Supplementary Information for

# Digital Light Processing 3D–printed Ceramic Metamaterials for Electromagnetic Wave Absorption

RuiZhou[1], Yansong Wang[2], Ziyu Liu[1], Yongqiang Pang[3], Jianxin Chen[1], Jie Kong[1, *]

[1]MOE Key Lab of Materials Physics and Chemistry in Extraordinary Conditions, Shaanxi Key Lab of Macromolecular Science and Technology, School of Chemistry and Chemical Engineering, Northwestern Polytechnical University, Xi'an 710072, P. R. China

[2]Key Laboratory of Optical System Advance Manufacturing Technology, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P. R. China

[3]School of Electronic Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, P. R. China

*Corresponding author. E–mail: kongjie@nwpu.edu.cn (Jie Kong)

## S1 Experimental Section

Size exclusion chromatography (SEC) measurement was performed on a system equipped with a Waters 515 pump, an autosampler and two MZ gel columns ($10^3$ and $10^4$ Å) with a flow rate of 0.5 mL min$^{-1}$ in THF (HPLC grade) at 25 °C. The detectors included a differential refractometer (Optilab rEX, Wyatt) and a multiangle light scattering detector (MALS, Wyatt) equipped with a 632.8 nm He−Ne laser (DAWN EOS, Wyatt). The refractive index increments of the polymers in THF were measured at 25 °C using an Optilab rEX differential refractometer.

Thermogravimetric analysis (TGA) and mass spectrometry (MS) analysis was performed on a simultaneous thermal device (STA, 449C Jupiter, Netzsch, Gerätebau GmbH, Selb, Germany) coupled with a quadrupole mass spectrometer (QMS, 403C Aëolos, Netzsch, Germany). The measurement was done under a steady flow of argon (40 ml/min), with a heating rate of 10 K/min at a range from ambient temperature to 1400 °C.

Powder X−ray diffraction (XRD) measurement was conducted on an X'Pert Pro Pro Powder diffractometer from PANalytical (Cu Kα radiation, 40 kV, 40mA) (D/Max2550VB+/PC). The X'Celerator Scientific RTMS detection unit was used for detection.

Imaging X−ray photoelectron spectroscopy (XPS) measurements were conducted on a K−Alpha spectrometer (Axis Ultra, Kratos Analytical Ltd., U.K.) and the core level spectra were measured using a monochromatic Al Kα X−ray source (hν = 1486.7 eV). The analyzer was operated at 23.5 eV pass energy and the analyzed area was 200−800 μm in diameter. The lowest energy resolution is 0.48 S−3 eV (Ag $3d_{5/2}$). Binding energy was referenced to the adventitious hydrocarbon C 1s line at 284.8 eV. The curve fitting of the XPS spectra was performed using the least−squares method.

