

Supporting Information

Single Crystal Growth and Phase Transition Mechanism of KCsMoP₂O₉ with Efficient Second Harmonic Generation via the Emerging Additional Periodic Phase Technology

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1. Distortion degree calculation

According to the refined structural data, there were one type of MoO₆ octahedron and two types of PO₄ tetrahedron in the KCMP crystal. Based on the bond length and bond angle of polyhedron at different temperature, the distortion degree Δd can be calculated using the following formula proposed by P. S. Halasyamani:¹

$$\Delta d = \frac{|(M-O1)-(M-O4)|}{|\cos \theta_1|} + \frac{|(M-O2)-(M-O5)|}{|\cos \theta_2|} + \frac{|(M-O3)-(M-O6)|}{|\cos \theta_3|} \quad (S1)$$

where M-O represents the bond length of polyhedron, and θ is the angle between bonds.

2. Dipole moment calculation

The direction of the polyhedral distortion can be analyzed by dipole moment, which was calculated using the bond-valence theory.²⁻⁶ Based on the bond length d_{ij} and occupied position of the MoO₆ octahedron for the KCMP crystal, the dipole moment can be calculated by the following formulas:

$$v_{ij} = \exp((r_0 - d_{ij}) / b) \quad (S2)$$

$$V_{ij} = \sum_j v_{ij} \quad (S3)$$

$$a + b = R \quad (S4)$$

$$ia = jb \quad (S5)$$

$$a = R / (1 + i / j) \quad (S6)$$

$$\mu = ne(C_{charge} - C_{grav}) \quad (S7)$$

where r_0 and b are valued as 1.907 and 0.37 for MoO₆ octahedron, respectively. Center of charge (C_{charge}) and center of gravity (C_{grav}) are determined by formula (S4-S6). a and b are the distance from the center of charge or gravity, R is the bond length, i and j are the atomic number. n is the number of electrons and e is the charge per electron (4.8×10^{-10} esu). The calculated results are shown in Tables S4-S5.

3. The first principle calculation

The calculations in this work were performed by adopting the Vienna ab initio Simulation Package (VASP) based on density functional theory (DFT) combined with projector augmented wave (PAW) pseudopotentials to describe the core electrons.⁷ The Mo $p^65s^24d^1$, Cs $5s^25p^66s^1$, K $3s^23p^64s^1$, P $2s^22p^3$, and O $2s^22p^4$ states were treated as the valence electrons. Structural configurations at different temperatures used for calculation were obtained from Rietveld refinement of the measured XRD patterns. Configuration optimization was performed using electron exchange and correlation within the generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) functional with an energy cutoff of 500 eV.⁸ And for structural relaxation, the energy and force convergence criteria were 1×10^{-5} eV and 0.01 eV/Å, respectively, and the Monkhorst-Pack K-point mesh was fixed as $9 \times 9 \times 2$ in the Brillouin zone for the structure. During the calculation of electronic properties, the above parameters and convergence conditions remain unchanged.

4. Maker Fringe Theory

The Maker fringe method was generally used to measure the nonlinear optical (NLO) coefficients, the power of second harmonic generation (SHG) could be expressed as:⁹

$$P_{2\omega}(\theta) = \frac{512\pi^3}{cA} d^2 P_\omega^2 f(\theta) \sin^2 \psi \quad (\text{S8})$$

where

$$f(\theta) = \frac{1}{(n_\omega^2 - n_{2\omega}^2)^2} t_\omega^4 T_{2\omega} P^2(\theta) R(\theta) \beta(\theta) \quad (\text{S9})$$

$$\psi = \frac{\pi l}{2} \frac{4}{\lambda_\omega} (n_\omega \cos \theta_\omega - n_{2\omega} \cos \theta_{2\omega}) \quad (\text{S10})$$

In equation (S8), c is the velocity of light in vacuum, A is the sectional area of fundamental light, d is the NLO coefficient, P_ω is the fundamental light power, $f(\theta)$ is a function of incident angle θ , while θ_ω and $\theta_{2\omega}$ denotes the corresponding refractive angles for the fundamental and SHG lights in the crystal, $\sin 2\Psi$ is the origin of the Maker fringes.

