Supporting Information

Enhanced negative permittivity by A-site heterovalent-ion doping in $La_{1-x-y}Ca_xK_yMnO_3$ perovskite

Meichun Fu, [a] Mei Han, [a] Yuan Zhang, [a] Beining Zheng *[b] and Shouhua Feng *[a]

Experimental

Materials

Lanthanum nitrate hexahydrate $La(NO_3)_3 \cdot 6H_2O$) was purchased from Macklin. Calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$), Manganese (II) chloride tetrahydrate($MnCl_2.4H_2O$), KOH were purchased from Sinopharm Chemical Reagent Co., Ltd. $KMnO_4$ was purchased from BEIJING SHIJI. All chemicals were utilized as purchased without further purifications.

The preparation of perovskite $La_{1-x-y}Ca_xK_yMnO_3$

The perovskite $La_{1-x-y}Ca_xK_yMnO_3$ was prepared via a hydrothermal disproportionation reaction. First, 250 mL 0.4 mol/L $La(NO_3)_3 \cdot 6H_2O$, 100 mL 0.4 mol/L $Ca(NO_3)_2 \cdot 4H_2O$, 250 mL 0.12 mol/L $KMnO_4$, 250 mL 0.56 mol/L $MnCl_2.4H_2O$ were prepared. And different volumes of the $La(NO_3)_3 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $KMnO_4$ solution were transferred to beakers and stirred in an ice bath at 4 ^oC, and 60 g KOH were also added slowly into the above mixture solution. Subsequently, different volumes of $MnCl_2.4H_2O$ solution were added and stirred about 10 min. Finally, the mixture solution was loaded into a 100 mL Teflon-lined stainless-steel autoclave, and reacted in an oven at 260 ^oC for 72 h. The impurities was cleaned by ultrasound and water, and then the target production was collected by magnet and dried at 80 ^oC for 24 h.

Materials Characterization

Powder X-ray diffraction (XRD) results were collected on the Rigaku D/Max 2550 V/PC X-ray powder diffractometer with Cu Kα irradiation (λ= 1.5418 Å), the test conditions were 50 kV and 200 mA at room temperature through stepwise scanning with the test Angle range was $10° \leq 2\theta \leq 80°$and the increment is 0.02^o. Field emission scanning electron microscopy (SEM) was measured by Helios NanoLab 600I microscope. X-ray photoelectron spectroscopy (XPS) was tested using the ESCALAB 250Xi electron spectrometer (Thermo Fisher Scientific) and Al Kα (1486.6 eV) was used as the X-ray excitation source. The soft X-ray absorption spectrum (XAS) of the O *K*-edge and Mn *L*-edge was measured at the BL12B-a beamline of the National Synchrotron Radiation Laboratory (NSRL, Hefei) in China. X-ray absorption spectra (XAS, including XANES and EXAFS) were collected at the SSRF's beamline BL14W1 of SSRF (Shanghai Synchrotron Radiation Facility) in China. LCR meter (Keysight E4980A, USA) equipped with Electrode-D of 16047E dielectric test fixture was used to analyse electrical and dielectric properties of samples in the frequency range from 20 Hz to 2 MHz with a self-built variable temperature test system range from room temperature to 300 ^oC. DC conductivity was measured by two needle method and AC conductivity was obtained by collecting and calculating the electrochemical impedance spectrum using impedance analyzer (SI 1260, Solartron, England).

Table S1. ICP test results of $La_{1-x-y}Ca_xK_yMnO_3$

ICP		
samples	theoretical feeding ratio	actual feeding ratio
LCKMO-1	$La_{0.22}Ca_{0.88}$ (excessive K)	$La_{0.27}Ca_{0.79}K_{0.09}MnO_3$
LCKMO-2	$La_{0.44}Ca_{0.66}$ (excessive K)	$La_{0.36}Ca_{0.69}K_{0.03}MnO_3$
LCKMO-3	$La_{0.66}Ca_{0.44}$ (excessive K)	$La_{0.52}Ca_{0.52}K_{0.08}MnO_3$
LCKMO-4	$La_{0.77}Ca_{0.33}$ (excessive K)	$La_{0.57}Ca_{0.44}K_{0.08}MnO_3$
LCKMO-5	$La_{0.88}Ca_{0.22}$ (excessive K)	$La_{0.63}Ca_{0.32}K_{0.11}MnO_3$
LCKMO-6	$La_{0.99}Ca_{0.11}$ (excessive K)	$La_{0.71}Ca_{0.20}K_{0.14}MnO_3$

