Supplementary Materials

Thermal Stability and Non-Linear Optical and Dielectric Properties of Lead-Free $K_{0.5}Bi_{0.5}TiO_3$ Ceramics

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A. Thermal stability

The chemical stability of the K_2CO_3, TiO_2, and Bi_2O_3 precursors was examined before synthesizing $K_{0.5}Bi_{0.5}TiO_3$ ceramics. Thermogravimetric analysis showed that titanium (IV) and bismuth (III) oxides are stable in the temperature range of 25 ÷ 1000 °C, while potassium carbonate starts to release the absorbed water molecules at 100 °C (Figure S1). Heating anhydrous K_2CO_3 above 800 °C enforces its decomposition, which is still incomplete at 1000 °C. The K_2CO_3 findings are consistent with the literature reports [S1, S2], indicating the potassium carbonate decomposition temperature under air is about 891 ÷ 896 °C and strongly depends on the heating rate. Thus, the TG analysis was considered when fixing the synthesis conditions of KBT ceramics.

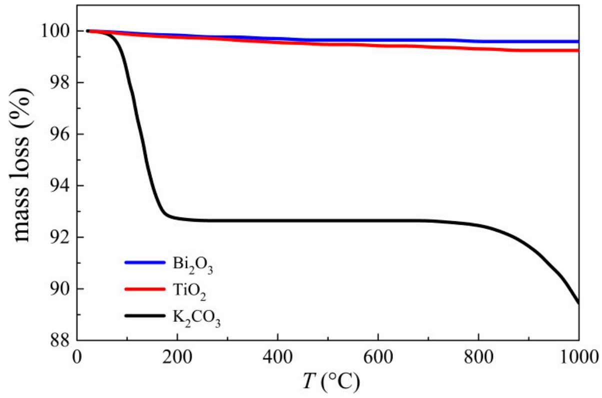
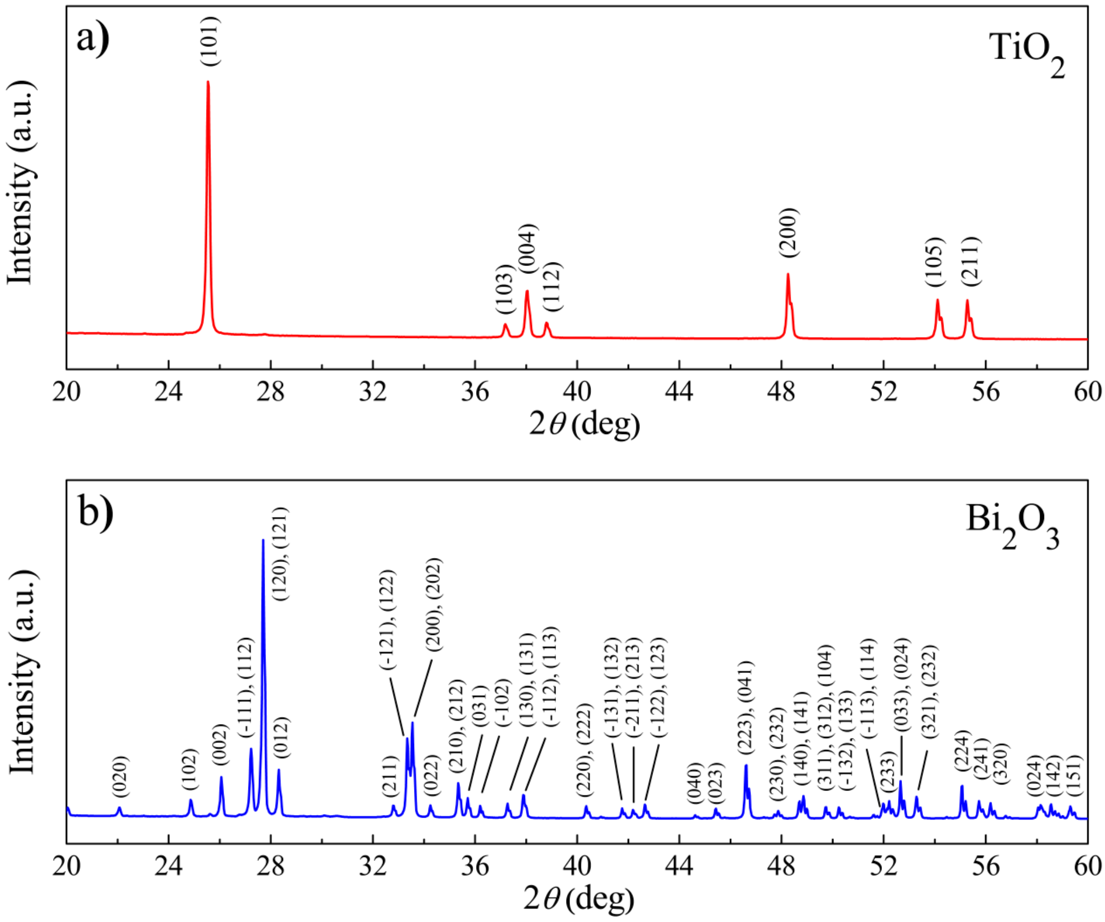


Figure S1. Thermogravimetric analysis of K_2CO_3, TiO_2, and Bi_2O_3 at ambient conditions.

