Electronic Supplementary Information:

Shape Controllable Synthesis of Bi-based Perovskite Superconductor Microcrystals via Mild Hydrothermal Method

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Contents

1. Experimental

1.1 Chemicals.

Chemicals of $NaBiO_3 \cdot 2H_2O$ (AR), $Bi(NO_3)_3 \cdot 5H_2O$ (99.0%), $Ba(OH)_2 \cdot 8H_2O$ (98.0%), $Ba(NO_3)_2$ (99.5%), $CO(NH_2)_2$ (99.0%), NH_4Cl (99.5%), CH_3COONH_4 (98.0%), and analytical grade of KOH were purchased from Sinopharm Chemical Reagent Co. Ltd. All of the chemicals were used as received without any further purification.

1.2 Synthesis.

Crystals of KBBNO were synthesized similar as that of in the reference with slight modification[1]. Two synthetic routes were performed to prepare the various KBBNO crystals with tuneable shapes. The ratio of reactant chemicals is 1:1:120 in molar ratio. **Route 1**: NH_4Cl was selected as shape controllable growing agent. Firstly, 0.3160 g $NaBiO_3 \cdot 2H_2O$ (1 mmol) solid was added in an glass beaker followed by the addition of 0.3155 g $Ba(OH)_2 \cdot 8H_2O$ (1 mmol). Then, 10 mL deionized water was dripped into the beaker with continuous magnetic stirring at room temperature. After the two reactants mixed thoroughly for about 10 min, 6.7332 g KOH solid was poured into the beaker and stirred for 15 min. the whole mixture was transferred to Teflon-lined stainless steel autoclaves with a capacity of 20 mL. Various share of NH_4Cl solid was poured in the reaction system quickly. The autoclaves were sealed with a Teflon-lined lead and then transferred into an oven kept at 240 ^oC for 72 h. We have also tried to tailor the crystal shape of KBBNO by CH_3COONH_4. However, no perovskite phase was formed. **Route 2**: The ratio of Bi:Ba:KOH is also kept to 1:1:120, while the Bi-source was added in two parts: $NaBiO_3 \cdot 2H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$ with a molar ratio of 1:0, 0.75:0.25, 0.50:0.50, 0.25:0.75 and 0:1, respectively. Adding sequence of the reactant chemicals is followed by that of in Route 1, without any facet directing agent adding in the reaction system. The reactant mixture was transferred into the same set of autoclave and kept at the same temperature for 72 h. Black color crystals were obtained by washing the hydrothermal products with deionized water for several times. The as-obtained samples were dried at 70 ^oC overnight. The samples were collected in a plastic sample tube without any post treatment. For eliminate the effect of NO_3^- contribution on the shape formation, $Ba(NO_3)_2$ was used to substitute $Ba(OH)_2$ with $NaBiO_3 \cdot 2H_2O$ as the only Bi-source. The reaction condition is kept the same as that of in Route 2. However, no perovskite phase could be formed.

1.3 Characterizations.

Sample composition was measured by induced couple plasma atomic emission spectroscopy (ICP-AES) and characteristic x-ray energy dispersive spectroscopy (EDS). Powder x-ray diffraction (PXRD) patterns were collected on a Rigaku D/Max 2500 V/PC X-ray diffractometer with a

radiation wavelength of 1.5418 Å (CuKα) with a tube voltage of 50 kV and current of 200 mA. The diffraction angle ranges from 10 ^{o} ≤ 2θ ≤ 90 ^{o} with an increment of 0.02 ^{o} for per step. Scanning electron microscope (SEM) images were collected with a Helios NanoLab 600i Dual Beam System (FEI Company, America) equipped with an Oxford EDS spectrometer. Secondary electron photos from SEM were measured with an accelerating voltage of 5 kV and a beam current of 86 pA. EDS data were collected with a 20 kV voltage and 1.4 nA current for continuous account of x-ray photons from 0-18 keV for 60 s. Pourbaix (E-pH) diagrams for the Bi-Ba-K-Na-H2O system were depicted based on the thermodynamic data provided by HSC Chemistry 6.0 software. The prediction of crystal morphologies were performed with Materials Studio 7.0 software. Geometric and energy calculation were determined by the Forcite and Morphology modules. A universal force field and Ewald summation method were applied for geometry optimization with an accuracy of 0.001 kcal/mol and buffer width of 0.5 $Å^2$. The attachment energy (E_{att}) and surface energy (E_{surf}) were calculated with the optimized geometry for the most important (MI) facets within the Ewald accuracy of 0.001 kcal/mol. Magnetic properties of the as-synthesized samples in zero-field-cooled (ZFC) and field-cooled (FC) processes were measured on a superconducting quantum interference device (SQUID) magnetometer (Quantum Design) from 4 K to 300 K. The applied field in FC process is 10 Oe.