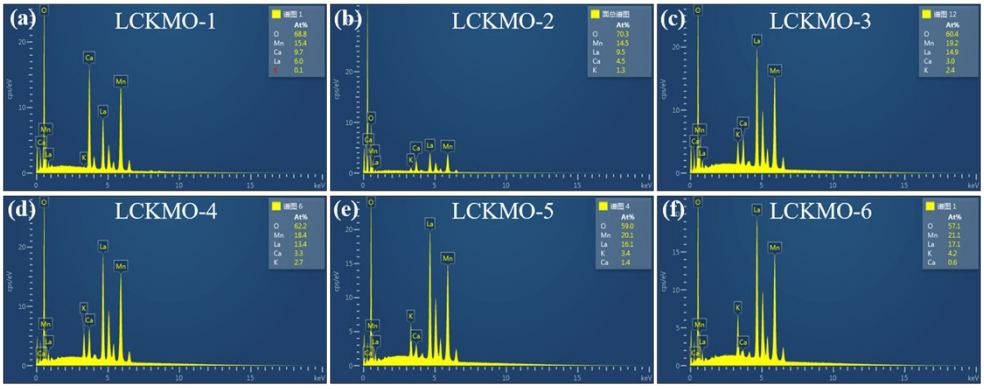

Fig. S1 Point analysis results of EDS energy spectrum for sample element content.

