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Supporting Information

Efficient Li⁺-doping strategy to optimize the band alignment of Cu₂ZnSn(S,Se)₄/CdS interface by Se&LiF co-selenization process

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Defect level calculation

The defect level (E_A) and the defect desitivity (N_t) can be estimated from the admittance results for device W/O and W/, respectively. The deep defects charge and discharge speed is slow, and they can contribute to the capacitance signal at high temperature and low frequency. However, under low temperature and high frequency test conditions, the deep defects will be frozen and unable to respond to capacitance signal. According to the dependence of capacitance signal and temperature, E_A and N_t can be extracted from the following equations.

$$\omega_0 = 2\xi_0 T^2 \exp\left(\frac{-E_A}{KT}\right) \quad (1)$$

$$E_\omega = kT \ln\left(\frac{2\beta_p N_v}{\omega}\right) \quad (2)$$

$$N_t(E_\omega) = -\frac{U_d}{qW_d} \cdot \frac{dC}{d\omega} \cdot \frac{\omega}{kT} \quad (3)$$

where ω_0 is the inflection point frequency. For each $C(f)$ curve, ω_0 is the maxima of $\omega \cdot dC/d\omega$ vs ω plot, ξ_0 is a temperature-independent thermal emission prefactor. β_p is the capture coefficient, N_v is the effective density of states in the valance band. ω is frequency, E_ω is the defect energy on the top of valence band maximum (VBM). U_d is the built-in voltage in the junction, W_d is the depletion region width, and k is the Boltzmann constant.

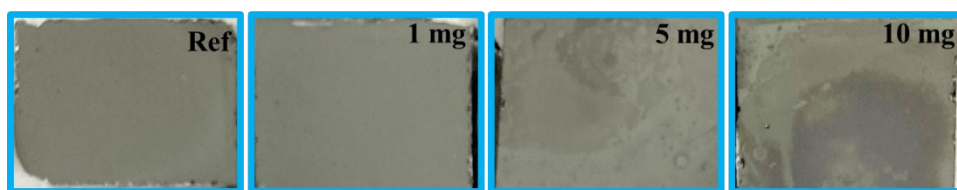


Fig. S1 Digital photographs of CZTSSe absorber films co-selenized at 570 °C for 20 min with LiF: 0 mg (Ref), 1 mg, 5 mg, 10 mg.

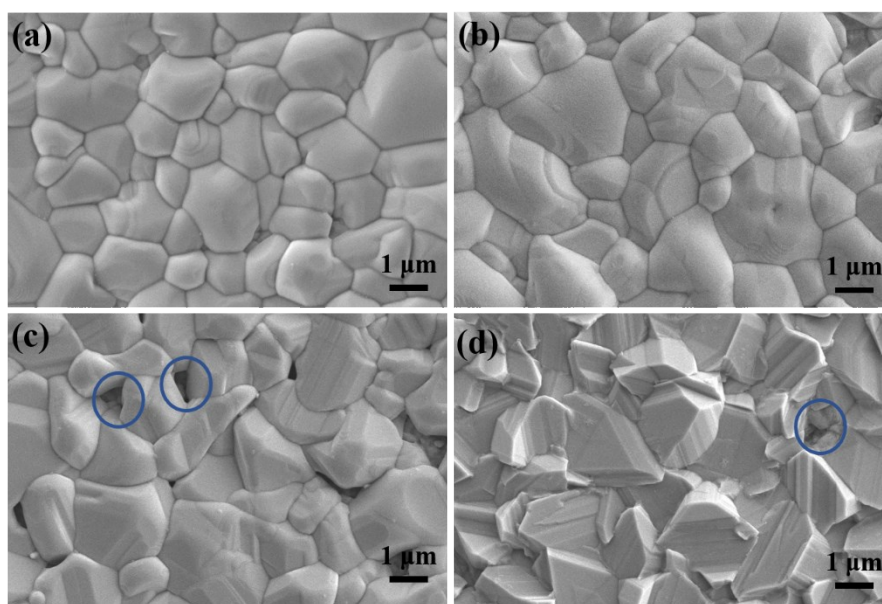


Fig. S2 (a-d) Top-view SEM images of CZTSSe absorber films co-selenized at 570 °C for 20 min with LiF: 0 mg (Ref), 1 mg, 5 mg, 10 mg.

