Electronic Supplementary Information

Supplementary figures and tables

Fig. S1. A sequence of Laue scan patterns across the sample. (**a-d**) at 4 different sites of the same plane of the sample(without tilting it), (**e-g**) at 3 different planes of the same sample by tilting it.
Fig. S2. Photographs of 0.375at.% Mn-doped KNN-based samples sintered at 1090 °C for 5–48 h.
Fig. S3. Photo of piezoelectric constant d_{33} value measured by two different d_{33} meters at room temperature for 0.375 at.% MnO_2-doped KNN-based single crystal.
Fig. S4. The degradation of d_{33} versus time for the Mn-doped KNN-based single crystal.
Fig. S5. Room temperature ferroelectric P-E loops of (1-x)(99.6KNN-0.4LB)-$x$$MnO_2$ crystals. (a) x = 0, (b) x = 0.375%.
Fig. S6. (a)Room temperature powder XRD patterns (with Co-Kα radiation) of (1-x)(99.6KNN-0.4LB)-$x$$MnO_2$ single crystal samples and (**b**)expanded XRD patterns at 2θ = 50-57 °.

Table S1. Comparison of piezoelectric and ferroelectric properties among developed piezoelectric ceramics and crystals.

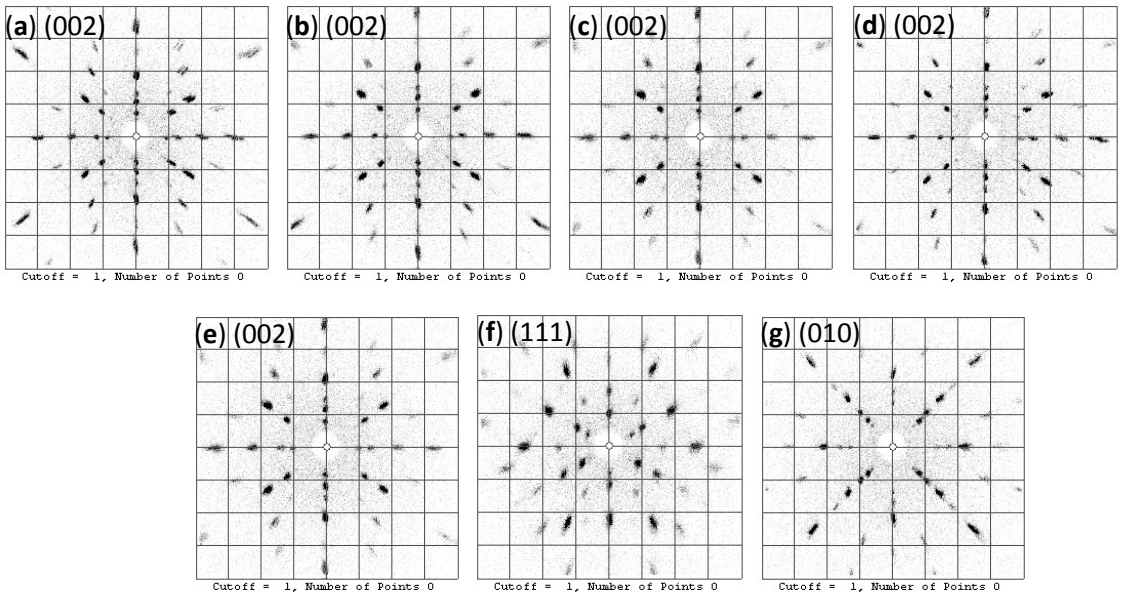

Fig. S1. A sequence of Laue scan patterns across the sample. (**a-d**) at 4 different sites of the same plane of the sample(without tilting it), (**e-g**) at 3 different planes of the same sample by tilting it.

Fig. S2. Photographs of 0.375at.% Mn-doped KNN-based samples sintered at 1090 °C for 5–48 h.

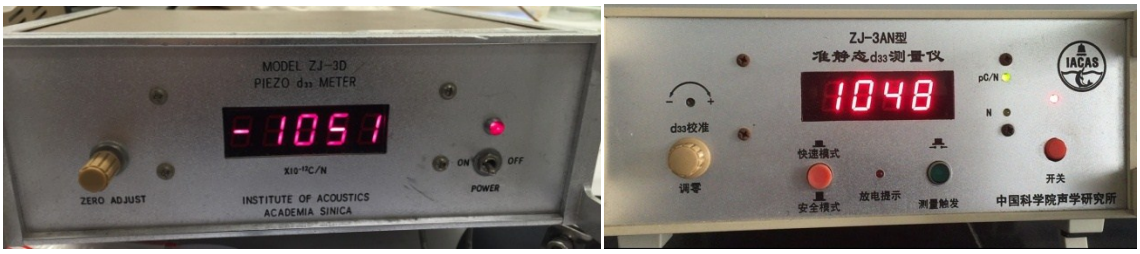

Fig. S3. Photo of piezoelectric constant d_{33} value measured by two different d_{33} meters at room temperature for 0.375 at.% MnO_2-doped KNN-based single crystal.