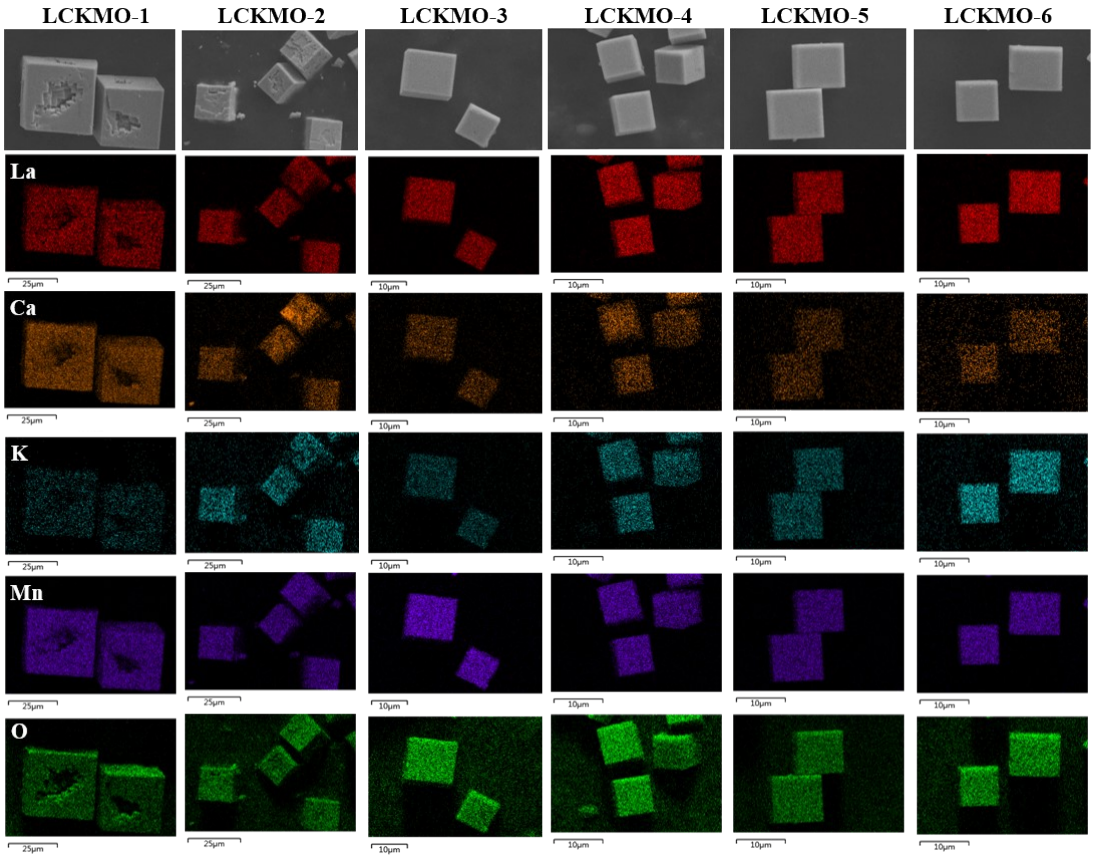

Fig. S2 EDS elemental mapping of the selected region shows the elemental distributions of La, Ca, K, Mn, O elements in the LCKMO.

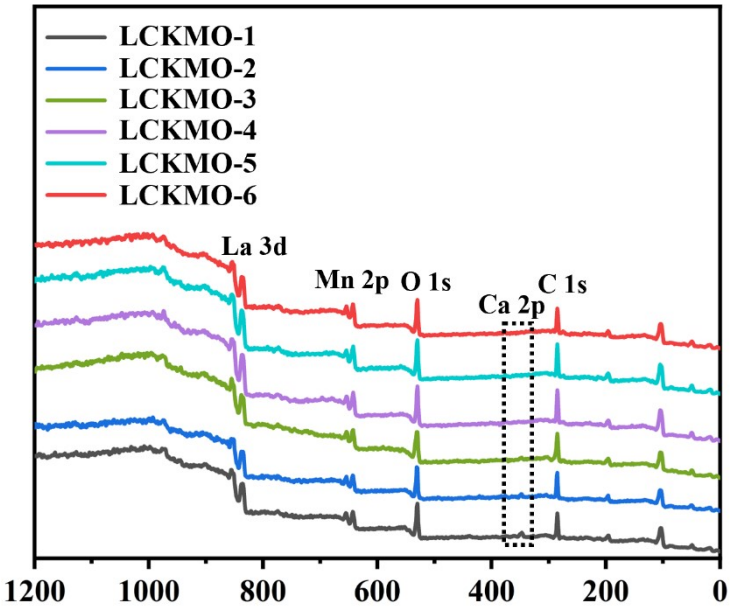

Fig. S3 XPS of survey spectra for LCKMO.

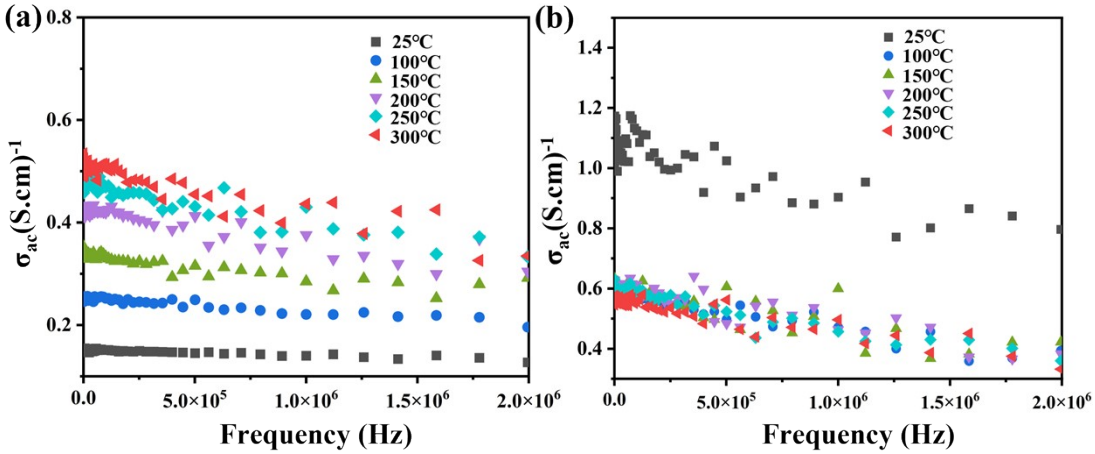

Fig. S4 a) AC conductivity of LCKMO-5 as a function of frequency at various temperatures. b) AC conductivity of LCKMO-6 as a function of frequency at various temperatures.

