



## Electrocaloric effect of alkali co-substituted $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ ceramics

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### ABSTRACT

We have investigated the electrocaloric properties of  $\text{K}^+$  and  $\text{Na}^+$  co-substituted  $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$  (SBN) ceramics using the indirect method. Tetragonal tungsten bronze  $(\text{K}_{0.5}\text{Na}_{0.5})_{2x}(\text{Sr}_{0.6}\text{Ba}_{0.4})_{5-x}\text{Nb}_{10}\text{O}_{30}$  (KNSBN) with  $x = 0.24$  was synthesized using dual-step sintering. Despite the low amount,  $\text{K}^+$  and  $\text{Na}^+$  co-substitution resulted in normal ferroelectric behaviour, showing no significant shift in the dielectric maximum temperature of 111 °C with increasing frequency. Maximum electrocaloric temperature change ( $\Delta T$ ) of 0.3 K was observed at an electric field of 30 kV/cm ( $\Delta E$ ) yielding the largest electrocaloric responsivity ( $\Delta T/\Delta E$ ) among SBN based ceramics. This relatively large value is in agreement with the larger pyroelectric coefficient of KNSBN compared to SBN based ceramics.

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### 1. Introduction

Recently, solid state cooling based on caloric materials received a lot of attention as an alternative for the conventional vapor compression based cooling technology due to its advantages such as lack of hazardous gases, compact size and high theoretical efficiency of the cooling cycle [1–4]. Among the caloric materials, electrocaloric materials are dielectric materials that show change in their dipolar entropy when an electric field is applied or withdrawn. The change of dipolar entropy upon the application of electric field results in a temperature change under adiabatic conditions; this phenomenon is called the electrocaloric effect [1,5]. The electrocaloric effect is large around the phase transitions in ferroelectric as well as antiferroelectric materials such as ferroelectric to paraelectric [6], antiferroelectric to ferroelectric [7] or ferroelectric to ferroelectric [8] phase transitions where large entropy changes take place. Ceramic and polymer ferroelectric materials in bulk as well as in thin and thick ceramic film forms are studied as electrocaloric materials [4]. Bulk ceramics have larger cooling capacity and larger electrocaloric responsivity than thin film counterparts, suited for the medium to large scale refrigeration systems [9]. Despite the large electrocaloric effect reported for Pb-based systems, due to the toxicity of Pb, research is also focused on Pb-free ferroelectrics for electrocaloric cooling applications. Pb-free systems that are extensively explored include  $\text{BaTiO}_3$  based systems such as  $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$  [10

],  $\text{BaHf}_x\text{Ti}_{1-x}\text{O}_3$  [6],  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$  [11] as well as  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  [12] and  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  [13] based materials.

Tetragonal tungsten bronze (TTB) ceramics have good dielectric, ferroelectric, pyroelectric and piezoelectric properties and versatile applications in electro-optics [14–17]. TTB structure with the general formula  $(\text{A}1)_2(\text{A}2)_4\text{C}_4\text{B}_{10}\text{O}_{30}$ , consists of  $\text{BO}_6$  octahedra linked by corner sharing, thereby creating three different interstitial sites for the A-site cations (two A1 (square), four A2(pentagonal), and four C(trigonal)) along the  $c$  axis (inset of Fig. 1) [18]. Due to the presence of these different interstitial sites, combinations of different cations can be introduced to the structure and the properties can be tuned. The [14]structure is called ‘stuffed’ when all 3 interstitial sites are occupied. When all A1 and A2 sites are occupied, the structure is named ‘filled’ and if 5 out of 6 total A sites are occupied then it is called ‘partially filled’ [14] or in many other references ‘unfilled’ [19]. We prefer to use the ‘unfilled’ term in this manuscript.

