Ceramics



Enhanced energy storage and photoluminescence properties in ErBiO₃-doped (Na_{0.5}Bi_{0.5})TiO₃-SrTiO₃ ceramics

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ABSTRACT

(1-*x*)(0.75Na_{0.5}Bi_{0.5}TiO₃-0.25SrTiO₃)-*x*ErBiO₃ (NBST-*x*EB, *x* = 0–0.04) ceramics were fabricated through a solid state reaction method. Scanning electron microscopy investigation shows that grain size of the ceramics decreases with increasing *x*. X-ray diffraction results reveal that all the ceramics are pseudocubic phase. An enhanced disordering of local structure by EB doping is revealed by Raman spectra. The NBST-*x*EB ceramics exhibit excellent dielectric stability within a wide temperature range after EB doping. A relatively high recoverable energy storage density (W_{rec}) of 1.834 J/cm³ with efficiency (η) of 71% are obtained for NBST-0.02 EB ceramics under a moderate electric field of 148 kV/cm. The W_{rec} and η of the NBST-0.02 EB ceramics exhibit excellent fatigue stability (10⁴) and temperature stability ($W_{rec} > 0.834$ J/cm³, $\eta > 64\%$) within 30–200 °C under 100 kV/cm. With the introduction of EB, the NBST-*x*EB ceramics also show strong photoluminescence properties due to the presence of Er³⁺.

Introduction

Dielectric capacitors with fast charge–discharge rates, good durability and temperature stability play an

important role in energy storage applications for micromation of electronic devices [1–8]. The total energy density (W_t), recoverable energy density (W_{rec}) and energy storage efficiency (η) of dielectric

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capacitors can be calculated according to Eqs. (1)–(3) [3, 4]

$$W_t = \int_{0}^{P_{\text{max}}} \text{EdP}$$
(1)

$$W_{\rm rec} = \int_{P_r}^{P_{\rm max}} {\rm EdP}$$
(2)

$$\eta = W_{\rm rec}/W \times 100\% \tag{3}$$

where E and P are electric field and polarization which can be obtained from the *P*-*E* hysteresis loops. $P_{\rm r}$ and $P_{\rm max}$ are remnant polarization and maximum induced polarization under a given E. In order to get a high $W_{\rm rec}$ and η , materials having slim P-E hysteresis loops with large P_{max} and small P_r are preferred. In normal ferroelectrics (FEs), large P_{max} often accompanies with large $P_{r_{\ell}}$ which results in small value in $W_{\rm rec}$ and η . However, relaxor ferroelectrics (RFEs) with short range ordered polar nano-regions (PNRs) show large P_{max} and small P_r simultaneously [9]. So the RFEs are considered to be ideal base materials for designing high performance electrical energy storage materials in recent years. For environmental concern, Na_{0.5}Bi_{0.5}TiO₃ (NBT) lead-free perovskite with complex ions occupying on its A-site attracts much attention because it can form solid solutions with many other lead-free perovskites, such as SrNb_{0.5}Sc_{0.5}O₃ (SNS) [10], SrNb_{0.5}Al_{0.5}O₃ (SNA) [11], NaTaO₃ (NT) [12] and SrTiO₃ (ST) [13–17]. The energy storage performance of pure NBT ceramics is poor because of the low dielectric break down strength ($E_{\rm b}$) and large $P_{\rm r}$. For dielectric ceramics, there are many strategies to improve $E_{\rm b}$ based on different breakdown processes [8, 18]. First, increasing band gap or phonon frequency. Large band gap can limit the electrons from the valence band to the conduction band and high phonon frequency means a quick energy loss rate [8]. Second, decreasing average grain size (AGS). The grain boundary regions will increase with decreasing AGS and a higher resistivity can be obtained because the grain boundaries can act as barriers to trap charge carriers [8, 18]. In addition, decreasing AGS can result in the pore size become small, which leads to a reduction of the local voltage applied on the pore and reduces the possibility of dielectric breakdown [8]. Third, inhibiting defects. Defects, such as impurities, pores, vacancies and so on, are always difficult to avoid during ceramic processing, especially in NBT ceramics because its A-site elements are volatile during sintering processing [19]. Compared with matrix material, the area containing defects usually exhibits a lower withstand voltage. Therefore, inhibiting defects is an effective way to improve $E_{\rm b}$. Generally, by incorporating some chemical compounds, the $E_{\rm b}$ can be significantly enhanced in NBT ceramics at the expense of decreasing P_{max} due to the negative correlation between dielectric permittivity (ε_r) and E_b [8]. However, although P_{max} is destroyed, these compounds not only can disturb long range ferroelectric order to generate PNRs leading to a decreasing P_{r} , but also can decrease the dielectric nonlinearity or delay the polarization saturation of NBT ceramics [8]. Therefore, by compound doping, the excellent energy storage properties (ESPs) can be achieved under a high E in NBT-based ceramics. For example, high $W_{\rm rec}$ of 6.64 J/cm³ and 4.21 J/cm³ were reported for 0.8NBT-0.2SNA ceramics and 0.8NBT-0.2NT ceramics under an extremely high E of 520 kV/cm [11] and 380 kV/cm [12], respectively.