In equation (S9), n_ω and $n_{2\omega}$ are the refractive indices under the fundamental and

harmonic wavelengths, respectively. t_ω and $T_{2\omega}$ are the transmission coefficients of fundamental wave and harmonic wave, respectively. $p(\theta)$, $R(\theta)$ and $\beta(\theta)$ are the projection factor, incident multiple-reflection correction and light beam size correction, respectively.

In equation (S10), l and λ_ω are the thickness of the tested crystal sample and wavelength of the fundamental light, respectively.

In order to fit the measured Maker fringes and obtain the NLO coefficients, a constant C was introduced as:¹⁰

$$C = \frac{512\pi^3}{cA} d^2 P_\omega^2 \quad (\text{S11})$$

where the power and the sectional area of the fundamental light were fixed. Herein, the magnitude of NLO coefficients of KCMP crystal could be determined relatively to d_{36} of KDP crystal according to the relationship between C and d in Equation (S11). Hence, the final coefficient equation can be expressed as:¹⁰

$$d(\text{sample}) = \sqrt{\frac{C(\text{sample})}{C(\text{KDP})}} d_{36}(\text{KDP}) \quad (\text{S12})$$

5. Additional Periodic Phase Theory

During the typical collinear frequency doubling process, the electric field $E_{2\omega}(z)$ of the SHG light is expressed as:¹¹

$$\frac{dE_{2\omega}(z)}{dz} = \frac{2i\omega}{cn_{2\omega}(z)} d_{\text{eff}}(z) E_\omega^2(z) e^{-i\Delta\varphi} \quad (\text{S13})$$

where $E_\omega(z)$ denotes the electric field of the fundamental field at the propagation length z . ω refers to the fundamental frequency. c represents the light velocity. $n_{2\omega}(z)$ and $d_{\text{eff}}(z)$ denote the refractive indexes of the SHG light and effective nonlinear coefficient at the propagation length z . $\Delta\varphi = k_2 z - 2k_1 z = \Delta k z$ is the phase difference between the fundamental and SHG lights with the wavevectors k_1 and k_2 , respectively. For the birefringence phase matching, $\Delta\varphi = \Delta k z = 0$. when $\Delta\varphi \leq \pi$, the energy will transfer from the fundamental light to the SHG, when $\Delta\varphi \geq \pi$, the energy will transfer from the SHG to the fundamental light. Therefore, the SHG output will oscillate with a phase

difference period of 2π .

The additional periodic phase (APP) technology can be expressed as follows: when the phase difference $\Delta\varphi_{PD}$ reaches π , the SHG process will be blocked, and an APP $\Delta\varphi_{APP}$ with the value of π or $-\pi$ will be added; after adding the APP, the phase difference in a certain period will be $\Delta\varphi_T = \Delta\varphi_{PD} + \Delta\varphi_{APP} = 2m\pi$ or 0 , here m is an integer. The APP can be achieved by periodically processing, which undermines the translational symmetry of the nonlinear crystals. In the unbroken regions, the frequency conversion can reach its maximum when $\Delta\varphi_{PD} = \pi$. There exists no continuous SHG effects in the processing regions, whereas the dispersion of the refractive indices exists with wavevectors k_1 and k_2 , thereby generating an APP $\Delta\varphi_{APP}$. When the fundamental and SHG lights propagate for a certain period, the phase difference between the fundamental and SHG lights should be $\Delta\varphi_{PD} + \Delta\varphi_{APP}$, which can reach 0 or $2m\pi$ to avoid the transferring of energy from the SHG light to the fundamental light. The period Λ can be calculated based on the following equations:

$$\Lambda = L_a + L_b \quad (S14)$$

$$\Delta\varphi = (k_2 - 2k_1)\Lambda = 2\pi \quad (S15)$$

Where L_a denotes the length of the periodic regions for the effective nonlinear interaction between the fundamental and SHG lights. L_b denotes the length of periodic regions where phase-difference is added and the conversion is blocked from the SHG to the fundamental light. The APP period length as a function of SHG wavelength for d_{33} -type KCMP crystal can be obtained and shown in Fig. S4. It shows that 515 nm SHG wavelength corresponds to the APP period of 20.6 μm .

