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Abstract

The piezoelectric property of [001]-oriented 0.5%MnO2-(K0.5Na0.5)NbO3 (Mn-KNN) crystals was studied as a function of domain size, being poled with different electric fields at 205 C (above orthorhombic to tetragonal phase transition temperature To-t). The piezoelectric coefficients d33 and relative dielectric constants er were found to increase from 270 pC/N to 350 pC/N and 730 to 850 with the domain size decreasing from 9 to 2 lm, respectively. The thermal stability of piezoelectric property was investigated, where the d33 value for [001]-oriented Mn-KNN crystals with domain size of 2 lm was found to decrease to 330 pC/N at depoling temperature of 150 C, with minimal variation of 6%. The results reveal that domain size engineering is an effective way to improve the piezoelectric properties of Mn-KNN crystals.

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Domain size engineering in 0.5%MnO_2-($K_{0.5}Na_{0.5}$)NbO_3 lead free piezoelectric crystals

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The piezoelectric property of [001]-oriented 0.5%MnO_2-($K_{0.5}Na_{0.5}$)NbO_3 (Mn-KNN) crystals was studied as a function of domain size, being poled with different electric fields at 205 °C (above orthorhombic to tetragonal phase transition temperature $T_{o\text{-}t}$). The piezoelectric coefficients d_{33} and relative dielectric constants ε_r were found to increase from 270 pC/N to 350 pC/N and 730 to 850 with the domain size decreasing from 9 to 2 μm, respectively. The thermal stability of piezoelectric property was investigated, where the d_{33} value for [001]-oriented Mn-KNN crystals with domain size of 2 μm was found to decrease to 330 pC/N at depoling temperature of 150 °C, with minimal variation of ~6%. The results reveal that domain size engineering is an effective way to improve the piezoelectric properties of Mn-KNN crystals. © *2015 AIP Publishing LLC*.
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I. INTRODUCTION

Sodium potassium niobate ($KNbO_3$-$NaNbO_3$) based solid solutions have been widely studied for the potential candidates of lead free ferroelectric materials due to the good piezoelectric properties and high Curie temperature.[1–13] In order to further enhance the piezoelectric properties, different dopants, such as Li^+, Ta^{5+}or single crystal growths have been considered,[3–7] in which the 0.5%MnO_2-($K_{0.5}Na_{0.5}$)NbO_3 (Mn-KNN) single crystals show higher piezoelectric/dielectric properties than those of pure ($K_{0.5}Na_{0.5}$)NbO_3 material, with comparable orthorhombic to tetragonal phase transition temperature and Curie temperature.[8–12] Domain size engineering is another important approach for obtaining enhanced piezoelectric properties in lead free piezoelectric single crystals.[13–18] The experimental results revealed that the enhanced piezoelectric coefficient was associated with high domain wall density, for example, the piezoelectric coefficient d_{31} was found to increase from −98 pC/N to −230 pC/N with domain sizes of 40 μm and 5.5 μm in $BaTiO_3$ crystals,[15] while the piezoelectric coefficient d_{33} was predicted to be greatly increased with nano-size domain configuration.[17] The theoretical simulation indicated that the piezoelectric coefficient was enhanced by reducing domain size, while an enhancement of piezoelectric coefficient in $BaTiO_3$ crystals with 90° twinned domain configuration was predicted using Ginzburg-Landau-Devonshire model.[16,17] In addition, the piezoelectric coefficient d_{33} and relative dielectric constant ε_r of [111]-poled tetragonal PIN-PMN-PT single crystals were reported to increase from 450 pC/N and 3000 to 1630 pC/N and 13 800 with the domain size of 50 μm and 500 nm, using domain size engineering technique, respectively.[18]

In the present work, the piezoelectric/dielectric properties were investigated in the domain size engineered [001]-oriented Mn-KNN lead free single crystal. As an experimental schedule, first, domain structures were *in-situ* observed in Mn-KNN single crystal under various electric fields at 205 °C and 25 °C. Second, the crystal samples were poled using field-cooled method and their piezoelectric/dielectric properties were measured. Finally, the temperature stability of electrical properties of the domain size engineered samples was evaluated.