The requirement of ultra-high *E* might be a handicap for the practical device applications [20, 21]. NBT-xST solid solution ceramics possess pinched P-E loops with large $P_{\rm max}$, small $P_{\rm r}$ and enhanced $E_{\rm b}$ (~ 100 kV/cm) at the ST content of 24–28 mol% [13–17]. By introducing the third component to form ternary solid solutions, enhanced (W_{rec} , η) of (2.03 J/ cm^{3} , 61.8%) and (1.746 J/ cm^{3} , 71%) were obtained for 0.76NBT-0.24ST-AgNbO3 0.72NBT-0.28STand BiAlO₃ ceramics under a moderate E = 120 kV/cm[13, 17]. By defect engineering with Bi-excess and Nadeficiency to compensate the volatilization of Bi during sintering, enhanced $E_{\rm b}$ and reduced $P_{\rm r}$ can be obtained without sacrifice of P_{max} in $0.75\text{Bi}_{(0.5+x)}$ - $Na_{(0.5-x)}TiO_3$ -0.25ST ceramics when the x is less than 0.02. Because of high electrical resistivity, the rare earth oxide Er_2O_3 is often used to enhance the E_b for ferroelectric ceramics [22-24]. Moreover, because of the special energy level of Er³⁺, Er³⁺-doped NBTbased ceramics show strong photoluminescence (PL) properties exhibiting strong green emission at \sim 550 nm and red emission at \sim 660 nm [25]. In addition, the PL intensity is usually used to value the PL properties [26], which is affected by many factors mainly including the concentration of Er³⁺, composition of matrix material, defects and so on [27]. Furthermore, it was reported that enhanced relaxor characteristics and refined grain size were obtained in K_{0.5}Na_{0.5}NbO₃ (KNN) ceramics via the doping of complex oxide $0.5 \text{Er}_2 \text{O}_3 - 0.5 \text{Bi}_2 \text{O}_3$ (or ErBiO₃,

abbreviated as EB hereafter), which leads to transparent ceramics with enhanced energy storage performance and PL properties [28, 29]. Inspired by these results, EB were chosen as a modifier for 0.75NBT-0.25ST ceramics in this work to realize the enhancement of $E_{\rm b}$ without significant decrease in $P_{\rm max}$ under a moderate E. Our results demonstrate that the ($W_{\rm rec}$, η) can be enhanced from (0.703 J/cm³, 45%) to (0.961 J/cm³, 63%) for 0.75NBT-0.25ST ceramics after 1 mol% EB doping under 100 kV/cm. The $E_{\rm b}$ of 148 kV/cm and $(W_{\rm rec}, \eta)$ of (1.834 J/ cm³,71%) were obtained after 2 mol% EB doping. Besides the enhanced ESPs, PL properties were also enhanced after EB doping, which makes EB-doped 0.75NBT-0.25ST a potential multifunctional material for electrical and optical applications.