## S2 Supplementary Figures

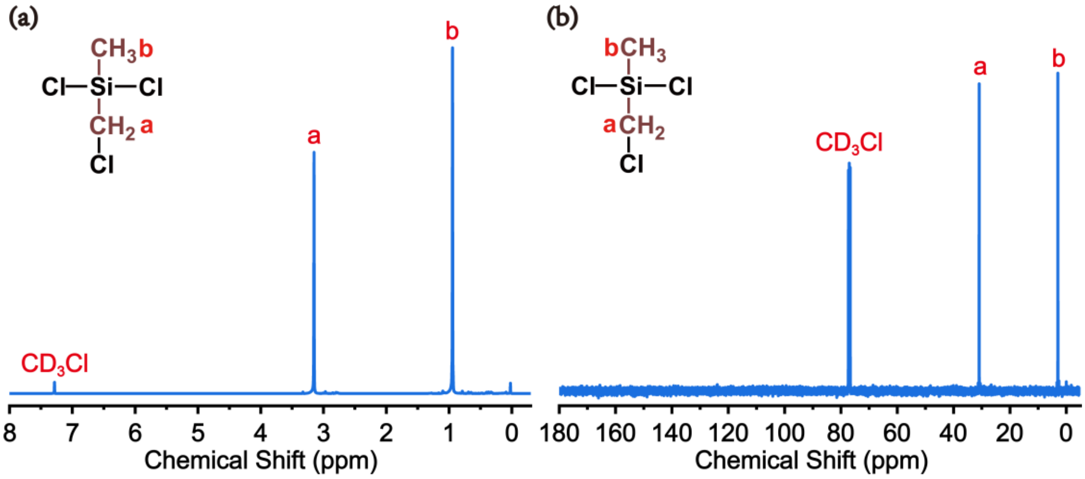

**Fig. S1** (**a**) $^1$H NMR spectrum and (**b**) $^{13}$C NMR spectrum of Dichloro(chloromethyl)methylsilane

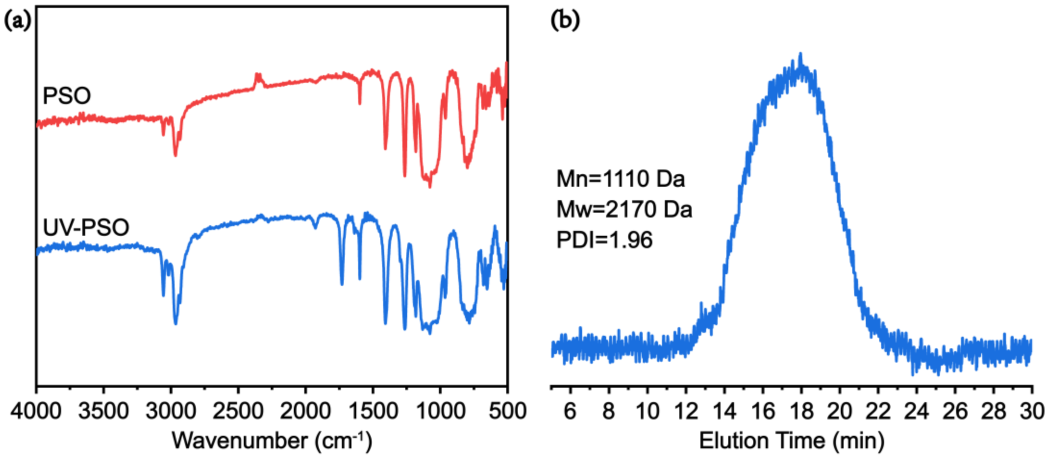

**Fig. S2** (**a**) FT−IR spectra of PSO and UV−PSO, (**b**) SEC trance of UV−PSO at a flow rate of 0.5 mL min$^{-1}$ in THF at 25 $^{o}$C