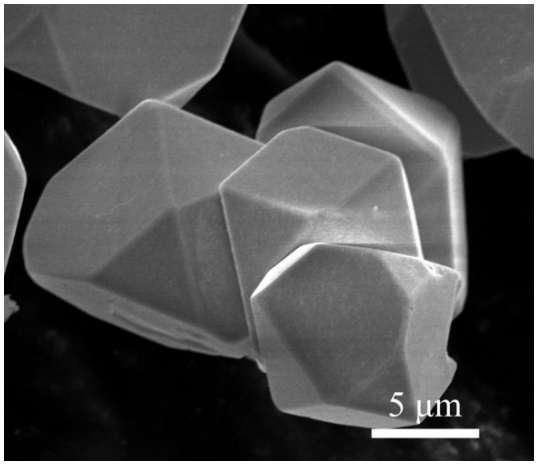


Figure S1 SEM graph of KBBNO crystal obtained with the NH_4Cl content of 0.8 g.

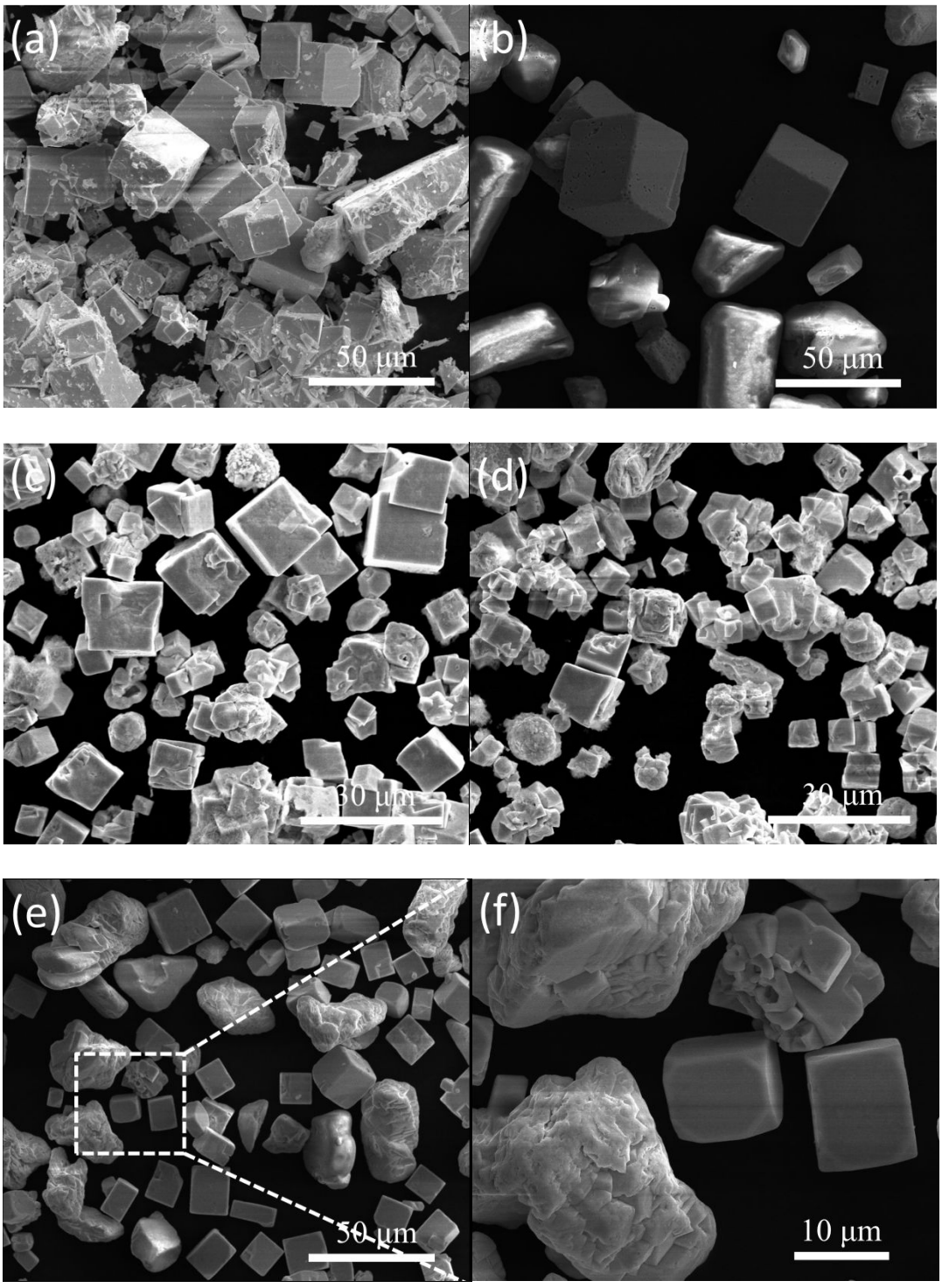


Figure S2 SEM graphs of urea-assistant synthesized KBBNO samples prepared with hydrothermal method. The adding amount of urea is (a) 0 g, (b) 1.5 g, (c) 1.7 g, (d) 1.8 g, (e and f) 1.9 g, respectively.

