Electronic Supplementary Information

Role of Free Volumes and Segmental Dynamics on Ion Conductivity of PEO/LiTFSI Solid Polymer Electrolytes Filled with SiO_2 Nanoparticles: A Positron Annihilation and Broadband Dielectric Spectroscopy Study

P. Utpalla[ǁ,†], S. K. Sharma[ǁ,†,*], S. K. Deshpande[‡], J. Bahadur[#,†], D. Sen[#,†], M. Sahu[ǂ], P. K. Pujari[ǁ,†,]

[ǁ]Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai, India-400085

[‡]UGC-DAE Consortium for Scientific Research, Mumbai, India-400085

[#]Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, India- 400085

[ǂ]Radioanalytical Chemistry Division, Bhabha Atomic Research Centre, Mumbai, India-400085

[†]Homi Bhabha National Institute, Anushaktinagar, Mumbai, India-400094

*Corresponding author: skumars@barc.gov.in

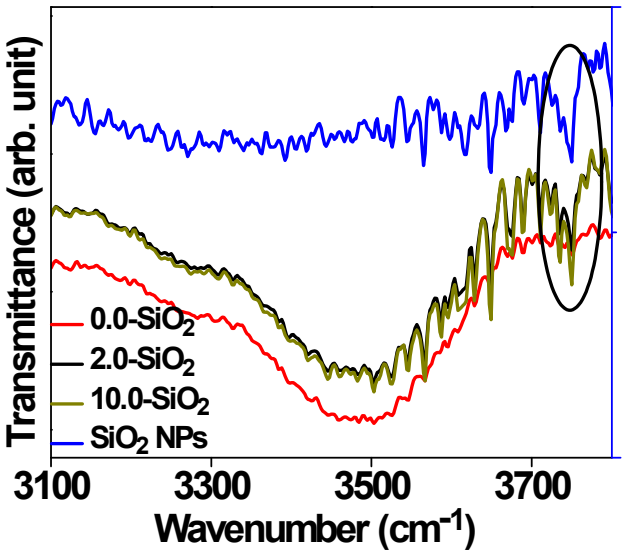


Figure S1: FTIR spectra of SiO_2 NPs and SPEs showing band in the range of 3740-3750 cm^{-1} corresponding to silanol groups.

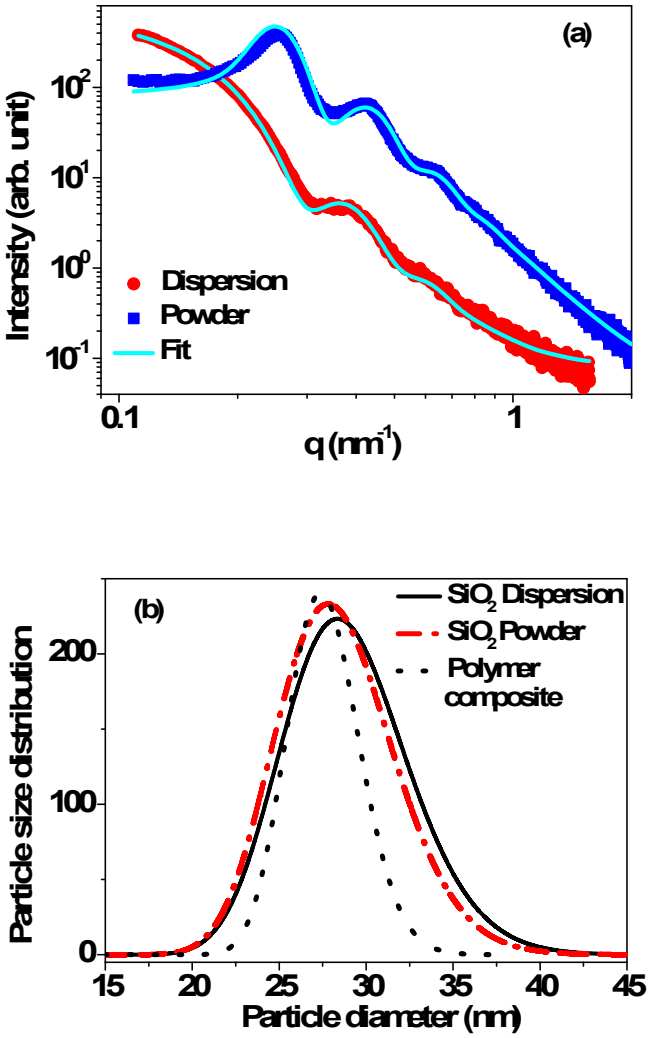


Figure S2: (a) The SAXS profile of the 2 wt.% silica dispersion and the dried silica nanopowder are depicted. The SAXS profiles have been fitted using eq. 6 in the manuscript (b) particle size distribution is estimated from both the profiles as well as estimated in the composite SPE.