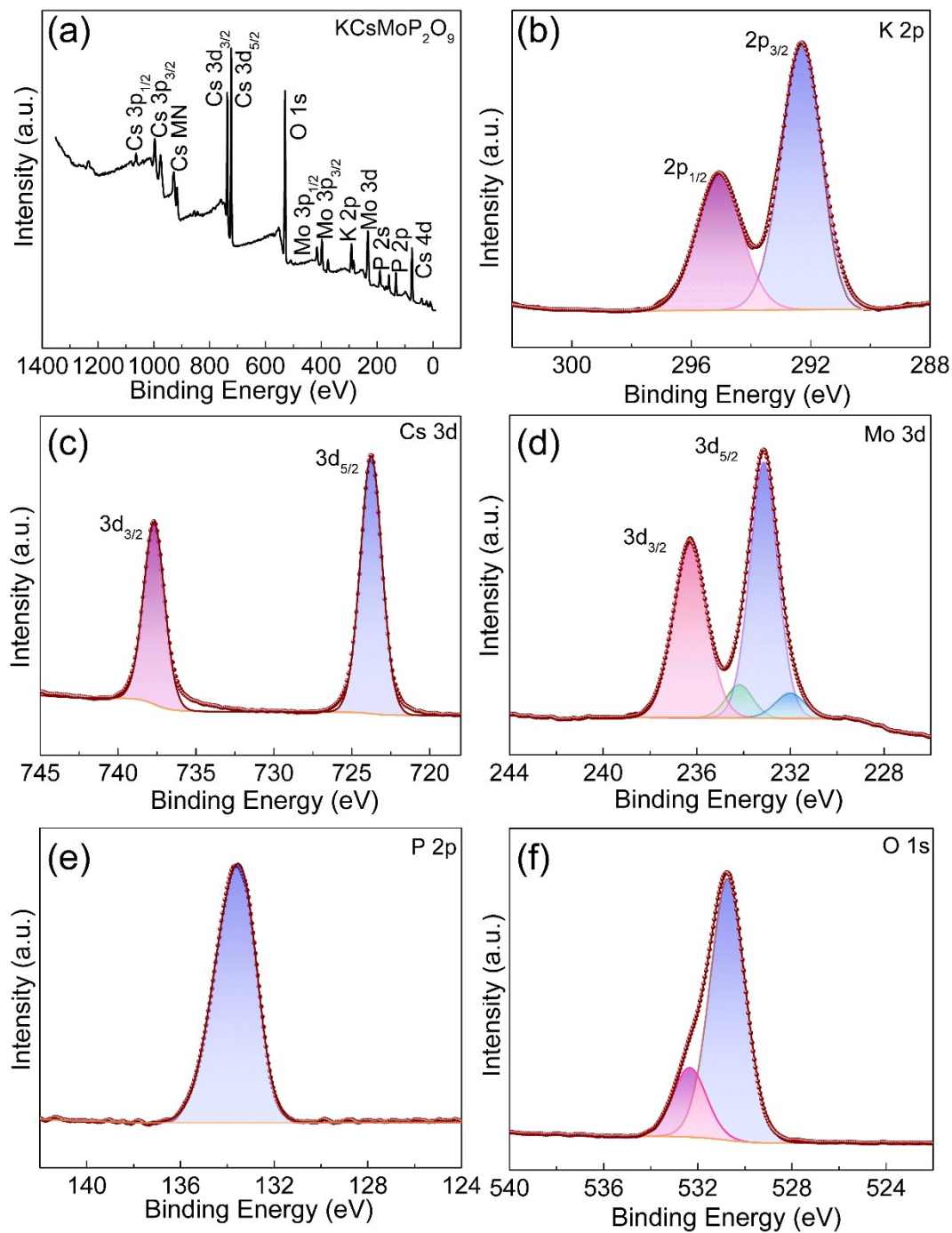


Fig. S1 (a) XPS spectra of the KCMP crystal; high-resolution energy spectra of (b) K 2p, (c) Cs 3d, (d) Mo 3d, (e) P 2p, and (f) O 1s.