II. EXPERIMENTAL

The 0.5%MnO_2-($K_{0.5}Na_{0.5}$)NbO_3 (Mn-KNN) crystals used in present work were grown by slow-cooling method.[12] The sizes of crystal samples for domain observation and electrical property measurements are 3 × 3 × 0.05 mm^3 and 3 × 3 × 0.5 mm^3, respectively. Gold electrodes were sputtered on the large surfaces of the samples. The domain structure was subsequently investigated using a polarizing light microscope (Olympus BX51) with heating-cooling stage (LINKAM). The piezoelectric coefficient (d_{33}) was measured using a piezo-d_{33} meter (ZJ-4A). Unipolar strain-electric field (S-E) was measured at 1 Hz using a modified Sawyer-Tower circuit by a lock-in amplifier (Stanford Research System, Model SR830). The high-field piezoelectric coefficient (d_{33}^*) was determined from the slope of S-E curve at the driving field of 10 kV/cm. The relative dielectric constant was calculated from the capacitance measured by an HP4284A multi-frequency LCR meter at 1 kHz. During thermal depoling experiments, the poled samples with gold electrodes were short-circuited and put in the furnace for 1 h at various high temperatures, then cooled down to room temperature and measured the d_{33} values using the piezo-d_{33} meter.

The various domain sizes were controlled by domain size engineering approach using field-cooled method, as summarized in Table I. First, the [001]-oriented samples were heated to 205 °C (>$T_{o\text{-}t}$), then electric fields of 0 to 18 kV/cm were applied, finally electric field was remained

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TABLE I. The piezoelectric/dielectric properties in [001]-oriented Mn-KNN crystals with different domain configuration.

Sample	Poling condition	Domain pattern	Domain size (μm)	$d_{33(\mathrm{meter})}$ (pC/N)	d^*_{33} (pm/V)	ε_r	tanδ (%)	$T_{\mathrm{o\text{-}t}}$ (°C)	T_c (°C)
Mn-KNN	120 °C/20 kVcm^{-1}	laminar	9	270	250	730	3	193	416
	205 °C/6kVcm^{-1}	laminar	6.5	285	260	750	3	193	416
	205 °C/10 kVcm^{-1}	laminar	4	300	290	780	3	193	416
	205 °C/12 kVcm^{-1}	twinned	2.5	320	320	800	3.5	193	416
	205 °C/18 kVcm^{-1}	twinned	2	350	360	850	3.5	193	416
KNN[a]	120 °C/20 kVcm^{-1}	laminar	25	160	/	240	2	208	423

[a]Reference 2.

and the temperature was decreased at a rate of 1 °C/min. Fig. 1(a) shows the experimental configuration to observe domain structures with applied electric field and the crossed polarizer/analyzer (P/A) pair. Figs. 1(b) and 1(c) show the spontaneous polarization (P_s) in orthorhombic (O-phase) and tetragonal (T-phase) phase of Mn-KNN crystals with applied electric field along [001] direction, respectively. With [001] applied electric field, new domain patterns with different domain sizes were fabricated in the Mn-KNN crystals. In order to optimize the poling condition, *in-situ* observation of domain structure has been carried out at various temperatures and electric fields.

III. RESULTS AND DISCUSSION

Fig. 2 shows the domain pattern of [001]-oriented Mn-KNN crystals as a function of temperature. Two types of domains were presented in the sample at room temperature, as shown in Fig. 2(a), one with domain walls parallel to [100] directions, the other tweed domain structure with domain walls parallel to [110], indicating the coexistence of orthorhombic phase 60°, 120°, and 90° domains. Upon increasing temperature, the ferroelectric phase transformation from orthorhombic to tetragonal was found to occur at 187 °C, where a laminar tetragonal 90° domain structure with boundaries along the [110] direction was observed, as shown in Fig. 2(b). The mixed tetragonal phase and orthorhombic phase domains persisted at 187.5 °C, as shown in Fig. 2(c). At 250 °C, the clear laminar tetragonal domain structure with size of 7 μm was observed, as given in Fig. 2(d).