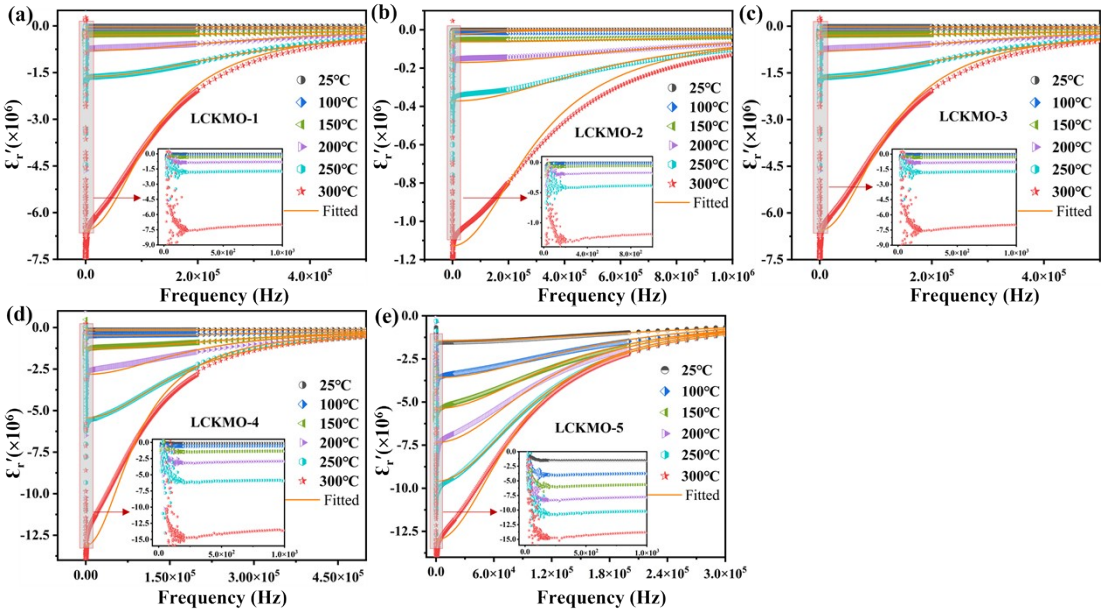

Fig. S5 The negative permittivity of LCKMO-1, 2, 3, 4, 5 as a function of frequency at various temperatures.

