes the coupling effect between electrical and thermal properties in the ferroelectric material. It is maximum at the critical point, the point where the compound changes its structure, basically structural instability produced due to compositional disorder and also due to external factors like the electric field, temperature [7]. Study of the ECE has been increased since the report of a giant ECE of $\Delta T = 12$ K was reported in $PbZrTiO_3$ thin films [8] and ferroelectric polymers [9]. These results pushes it for further materials like for different organic and inorganic relaxor, ferroelectric, and antiferroelectric materials has been widely investigated [10–12]. Different types of ferroelectric materials such as ceramics, thin/thick films, the single crystal and polymers were explored for ECE study [13]. The largest ECE was observed in thin films [10,14], but it has limited heat extraction capacity [15]. Since the cooling capacity of bulk ceramic is larger than the thin films, therefore, the bulk has a significant advancement over the thin films for practical cooling applications [16,17]. Additionally, the electrocaloric responsivity ($\zeta = \Delta T/\Delta E$) of bulk ceramics is larger than of polymers, thin films and single crystals [18]. Since in ABO_3 structure, hybridisation between B site atom and the oxygen atom is one of the reason for exhibiting favourable electrocaloric effect, a compound with smaller ion and larger charge show the good EC effect [19]. Among the ferroelectrics, lead-based ceramics have large electrocaloric responsivity and the extensive temperature range of ΔT due to the presence of the morphotropic phase region and polar nanoregions [20,21]. However, the use of such lead-based electrocaloric materials is restricted due to the concern of lead toxicity. Therefore, various lead-free ferroelectric ceramics with identical properties such as $BaTiO_3$, $K_{0.5}Na_{0.5}NbO_3$, $K_{0.5}Bi_{0.5}NbO_3$ and $Na_{0.5}Bi_{0.5}TiO_3$ based solid solutions were studied to explore their EC response [11,12,22].

Among all, lead-free alkaline niobate such as $K_{0.5}Na_{0.5}NbO_3$ (KNN) based ceramics has demonstrated the excellent EC effect with remarkable properties in energy storage [23,24], excellent piezoelectric properties and higher polarization value than the $BaTiO_3$ [25] like ceramics as found through simulations. Li et al. [23] reported ΔT of 0.41 K at 353 K under 20 kV/cm field in $(Na_{0.52}K_{0.46})(Nb_{0.90}Sb_{0.08})O_3$ - $0.02LiTaO_3$ ceramics. Recently, $0.9K_{0.5}Na_{0.5}NbO_3$ - $0.1Sr(Sc_{0.5}Nb_{0.5})O_3$ have shown ΔT of 0.28 K at 25 kV/cm [24]

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whereas for $0.85K_{0.5}Na_{0.5}NbO_3$ - $0.15SrTiO_3$, ΔT is found to be 1.9 K at 340 K under 159 kV/cm field by direct measurement method [26]. Recently, the $K_{0.5}Na_{0.5}NbO_3$- $SrZrO_3$ solid solution have display interesting ferroelectric properties [27].

$K_{0.5}Na_{0.5}NbO_3$ and $SrZrO_3$ have the orthorhombic and cubic structure, respectively. The substitution of $SrZrO_3$ in KNN creates disorder in the crystal, the critical point appears, which also makes the normal ferroelectric KNN to the relaxor solid solution KNN-xSZ and more promiseable for ECE. The transition temperature shifts toward the room temperature with a broad scale; makes this solid solution more favourable. The $K_{0.5}Na_{0.5}NbO_3$ - $SrZrO_3$ solid solution exhibits high dielectric permittivity and less loss in the wide temperature range [27]. There is no report on the electrocaloric response of this system. In this article, the electrocaloric response of (1-x) $(K_{0.5}Na_{0.5})NbO_3$ - $xSrZrO_3$ (KNN-xSZ) has been studied using Maxwell approach. Further, the EC responsivity, the coefficient of performance and electrical storage energy with the efficiency have been calculated and discussed to understand the materials versatile properties towards in electronic devices for cooling and energy-storage applications.

2. Experimental procedures

Lead-free KNN-xSZ (x = 0.05, 0.10 and 0.15) powders were synthesized using a conventional solid-state route [24,28,29]. Highly pure (~ 99%) K_2CO_3, Na_2CO_3, Nb_2O_5, $SrCO_3$ and $Zr(C_5H_7O_2)_4$ were used as the initial precursors. The raw reagents were weighted according to stoichiometric ratio. The homogenized mixture of precursors were grinded for 8 h by mortar and pestle (agate). Mixed precursor were calcined at 1173 K for 4 h. The calcined powder was further mixed with 5 wt.% polyvinyl alcohol solution (PVA) and formed into the 10 mm diameter disk of 1 mm thickness from using a cylindrical steel die under 125 kN uniaxial pressure. The green pellet were sintered at 1423 K for 6 h using the double crucible method to suppress the volatile nature of alkali oxides [30]. The experimental density of the sample was calculated using Archimedes principle and found to be 4.37, 4.32, 4.31 g/cm^3 in KNN-xSZ for x = 0.05, 0.10, 0.15. The surface of the sintered pallet was grinded and cleaned to do the SEM characterisation. Top and bottom faces of sintered pellets were smoothened by 0.25 μm diamond paste, and silver paste was applied for electrical measurements which were dried first at 423 K and then at 723 K for 10 min.