Fig. 3 shows the tetragonal domain structure in [001]-oriented Mn-KNN crystals at different electric fields along [001] direction at 205 °C (above the polymorphic phase transition temperature $T_{\mathrm{o\text{-}t}}$). It was found that higher electric field favor smaller domain size, meanwhile the domain pattern remained the same. The domain size was about 7 μm in tetragonal Mn-KNN crystals at zero electric field, as shown in Fig. 3(a), decreasing to about 2.5 μm, 1.7 μm, and 1.5 μm with electric field strengths at 6 kV/cm, 12 kV/cm, and 18 kV/cm, as shown in Figs. 3(b)–3(d), respectively. As shown in Figs. 4(a)–4(d), the samples with domain sizes of 9, 6.5, 2.5, and 2 μm were obtained when the samples were cooled down to room temperature, corresponding to the domain structures shown in Fig. 3. Based on the domain

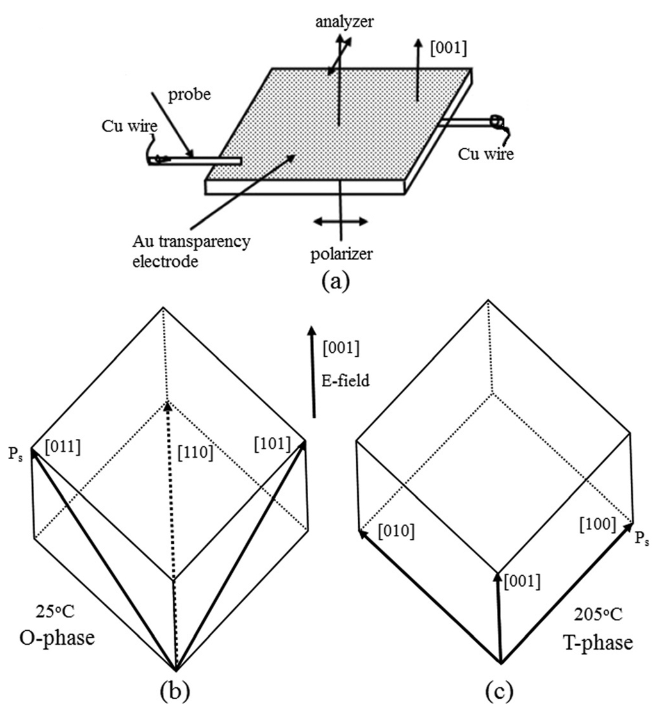

FIG. 1. (a) Schematic diagram for domain observation under electric field using a polarizing light microscope, spontaneous polarization in (b) orthorhombic and (c) tetragonal Mn-KNN crystals under applied electric field along [001] direction.

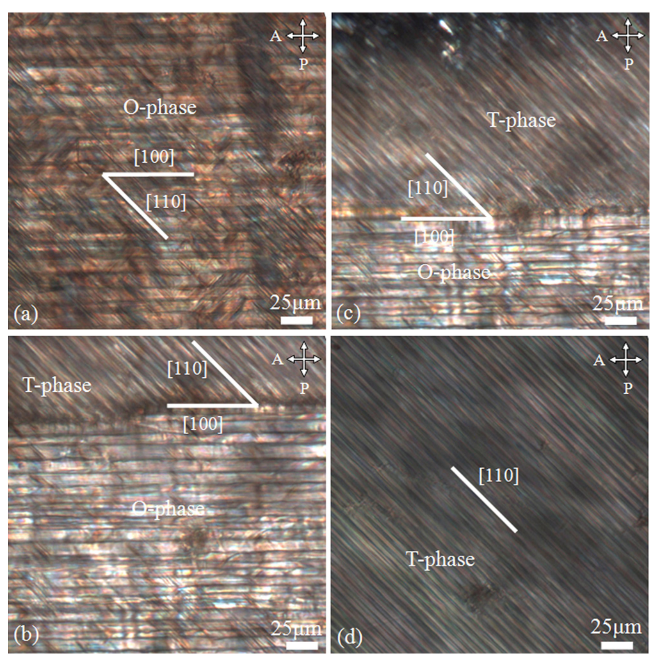

FIG. 2. Real-time domain observation in [001]-oriented Mn-KNN crystals at (a) 25 °C, (b) 187 °C, (c) 187.5 °C, and (d) 250 °C.