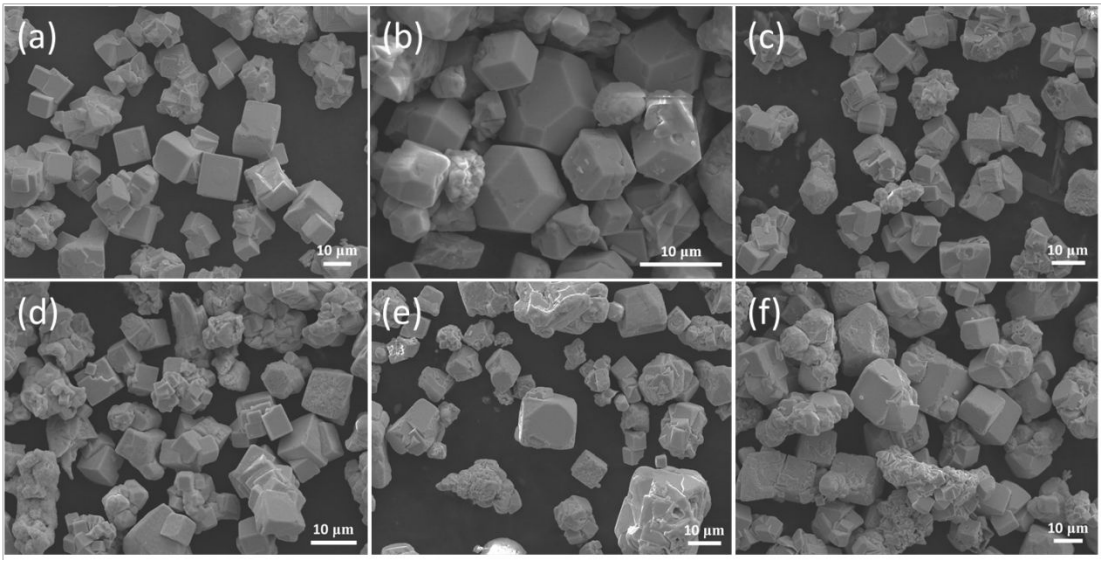


Figure S3 SEM graphs of NH_4Cl-assistant synthesized KBBNO samples with $BaCl_2$ as the only Ba source. The adding amount of NH_4Cl is (a) 0 g, (b) 0.2 g, (c) 0.4 g, (d) 0.6 g, (e) 0.8 g, and (f) 1.0 g, respectively.

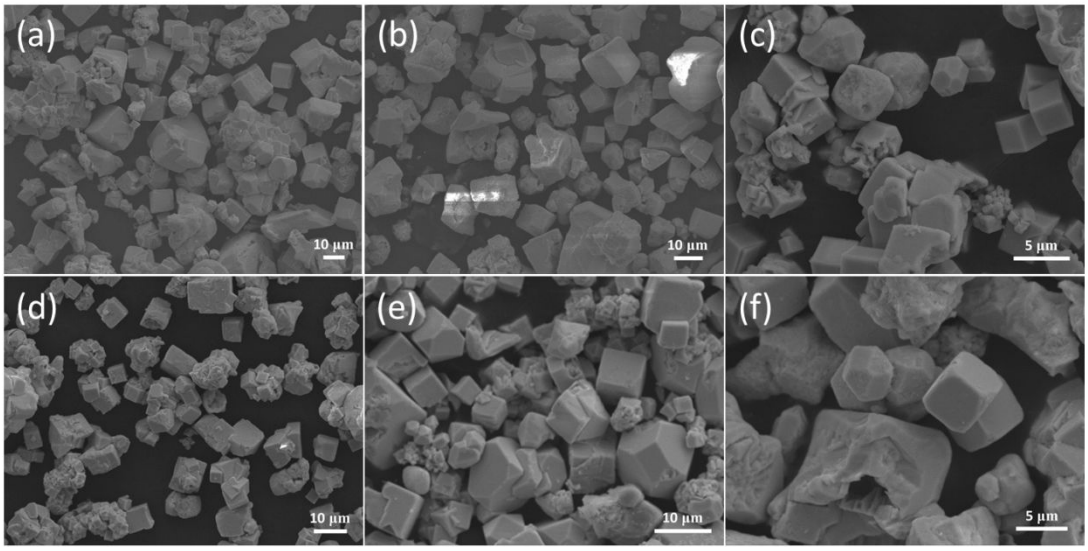


Figure S4 SEM graphs of NH_4Cl-assistant synthesized KBBNO samples with $Ba(NO_3)_2$ as the only Ba source. The adding amount of NH_4Cl is (a) 0 g, (b) 0.2 g, (c) 0.4 g, (d) 0.6 g, (e) 0.8 g, and (f) 1.0 g, respectively.

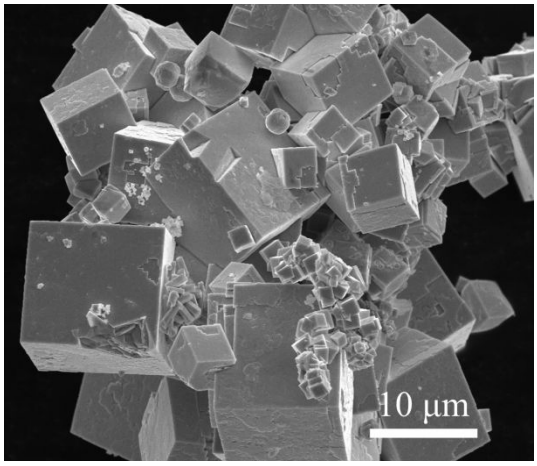


Figure S5 SEM graph of KBBNO crystal obtained with $Bi(NO_3)_3$ as the sole Bi-source.

