Broadband dielectric behavior of MIL-100 metal-organic framework as a function of structural amorphization

Arun Singh Babal, a Barbara E. Souza, a Annika F. Möslein, a Mario Gutiérrez, a
Mark D. Frogley, b and Jin-Chong Tan a,*

a Multifunctional Materials and Composites (MMC) Laboratory, Department of Engineering Science, University of Oxford, Parks Road, Oxford, OX1 3PJ, United Kingdom

b Diamond Light Source, Harwell Campus, Chilton, Oxford, OX11 0DE, United Kingdom

*E-mail: jin-chong.tan@eng.ox.ac.uk
Contents

1. Powder X-ray diffraction (XRD) ................................................................................. 3

2. Fourier-transform infrared spectroscopy (ATR-FTIR) ................................................ 4

3. Thermogravimetric analysis (TGA) .............................................................................. 6

4. Dielectric properties ...................................................................................................... 7
   4.1 Basolite F300 .......................................................................................................... 7
      4.1.1 Real Part of Dielectric Constant ($\varepsilon'$) ....................................................... 7
      4.1.2 Imaginary Part of Dielectric Constant ($\varepsilon''$) ............................................... 10
      4.1.3 Dielectric Loss (tan $\delta$) ............................................................................... 13
   4.2 MIL-100-MG .......................................................................................................... 16
      4.2.1 Real Part of Dielectric Constant .................................................................... 16
      4.2.2 Imaginary Part of Dielectric Constant ............................................................ 19
      4.2.3 Dielectric Loss ................................................................................................ 22
   4.3 Comparative dielectric loss ...................................................................................... 25

5. Reflectivity spectra $R(\omega)$ in the far-IR and mid-IR regions ........................................ 26

6. Refractive index in THz region .................................................................................... 27

7. The imaginary part of dielectric constant in the THz region .......................................... 28

8. AC conductivity ........................................................................................................... 29
   8.1 Basolite F300 ........................................................................................................... 29
   8.2 MIL-100-MG ........................................................................................................... 32
1. Powder X-ray diffraction (XRD)

Figure S1: The XRD patterns for: (a) Basolite F300 and (b) MIL-100-MG pellets, both normalized with respect to the highest data point. (c) XRD patterns in absolute intensities for
MIL-100-MG pellets. Inset of table shows the pellet crystallinity (%), estimated from the area ratio of the crystalline peaks to the total area found under the XRD pattern.

2. Fourier-transform infrared spectroscopy (ATR-FTIR)
Figure S2: (a) The pressure-dependent ATR-FTIR spectra for Basolite F300 pellets, (b) Derivative of peak shift over pelleting pressure.
3. Thermogravimetric analysis (TGA)

Figure S3: The pressure-dependent thermal stability measurement (TGA) for Basolite F300 pellets.
4. Dielectric properties

4.1 Basolite F300

4.1.1 Real Part of Dielectric Constant ($\varepsilon'$)
Supporting Information / 20 Jan 2021

Figure S4: The real part of dielectric constant for Basolite F300 pellets prepared under a compression load of: (a) 0.5-ton, (b) 1-ton, (c) 2-ton, (d) 3-ton (e) 5-ton (f) 7-ton, and (g) 10-ton, corresponding to the pressure of 36.96, 73.92, 147.84, 221.76, 369.6, 517.44 and 739.20 MPa, respectively.
4.1.2 Imaginary Part of Dielectric Constant ($\varepsilon''$)

(a) Dielectric Constant ($\varepsilon''$) vs. Frequency ($f$) / MHz for Basolite F300-0.5t

(b) Dielectric Constant ($\varepsilon''$) vs. Frequency ($f$) / MHz for Basolite F300-1t

(c) Dielectric Constant ($\varepsilon''$) vs. Frequency ($f$) / MHz for Basolite F300-2t
Figure S5: The imaginary part of dielectric constant for Basolite F300 pellets prepared under a compression load of: (a) 0.5-ton, (b) 1-ton, (c) 2-ton, (d) 3-ton (e) 5-ton (f) 7-ton, and (g) 10-ton, respectively.
4.1.3 Dielectric Loss (\(\tan \delta\))
**Figure S6:** The dielectric loss for Basolite F300 pellets prepared under a compression load of:

(a) 0.5-ton, (b) 1-ton, (c) 2-ton, (d) 3-ton (e) 5-ton (f) 7-ton, and (g) 10-ton, respectively.
4.2 MIL-100-MG

4.2.1 Real Part of Dielectric Constant
Figure S7: The real part of dielectric constant for MIL-100-MG pellets prepared under a compression load of: (a) 0.5-ton, (b) 1-ton, (c) 2-ton, (d) 3-ton (e) 5-ton (f) 7-ton, and (g) 10-ton, corresponding to the pressure of 36.96, 73.92, 147.84, 221.76, 369.6, 517.44 and 739.20 MPa, respectively.
4.2.2 Imaginary Part of Dielectric Constant

![Graphs showing the imaginary part of the dielectric constant for different samples over frequency.](image-url)
Figure S8: The imaginary part of dielectric constant for MIL-100-MG pellets prepared under a compression load of: (a) 0.5-ton, (b) 1-ton, (c) 2-ton, (d) 3-ton (e) 5-ton (f) 7-ton, and (g) 10-ton, respectively.
4.2.3 Dielectric Loss

(a) Dielectric Loss (tan δ) vs. Frequency (f) / MHz for MIL-100-MG-0.5t

(b) Dielectric Loss (tan δ) vs. Frequency (f) / MHz for MIL-100-MG-1t

(c) Dielectric Loss (tan δ) vs. Frequency (f) / MHz for MIL-100-MG-2t
Figure S9: The dielectric loss for MIL-100-MG pellets prepared under a compression load of:
(a) 0.5-ton, (b) 1-ton, (c) 2-ton, (d) 3-ton (e) 5-ton (f) 7-ton, and (g) 10-ton, respectively.
4.3 Comparative dielectric loss

Figure S10: Dielectric loss of MOF pellets as a function of pelleting pressure and temperature:
(a) Basolite F300 and, (b) MIL-100-MG pellets specific frequencies (0.01, 0.1, and 1 MHz).
5. Reflectivity spectra $R(\omega)$ in the far-IR and mid-IR regions

Figure S11: Reflectance spectra of MIL-100-MG pellets. Inset: (a) reflectivity spectra in the near-IR region, (b) joining of the far-IR and mid-IR spectra at 517 cm$^{-1}$ (~15.5 THz), (c) pelleting pressure-dependent redshift in transition mode of peaks obtained from the Gaussian peak fitting and (d) plot for pressure-dependent peak shift in peak positions.
6. Refractive index in THz region

Figure S12: (a) Real and (b) imaginary parts of the refractive index of MIL-100 pellets in IR frequency range. Inset (c)-(d) shows the optically insensitivity of the framework in near-IR region.
7. The imaginary part of dielectric constant in the THz region

Figure S13: The imaginary part of dielectric constant ($\varepsilon''$) in the IR frequency range for MIL-100 pellets. Inset (a) shows the $\varepsilon''$ spectrum in the near-IR region. Inset (b) doesn’t show any shift in the transition mode, whereas, in inset (c)-(d) the redshift is evident in the transition modes caused by the pelleting force-induced amorphization.
8. AC conductivity

8.1 Basolite F300

![AC Conductivity Graphs for Basolite F300](image)

- Basolite F300-0.5t
- Basolite F300-1t
- Basolite F300-2t

**AC Conductivity**
Figure S14: The AC conductivity of Basolite F300 pellets prepared under a compression load of: (a) 0.5-ton, (b) 1-ton, (c) 2-ton, (d) 3-ton (e) 5-ton (f) 7-ton, and (g) 10-ton, corresponding to the pressure of 36.96, 73.92, 147.84, 221.76, 369.6, 517.44 and 739.20 MPa, respectively.
8.2 MIL-100-MG
Figure S15: The AC conductivity of MIL-100-MG pellets prepared under a compression load of: (a) 0.5-ton, (b) 1-ton, (c) 2-ton, (d) 3-ton, (e) 5-ton, (f) 7-ton, and (g) 10-ton, corresponding to the pressure of 36.96, 73.92, 147.84, 221.76, 369.6, 517.44 and 739.20 MPa, respectively.