Among the tetragonal bronze family, mainly strontium barium niobate ( $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ ), in short SBN, has been studied for electrocaloric cooling. In SBN, C site is empty and A1 and A2 sites are not fully occupied (5 out of 6 total A sites are occupied) therefore the structure can be considered as ‘unfilled’. With the increase of Sr content, SBN shows a transition from normal ferroelectric to relaxor ferroelectric state around  $x = 0.5$ . Le Goupil et al. studied the electrocaloric effect of  $\text{Sr}_{0.75}\text{Ba}_{0.25}\text{Nb}_2\text{O}_6$  single crystals, which shows relaxor ferroelectric characteristics, using direct measurements. They obtained a maximum  $\Delta T$  of  $\approx 0.4$  K under 10 kV/cm, when the electric field is applied along the polar direction of SBN [20]. Tang et al. [21] studied electrocaloric effect of  $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$  ceramics ( $x = 0.4, 0.5$  and  $0.6$ ) and re-

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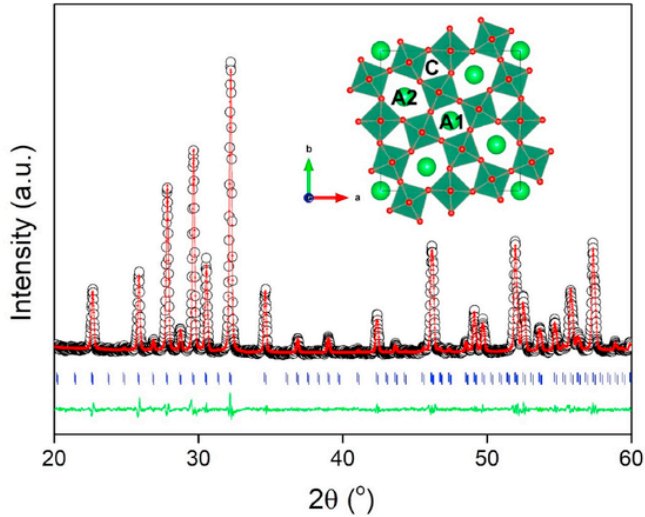


Fig. 1. Le Bail fit of the XRD spectra of dual-step sintered KNSBN. Observed XRD intensity (circles), calculated intensity (solid line), and the difference of observed and calculated patterns,  $Y_{obs} - Y_{cal}$  (solid line at the bottom). Tick marks represent the positions of allowed Bragg reflections in  $P4mm$  space group. Inset shows the tetragonal tungsten bronze structure viewed along the  $c$ -axis.

ported that  $Sr_{0.6}Ba_{0.4}Nb_2O_6$  has the highest  $\Delta S$  (0.39 J/kg) and  $\Delta T$  (0.32 K) under the 60 kV/cm. They also showed that  $Sr_{0.6}Ba_{0.4}Nb_2O_6$  composition has the best pyroelectric energy harvesting performance. It is reasonable to expect a material with better pyroelectric properties to show better electrocaloric properties since pyroelectric properties and electrocaloric effect are commensurate [21,22]. To obtain better pyroelectric properties,  $Sr_xBa_{1-x}Nb_2O_6$  system was doped with various cations e.g.  $Y^{3+}$ ,  $La^{3+}$ ,  $Ce^{3+}$ ,  $Pr^{3+}$ ,  $Nd^{3+}$ ,  $Sm^{3+}$ ,  $Eu^{3+}$ ,  $Gd^{3+}$ ,  $Tm^{3+}$ ,  $Dy^{3+}$ ,  $Er^{3+}$ ,  $Yb^{3+}$ ,  $K^+$  and  $Na^+$  [23,24]. Yao et al. [23] reported that pyroelectric properties of  $Sr_{0.5}Ba_{0.5}Nb_2O_6$  increase with the  $Gd^{3+}$  dopant from 49  $\mu C/m^2K$  to 168  $\mu C/m^2K$  at room temperature however the origin of this improvement was not discussed. In another study,  $Sr_{0.6}Ba_{0.4}Nb_2O_6$  was doped using two alkali cations  $K^+$  and  $Na^+$  with the formula  $(K_{0.5}Na_{0.5})_{2x}(Sr_{0.6}Ba_{0.4})_{5-x}Nb_{10}O_{30}$  ( $0.24 \leq x \leq 1.0$ ) (KNSBN) [24]. The composition with  $x = 0.24$  yielded the highest pyroelectric coefficient ( $p$ ) of 284  $\mu C/m^2K$  at room temperature and the lowest transition temperature at 130 °C among the series. This room temperature  $p$  is even larger than that of  $Sr_{0.6}Ba_{0.4}Nb_2O_6$  ceramics. More interestingly, even though when the Sr content in  $Sr_xBa_{1-x}Nb_2O_6$  exceeds  $x \geq 0.5$ , a transition from normal ferroelectric to relaxor ferroelectric behavior is induced; in the case of KNSBN, it was shown that normal ferroelectric character is kept even at the lowest  $Na^+$  and  $K^+$  doped composition of  $x = 0.24$  [24] as we will discuss later.