Experimental procedure

 $(1-x)(0.75Na_{0.5}Bi_{0.5}TiO_3-0.25SrTiO_3)-xErBiO_3$ (NBSTxEB) ceramics were fabricated through a solid state reaction method. Raw materials of TiO₂ (\geq 98%), $Bi_2O_3 (\geq 99\%)$, $Na_2CO_3 (\geq 99.8\%)$, $SrCO_3 (\geq 99\%)$ and $\text{Er}_2\text{O}_3 (\geq 99.9\%)$ were dried at 120 °C for 2 h. Then the raw materials were weighed according to the mole ratio of x = 0, 0.01, 0.02, 0.03 and 0.04. The mixed raw materials were ball milled for 1 h with alcohol. After ball milling, the mixed raw materials were dried and calcined at 900 °C for 3 h to obtain ceramic powders. Then the ceramic powders were ground and ball milled for 8 h. After ball milling, the ceramic powders were pressed into pellets with dimensions of $\Phi 10 \text{ mm} \times 1 \text{ mm}$ under a cold isostatic pressure of 250 MPa. Finally, these pellets were sintered at 1150-1200 °C for 2 h.

The sintered ceramics were polished with parallel surfaces and sliver electrodes were fired on both parallel surfaces at 600 °C for 0.5 h. Temperature dependent dielectric properties were measured by using a DMS-500 (Partulab). In order to measure the ferroelectric properties under high *E*, gold electrodes were sputtered on the polished parallel surfaces of the samples with a small upper electrode and a large bottom electrode. The small electrode was obtained by using 3.00 mm mask during sputtering process. The large electrode (~ 9 mm) was sputtered on the surface of the samples without the mask. The *P*–*E* loops were measured at 10 Hz with a Precision LC II (Radiant Technologies Inc, USA). Microstructures

of the NBST-*x*EB ceramics were observed by a scanning electron microscopy (SEM, Magellan 400, FEI, USA) equipped with an energy dispersive spectrometer (EDS, Max150, Oxford-X, UK). X-ray diffraction (XRD) data were measured by using a Rigaku D/max-2500/PC system. Lattice vibration related with local structures of the NBST-*x*EB ceramics were measured by using a Raman spectrometer (LabRAM HR Evolution Raman) with a 473 nm exciting laser. The Raman spectra were taken on three spots for ach composition and error analyses were performed. In addition, the Raman spectrometer was used to collect the photoluminescence spectra.

Results and discussion

SEM micrographs and grain size distribution of the NBST-xEB ceramics are shown in Fig. 1a-e. Inhomogeneous grain size can be seen for the NBST ceramics in Fig. 1a. After doping of EB, the grain size distribution become uniform and all the ceramics exhibit a dense microstructure without obvious pores. The secondary phases with lamellar structure is present in the micrographs for $x \ge 0.02$, which could be the Bi-rich phase as evidenced in our following XRD results. Except for the Bi-rich phase region, the results of SEM-EDS demonstrate NBST-0.02 EB ceramics have good chemical uniformity as shown in Fig. 1h–j. With increasing x, average grain size (AGS) of NBST-xEB ceramics decreases from 1.99 μ m to 1.30 μ m for x = 0 and 0.01 and continues to decrease for x = 0.02, as shown in Fig. 1f. Then the average grain size slightly increases for x = 0.03 and 0.04. After doping EB, part of Er and Bi ions might enter perovskite A-site, which compensates the volatilization of Na and Bi in NBST and reduce the concentration of oxygen vacancies. The increasing atomic mass on the A-site and decreasing concentration of oxygen vacancies will hinder substance and energy transfer across grain boundary during sintering process, which results in the reduced AGS in EB-doped NBST ceramics [19]. The reduced AGS is beneficial to enhancement of E_b due to high density of grain boundary which acts as barriers to trap more charge carriers [22].

XRD patterns of NBST-*x*EB ceramics are shown in Fig. 2a. Pure perovskite phases are found for NBST-*x*EB ceramics with x = 0 and 0.01. Additional



Figure 1 The SEM images of NBST-*x*EB ceramics: **a** x = 0, **b** x = 0.01, **c** x = 0.02, **d** x = 0.03 and **e** x = 0.04. Insets are the grain size distribution corresponding to respective bulk ceramics.