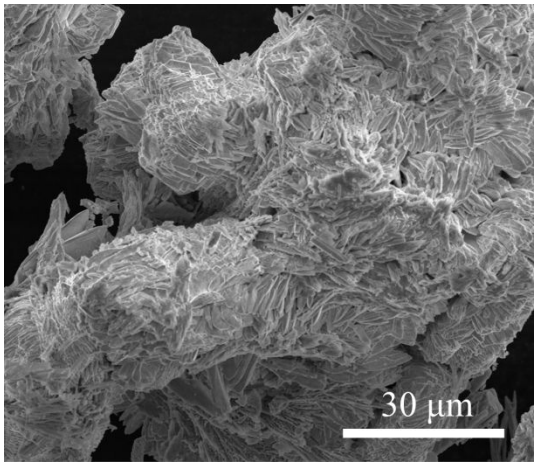


Figure S6 SEM graph of mixture of (oxy)hydroxides of Bi and Ba with $NaBiO_3$+$Ba(NO_3)_2$ as the reactant for Bi and Ba source, respectively.

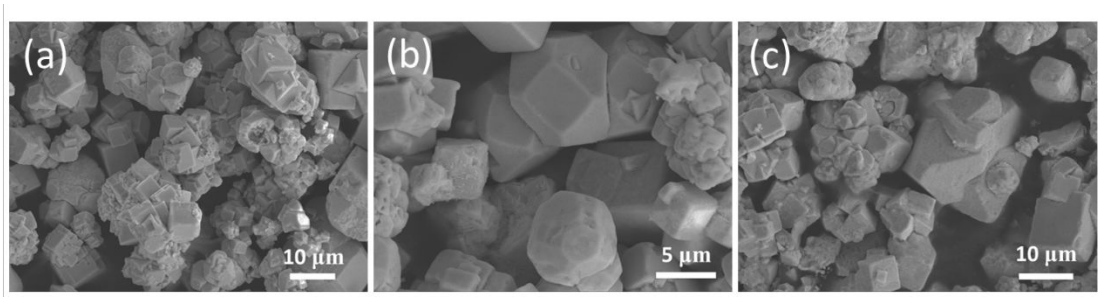
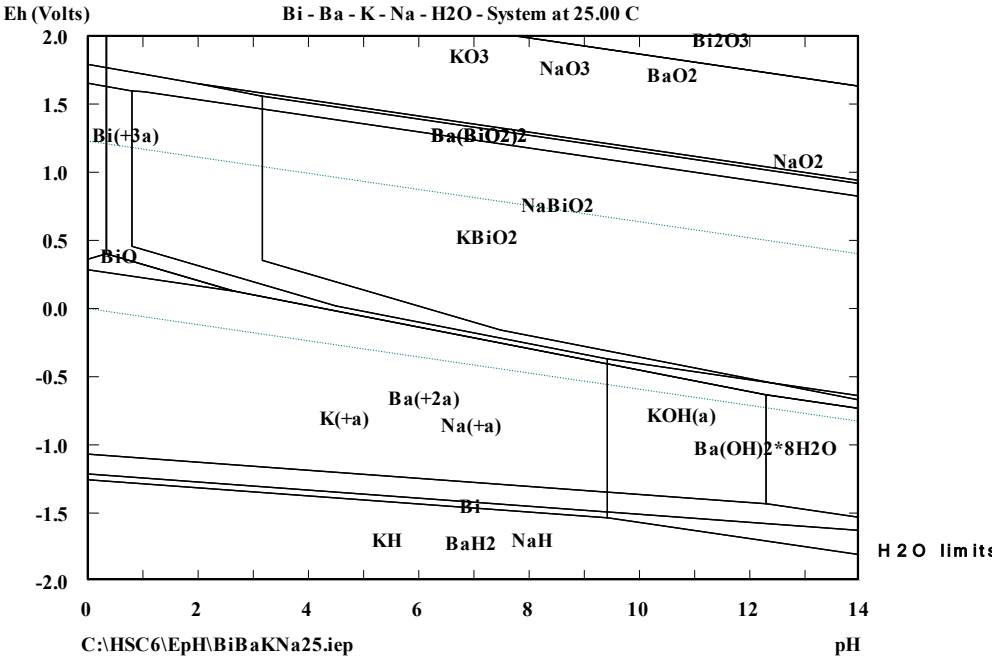
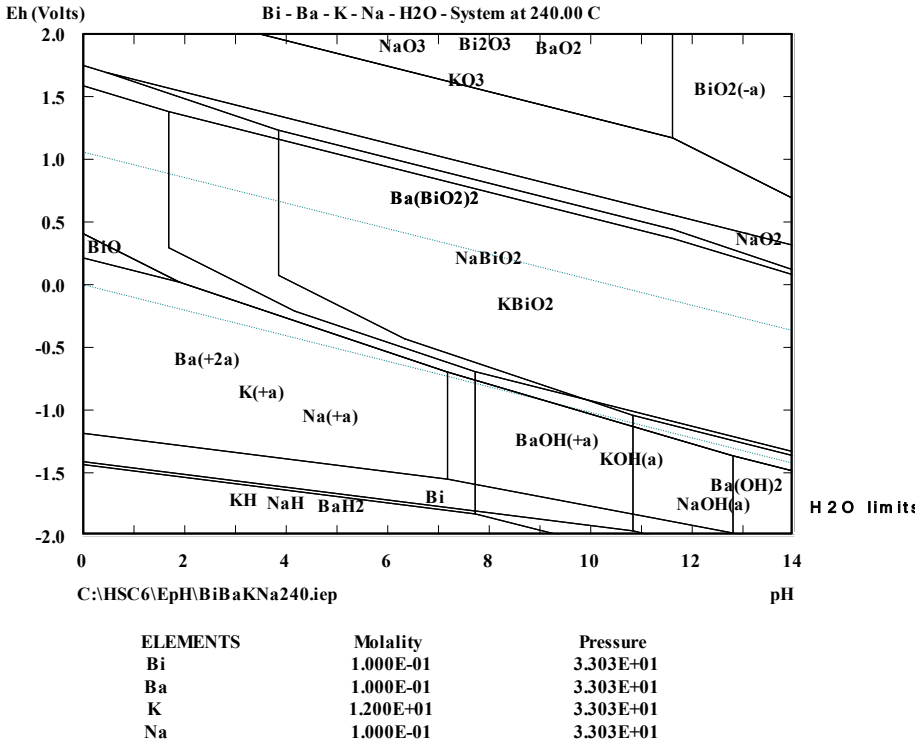