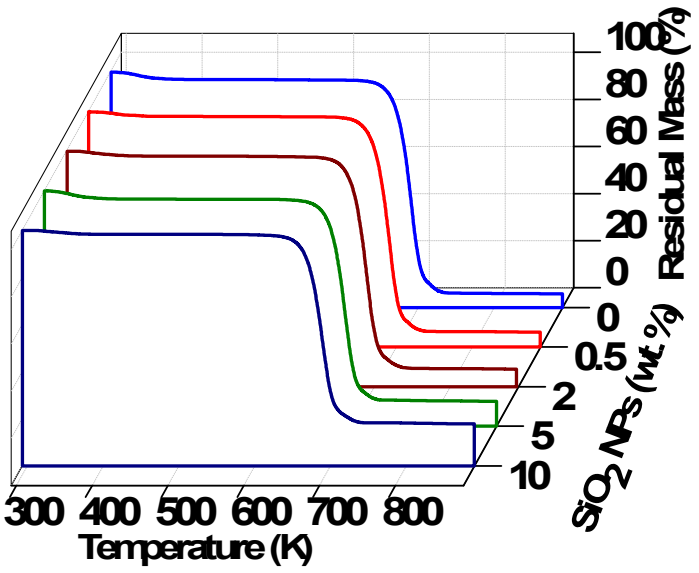


Figure S3: TGA curves of PEO based electrolytes with different loadings of SiO_2 NPs (0.0 -10.0 wt.%).

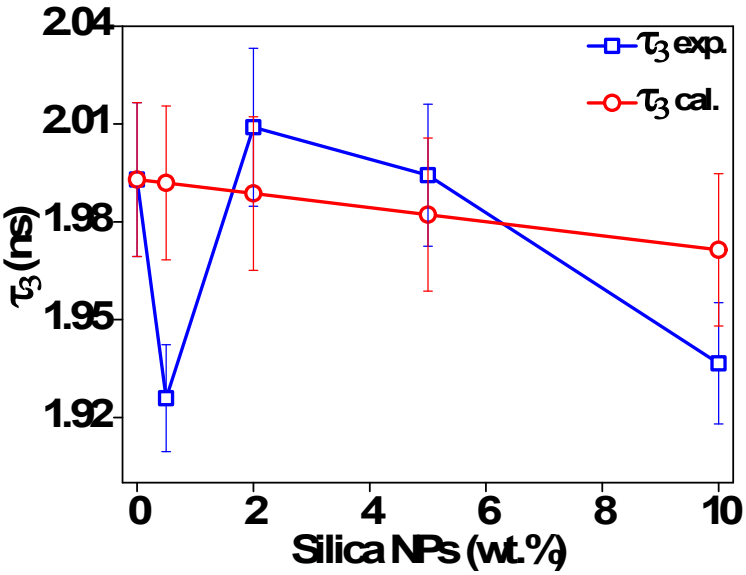


Figure S4: *o*-Ps lifetime as a function of SiO_2 NPs loading. The red circle symbol shows the calculated *o*-Ps lifetime considering SPEs as mixture of PEO-5wt.% LiTFSI and SiO_2 NPs using eq. $\tau_{cal} = x\tau_{silica} + (1-x)\tau_{silica\text{-}0}$, where x is the weight fraction of SiO_2NPsin the electrolyte. Lines are guide to the eye.

