Room temperature multiferroicity in Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_9$+$\delta$

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Magnetoelastic multiferroics are materials that have coupled magnetic and electric dipole orders, which can bring novel physical phenomena and offer possibilities for new device functions. In this report, single-crystalline Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_9$+$\delta$ nanobelts which are isosstructural with the high-temperature superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ are successfully grown by a hydrothermal method. The regular stacking of the rock salt slabs and the BiFeO$_3$-like perovskite blocks along the c axis of the crystal makes the Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_9$+$\delta$ nanobelts have a natural magnetoelastic–dielectric superlattice structure. The most striking result is that the bulk material made of the Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_9$+$\delta$ nanobelts is of multiferroicity near room temperature accompanied with a structure anomaly. When an external magnetic field is applied, the electric polarization is greatly suppressed, and correspondingly, a large negative magnetocapacitance coefficient is observed around 270 K possibly due to the magnetoelastic coupling effect. Our result provides contributions to the development of single phase multiferroics.
Bi\(_{4.2}\)K\(_{0.8}\)Fe\(_2\)O\(_9\) nanobelts can be suppressed by magnetic fields via magnetoelastic coupling. It is notable that the Bi\(_{4.2}\)K\(_{0.8}\)Fe\(_2\)O\(_9\) compound cannot be synthesized by a conventional solid state reaction method (see Supplementary Information), and it only can be grown within a nanoscale through a hydrothermal method so far.

**Results**

Figure 1 shows X-ray diffraction (XRD) patterns of the Bi\(_{4.2}\)K\(_{0.8}\)Fe\(_2\)O\(_9\) nanobelts. For the data in Fig. 1a, the nanobelts have been fully ground to reduce the preferred orientation from the belt-like shape. The diffraction patterns are similar to that of the Bi2212 as well as its isostructural compound Bi\(_{2-x}\)Sr\(_x\)Fe\(_2\)O\(_y\) (BSFO, JCPDS card No. 86-0286)\(^\text{15,16}\), and the lattice parameters are about \(a = 5.470\,\text{Å}, b = 5.468\,\text{Å}, c = 32.592\,\text{Å}\) (space group \(Fm\overline{3}m\)) for the average structure. Meanwhile, if the as-synthesized nanobelts are laid flat on a substrate with no grind, the intensity of the (001) diffraction pattern increases markedly, and the diffraction patterns of the other directions almost disappear as shown in Fig. 1b. These results demonstrate that the samples may have a good single-crystalline structure with the \(c\) axis perpendicular to the surface plane of the nanobelts. In addition, the structure of the Bi\(_{4.2}\)K\(_{0.8}\)Fe\(_2\)O\(_9\) nanobelts is long-term stable at room temperature, but when heated to about 720 K, the Bi\(_{4.2}\)K\(_{0.8}\)Fe\(_2\)O\(_9\) nanobelts will be decomposed mainly to BiFeO\(_3\) and Bi\(_2\)O\(_3\)(KBiO\(_2\))\(_3\), as depicted in Supplementary Fig. S1.

To further examine the structure, the microstructure of the sample is investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figs. 2a and 2b show the overview images of the nanobelts, the lengths of the nanobelts vary from a few to several dozen micrometers and more morphology images can be seen in Supplementary Fig. S2. The energy-dispersive X-ray spectroscopy (EDS) analyses on each single nanobelt reveal the presence of Bi, K and Fe with an average atomic ratio close to 4.2 : 0.8 : 2 (see Supplementary Fig. S3), and K ions are introduced to the lattice by self-assembly during the hydrothermal process, which may be helpful to keep the structure and chemical valences steady. Fig. 2c and Supplementary Fig. S4 show the high-resolution TEM images focusing on the surface plane of a nanobelt, it is noted that the nanobelts grow along [100] direction (a-axis) and have a commensurately modulated structure with 4 time periodicity of the subcell lattice parameter \(b\), which can be also confirmed from the result of selected area electron diffraction (SAED) patterns along the [001] and [100] zone axes as displayed in Figs. 2d and 2e. From the satellite spots in Fig. 2e the modulation can finally be characterized by a wave vector \(q^* = (0, 0.25, 1)\). Fig. 2f presents the SAED patterns of the [010] zone axis of a single nanobelt, in which the satellite spots are invisible due to the projection direction. It can be inferred the structural modulate wave make the \(<100>\) facets have higher surface energy than the \(<010>\) facets. Since the \(<010>\) facets have the lowest surface energy due to the large BiO interlayer distance\(^\text{15}\), thus a belt-like structure is forming. Taken together, a nanosized single crystal is obtained through our synthetic route, and their average structure constructed by analyzing the XRD, SAED patterns and high-resolution TEM images, is shown in Fig. 3 without considering the modulated structure, and the calculated XRD patterns based on this preliminary structure model using a Rietveld method are presented in Supplementary Fig. S5, which basically agrees with experimental points. Hence the structure of the nanobelts could be of the “… perovskite layer – rock salt layer – perovskite layer – rock salt layer…” configuration along the \(c\) axis of the crystal and one can find the perovskite layer is similar to the structure of BiFeO\(_3\)\(^\text{15,16}\), indicating a possibility for multiferroic characteristics.