In this study, motivated by the normal ferroelectric-like behavior and large pyroelectric coefficient reported earlier, we investigate the electrocaloric properties of  $(K_{0.5}Na_{0.5})_{2x}(Sr_{0.6}Ba_{0.4})_{5-x}Nb_{10}O_{30}$  with  $x = 0.24$  using the indirect method and report that in agreement with its large pyroelectric coefficient, KNSBN also shows large electrocaloric effect compared to SBN based ceramics. We use a simplified version of the chemical formula in order to compare more easily with the parent  $Sr_{0.6}Ba_{0.4}Nb_2O_6$  composition:  $(K_{0.5}Na_{0.5})_{0.096}(Sr_{0.6}Ba_{0.4})_{0.952}Nb_2O_6$ . Dual step sintering was applied to avoid abnormal grain growth since it has been shown that in the  $Sr_xBa_{1-x}Nb_2O_6$  system the liquid phase can easily form during the sintering process which might cause abnormal grain growth [25–27]. It is known that abnormal grain growth might result in deterioration of the dielectric and ferroelectric properties [26,28]. While we focus on the electrocaloric properties of the sample obtained by dual-step sintering, we also provide a comparison of the microstructure, dielectric and ferroelectric properties of this sample with the sample obtained using conventional sintering.

## 2. Experimental

KNSBN was prepared from  $K_2CO_3$  ( $\geq 99.0\%$ , Isolab Chemicals),  $Na_2CO_3$  ( $\geq 99.8\%$ , Isolab Chemicals),  $SrCO_3$  ( $\geq 99.5\%$ , Enteknomaterials),  $BaCO_3$  ( $\geq 99.5\%$ , Enteknomaterials), and  $Nb_2O_5$  ( $\geq 99.5\%$ , Alfa Aesar). Starting powders were mixed in ethanol using planetary ball milling (Retsch PM 100) in a nalgene bottle with zirconia balls for 18 h. The mixed powder was dried and calcined at 1100 °C for 6 h. The calcined powder was mixed with 5 wt% polyvinyl alcohol as the binder and formed into the pellets using uniaxial pressing. Binder burnout was performed at 600 °C for 5 h with a heating rate of 1 °C/min. For the dual-step sintered sample, first pre-sintering was carried out at 1150 °C for 4 h with a heating rate of 5 °C/min. Then, the sample was again sintered at 1270 °C for 2 h with a heating rate of 5 °C/min. Pre-sintering step was not applied for the conventionally sintered sample i.e. after binder burnout the sample was directly sintered at 1270 °C for 2 h with a heating rate of 5 °C/min. The density of pellets were measured using the Archimedes method. Phase analysis of samples was done by X-ray diffraction (Panalytical X'Pert Pro) and unit cell parameters were obtained from Le Bail fits using Rietica [29]. Polishing and thermal etching were applied for microstructural observation. The morphology of the sample was analyzed by a scanning electron microscope (SEM, Quanta 250 FEG). The average grain size was calculated using the linear intercept method.

For the electrical measurements, both sides of the pellet were coated with silver epoxy. The dielectric constant of the sample was measured using an LCR-meter (Keysight E4980AL) between 50 and 200 °C at 100 Hz, 1 kHz, 10 kHz and 100 kHz. Ferroelectric hysteresis loops were measured using a commercial ferroelectric tester (Aixact TF Analyzer 1000) at 10 Hz between room temperature and 160 °C.