Figure S7 SEM graphs of KBBNO crystals with $BiCl_3$ as a co-source of (a) 10%, (b) 20%, and (c) 30% molar ratio in Bi(III)/(Bi(III)+Bi(V)), respectively.



ELEMENTS	Molality	Pressure
Bi	1.000E-01	1.000E+00
Ba	1.000E-01	1.000E+00
K	1.200E+01	1.000E+00
Na	1.000E-01	1.000E+00

Figure S8 Pourbaix diagram of the Bi-Ba-K-Na-H_2O system at the pressure of 1 bar and temperature of 25 ^{o}C.



ELEMENTS	Molality	Pressure
Bi	1.000E-01	3.303E+01
Ba	1.000E-01	3.303E+01
K	1.200E+01	3.303E+01
Na	1.000E-01	3.303E+01

Figure S9 Pourbaix diagram of the Bi-Ba-K-Na-H_2O system at the pressure of 33.03 bar and temperature of 240 ^{o}C.

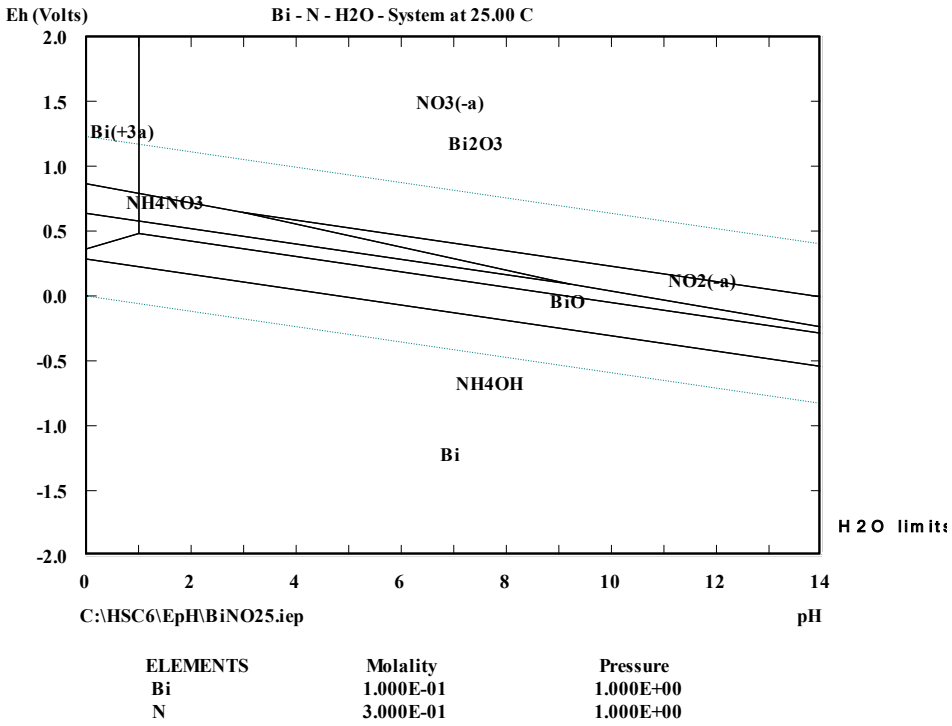
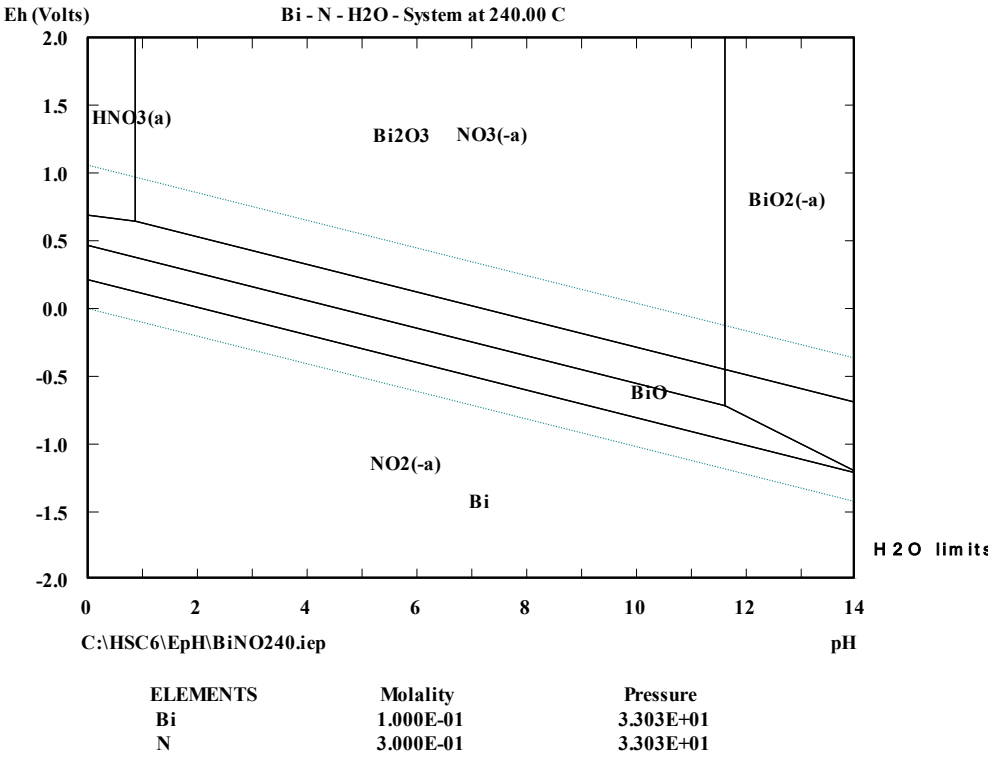