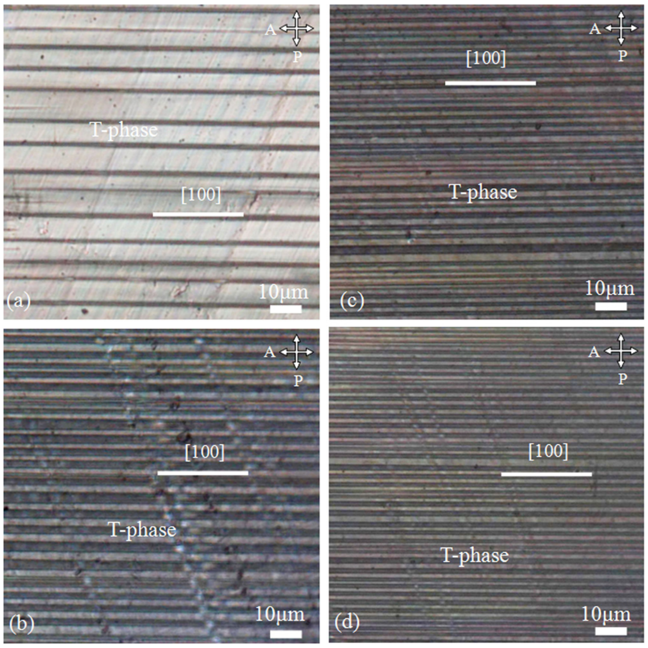

FIG. 3. Real-time domain observation in [001]-oriented Mn-KNN crystals at 205 °C under various electric field applied along [001] direction (a) E = 0 kV/cm, (b) E = 6 kV/cm, (c) E = 12 kV/cm, and (d) E = 18 kV/cm.

observation results, the optimum poling condition for achieving different domain sizes and domain patterns, including the poling temperature and applied electric field strength, were summarized in Table I. It is interesting to note that the laminar domain pattern changed to twinned domain structure when the poling electric field was above 10 kV/cm, with the temperature decreasing from 205 °C to room temperature, as shown in Figs. 4(c) and 4(d), which was reported to account for the enhanced piezoelectric properties.[17]

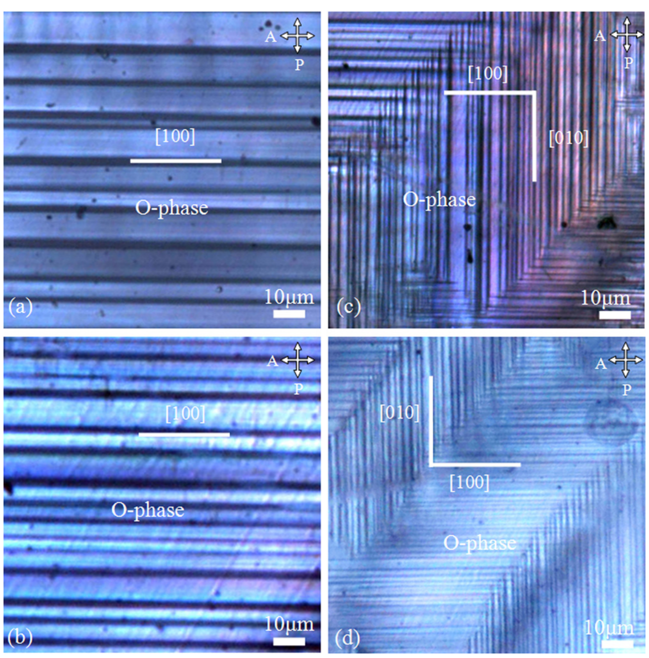

FIG. 4. Domain patterns of [001]-oriented Mn-KNN crystal with various domain sizes (a) 9 μm, (b) 6.5 μm, (c) 2.5 μm, and (d) 2 μm.

Figs. 5(a)–5(e) show the unipolar strain behavior of Mn-KNN crystals at a field of 10 kV/cm for samples with average domain sizes of 9, 6.5, 4, 2.5, and 2 μm, respectively. The high-field piezoelectric coefficient d_{33}^* calculated from the strain-field curve was found to increase with decreasing the domain size, being 360 pm/V for samples with average domain size of 2 μm. It can be seen that the enhancement of piezoelectric coefficient d can be partly attributed to the increase of relative dielectric constant, since the coefficient d of perovskite ferroelectrics is proportional to $PQ\varepsilon$ (P is spontaneous polarization, Q is electrostrictive coefficient).[19] In addition, the orthorhombic to tetragonal phase transition temperature and Curie temperature were found to maintain the same values with decreasing the domain size from 9 to 2 μm, as shown in Table I.