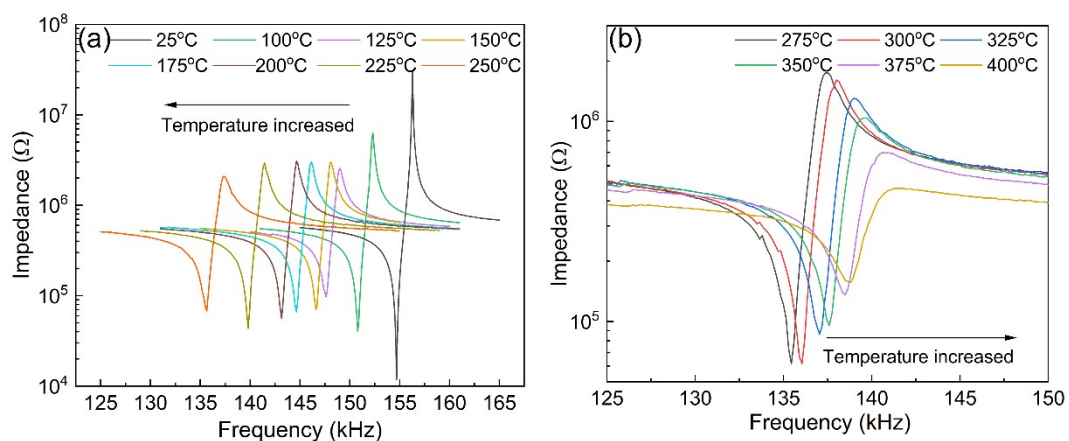


Fig. S2 The impedance spectroscopy at different temperature.

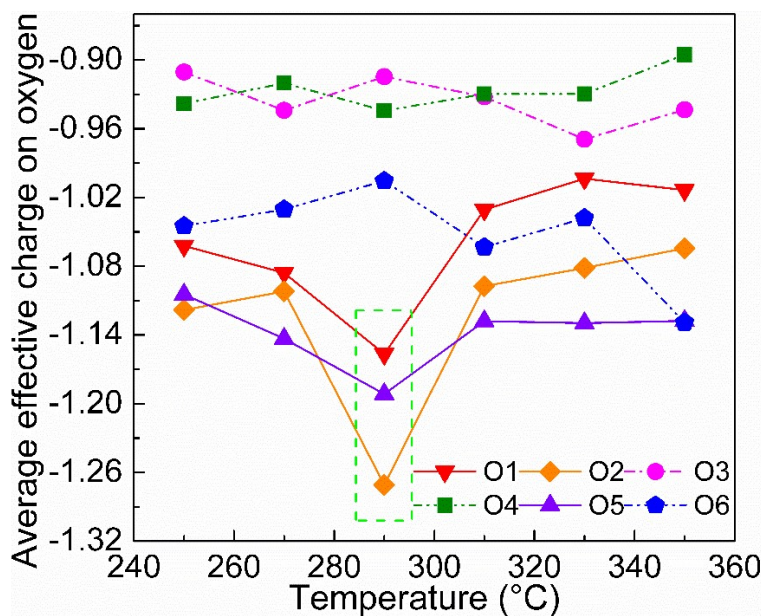


Fig. S3 The variation of average effective charge on oxygen with temperature for KCMP crystal.