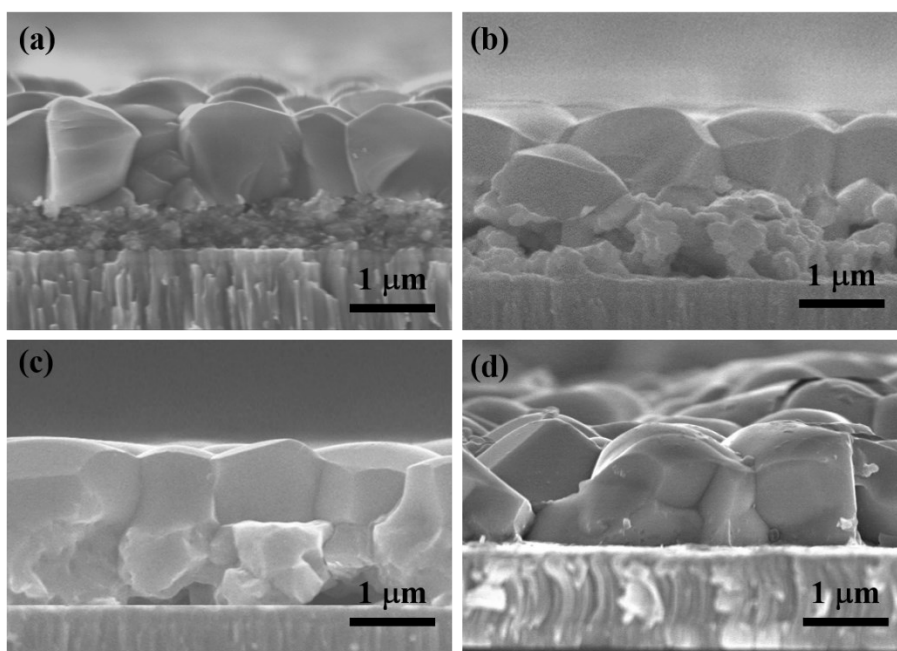


Fig. S3 (a-d) Cross-sectional SEM images of CZTSSe absorber films co-selenized for 20 min while adding 1 mg of LiF at different annealing temperatures: 480 °C, 510 °C, 550 °C, 570 °C.