diffraction peaks corresponding to Bi₂Ti₂O₇ phase exist for x = 0.02-0.04, which might be the secondary phase as observed by the SEM results. (111) and (200) diffraction peaks which are referred to a perovskite cubic lattice are magnified in Fig. 2b, c. There is no obvious splitting for both (111) and (200) diffraction peaks, which indicates the perovskite phases of NBST-*x*EB ceramics are close to cubic structure or so called pseudocubic structure in literatures [14, 15]. With increasing *x*, the 2 θ of (111) and (200) peaks shift toward higher angle direction because unit cell becomes smaller when the smaller Er³⁺ enters into

f The average grain size as function of EB content. **g**–**m** The microstructure and corresponding EDS mapping images for NBST-0.02 EB ceramics.

the A-site of perovskite. Effects of EB doping on the local structure are revealed by Raman spectra, as shown in Fig. 3a. According to the vibration mode, the Raman spectra of NBST-*x*EB can be divided into four regions corresponding to A-site vibration $(100-200 \text{ cm}^{-1})$, B–O bond vibration $(200-400 \text{ cm}^{-1})$, BO₆ octahedral vibration $(400-700 \text{ cm}^{-1})$ and A₁ + E vibration $(700-900 \text{ cm}^{-1})$ [14], which can be deconvoluted into eight Lorentz peaks as represented in Fig. 3a for NBST-0.04 EB ceramics. Raman shift, integrated intensity and full width at half maximum (FWHM) as functions of *x* for the deconvoluted peaks





Figure 3 a Raman spectra of the NBST-xEB ceramics and representative deconvoluted results for the NBST-0.04 EB ceramics. **b**–**d** Raman shift, integrated intensity and FWHM as functions of EB content x for peaks 1, 2 and 3.

corresponding to the A-site and B-O bond vibrations are shown in Fig. 3b, d. All the three parameters of Raman spectra monotonically change with increasing x, which clearly indicates that Er^{3+} and Bi^{3+} are incorporated into perovskite lattice of NBST ceramics. The B-O bond vibration is closely related to the structure and dielectric properties of NBT-based materials [14, 30-32], which are deconvoluted into peak 2 and 3. With increasing *x*, the Raman shift of peaks 2 and 3 gradually shifts toward low wavenumber, indicating the softening of the Ti-O vibrations mirroring the de-coupling of the Ti-O bonds [30]. Considering the polarity of NBT-based ceramics is mainly originated from the strong coupling of the Bi–O and Ti–O bonds [33], therefore, the de-coupling of the Ti-O bonds will lead to the

descending dielectric and ferroelectric properties. The integrated intensities of the peaks 1, 2 and 3 monotonically decrease with increasing x, which implies that the perovskite structure changes gradually toward a cubic one as evidenced by XRD in Fig. 2b, c. The FWHM of peak 1 increases with increasing x, which might provide an experimental evidence that the disordering on the A-site are enhanced due to Er^{3+} entering the A-site. The broadened and diffused Raman spectra indicate enhanced disordering of local structures in NBST-*x*EB ceramics after EB doping [14, 30–32].

Figure 4a–e shows the temperature dependent dielectric permittivity (ε_r) and loss factor ($tan\delta$) for NBST-*x*EB ceramics under various frequencies. Below 150 °C, a strong frequency dispersion can be



Figure 4 The dielectric constant (ε_r) and loss factor ($tan\delta$) as functions of temperature for NBST-*x*EB ceramics under different frequencies: **a** x = 0, **b** x = 0.01, **c** x = 0.02, **d** x = 0.03 and **e** x = 0.04. (**f**) The λ —*T* curves of NBST-*x*EB ceramics at 1 kHz.