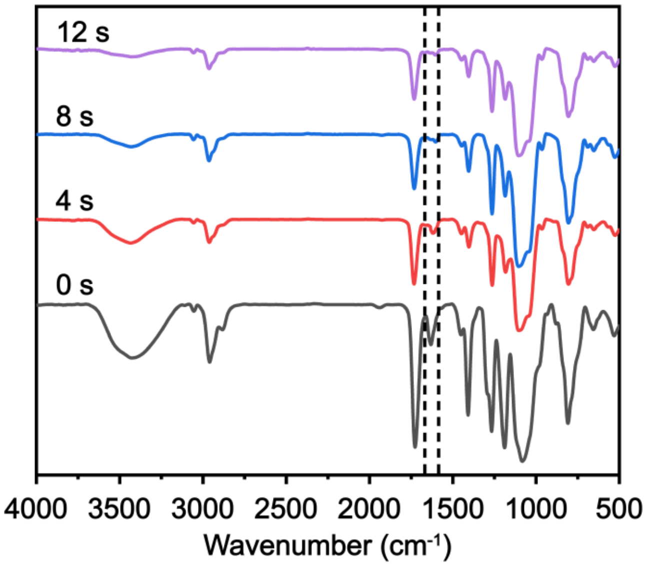

**Fig. S3** The FT−IR spectra with different curing time

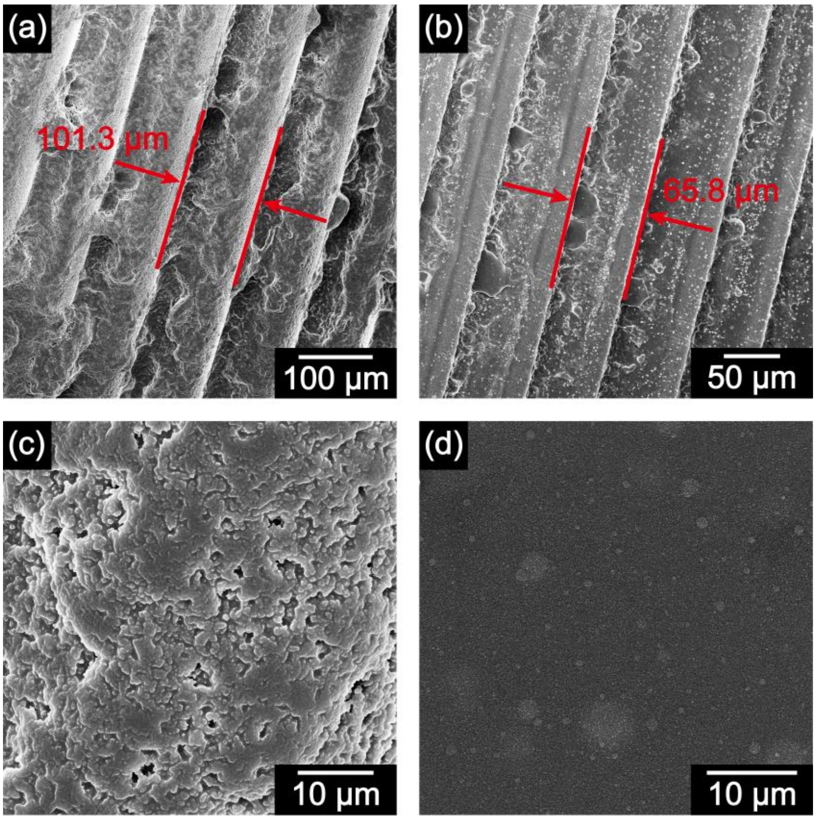

**Fig. S4** (**a**) (**c**) SEM images of green body and (**b**) (**d**) corresponding ceramics  pyrolyzed at 1200 °C in argon atmosphere