The X-ray diffraction of the sintered sample was examined by the Powder X-ray diffractometer (Rigaku mini Flex 600, Japan). The morphology and elemental analysis of the bulk sample were obtained by SEM (Zeiss EVO-40) with the attachment of energy dispersive X-ray spectroscopy (EDS, Bruker, S4 PIONEER). Espirit 1.8.1 software used in imaging and analysis the EDS spectrum and calibrated with a gold sample. The temperature dependent dielectric permittivity was observed using an impedance analyzer (E4990A, Keysight Technologies) from 90 K to 690 K in a customized furnace for the frequencies from 50 Hz to 1 MHz. The polarization-electric field (P-E) hysteresis loops were recorded at 50 Hz using the ferroelectric test system (Marine India) in the temperature range 303 K–403 K. The differential scanning calorimeter (DSC 3, Mettler Toledo) was used for calorimetric measurement to calculate the specific heat capacity C_P.

3. Results and discussion

Fig. 1a displays the room temperature X-ray diffraction pattern of KNN-xSZ (x = 0.05, 0.10, 0.15) solid solution sintered powder for 2θ of 20–70°. It is clear from Fig. 1a that all samples have ABO_3 typed perovskite structure. The obtained peaks are of high intensity which proves to be the highly crystallinity of the sample, among all KNN-0.1SZ is more crystalline and peaks have indexed with the orthorhombic phase of $K_{0.5}Na_{0.5}NbO_3$ [31] [ICDD PDF card no. 01-077-0038] and $K_6(Nb_{10.88}O_{30})$ [32] [ICDD PDF card no. 01-087-1856]. According to crystal chemistry principle and size-large cations, radius-matching rule, i.e. A site occupies by Na^+ (0.139 nm, CN = 12), K^+ (0.164 nm, CN = 12), and Sr^{2+} (0.144 nm, CN = 12) whereas Nb^{5+} (0.064 nm, CN = 6) and Zr^{4+} (0.072 nm, CN = 6) with comparatively lesser sizes occupy the B sites of ABO_3 perovskite structure. Pure KNN shows the orthorhombic structure with the lattice constant a (Å) = 7.9751, b (Å) = 7.8620, c (Å) = 7.9565 and (202), (020) peak splitting about 45° is visible in Fig. 1b. The increasing doping of $SrZrO_3$ content changes the orthorhombic

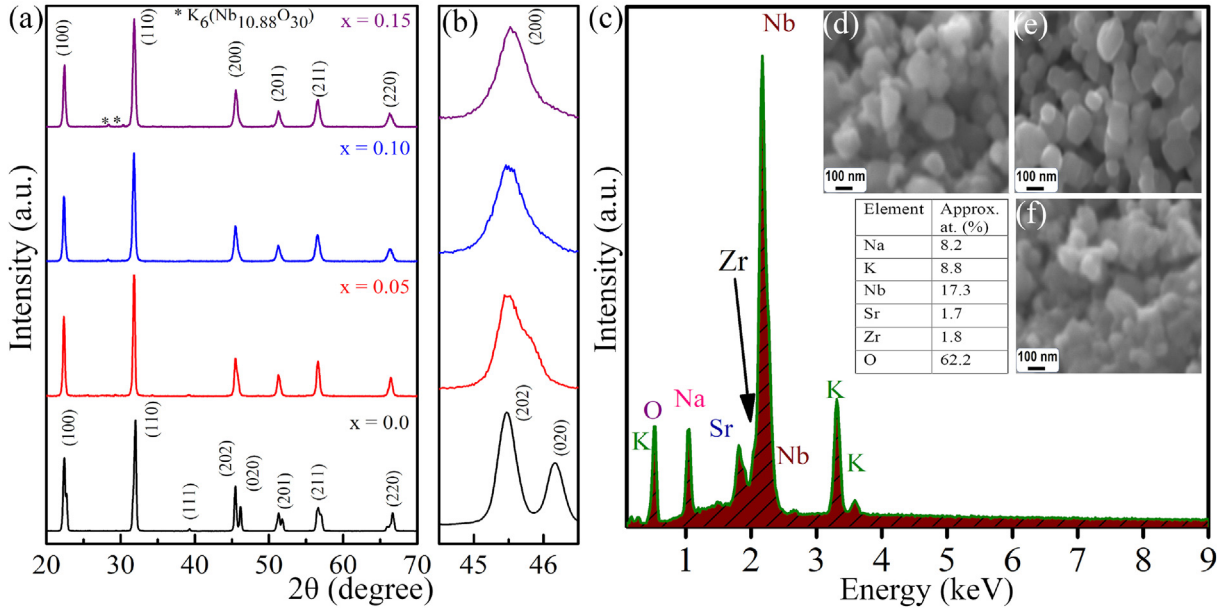

Fig. 1. The room temperature X-ray diffraction pattern of KNN-xSZ (x = 0.00, 0.05, 0.10, 0.15) for 2θ, 20° - 70°(a), 44.5° - 46.5°(b), EDS(c) profile of KNN-0.1SZ and SEM micrographs for x = 0.05(d), 0.10(e) and 0.15(f) for KNN-xSZ ceramics.