Figure S10 Pourbaix diagram of the Bi-N-H_2O system at the pressure of 1 bar and temperature of 25 ^{o}C.



ELEMENTS	Molality	Pressure
Bi	1.000E-01	3.303E+01
N	3.000E-01	3.303E+01

Figure S11 Pourbaix diagram of the Bi-N-H_2O system at the pressure of 33.03 bar and temperature of 240 ^{o}C.

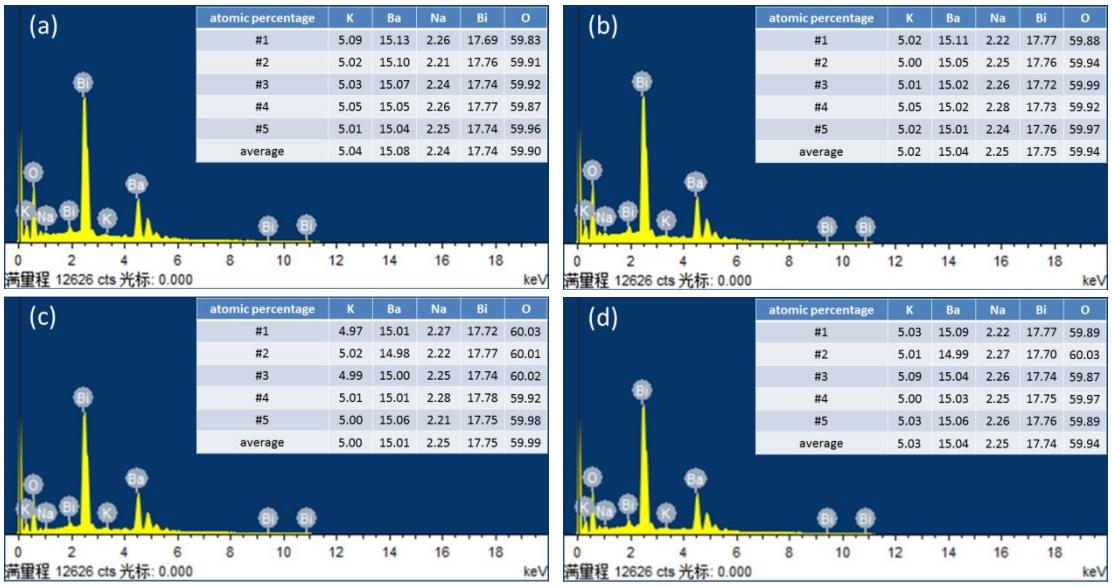


Figure S12 Energy dispersive spectroscopy (EDS) and atomic percentage of KBBNO crystal with (a) cubic, (b) truncated cube, (c) cuboctahedron and (d) truncated octahedral shape.