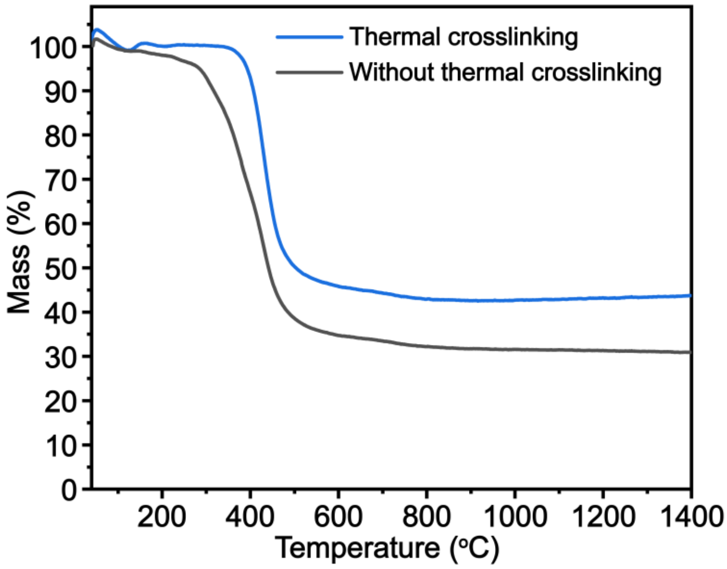

**Fig. S5** TGA curves of thermal crosslinking and without thermal crosslinking 3D printing samples

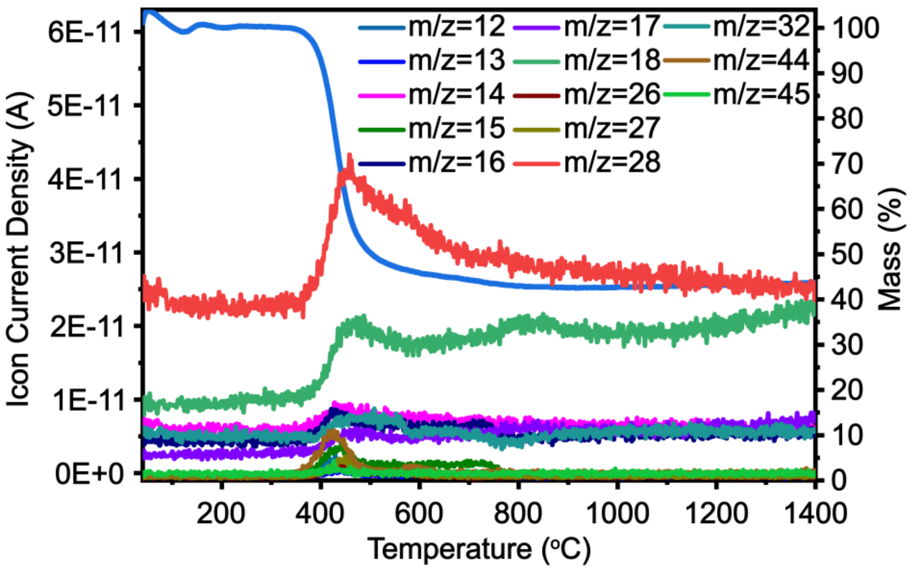

**Fig. S6** TGA−MS spectra of green bodies with thermal crosslinking

As shown in **Fig. S5**, the slight mass loss of the no thermal crosslinking sample before 200 ºC is mainly caused by the volatilization of residual small molecules and adsorbed water (less than 3%). From 200 ºC, sample start to be degraded, while the thermal crosslinking sample begin to degrade at 350 ºC. When the temperature increasing to 500 ºC, the mass loss of thermal crosslinking sample is less than 55%, while the mass loss of the sample without thermal crosslinking is more than 65%. The thermal crosslinking of silicon vinyl provides a higher crosslinking density for the sample, thus reducing the mass loss during pyrolysis. From 500 ºC to 1400 ºC, both of the two samples barely show a mass loss (less than 5%). The thermal crosslinking sample has 43.74% ceramic yield. Furthermore, the TG−MS spectrometry in **Fig. S6** indicated the thermolysis was mainly accompanied by the decomposition products of hydrocarbons, $CH_x^+$ (x=0−3, m/z=12−15), $CH_4$ (m/z=16), $C_2H_x^+$ (x=2, 3, 4 and 6, m/z=26, 27, 28 and 30) as well as $H_2$ (m/z=2), $OH^-$ (m/z=17), $H_2O$ (m/z=18), $O_2$ (m/z=32), $CO_2$ (m/z=44) and other oligomer fragments (m/z=45). The evolution of $CH_4$, $H_2$, $CH_x^+$, $C_2H_x^+$ in the range from 300 ºC to 500 ºC was ascribed to decomposition of $Si{-}CH_3$ groups, $-CH_2-$ groups and cleavage of C−C bonds. The $O_2$, CO and $CO_2$ were manly attributed to decomposition of C=O, −O− and the oxidation reaction. A small amount of −OH groups was due to the decomposition of Si−OH.

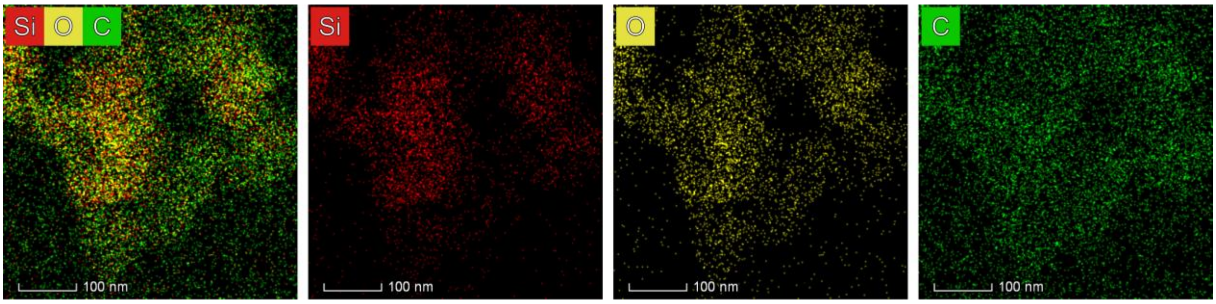

**Fig. S7** The element mappings of Si, O, and C of the ceramic parts pyrolyzed at 1200 °C in argon atmosphere, respectively