The piezoelectric coefficients d_{33} for [001]-oriented Mn-KNN crystals as a function of domain size are shown in Fig. 6. Similar with the simulation in Ref. 18, the exponential decay function is used to fit the experimental data, and the relationship between the piezoelectric coefficient and domain size follows the formula:

$$d_{33} = 250 + 320\exp(-W_d/1.6),$$

where W_d is defined as domain size (width). From the formula, the d_{33} value would be significantly increased from 270pC/N to 550pC/N with the domain size decreasing from 9 μm to 0.1 μm, below which, the d_{33} value will be saturated.

It was generally accepted that the increased non-180° ferroelastic domain wall density was the dominant factor to

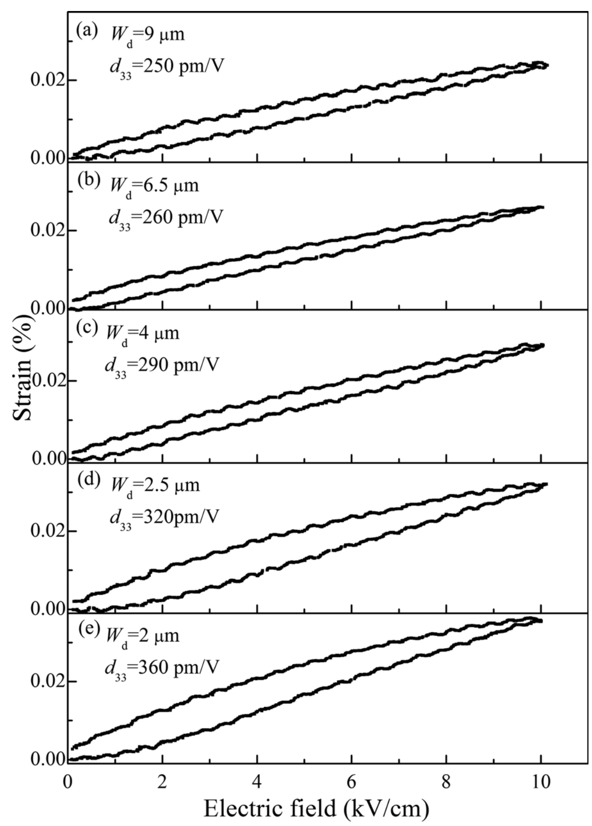

FIG. 5. Unipolar strain in [001]-oriented Mn-KNN crystal with different domain size (W_d) (a) 9 μm, (b) 6.5 μm, (c) 4 μm, (d) 2.5 μm, and (e) 2 μm.

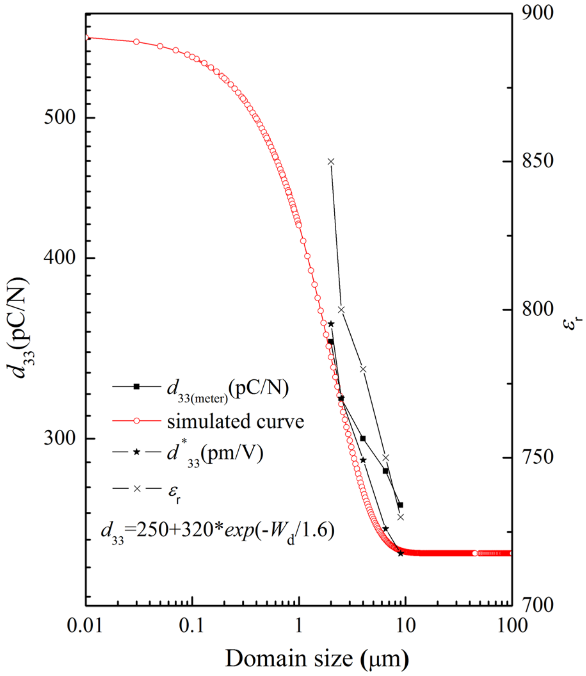

FIG. 6. The piezoelectric coefficient d_{33} and relative dielectric constant ε_r as a function of domain size (W_d) in [001]-oriented Mn-KNN crystal.