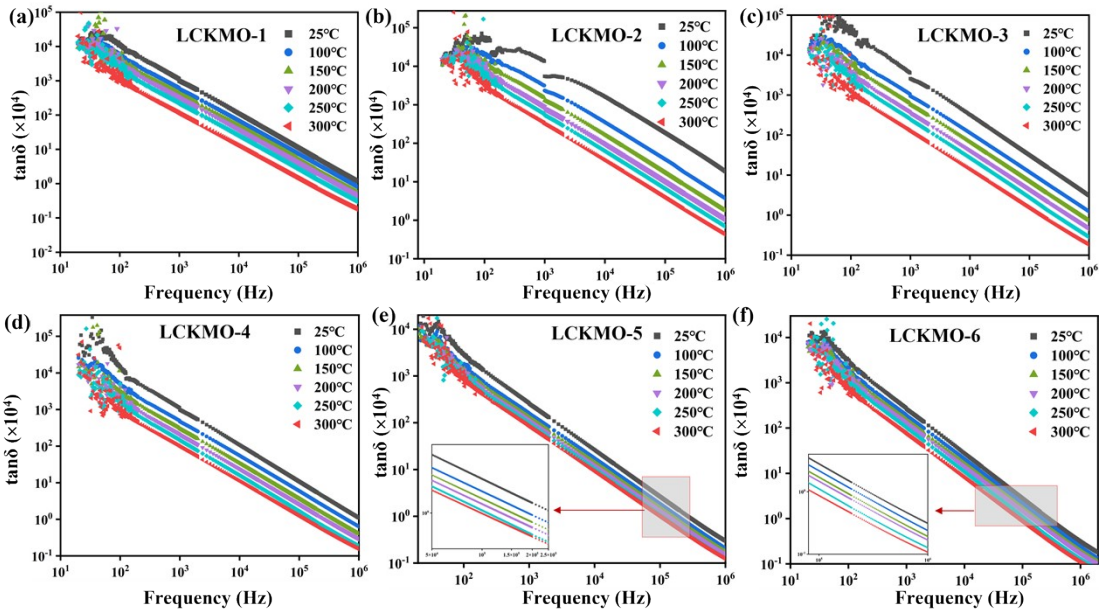

Fig. S6 a-f) The dielectric loss (tan δ) of perovskite LCKMO as a function of frequency at various temperatures.

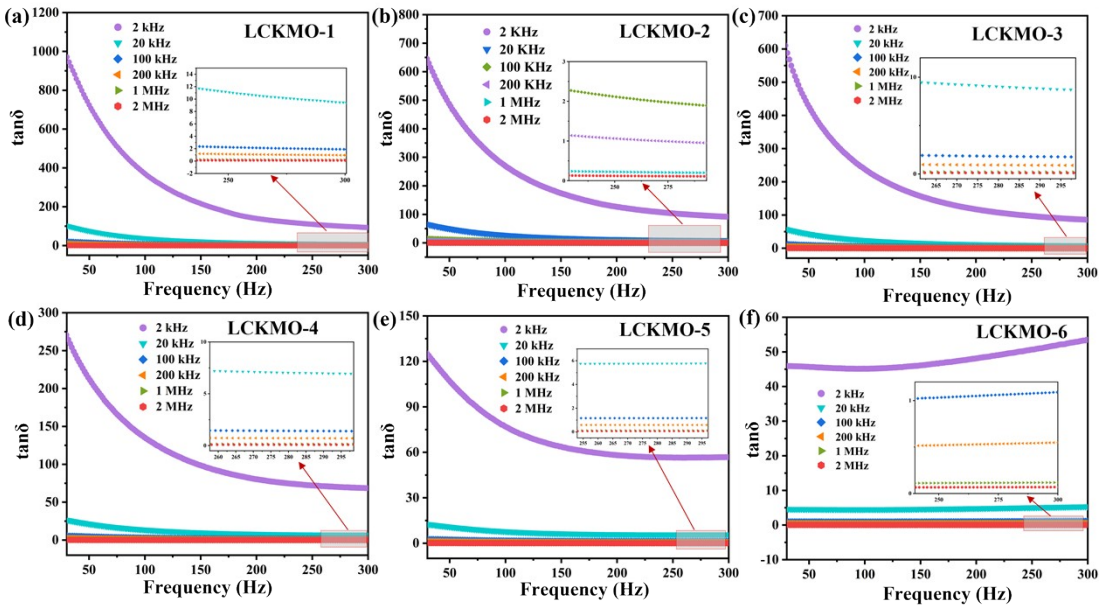

Fig. S7 a-f) Temperature-dependent the dielectric loss (tan δ) of perovskite LCKMO.

Table S2. peak area results of O 1s for $La_{1-x-y}Ca_xK_yMnO_3$

samples	O_{III} (O_{Lat})	O_{II} (O_{Ads})	O_I (H_2O)
LCKMO-1	54.00%	40.03%	5.97%
LCKMO-2	57.45%	25.30%	17.25%
LCKMO-3	42.63%	36.80%	21.57%
LCKMO-4	57.27%	32.91%	9.82%
LCKMO-5	61.40%	28.06%	10.54%
LCKMO-6	62.82%	21.04%	16.14%