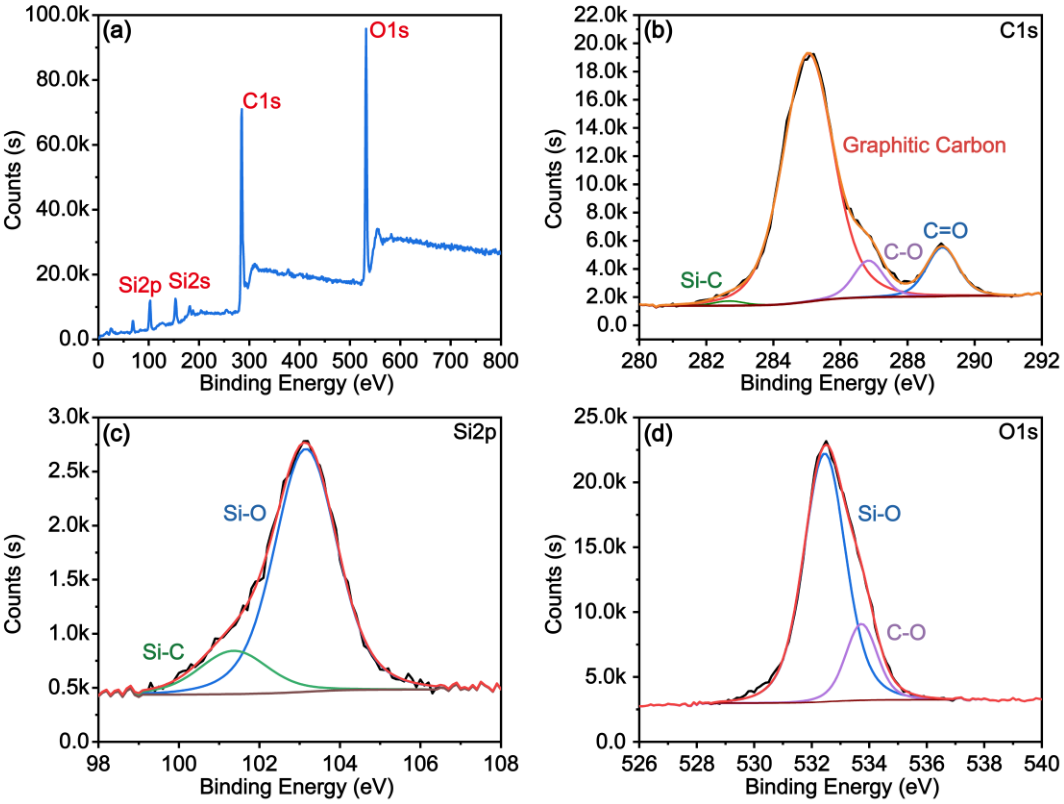

**Fig. S8** XPS spectra of the ceramic parts pyrolyzed at 1200 °C in argon atmosphere. (**a**) XPS spectrum, (**b**) C 1s spectrum, (**c**) Si 2p spectrum, (**d**) O 1s spectrum