Electrocaloric temperature change ( $\Delta T$ ) of the sample was calculated using the indirect method based on Maxwell's equations (Eq. (1)).

$$\Delta T = -\frac{1}{\rho} \int_{E_1}^{E_2} \frac{T}{c} \left( \frac{\partial P}{\partial T} \right)_E dE \quad (1)$$

where  $P$  is the electrical polarization,  $E_1$ ,  $E_2$  are initial and final electric field,  $c$  is the heat capacity,  $\rho$  is the density and  $T$  is the temperature.

## 3. Results and discussion

### 3.1. Structural characterization

Le Bail fit to the X-ray diffraction spectra of dual-step sintered KNSBN is shown in Fig. 1. All observed peaks belong to the tetragonal tungsten bronze structure. Lattice parameters were obtained from the Le Bail fit using the tetragonal tungsten bronze structure of SBN with the space group  $P4mm$  as the standard [30]. The fit quality was good, evidenced by the difference curve and the low  $R_{wp}$  of 4.44%. Lattice parameters  $a$  and  $c$  were obtained as 12.449(6) Å and 3.933(9) Å, respectively, in agreement with KNSBN compositions reported in Refs. [24].

Fig. 2 shows SEM micrograph of the surface of the sample sintered using dual step sintering. While the abnormal grain growth could be prevented: i.e. giant grains of 100  $\mu m$  size were not observed [27], grain size distribution is broad and not homogeneous. Similar microstructure was reported for some SBN compositions synthesized using dual sintering [31]. The average grain size was estimated to be  $\sim 2 \mu m$  (Fig. 2). The measured density of the sample was  $\sim 91\%$  of the theoretical density. We note that following conventional sintering with the same calcination temperature and the single sintering step at 1270 °C for 2 h, we have obtained a microstructure (Fig.S2(b)) with cracks and inhomogeneities, suggesting liquid phase formation and abnormal grain growth. Adding a pre-sintering step (i.e. dual-step sintering) approximately 100 °C below the normal sintering temperature

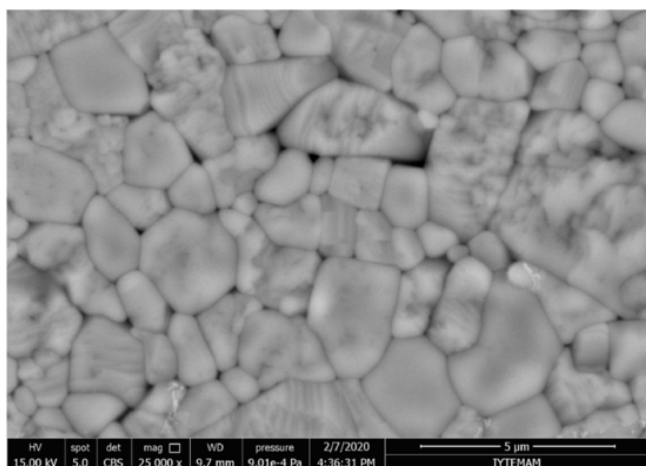


Fig. 2. SEM surface micrograph of dual-step sintered KNSBN.

is reported to prevent liquid phase formation since the liquid phase formation is triggered by incomplete calcination [27]. Comparison of the sintering profiles and microstructures of the two samples obtained using conventional and dual-step sintering is provided in the supplementary material (Fig. S1 and S2).

### 3.2. Dielectric properties

Dielectric constant ( $\epsilon$ ) and dielectric loss ( $\tan \delta$ ) of dual-step sintered KNSBN in the temperature range of 50–200 °C and at various frequencies (100 Hz, 1 kHz, 10 kHz, and 100 kHz) are presented in Fig. 3. Dielectric constant shows a broad peak at the transition temperature ( $T_m$ ) around 111 °C. In agreement with the study of Yao et al. [24], dielectric peak position does not shift significantly towards higher temperatures with increasing frequency, pointing to a normal ferroelectric with diffuse phase transition character rather than a ferroelectric relaxor. This is in contrast to what has been reported for  $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$  ceramics, where a clear shift in the broad dielectric maximum to higher temperatures is reported [32,33]. The maximum value of our dielectric constant is smaller than that reported in Ref. [24]. This could be due to the slightly smaller average grain size of our samples (2  $\mu\text{m}$  compared to 5  $\mu\text{m}$ ). It is well known that the larger grain size can yield better dielectric and ferroelectric properties [27,34].  $T_m$  we obtained is also lower than that reported in the earlier report [24]. This lower transition temperature might have resulted from the slightly lower grain