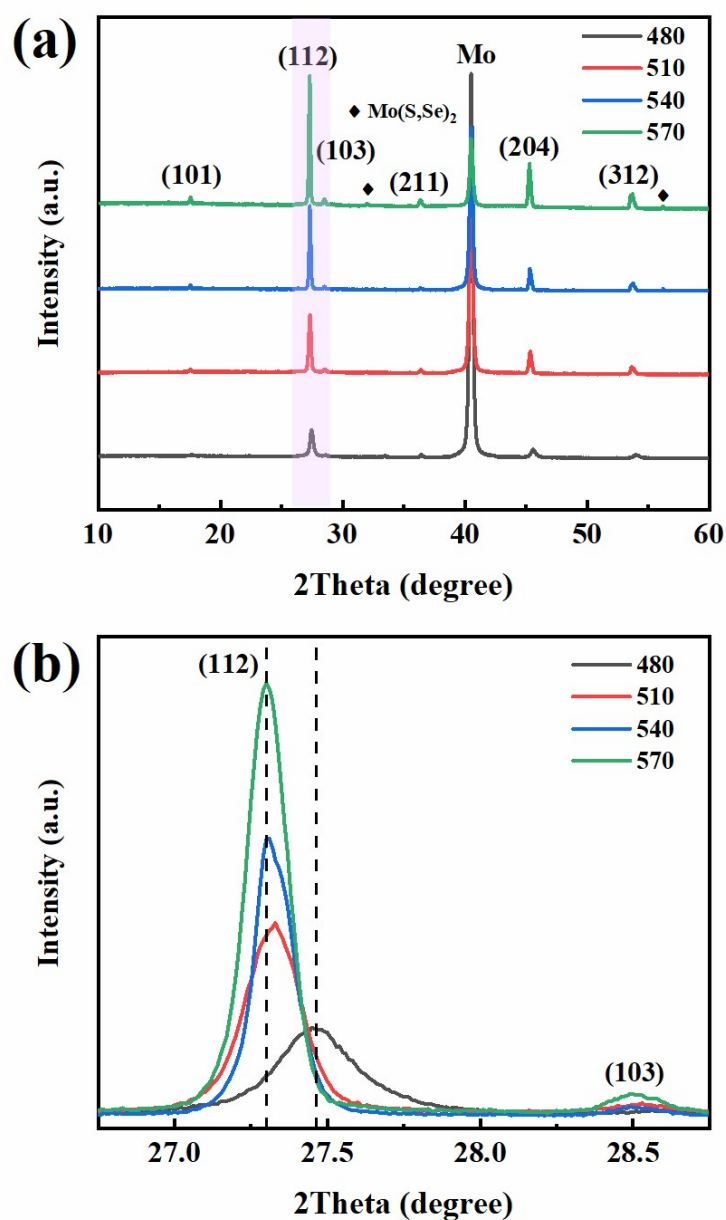


Fig. S4 (a) XRD patterns of CZTSSe absorber films co-selenized for 20 min while adding 1 mg of LiF with LiF at 480 °C, 510 °C, 540 °C, 570 °C. (b) The (112) diffraction peaks for all the samples are enlarged to show peak shift.

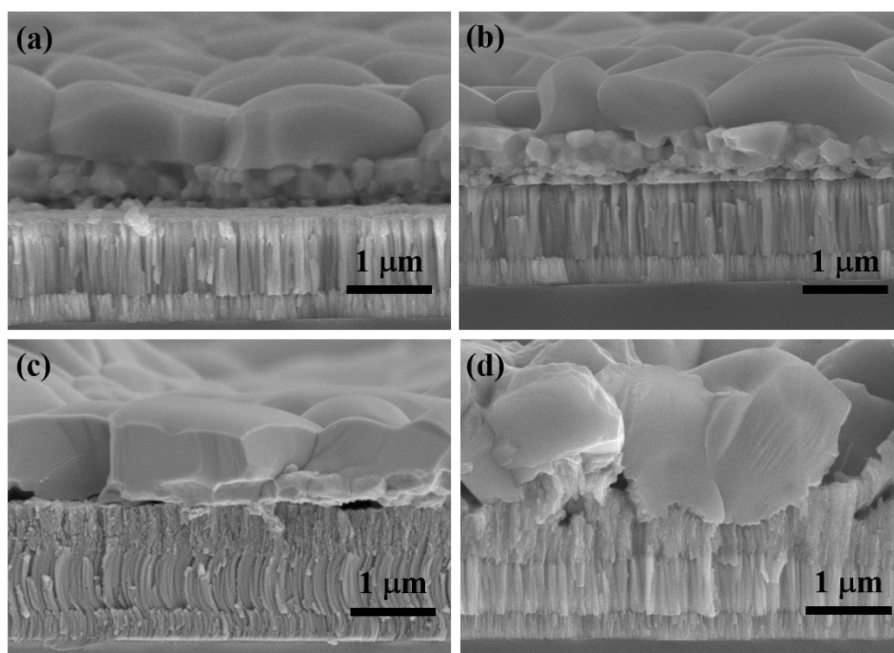


Fig. S5 (a-d) Cross-sectional SEM images of CZTSSe absorber films co-selenized at 570 °C while adding 1 mg of LiF at different annealing time: 10 min, 15 min, 20 min, 25 min.