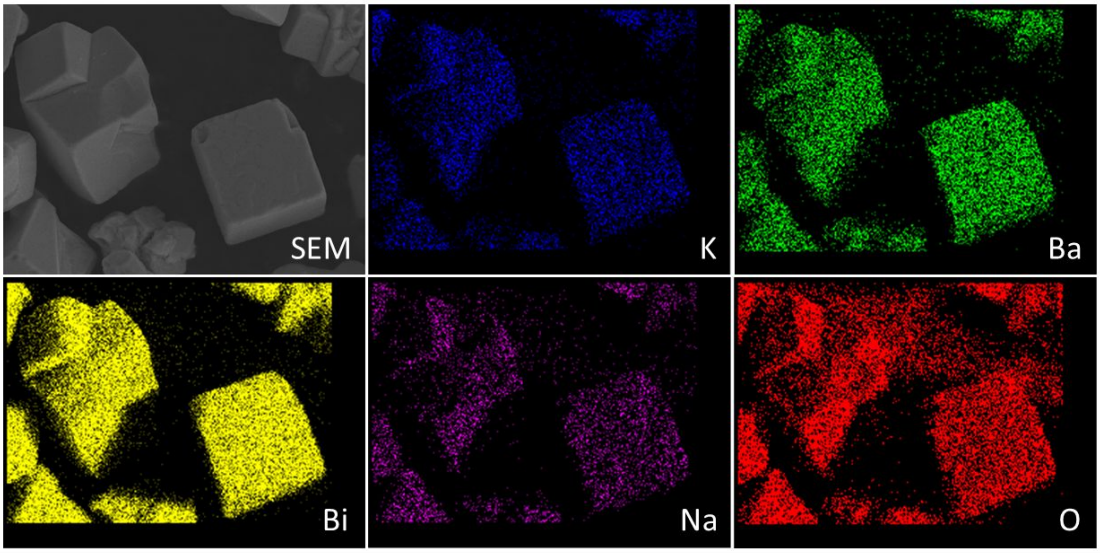


Figure S13 Elemental distribution of cubic shape KBBNO crystals with SEM graph and K, Ba, Bi, Na, O element, respectively collected according to energy dispersive spectroscopy (EDS) results.

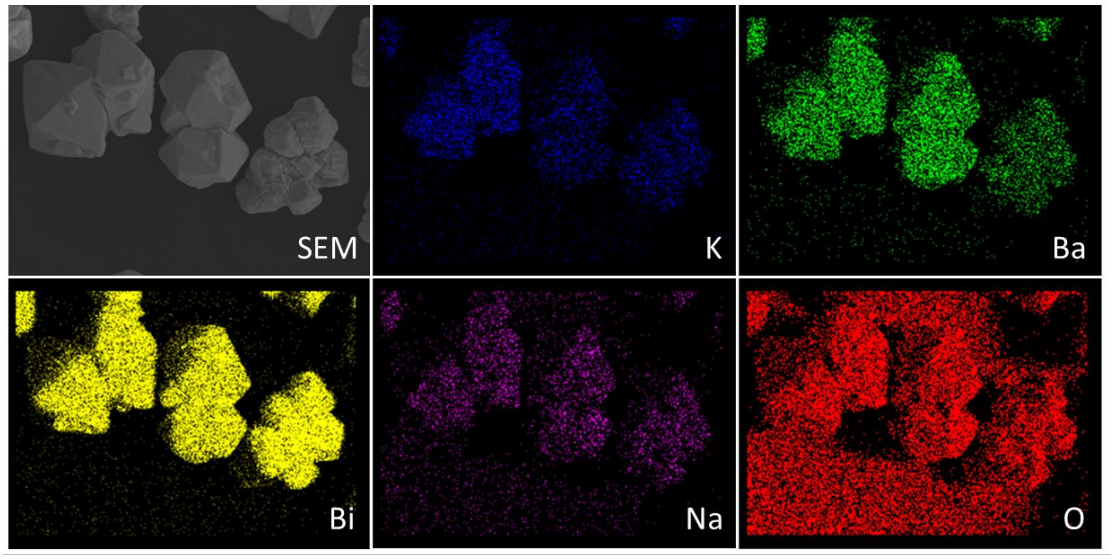


Figure S14 Elemental distribution of octahedral shape KBBNO crystals with SEM graph and K, Ba, Bi, Na, O element, respectively collected according to energy dispersive spectroscopy (EDS) results.