seen on both ε_r and tan δ for NBST ceramics. The temperature corresponding to the dielectric peaks within the frequency dispersion range increases with increasing frequency, which shows some similarity with that of typical relaxor ferroelectrics [34, 35]. The ε_r decreases significantly with EB doping, which can be attributed to the weakening Ti-O bonds as evidenced by the Raman spectra. In addition, the frequency dispersion shows two different features. First, the temperature range of frequency dispersion slightly extends to high temperature. Second, the temperature corresponding to the dielectric peak gradually becomes frequency independent and merged into a very broad dielectric platform with increasing x to 0.04. $\lambda = (\varepsilon_{r,T} - \varepsilon_{r,150 \circ C}) / \varepsilon_{r,150 \circ C}$ is often used to describe the temperature stability of hightemperature dielectric capacitors because 150 °C is a benchmark operating temperature [36-38]. Figure 4f shows the λ as a function of temperature (*T*) for NBST-xEB ceramics at 1 kHz and the shaded area represents the λ value between 5 and -15%. $\varepsilon_{r,150 \circ C_{\ell}}$ $tan\delta_{150}$ $\sim_{\rm C}$ and T (-15% < λ < 5%) of NBST-*x*EB ceramics at 1 kHz are collected in Table 1. The temperature stability range are broadened by EB doping in NBST ceramics and all the ceramics have a high $\varepsilon_{r,150 \ ^{\circ}C}$ (> 1290) and low $tan\delta_{150 \ ^{\circ}C}$ (< 0.03). Therefore, NBST-*x*EB ceramics can be used as potential high-temperature dielectric capacitor materials.

Figure 5a, b shows the *P*–*E* loops and switching current (*I*)–*E* loops measured at room temperature under 100 kV/cm for NBST-*x*EB ceramics. The *P*–*E* loops become slimmer as EB content increases. P_{max} , P_{r} and $\Delta P = P_{\text{max}} - P_{\text{r}}$ gradually decrease with increasing EB content, as shown in Fig. 5c. These results indicate that doping EB can disturb long-

Table 1 The values of $\varepsilon_{r,150 \circ C}$, $tan\delta_{150 \circ C}$ and T $(-15\% < \lambda < 5\%)$ of NBST-xEB ceramics at 1 kHz

Compositions	€ _{r,150} °C	$tan\delta_{150}$ °C	$T (-15\% < \lambda < 5\%)$
x = 0	4286.8	0.0089	99–277 °C
x = 0.01	2369.8	0.0161	94–325 °C
x = 0.02	1659.3	0.0185	88–327 °C
x = 0.03	1648.8	0.0133	64–345 °C
x = 0.04	1295.9	0.0283	78–400 °C





range ferroelectric ordering in NBST ceramics and enhance the disordering of the local structures as evidenced by the Raman spectra in Fig. 3. Four peaks $(\pm E_1 \text{ and } \pm E_2)$ on the *I*–*E* loops are seen for NBST ceramics in Fig. 5b. The peaks occurring at $\pm E_1$ indicate the *E* induced phase transition from RFE to FE, while the reversible transition from FE phase to RFE occurs at $\pm E_2$ [36].With increasing EB content, the $\pm E_1$ peaks gradually fade, which indicates RFE is maintained without long range ordered FE induced under 100 kV/cm. Figure 5d shows the $W_{\rm rec}$ and η calculated according to Eqs. (1-3) for NBST-xEB ceramics under 100 kV/cm. The (W_{rec} , η) of NBST ceramics can be enhanced from $(0.703 \text{ J/cm}^3, 45\%)$ to (0.961 J/cm³,63%) by 1 mol% EB doping. The improvement of (W_{rec}, η) is as high as (37%, 40%). With further increasing x, the $W_{\rm rec}$ decreases while the η increases slightly.

Unipolar *P*–*E* loops were measured for the NBST*x*EB ceramics before breakdown, as displayed in Fig. 6a. The highest (W_{rec} , η) of (1.834 J/cm³, 71%) are obtained for NBST-0.02 EB ceramics under a maximum E_b of 148 kV/cm. The excellent ESPs obtained at x = 0.02 which can be attributed two factors: one is the enhanced E_b due to the refined grain size and enhanced electrical resistivity by EB doping [22–24];

another important factor is the enhanced disordering of the local structures as evidenced by the Raman spectra in Fig. 3. The enhanced disordering of the local structures might generate nanodomains and PNRs [35]. Compared with large-scale ferroelectric domains, these nanodomains and PNRs not only can be aligned under a given E, but also can back to its original state when E is unloaded [8]. Therefore, for x = 0.02, a relatively large P_{max} and small P_{r} can be obtained under 148 kV/cm. However, nanodomains and PNRs might be further refined and even eliminated with increasing x, which leads to a significantly reduced P_{max} under a given E [39]. Therefore, although the enhanced $E_{\rm b}$ is also obtained for x = 0.03and 0.04, the $W_{\rm rec}$ of 1.457 J/cm³ and 1.421 J/cm³ are relatively lower than that of x = 0.02 due to a small P_{max} . The comparison of W_{rec} between NBST-0.02 EB ceramics and recently reported NBT-based ceramics is shown in Fig. 6c [10, 40–49]. It can be seen that the $W_{\rm rec}$ of NBST-0.02 EB ceramics possesses a considerable advantage under a relatively low *E*.