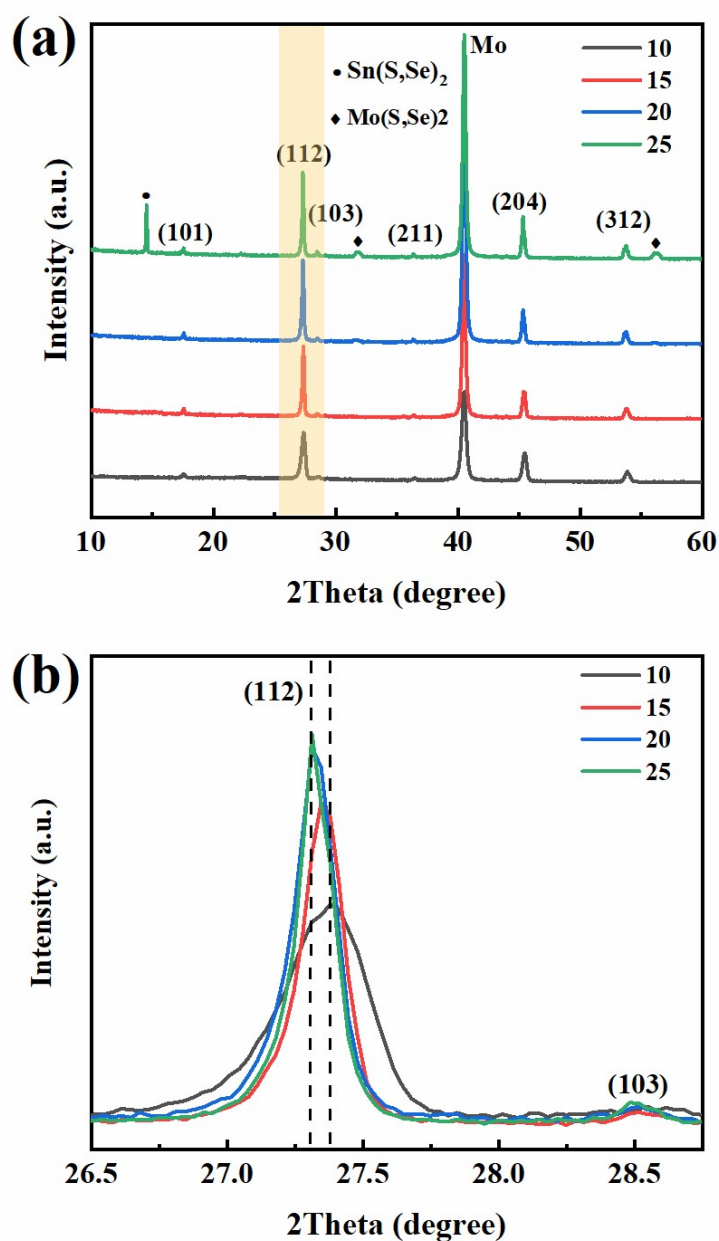


Fig. S6 (a) XRD patterns of CZTSSe absorber films co-selenized at 570 °C while adding 1 mg of LiF at different annealing time with LiF at 10 min, 15 min, 20 min, 25 min. (b) The (112) diffraction peaks for all the samples are enlarged to show peak shift.

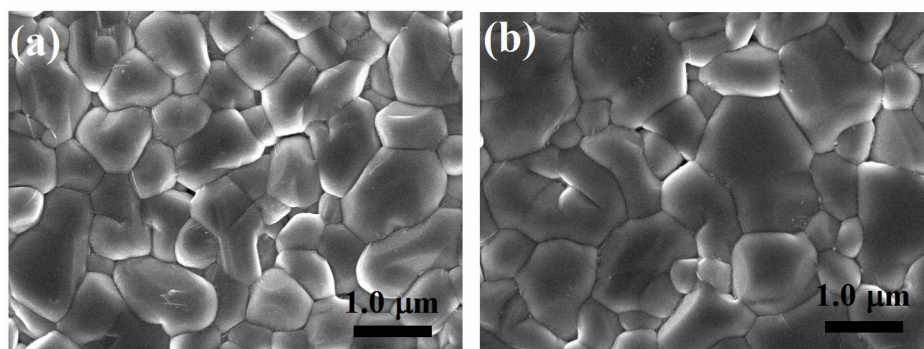


Fig. S7 Top-view SEM images of samples W/O and W/, respectively.

Table S1 Elemental composition ratios of sample W/O and W/. Results were obtained from top-view EDX measurements.