Figure 4a shows the magnetic hysteresis loops of the Bi\(_{4.2}\)K\(_{0.8}\)Fe\(_2\)O\(_9\) nanobelts at 300 K and 2 K. At room temperature, the magnetization (\(M\)) – applied magnetic field (\(H\)) curve is almost linear between –50 kOe and +50 kOe with a small coercive magnetic field (\(H_c\)) about 50 Oe. This implies the magnetic ground state of Bi\(_{4.2}\)K\(_{0.8}\)Fe\(_2\)O\(_9\) may be antiferromagnetic accompanied with weakly ferromagnetically coupled spins possibly located at the surface of the nanobelts, bringing a weak ferromagnetism to the system\(^\text{19}\). At 2 K, a more obvious hysteresis loop with a \(H_c\) of about 600 Oe indicates the ferromagnetism is enhanced at low temperatures. The top inset of Fig. 4a shows the temperature (\(T\)) dependencies of zero field cooled (ZFC) and field cooled (FC) magnetizations at 50 Oe for the Bi\(_{4.2}\)K\(_{0.8}\)Fe\(_2\)O\(_9\) nanobelts. The ZFC curve shows a peak near \(T_p\) = 40 K and a separation from the FC curve below \(T_p\), indicating the appearance of spin-glass-like behavior at low temperatures. It is notable that an exchange bias phenomenon is observed in Bi\(_{4.2}\)K\(_{0.8}\)Fe\(_2\)O\(_9\) nanobelts at 300 K and 2 K when \(M-H\) curves are...
measured in the FC mode with the cooling fields $H_{FC} = \pm 50$ kOe as shown in Figs. 4b and 4c, which could be explained by the exchange coupling between the inside antiferromagnetic spins and the surface ferromagnetic-like spins. The disordered magnetic structure at the surface of the Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$ nanobelts is responsible for the spin-glass-like behavior at low temperature. It should be mentioned that the nanorization can greatly affect the magnetization behavior of the magnetic materials in a variety of ways$^{20,21}$, and in addition a small amount of iron oxide impurities, which even if cannot be detected by XRD, could also give rise to a weak ferromagnetism as well as exchange bias$^{22,23}$.$^*$ Therefore, the weak-ferromagnetic phenomenon in Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$ nanobelts needs further investigation.

One of the most important results is that an evident ferroelectric behavior for the bulks made of the Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$ nanobelts is obtained at room temperature as characterized by polarization hysteresis in Fig. 5a. A remanent polarization ($P_r$) of about 0.7 $\mu$C cm$^{-2}$ and a coercive electric field ($E_c$) of about 4 kV cm$^{-1}$ at room temperature can be clearly observed. The current switching peaks in the electric field ($E$) dependent charge current density ($J$) curve further confirm the ferroelectricity. As the structure of the perovskite block is close to that of BiFeO$_3$, the ferroelectricity of the new compound might have a similar physical mechanism, that the “lone pairs” of the Bi ions in the perovskite blocks might give rise to an off-center distortion$^{24,25}$. In Fig. 5b the temperature profiles of the electric polarization calculated by the pyroelectric current measurements show a broadening transition about from 320 K to 220 K with a steep around 270 K. The polarization can be switched with opposite poling electric fields, and the saturated polarization reaches 5.65 $\mu$C cm$^{-2}$ at 120 K. Correspondingly, as shown in Fig. 5c, the temperature profile of teragonality $c/a$ of the structure has a slope change at 270 K, and below 270 K the value of $c/a$ increases evidently with the decreasing temperature, indicating ferroelectric distortion with an elongation of

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**Figure 3** | Average structure scheme of Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$. The structure of the new compound is constructed through the analysis of characterization results, and is isostructural with the high-temperature superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, which make it have a natural magnetoelectric–dielectric superlattice configuration along the c axis of the crystal.