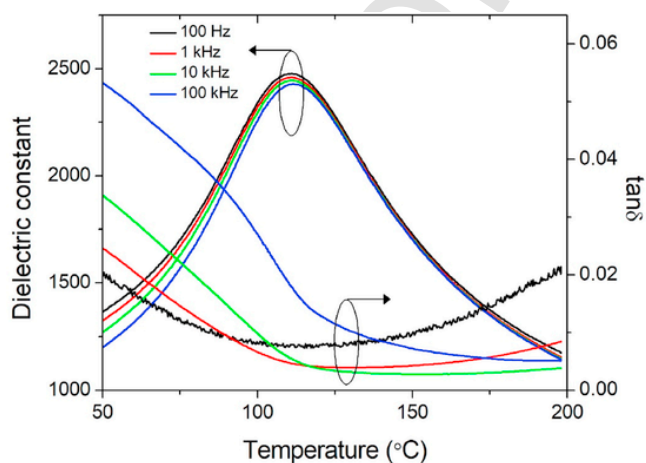


Fig. 3. Temperature dependence of dielectric constant and dielectric loss of dual-step sintered KNSBN at different frequencies.

size of our samples. It was reported that Ce doping suppresses grain growth in  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$  ceramics and in turn causes a significant decrease in Curie temperature due to the larger internal stress in fine grained samples [35]. The dielectric loss of the sample decreased with increasing temperature until the temperature of the dielectric maximum and then reaches a plateau for 10 and 100 kHz. The temperature of the plateau shifts to higher temperatures with increasing frequency. At 100 Hz and 1 kHz, an increase of dielectric loss at high temperatures was observed which might be related to the increasing dc conductivity at these temperatures [36]. Dielectric loss was smaller than 0.022 over the whole temperature range. Comparison of the temperature dependence of the dielectric constant of the samples obtained using conventional and dual-step sintering is provided in Fig. S3. Dielectric constant of the dual-step sintered sample is larger than that of the conventionally sintered one, while its dielectric maximum temperature is lower. Similar behaviour was reported for SBN ceramics and explained in terms of the internal stress developed in fine-grained samples (obtained by dual-step sintering) during cooling [27].

As mentioned in the introduction section, in the SBN system,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  occupy A1 and A2 sites while C site of TTB structure is empty. Five of the six A-site positions are occupied: A1 sites are filled by  $\text{Sr}^{2+}$  ions, whereas both  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  can occupy A2 site. There is a strong correlation between the occupancy of the A1 and A2 sites and the relaxor ferroelectric character of the material. Normal ferroelectric behavior with no frequency dispersion of the dielectric peak was observed for  $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$  when  $x = 0.20$  ( $\text{Sr}/\text{Ba} = 1/4$ ). In that case, four A2 sites are occupied by  $\text{Ba}^{2+}$  while one of the two A1 sites is occupied by one  $\text{Sr}^{2+}$  and thus, an ordered and even distribution of ions is obtained [19]. When the composition moves away from  $x = 0.25$ , cation distribution becomes disordered and relaxor ferroelectric behavior is observed with the signature of frequency dispersion of the dielectric maximum. The strength of frequency dispersion in  $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$  system increases with strontium content [19,37]. It has been established that the origin of the relaxor behavior in SBN is the ‘quenched electric random fields related to randomly distributed vacancies on the A-sites’ [38]. One way to decrease the disorder and frequency dispersion is introducing alkali ions such as  $\text{Na}^+$  and  $\text{K}^+$ . Introduction of  $\text{Na}^+$  and  $\text{K}^+$  to the structure causes the filling of vacant A1 and A2 sites since for each divalent cation, two monovalent  $\text{Na}^+$  or  $\text{K}^+$  are introduced while small C sites remain unoccupied [33,39]. This decrease in the vacant sites is reported to cause the suppression of relaxor ferroelectric properties and induces diffuse phase transition [33]. In our case, the amount of  $\text{Na}^+$  or  $\text{K}^+$  introduced at the A-sites is quite small however is enough to decrease the frequency dispersion and induce normal ferroelectric behavior with diffuse phase transition character.