Sample	Cu/(Zn+Sn)	Zn/Sn	Se/(S+Se)
W/O	0.792	1.11	0.917
W/	0.758	1.07	0.928

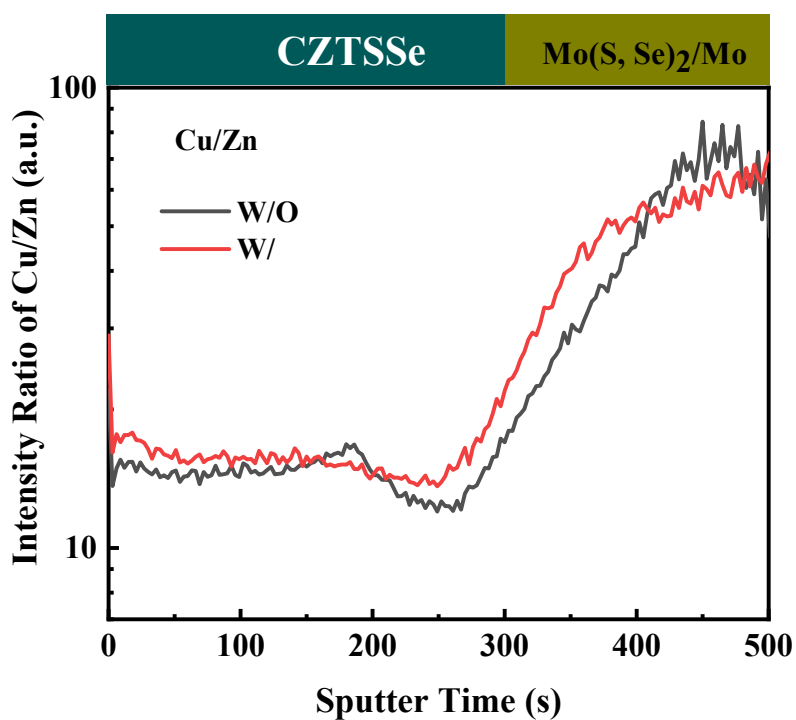


Fig. S8 Intensity ratios of Cu/Zn for samples W/O and W/, respectively.

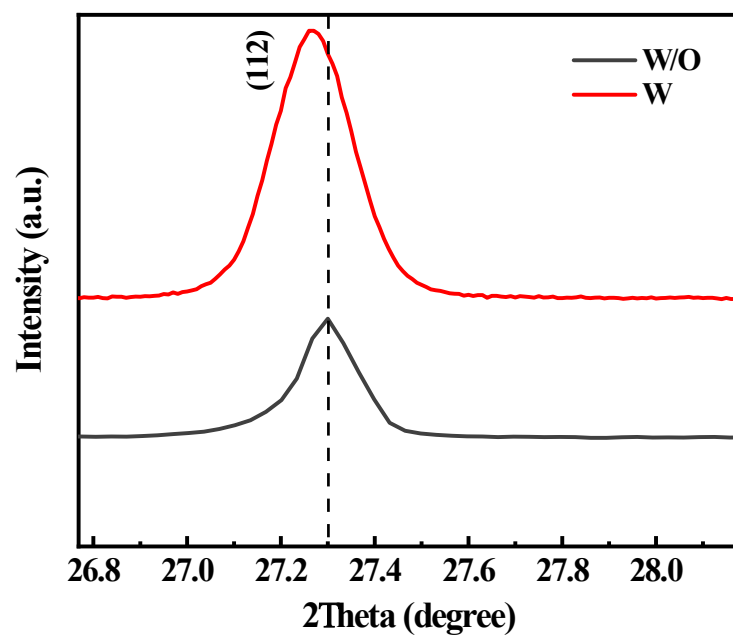


Fig. S9 The enlarged view (112) peaks of samples W/O and W/, respectively.

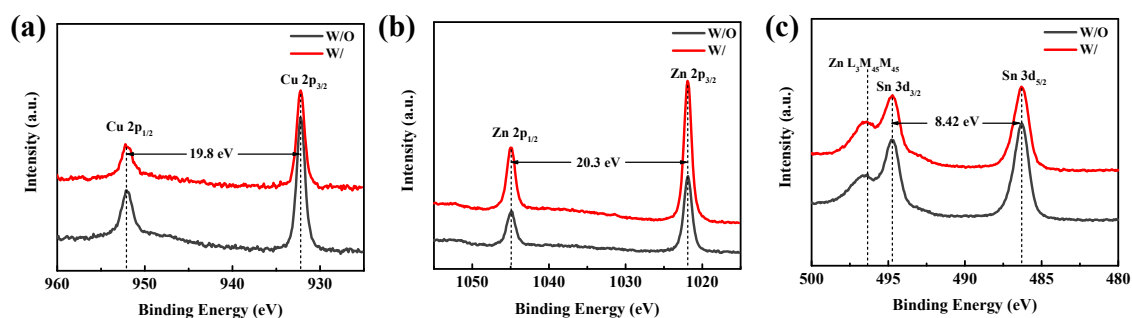


Fig. S10 (a-c) High-resolution XPS spectra of the Cu 2p, Zn 2p, Sn 3d core level of samples W/O and W/. The Zn L₃M₄₅M₄₅ Auger peak at 496.3 eV can be observed on the left side of the Sn 3d core level spectrum.