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**Figure 4** | Magnetic properties of the Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$ nanobelts. (a), the $M$–$H$ curves of the nanobelts at 300 K and 2 K. The top inset shows the temperature dependencies of ZFC and FC magnetizations at 50 Oe, and the bottom inset represents an enlarged view of the $M$–$H$ curve at 300 K. (b–c), exchange bias effect in Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$ nanobelts at 300 K (b) and 2 K (c), respectively. The $M$–$H$ curves are measured in a field cooling mode with the cooling fields $H_{FC} = \pm 50$ kOe (red solid square) and −50 kOe (blue open circle), respectively.

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**Figure 5** | Ferroelectric properties of the Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$ nanobelts. (a) $P$–$E$ and $J$–$E$ loops of the bulks made of the Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$ nanobelts at 300 K. (b) Temperature dependence of electric polarization in zero (blue line) and 50 kOe (red line) magnetic fields, and the value of the polarization was acquired by integrating the pyroelectric current. For the measurements the nanobelts were pressed into a bulk with a cuboid shape ($2 \times 2 \times 0.5$ mm$^3$) under a pressure of 20 MPa at room temperature. (c) Temperature dependent $c/a$ measurements for the Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$ nanobelts, the yellow wide line is guide to eyes.
the $c$ axis\textsuperscript{24}. From Fig. 5c together with the SEM images of the cross-section of a Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$ bulk shown in the Supplementary Fig. S6 where there are a certain amount of nanobelts with $c$-axes perpendicular to the pressure surface, we consider that the polarization behaviors of the nanobelts with $c$-axes perpendicular to the pressure surface will dominate polarization loop shape, and thus a near-square loop shape is obtained. Furthermore, it is very interesting that the ferroelectric polarization is distinctly suppressed under a magnetic field of 50 kOe (see Fig. 5b), indicating a possible strong magnetoelectric coupling in this system.

Figures 6a–b show the temperature dependencies of dielectric constant ($\varepsilon'$) and dielectric loss ($\tan\delta$) of the bulks made of the Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$ nanobelts, respectively. The most remarkable feature is that the peak position near 270 K in each $\varepsilon'$–$T$ curves is frequency independent, but the peak height $\varepsilon'$ (270 K) decrease sharply with the increasing frequencies. It is known that a ferroelectric phase transition can make the dielectric constant divergent, so the peaks of the $\varepsilon'$–$T$ curves may be further evidence for the ferroelectric transition of the Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$ nanobelts. M. Dawber et al. have reported that in their PbTiO$_3$–SrTiO$_3$ superlattice system the ferroelectric transition temperature decreases with decreasing FE layer volume fraction, and the Curie point of PbTiO$_3$–SrTiO$_3$ superlattice can be tuned from 1000 K to 300 K\textsuperscript{25}. Suppose the ferroelectricity of the nanobelts originates from the BiFeO$_3$-like perovskite layers, the insertion of the rock salt [Bi$_2$O$_2$]$^{2+}$ layers may tune the ferroelectric Curie temperature to near room temperature, and make the Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$ nanobelts be a high $k$-dielectric capacitor material with the operating temperature near room temperature, and keep the dielectric loss to be quite low (see Fig. 6b). On the other hand, the K ions in the crystal lattices may also affect the ferroelectric Curie point as well as the polarization. Similar to the $P$–$T$ curves (see Fig. 5b), the peaks of the $\varepsilon'$–$T$ curves (see Fig. 6a) are very broadening with a temperature range from 200 K to 320 K, which may be due to the heterogeneity of the local structure of the Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$ nanobelts. When a magnetic field of 50 kOe is applied as shown in Fig. 6c, the dielectric hump is greatly suppressed but the peak temperature remains almost unchanged, revealing a magnetic manipulation of dielectric properties around the ferroelectric transition region. Fig. 6d shows the temperature dependence of the magneto-dielectric effect (MD) which is defined as

\begin{equation}
MD = \frac{\varepsilon'(50 \text{ kOe}) - \varepsilon'(0)}{\varepsilon'(0)} \times 100\%.
\end{equation}

It is notable that the MD coefficient is about $-20\%$ at 300 K and $-64\%$ at 270 K for the frequency of 1 kHz, which is at least two orders of magnitude higher than those of BiFeO$_3$ ceramics\textsuperscript{26,27}. While for the temperature region below 100 K, the MD coefficient is almost frequency independent and only about $-1\%$. The temperature dependence of $dc$ resistivity $\rho$ of the samples at zero magnetic field and 50 kOe is shown in the inset of the Fig. 6c. Although the resistance of the nanobelts decreases slightly in the temperature range from 280 K to 330 K under a field of 50 kOe, the MD effect in the nanobelts cannot be originated by a well-known Maxwell–Wagner capacitor configuration with considering the magnetoresistance (MR) effect\textsuperscript{28,29}. Firstly, for a negative MR dominated by the grains of the bulk samples in such a scenario, it will generally cause a positive MD effect\textsuperscript{30}, but the MD coefficient shown in Fig. 6d is always negative in our case. Secondly, in spite of a MR related to spin-polarized tunneling across grain boundaries or interfaces may induce a negative MD coefficient, the dielectric loss should increase with increasing magnetic fields\textsuperscript{28}. On the contrary, the dielectric loss of the nanobelts is actually reduced under a magnetic field, see Supplementary Fig. S7. Moreover, the MD effect of the nanobelts exists for the whole temperature range measured as described in Fig. 6d, while the MR only occurs within the temperature range from 280 K to 330 K, further confirming that the magnetocapacitance