### 3.3. Ferroelectric and electrocaloric properties

In Fig. 4 ferroelectric hysteresis loops of dual-step sintered KNSBN measured at 10 Hz and different temperatures are shown. At room temperature, the sample exhibits a typical hysteresis loop. Hysteresis loops become slimmer with increasing temperature and at and above  $T_m = 111$  °C, they fully close-up and at the highest measurement temperature of 160 °C an almost linear loop is observed, suggesting that the paraelectric state is reached. The value of the maximum polarization is comparable to SBN ceramics [40] when compared to the same electric field. A comparison of the hysteresis loops of the samples obtained using conventional and dual-step sintering is provided in Fig. S4. It can be observed that while the maximum polarization of the dual-step sintered sample is larger, its coercive is smaller than that of the conventionally sintered sample. These differences are related to the higher density (91 vs. 86%), better crystallinity and relatively homogeneous microstructure of the dual-step sintered sample.

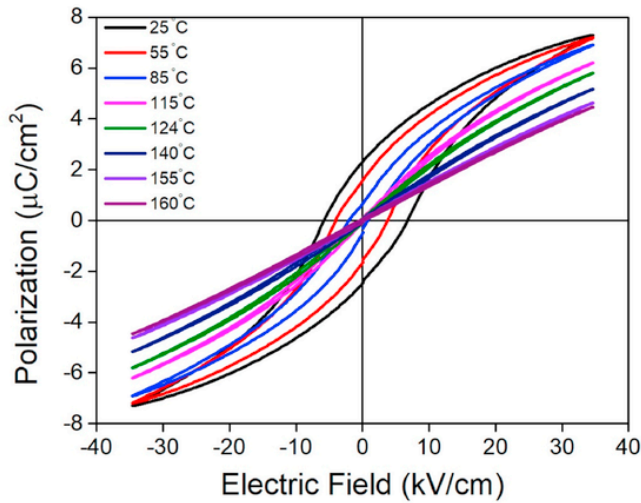


Fig. 4. Ferroelectric hysteresis loops of dual-step sintered KNSBN at different temperatures measured at 10 Hz.

Electrocaloric temperature change ( $\Delta T$ ) of the dual-step sintered sample was calculated by the indirect method, using equation (1). For the calculation, first  $\left(\frac{\partial P}{\partial T}\right)_E$  was obtained. In order to do this, the temperature dependence of the electrical polarization at different electric fields were plotted using the data from the upper branches of the hysteresis loops, as illustrated in Fig. 5(a). The curves were fitted with 6th order polynomials and then the fitted curve is differentiated.  $\Delta T$  was then calculated using equation (1). In the calculation, measured density ( $\rho$ ) of 4.81 g/cm<sup>3</sup> was used. Heat capacity ( $c$ ) value of 330 J/kgK was taken from Ref. [24] which is the value reported for the KNSBN