B. Structural characterization

Figure S2 shows the X-ray diffraction patterns for precursors in the 2θ range of 20º ÷ 60º. XRD data matches the following crystallographic cards: ICDD PDF4+; 00-004-0477 for TiO_2, ICDD PDF4+; 01-072-0398 for Bi_2O_3, and ICDD PDF4+; 04-014-3875 for K_2CO_3, respectively.



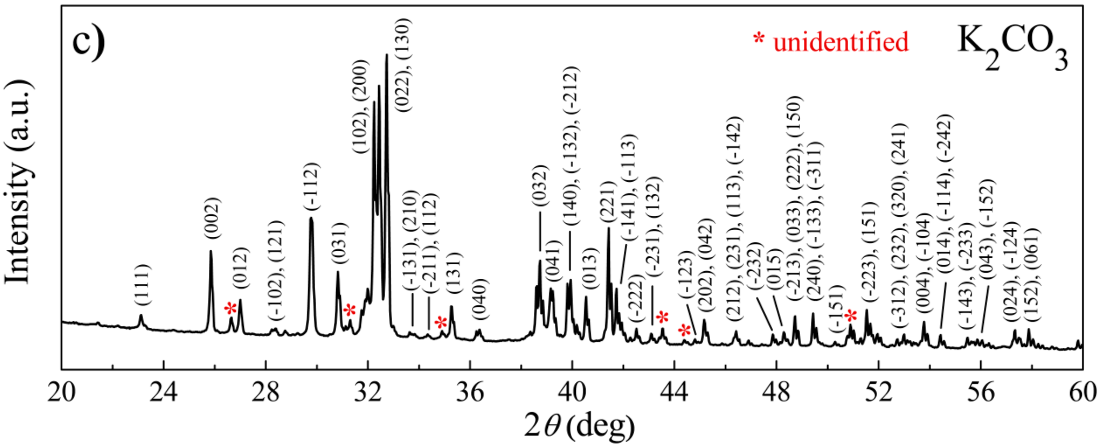


Figure S2. X-ray diffraction patterns of (**a**) tetragonal TiO_2 and monoclinic (**b**) Bi_2O_3, (**c**) K_2CO_3 precursors.

X-ray diffraction patterns collected for TiO_2 (Fig. S2a) and Bi_2O_3 (Fig. S2b) precursors show pure phases; nevertheless, it is possible to recognize some unknown lines for K_2CO_3 (Fig. S2c).These results should be considered when fabricating KBT since a foreign admixture can modify calcined or sintering temperature.

C. Optical vibrational spectroscopy

Table S1. Experimental and theoretical vibrational bands for 2x2x2 supercell of KBT.

Experiment		**DFT calculations**			
ν_{IR} [cm^{-1}]	ν_{RS} [cm^{-1}]	ν [cm^{-1}]	ν_{IR} [cm^{-1}]	ν_{RS} [cm^{-1}]	**Remarks**
819	819	816 812 802 802 748		803	ν_s(Ti–O) stretching
656	638	698 698 618 609		699 618	ω(O–Bi–O) wagging ν_s(Ti–O–Ti) stretching
564		595 588 588 579 579	578 507		ν_{as}(Ti–O–Ti) $\nu_s$stretching
540	528	540 533 508 508 503 496 491 484 481 476 476 467 464 462 447 447 444 438 438 435 429		537 493 435	δ(O–Ti–O) bending deformation modes ν_{as}(Ti–O–Ti) $\nu_s$stretching
410		404 401 401 400 384 383 383 372	383		skeletal bending deformations
389		367 367 360	358		
	343	348 348 344 344 343 342 333 333 332 322.7 327.1 327 327		360 301	
324		308 304 300 300 299.7 295 295 295 282 275 271 266 261 256 256 255	303		skeletal bending deformations
275	273	240 231 230 230	230	230	skeletal bending deformations
228		183 183 180 174 174 170 169 168.6 168 168 166 163 162 162 159	184		torsion modes
	206	207 204 201 201 197		197	torsion modes
195					
	142	149 149 148 147 143 143 116		114	

		108 108 103 91 86 84 84	107	lattice modes (ν_L)
	66	57 57 47 47		
		0 0 0		acoustic modes

References

[S1] Zhang, J.; Qi, M.; Zhang, G.; Hu, H.; Xie, L.; Ma, X. Co - production of hydrogen and fibrous carbons by methane decomposition using K_2CO_3/carbon hybrid as the catalyst, *International Journal of Hydrogen Energy* **2017**, 42, 11047 – 11052, https://doi.org/10.1016/j.ijhydene.2017.03.113.

[S2] Lehman, R.L.; Gentry, J.S.; Glumac, N.G. Thermal stability of potassium carbonate near its melting point, *Thermochimica Acta* **1998**, 316(1), 1 – 9, https://doi.org/10.1016/S0040-6031(98)00289-5.