Figure 7a, b shows the temperature dependent *P*–*E* loops and (W_{rec} , η) for NBST-0.02 EB ceramics from 30 to 200 °C under 100 kV/cm. The *P*–*E* loops gradually become linear as temperature increases. (W_{rec} , η) increase from (0.834 J/cm³,64%) to (0.967 J/cm³,



Figure 6 a The unipolar *P-E* loops of NBST-*x*EB ceramics before breakdown. **b** The corresponding W_{rec} and η as functions of EB content. **c** The comparison of W_{rec} between NBST-0.02 EB ceramics and recently reported NBT-based ceramics.



Figure 7 a and **b** the temperature stability of NBST-0.02 EB ceramics from 30 to 200 °C under 100 kV/cm. **c** and **d** the fatigue stability of NBST-0.02 EB ceramics from 1 to 10⁴ under 100 kV/cm.





90%) with increasing temperature from 30 to 200 °C. These results demonstrate that ESPs of NBST-0.02 EB ceramics exhibit excellent temperature stability within temperature range of 30-200. Figure 7c, d displays the *P*–*E* loops and (W_{rec} , η) of NBST-0.02 EB ceramics with the loaded cycles from 1 to 10^4 under 100 kV/cm. It can be seen that the P-E loops are almost unchanged from 1 to 10⁴ cycles. The variations of $W_{\rm rec}$ and η are only 1.19% and 2.16%, indicating excellent fatigue stability of ESPs for NBST-0.02 EB ceramics.

Photoluminescence (PL) properties of NBST-xEB ceramics are shown in Fig. 8a. NBST ceramics does not show any PL properties. After EB doping, NBSTxEB ceramics exhibit two green emissions $({}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ at ~ 530 nm and ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ at ~ 549 nm) and one red emission (${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ at ~ 665 nm) excited under 473 nm light, which is similar to the previously reported results in Er-doped NBT-based ceramics [25, 50]. The mechanism of PL properties for EB-doped ceramics can be well illustrated by the energy level scheme of Er³⁺ ion, as shown in Fig. 8b. The electrons located at the ground state (${}^{4}I_{15/2}$) can be excited to ${}^{4}F_{7/2}$ level upon 473 nm light excitation, then these electrons can quickly relax to ${}^{2}H_{11/2}$, ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ levels by nonradiative manner due to the small energy gaps and unstable ${}^{4}F_{7/2}$ level [25]. Finally, most of them recombine and back to the ground state $({}^{4}I_{15/2})$ leading to two green emissions $({}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ at ~ 530 nm and ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ at ~ 549 nm) and one red emission $({}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ at ~ 665 nm) [25]. The variations for emission intensities of the wavelength at 549 nm (green) and 665 nm (red) with EB content are shown in an inset of Fig. 8. The green and red emission intensities increase and reach a maximum value at x = 0.03, then decrease with further increasing of x which might result from concentration quenching of Er³⁺ [51].

Conclusions

This study reveals that EB is an effective structure and property modifier for the NBST ceramics. The grain size can be refined by EB doping. Cation disordering on the A-site of perovskite is enhanced while the distortion from cubic structure is reduced with increasing EB content. Therefore, the P_r can be significantly decreased by EB doping. The relatively high $W_{\rm rec}$ of 1.834 J/cm³ and η of 71% under a moderate E of 148 kV/cm are obtained for NBST-0.02 EB ceramics, exhibiting excellent temperature (30-200 °C) and fatigue stabilities (10^4) under 100 kV/cm. Moreover, with the EB doping, all ceramics show strong PL properties. Thus, the NBSTxEB ceramics can be considered as potential electricoptical multifunctional materials.

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Data availability statement

The datasets generated during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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