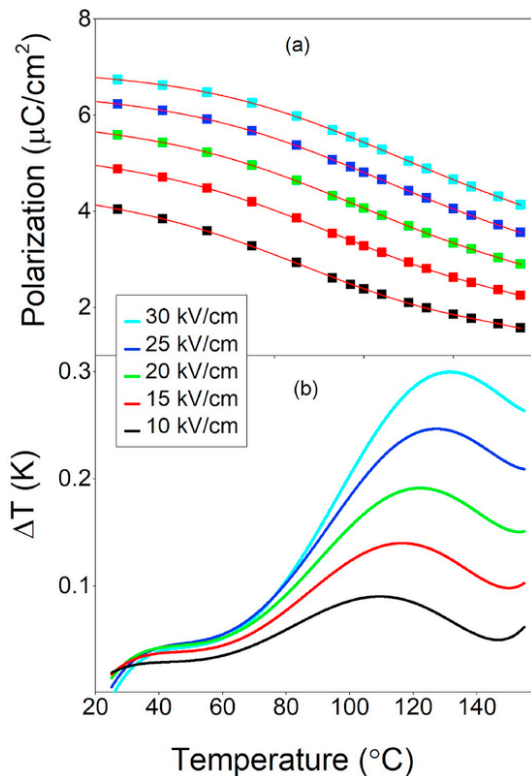


Fig. 5. (a) Electrical polarization of dual-step sintered KNSBN as a function of temperature at different electric fields. The solid line is a fit to a sixth-degree polynomial, (b) Electrocaloric temperature change ( $\Delta T$ ) of dual-step sintered KNSBN as a function of temperature at different electric fields.

of the same composition. The temperature evolution of  $\Delta T$  under different electric fields is shown in Fig. 5(b).  $\Delta T$  shows a broad peak at around  $T_m = 111$  °C under 10 kV/cm  $\Delta T$  peak shifts to higher temperatures as the electric field is increased.  $\Delta T$  reaches 0.3 K under 30 kV/cm at around 133 °C and the calculated electrocaloric responsivity or strength ( $\Delta T/\Delta E$ ) is 0.1 K\*mm/kV at this temperature. Even though this value is modest among Pb-free ceramics, it is the largest among SBN based ceramics as we discuss below. We note that the dual-step sintered sample underwent dielectric breakdown above 30 kV/cm. This relatively low dielectric breakdown strength is likely to originate from the slightly low density of the sample since density is one of the key factors controlling the breakdown strength [41]. Conventionally sintered sample had even lower breakdown strength as it underwent dielectric breakdown at high temperatures. Therefore its electrocaloric property measurements couldn't be completed. This must be caused by its inhomogeneous microstructure.

In Table 1, the electrocaloric properties of KNSBN are compared with different SBN compositions in ceramic and single crystal form. In order to compare the electrocaloric effect,  $\Delta T/\Delta E$  values for each material are listed. In addition to the measurement method, the nature of the material i.e. whether the material behaves as a ferroelectric relaxor or normal ferroelectric is also included in the table. KNSBN shows better electrocaloric responsivity than all SBN ceramic compositions reported so far however as expected single crystal SBN compositions outplay KNSBN ceramic. We stress that all SBN compositions listed in Table 1 are mostly relaxor ferroelectrics unlike the KNSBN composition we report here. Indirect measurement of electrocaloric effect based on Maxwell's relations is not accurate for relaxor ferroelectrics nevertheless it is still used to estimate the electrocaloric effect. Direct measurement was shown to yield larger electrocaloric temperature change for many ceramics compared to the indirect method [42–44]. Large  $\Delta T$  of KNSBN is in accordance with its large room temperature pyroelectric coefficient ( $p$ ) reported by Yao et al. (284  $\mu\text{C}/\text{m}^2\text{K}$ ). KNSBN's room temperature pyroelectric coefficient is greater than that of  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$  ceramics (200  $\mu\text{C}/\text{m}^2\text{K}$ ) [17], which has the largest  $p$  among SBN compositions. And this difference does not originate from a proximity effect to the Curie temperature.  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$  ceramics has a  $T_C$  of around 80 °C [17] which is lower than KNSBN. This difference between  $p$  of KNSBN and SBN ceramics points out to a sharper change of electrical polarization in KNSBN and partially accounts for the large  $\Delta T$  obtained in this study. The difference in  $\Delta T$  between single crystals and ceramics can be anticipated by looking at the large value of  $p$  of  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$  single crystal: 550  $\mu\text{C}/\text{m}^2\text{K}$  [45]. SBN has strongly anisotropic electrical properties and is polar only along [001] direction. In ceramics, randomly oriented grains result in an average value of all directions which causes a decrease in pyroelectric coefficient.