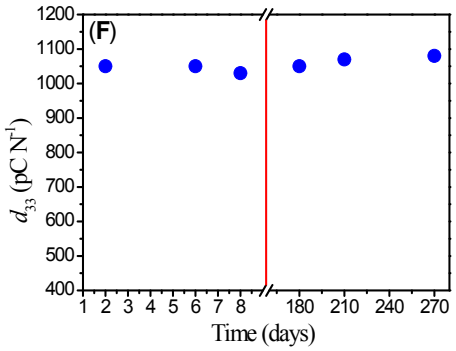

Fig. S4. The degradation of d_{33} versus time for the Mn-doped KNN-based single crystal.

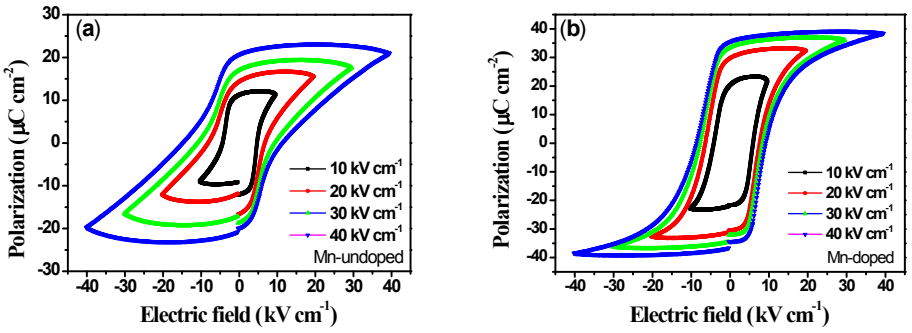

Fig. S5. Room temperature ferroelectric P-E loops of (1-x)(99.6KNN-0.4LB)-$x$$MnO_2$ crystals. (**a**) x = 0, (**b**) x = 0.375%.

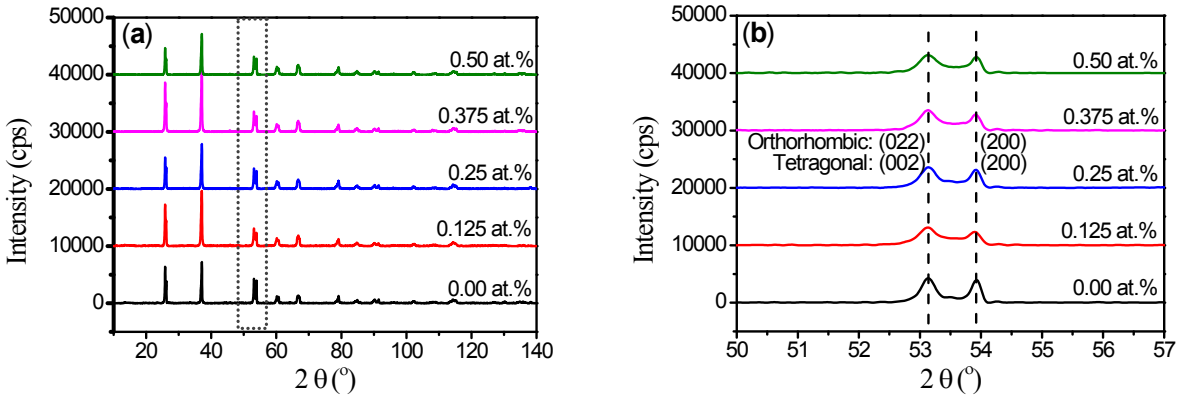

Fig. S6. (**a**)Room temperature powder XRD patterns (with Co-Kα radiation) of (1-*x*)(99.6KNN-0.4LB)-*x*MnO_2 single crystal samples and (**b**)expanded XRD patterns at 2θ = 50-57 °.

Table S1. Comparison of piezoelectric and ferroelectric properties among developed piezoelectric ceramics and crystals.

Composition	d_{33}(pC N^{-1})	ε_r	T_c(°C)	Growth method
KNN-LB: Mn crystal	1050	675	403	SFSSCG(this work)
KNL4Ncrystal	689	~450	432	SFSSCG[32]
KNN-LB crystal	260	~3000	405	SFSSCG[11]
KNNTL: Mn crystal	545	362	235	TSSG[25]
$KNNLiNbO_3$ crystal	405	185	426	Bridgeman[21]
KNN: Mn crystal	270	730	416	Flux[22]
Textured LF4T ceramic	416	1570	253	Textured process[6]
KNNS-BNKZ ceramic	490	>2000	227	Ceramic process[13]
KNNS-BZ-BKH	570	/	~190	Ceramic process[14]