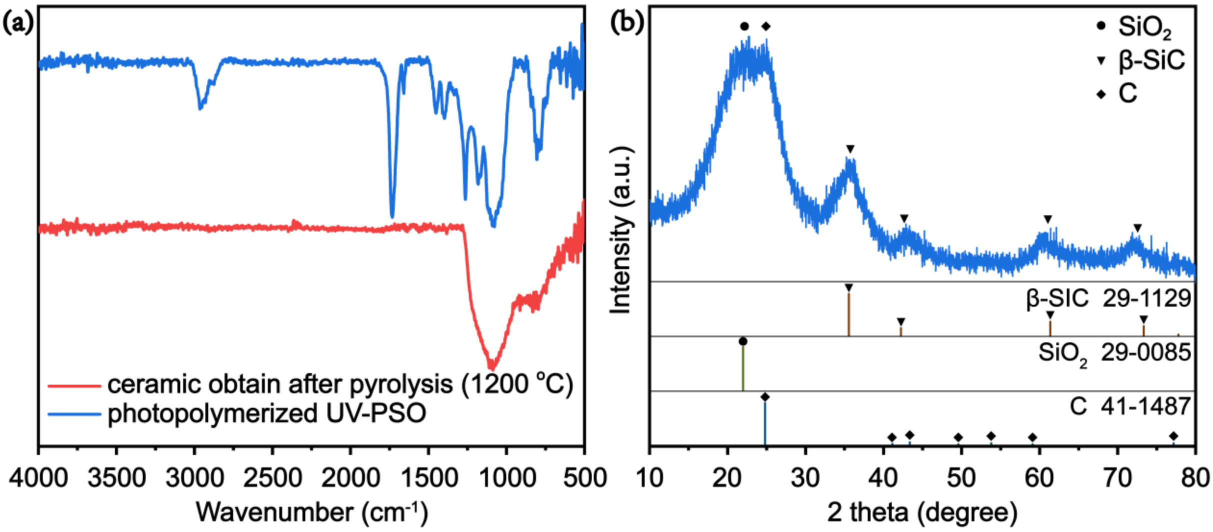

**Fig. S9** (**a**) FT−IR spectra of the photo−polymerized UV−PSO before and after pyrolysis at 1200 ºC under argon atmosphere; (**b**) X−ray diffraction pattern recorded on the UV−PSO ceramic after pyrolysis at 1200 ºC under argon atmosphere