the enhanced piezoelectric property in domain size engineered $BaTiO_3$ single crystals.[15] In addition, the simulation data in Ref. 17 also revealed that the high density of 90° twinned domain boundaries accounted for the improved piezoelectric coefficients. In present work, experimental results revealed that the enhanced piezoelectric coefficients were associated with the domain size decreasing. However, as a concomitant phenomenon, the domain wall thickness became thinner with smaller domain size. Thus, from the viewpoint of free energy, the domain state will be unstable in the domain size engineered samples with fine domain size. However, the domain wall thickness cannot be exactly measured by polarizing light microscope because of the misalignment between light beam and domain walls. In classic theory, the relationship between domain wall thickness and temperature was predicted as[20,21]

$$W_t \propto (T - T_c)^{-1},$$

where W_t is defined as domain wall thickness. The domain wall thickness becomes larger when the temperature is far above Curie temperature (T_c). The domain wall thickness will be monotonically increased with domain wall energy density increase as a function of temperature from room temperature to O-T polymorphic phase transition temperature. That is to say, the domain state in domain size engineered Mn-KNN crystals is unstable with increasing temperature.

In order to evaluate the thermal stability of the piezoelectric properties for [001]-oriented Mn-KNN crystals with various domain size, the thermal depoling on piezoelectric coefficient (d_{33}) with domain sizes of 9, 6.5, and 2 μm were performed and the results are given in Fig. 7. For the sample with domain size of 2 μm, the value of d_{33} slightly decreased from 350pC/N to 330pC/N at depoling temperature of 150 °C, above which, the value was sharply decreased to 250 and

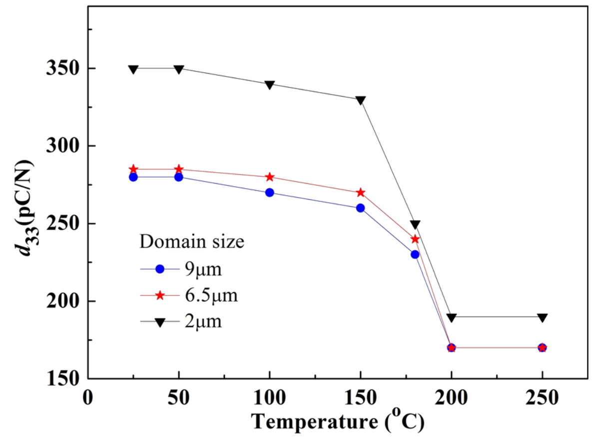

FIG. 7. Thermal depoling on piezoelectric coefficient d_{33} in [001]-oriented Mn-KNN crystal.

190pC/N at 180 and 200 °C, respectively. For the samples with domain size of 6.5 μm, the d_{33} value was decreased to 270 and 170pC/N at 150 and 200 °C, respectively. For the sample with domain size of 9 μm, the d_{33} value was decreased to 260 and 170 pC/N at 150 and 200 °C, respectively. Of particular interest is that there was slightly change of the domain structure in the Mn-KNN crystals with domain size of 9, 6.5, and 2 μm from 25 to 150 °C. The possible reason of this phenomenon is that the increase of domain wall thickness is below the resolution of optical method. Above 150 °C, the phenomenon of the sharply decrease of d_{33} value in all the samples was thought to be related to the unstable domain state at the temperature near to O-T polymorphic phase transition temperature.

IV. CONCLUSIONS

Various domain configurations in Mn-KNN single crystals have been prepared using field-cooled poling method, the laminar domain pattern with size of 9 μm was found to change to twinned domains with size of 2 μm, when the temperature decreased from 205 °C to room temperature at poling electric field of 18 kV/cm. The piezoelectric/dielectric properties were clearly improved for the samples with embedded twinned domains, showing minimal property variations during thermal depoling measurement. Based on the experimental results, domain size engineering is expected to achieve large piezoelectric response in KNN based lead free material with nano-size domain configuration, while maintaining the high polymorphic phase transition temperature and Curie temperature.

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