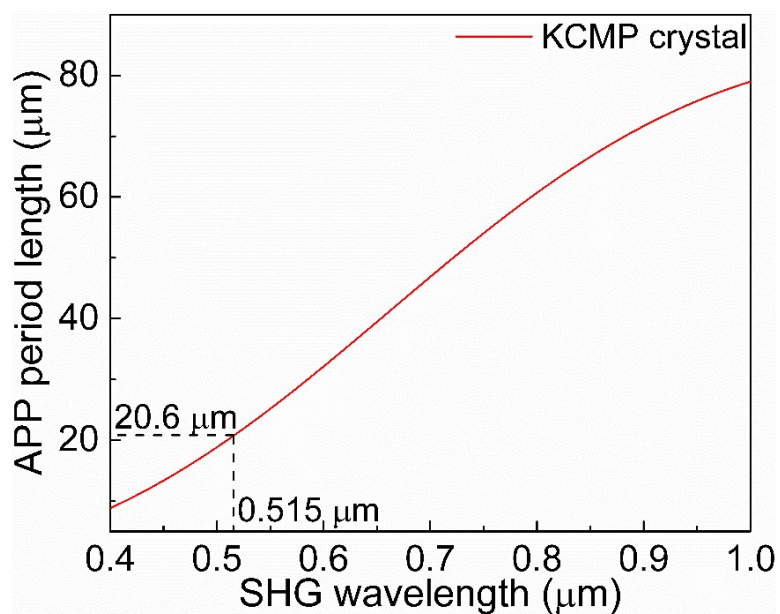


Fig. S4 The APP period length as a function of SHG wavelength for d_{33} -type KCMP crystal.

Table S1 XPS analysis of elements K 2p, Cs 3d, Mo 3d, P 2p and O 1s in KCMP crystal.

Elements		BE (eV)	FWHM (eV)	Area Percent (%)	Valenc e																																			
K	2p _{1/2}	295.07	1.81	8.32	+1																																			
	2p _{3/2}	292.34	1.54			Cs	3d _{3/2}	737.67	1.73	9.37	+1	3d _{5/2}	723.76	1.70	3d _{3/2}	236.29	1.67	Mo	3d _{5/2}	233.14	1.41	6.37	+6	3d _{3/2}	234.18	1.33	+5	3d _{5/2}	232.01	1.5	+4	P	2p	133.67	1.99	16.67	+5	O	1s	532.35
Cs	3d _{3/2}	737.67	1.73	9.37	+1																																			
	3d _{5/2}	723.76	1.70																																					
	3d _{3/2}	236.29	1.67																																					
Mo	3d _{5/2}	233.14	1.41	6.37	+6																																			
	3d _{3/2}	234.18	1.33		+5																																			
	3d _{5/2}	232.01	1.5		+4																																			
P	2p	133.67	1.99	16.67	+5																																			
O	1s	532.35	1.69	59.28	-2																																			

530.74	1.76
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Table S2 The refractive indices of the KCMP crystal measured at five different wavelengths.

Wavelength (μm)	n_o	n_e	Δn
0.406	1.6755	1.6663	0.0092
0.514	1.6515	1.6427	0.0088
0.636	1.6390	1.6307	0.0083
0.965	1.6259	1.6188	0.0071
1.547	1.6176	1.6105	0.0071

Table S3 Sellmeier coefficients derived from the measured refractive indices.

Sellmeier coefficient	A	B	C	D
s				
n_o	2.62167	0.02522	0.02985	0.00659
n_e	2.60362	0.02149	0.04151	0.00794

Table S4 Calculation results for the valence bonds of the MoO_6 octahedron.

	d_{ij}	v_{ij}
Mo-O1	1.6886	1.8045
Mo-O2	1.6982	1.7583
Mo-O3	2.1708	0.4902
Mo-O4	1.9916	0.7956
Mo-O5	2.1597	0.5051
Mo-O6	1.9912	0.7965
$\sum V_{ij}$		6.15

Table S5 Calculation results for the dipole moment of the MoO_6 octahedron.

	$x(a)$	$y(b)$	$z(c)$	Debye
MoO_6	-0.3248	-0.6335	-1.5152	1.6115

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