Table S3 Photovoltaic performance and Voc deficit for CZTSSe-based solar cells. *x*: unknown

	V_{oc} (V)	E_g (eV)	V_{oc} -deficit (V)	η (%)	Li^+ -doping strategy	Ref
CZTSSe	0.531	1.13	0.599	11.6		1
CZTSSe	0.496	1.11	0.614	11.5		2
CZTSSe	0.449	1.04	0.591	11.8		3
CZTSSe	0.459	1.23	0.771	6	precursor-doping	4
CZTSSe	0.408	1.04-1.09	^a ≥ 0.632	6.7		5
CZTSSe	0.380	1.08	0.7	6		6
CZTSSe	0.398	<i>x</i>	^b ≥ 0.602	5.21	soaking	7
CZTSSe	0.477	1.06	0.583	11.63	co-selenization	This work

^a The minimum V_{oc} -deficit was calculated based on the minimum band gap of 1.04 eV mentioned in the literature.

^b The minimum V_{oc} -deficit was calculated assuming $x = 1.0$ eV.

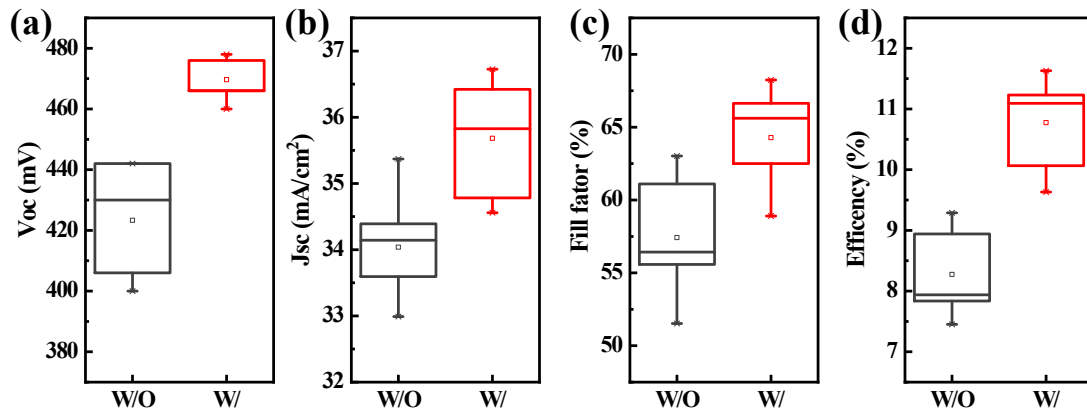


Fig. S11 (a-d) The statistic photovoltaic performances of the V_{oc} , J_{sc} , Fill factor and efficiencies of the devices W/O and W/.

Table S4 Statistics of CZTSSe solar cell parameters for 18 cells for devices W/O and W/.

	V_{oc} (V)		J_{sc} (mA/cm ²)		FF (%)		η (%)	
	W/O	W/	W/O	W/	W/O	W/	W/O	W/
Cell #1	0.4	0.46	34.61	36.73	57.14	58.9	7.91	9.95
Cell #2	0.406	0.478	34.29	36.6	55.79	63.47	7.77	11.1
Cell #3	0.412	0.466	34.14	34.56	56.43	62.51	7.94	10.07
Cell #4	0.43	0.476	35.37	36.42	51.52	66.64	7.84	11.54
Cell #5	0.442	0.477	34.39	36.34	61.11	67.09	9.29	11.63
Cell #6	0.442	0.472	33.59	35.83	55.58	65.61	8.25	11.09
Cell #7	0.442	0.466	33.15	34.58	61.93	66.62	9.07	10.74
Cell #8	0.43	0.466	32.99	34.78	63.03	59.43	8.94	9.63
Cell #9	0.406	0.466	33.81	35.32	54.29	68.24	7.45	11.23

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