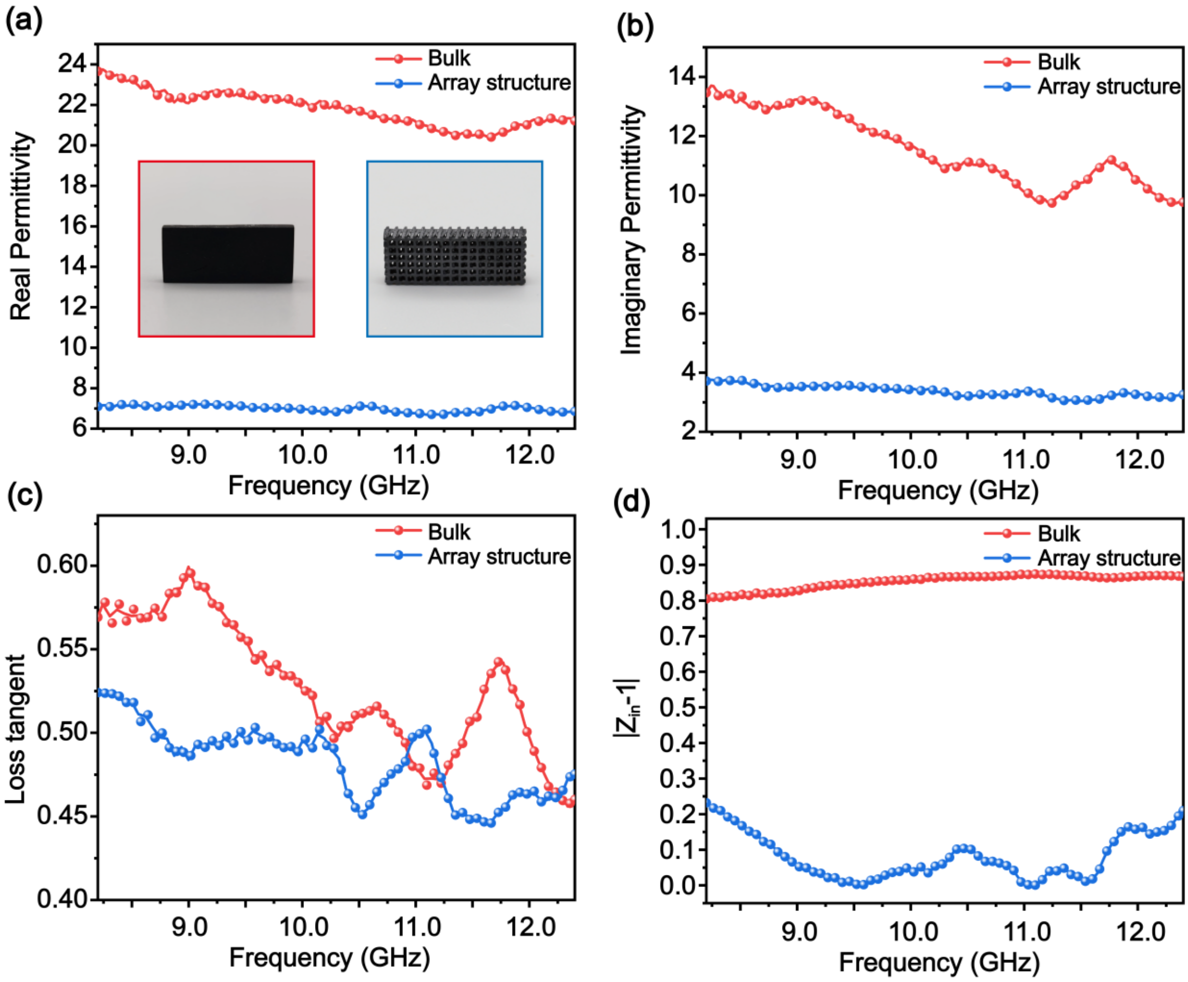

**Fig. S10** The (**a**) real part, (**b**) imaginary part of permittivity and (**c**) loss tangent for 3D printed bulk ceramic sample and cross helix array structure ceramic sample; (**d**) modulus of $|Z_{in} - 1|$of samples at optimal thickness corresponding to RC$_{min}$ in the frequency range 8.2−12.4 GHz

**Fig. S11** Si−O−C ceramic metamaterial structure fabricated for EM wave absoption in X−Ku band

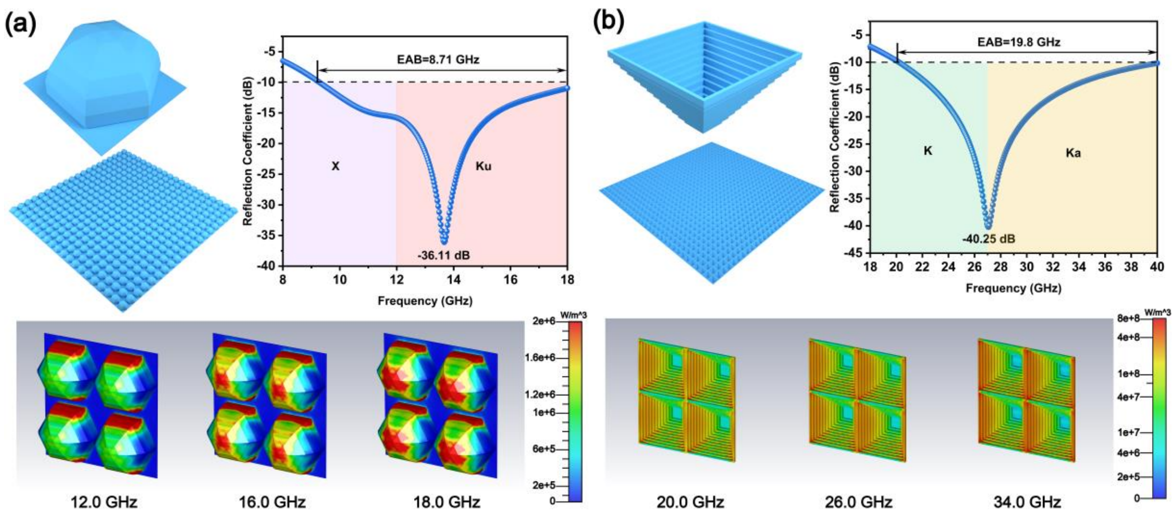

**Fig. S12** Different metastructures for microwave absorbing in X, Ku, K, Ka bands and the corresponding RC data by simulations, based on the dielectric constant of the bulk sample