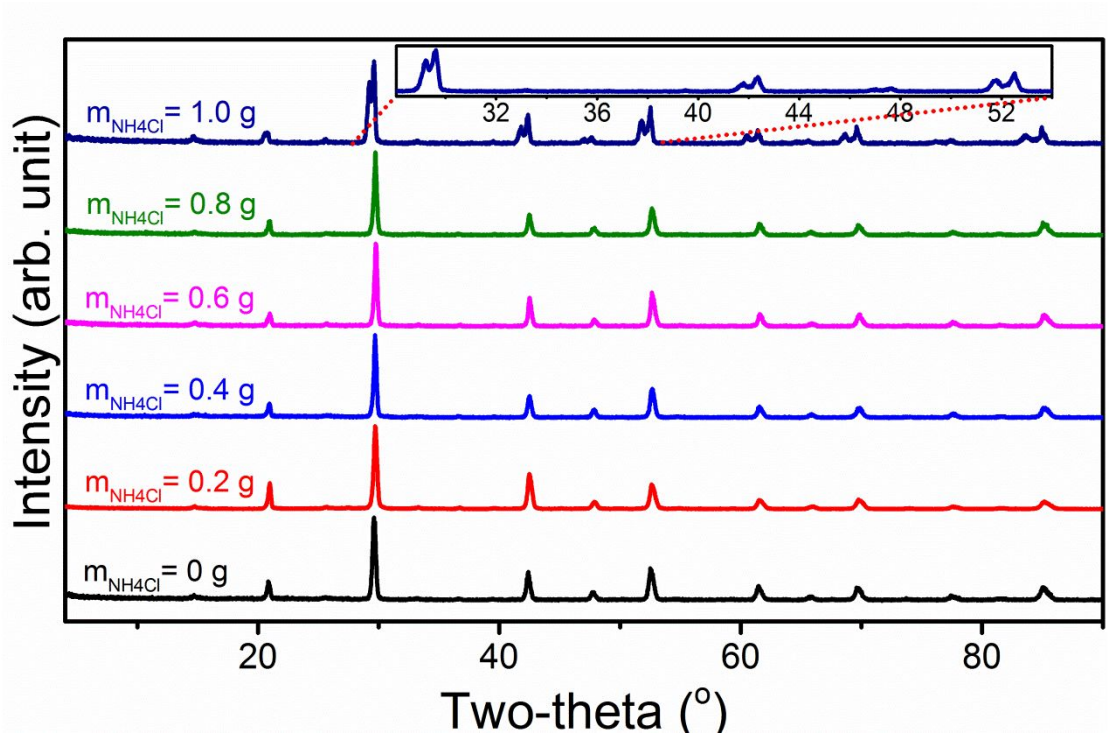


Figure S15 PXRD patterns of hydrothermally synthesized KBBNO crystals obtained in various NH_4Cl amount. Inset shows an enlarged view of the diffraction pattern when the NH_4Cl amount is 1.0 g.

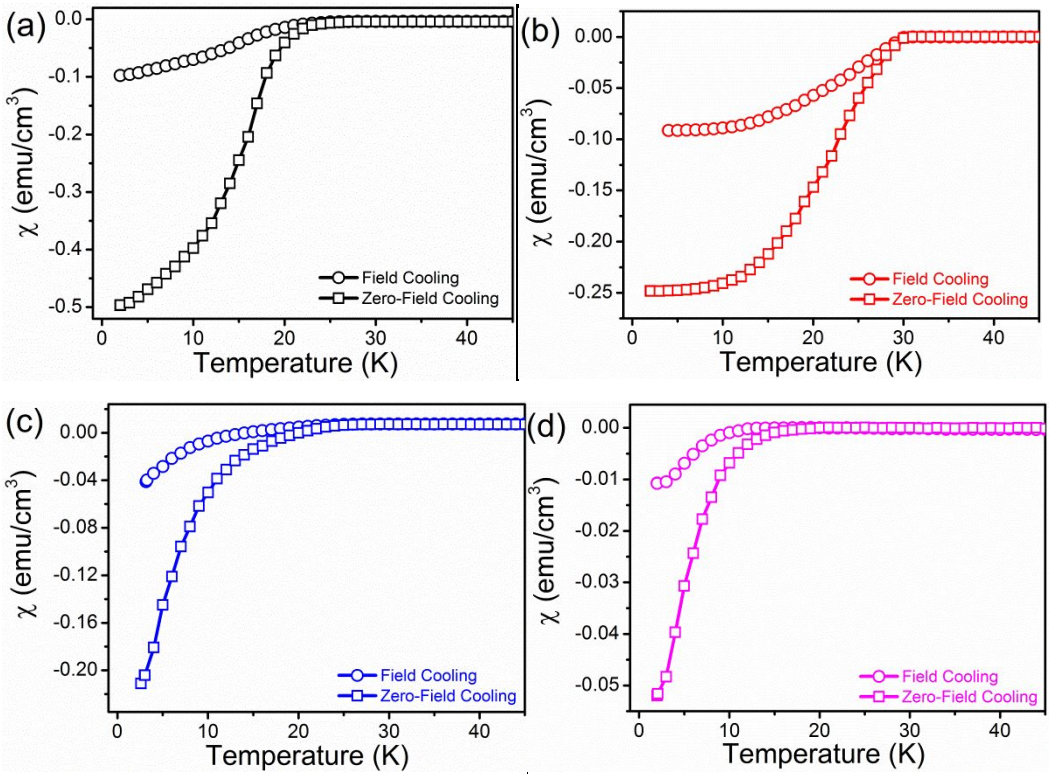


Figure S16 Temperature dependent magnetic susceptibility of various shapes of KBBNO samples measured in field cooling and zero-field cooling process in a magnetic field of 10 Oe: (a) cubic, (b) truncated cubic, (c) cuboctahedron, and (d) truncated octahedron, respectively.

References

[1] Rubel, M. H. K.; Takei, T.; Kumada, N.; Ali, M. M.; Miura, A.; Tadanaga, K.; Oka, K.; Azuma, M.; Yashima, M.; Fujii, K.; Magome, E.; Moriyoshi, C.; Kuroiwa, Y.; Hester, J. R.; Avdeev, M. Hydrothermal Synthesis, Crystal Structure, and Superconductivity of a Double-Perovskite Bi Oxide. *Chem. Mater.* **2016**, *28*, 459-465.

[2] Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff. W. M. UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations. *J. Am. Chem. Soc.* **1992**, *114*, 10024.