**Figure 6 | Magnetocapacitance effect in Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$ nanobelts.** (a–b) Temperature dependence of dielectric constant $\varepsilon'$ (a), and dielectric loss $\tan\delta$ (b) of the bulks made of the Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_{9+\delta}$ nanobelts at 1 kHz, 10 kHz, 50 kHz, 100 kHz, 500 kHz and 1 MHz measured in zero magnetic field. (c) Temperature dependence of $\varepsilon'$ at 1 kHz under zero (red points) and 50 kOe (olive points) magnetic fields, respectively. The inset of (c) shows the temperature profiles of $dc$ resistivity $\rho$ at zero (red line) and 50 kOe (olive line), respectively. (d) The corresponding temperature dependence of the magnetocapacitance effect of the samples.
observed cannot be explained in terms of the MR of the samples. Therefore, we attribute the MD phenomenon in Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_9$ nanobelts with ME–DE type layered structure to be a system. Therefore, our synthetic route may also open a window for applications.

Methods

The Bi$_{4.2}$K$_{0.8}$Fe$_2$O$_9$ nanobelts with ME–DE type layered structure were prepared by a surfactant-free hydrothermal synthesis method. All chemicals were of analytical grade and used without further purification. In a typical procedure, an aqueous solution of 5 mL was first prepared by dissolving 0.4 mmol Bi(NO$_3$)$_3$ · 5H$_2$O, 0.19 mmol Fe(NO$_3$)$_3$ · 9H$_2$O, and 1 mL nitric acid in distilled water. The mixture was dropped into KOH solution (15 mL) as slowly as possible under magnetic stirring and the final concentration of KOH was 12 M. The suspension solution was transferred to a stainless steel Teflon-lined autoclave of 25 mL capacity. The reaction was performed by heating the autoclave at 190°C for 90 min with a heating rate of 2°C min$^{-1}$. After it was cooled to ambient temperature naturally, the final products were collected by centrifugation, washed several times with distilled water and ethanol, and dried at 120°C for 6 h in air before further characterizations.

The structure of the synthesized nanobelts was recorded with an X-ray diffractometer using Cu Kα radiation. The microstructural and energy-dispersive X-ray spectroscopy (EDS) analysis was examined by scanning electron microscopy and high-resolution transmission electron microscopy.

The magnetic properties were determined with a commercial magnetometer. The P–E hysteresis loops were measured at 5 Hz using a standard ferroelectric tester. For the electric measurement, the nanobelts were fully pulverized in an agate mortar using absolute ethanol as the grinding aid, then the obtained powder was pelletized to a bulk with a tetragonal shape (2 × 2 × 0.5 mm$^3$), the density is 5.4 mg mm$^{-3}$ which is about 70% of the theoretical value) in a stainless steel mold at room temperature under a vertical pressure of 20 MPa and a pressure-holding time of 6 hours, then silver electrodes were deposited onto the opposite 2 × 2 mm$^2$ pressure surfaces. The dielectric constant was measured using an LCR (inductance–capacitance–resistance) meter. The temperature dependence of electric polarization was obtained by measurements of pyroelectric current. The sample is cooled down from 400K to a given low temperature in an electric field of 2 kV cm$^{-1}$, then the poling electric field was removed and the samples were short-circuited for 4 hours. Then, the samples were heated at a constant rate (3 K min$^{-1}$), and the pyroelectric currents were measured. The pyroelectric currents and the dc resistance of the samples were determined with an electrometer.
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**Author contributions**

X.G.L. conceived the project and designed the experiments. S.N.D. performed the syntheses and experimental measurements. Y.J.S., S.N.D. and J.Q.L. performed the characterizations and structural analysis. Y.P.Y. and Y.K.L. contributed to the ferroelectric measurements. S.N.D. and X.G.L. wrote the paper. All authors contributed through scientific discussions.

**Additional information**

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**Competing financial interests:** The authors declare no competing financial interests.

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