We suggest that the origin of the electrocaloric effect and the large pyroelectric coefficient in KNSBN must be related to the stabilization of ferroelectricity upon  $\text{K}^+$  and  $\text{Na}^+$  co-substitution. It has been reported that remanent polarization increases as the amount of  $\text{K}^+$  and  $\text{Na}^+$  increases in KNSBN ceramics [24], which is an indication of the stabilization of ferroelectricity upon doping. In our case, we also observe a relatively large remanent polarization, an increase in the Curie temperature compared to undoped  $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$  as well as disappearance of the shift of dielectric maximum with increasing frequency; all of which support the stabilization of the ferroelectricity. A similar increase of remanent polarization was observed in  $\text{Ca}_x\text{Sr}_{0.3-x}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$  ceramics where  $\text{Ca}^{2+}$  doping was suggested to stabilize the ferroelectricity of the material, evidenced by an increase in Curie temperature and remanent polarization with the doping. In addition, the pyroelectric coefficient also increased with increasing  $\text{Ca}^{2+}$  content [46]. Based on these reports and the observation of normal ferroelectric behavior in our KNSBN, we suggest the relatively large electrocaloric responsivity we measure on KNSBN as well as the previously reported large pyroelec-

**Table 1**  
Comparison of electrocaloric properties for different SBN related materials.

Material	Form	T <sub>c</sub> or T <sub>m</sub> (°C)	ΔT (K)	E (kV/cm)	ΔT/ΔE (K*mm/kV)	Method/Material Type	Ref.
Sr <sub>0.5</sub> Ba <sub>0.5</sub> Nb <sub>2</sub> O <sub>6</sub>	ceramic	50	0.35	100	0.035	indirect/relaxor	[47]
Sr <sub>0.6</sub> Ba <sub>0.4</sub> Nb <sub>2</sub> O <sub>6</sub>	ceramic	134	0.32	60	0.053	indirect/relaxor	[21]
Sr <sub>0.698</sub> Gd <sub>0.002</sub> Ba <sub>0.3</sub> Nb <sub>2</sub> O <sub>6</sub>	ceramic	40	0.085	15	0.056	indirect/relaxor	[48]
Sr <sub>0.6</sub> Ba <sub>0.4</sub> Nb <sub>2</sub> O <sub>6</sub>	Single crystal	< 35	0.42	10	0.42	direct/relaxor	[20]
Sr <sub>0.61</sub> Ba <sub>0.39</sub> Nb <sub>2</sub> O <sub>6</sub> + 1.4 %Ce	Single crystal	< 30	0.85	28	0.303	direct/relaxor	[49]
KNSBN	ceramic	133	0.30	30	0.1	indirect/normal ferroelectric	This work

tric coefficient, must be related to the stabilization of ferroelectricity with doping. To better understand the origin of large  $p$  and electrocaloric responsivity of KNSBN ceramics, however, more work on the possible correlation between the filling of A-site positions with K<sup>+</sup> and Na<sup>+</sup> and the increase in the pyroelectric coefficient and preferably direct measurement of the electrocaloric effect to compare the electrocaloric temperature change of SBN and KNSBN, are necessary.

#### 4. Conclusions

We have investigated the electrocaloric properties of K<sup>+</sup> and Na<sup>+</sup> co-doped SBN. Despite the low amount of alkali doping, KNSBN showed normal ferroelectric like behavior with no significant shift of dielectric maximum temperature with increasing frequency. KNSBN shows a maximum ΔT of 0.3 K under 30 kV/cm which corresponds to an electrocaloric responsivity of 0.1 K\*mm/kV around 130 °C. This value is larger than those of SBN ceramics and is in agreement with the larger pyroelectric coefficient value of KNSBN compared to SBN ceramics. We suggest that the relatively large ΔT and  $p$  originates from the stabilization of ferroelectricity upon doping.

#### CRedit authorship contribution statement

**Arif Kurnia:** Data curation, Writing - original draft. **Emriadi:** Writing - review & editing. **Nandang Mufti:** Supervision, Writing - review & editing. **Zulhadjri:** Supervision, Writing - review & editing. **Umud Adem:** Conceptualization, Supervision, Writing - review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

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