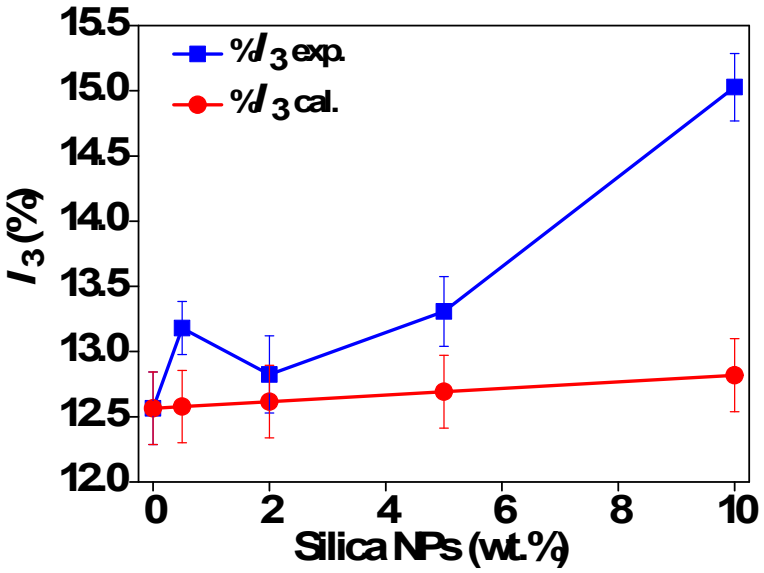
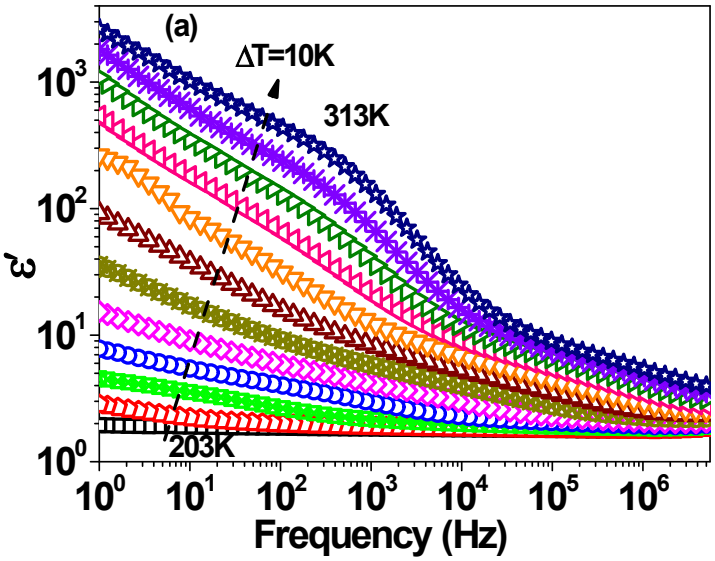
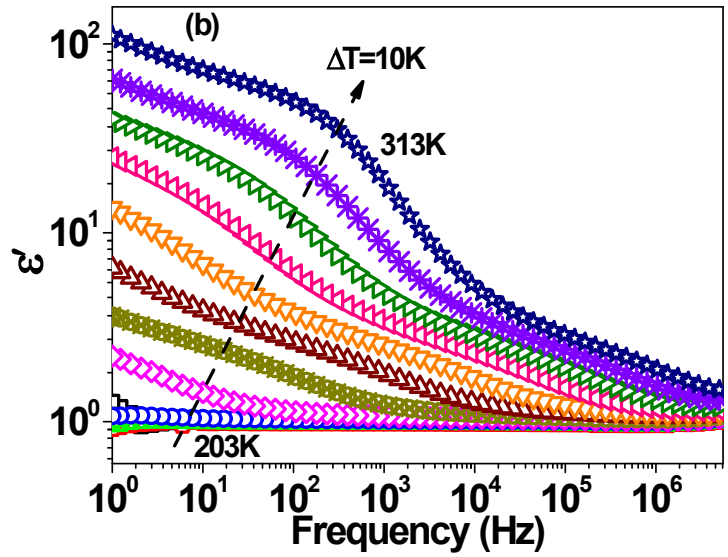
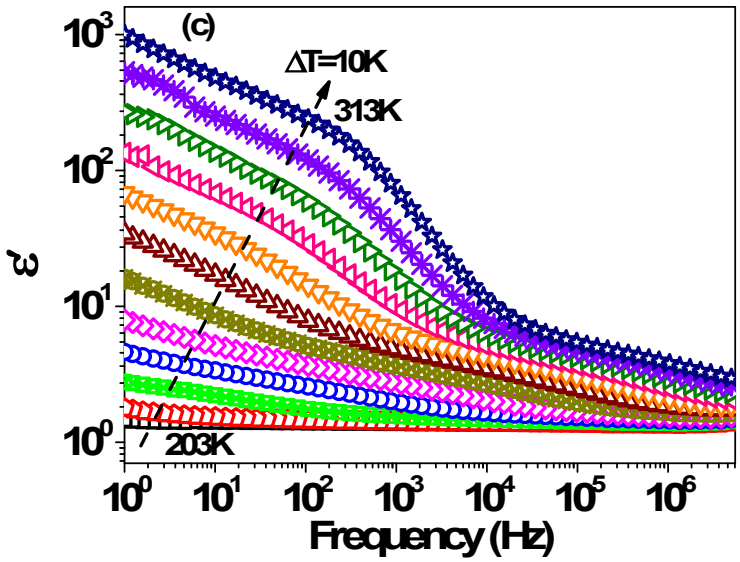


Figure S5: *o*-Ps intensity as a function of SiO_2 NPs loading. The red circle symbol shows the calculated *o*-Ps lifetime considering SPEs as mixture of PEO-5wt.% LiTFSI and SiO_2 NPs using eq. $I_{cal} = xI_{silica} + (1-x)I_{silica-0}$, where *x* is the weight fraction of SiO_2NPs in the electrolyte. Lines are guide to the eye.




(b)
ΔT=10K
313K
203K
ε
Frequency (Hz)


(c)
ΔT=10K
313K
203K
ε
Frequency (Hz)

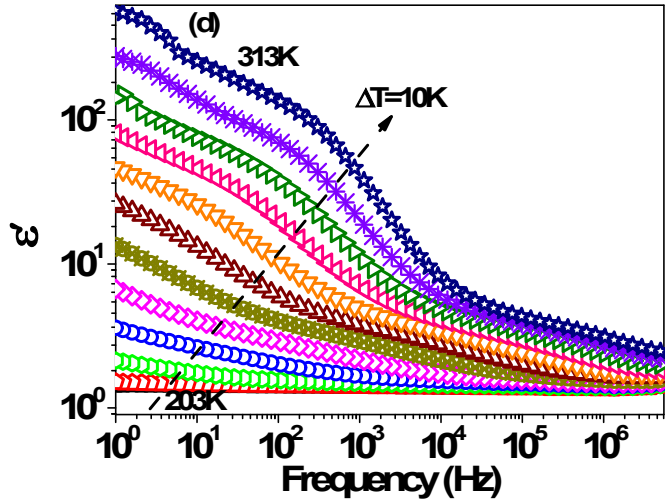
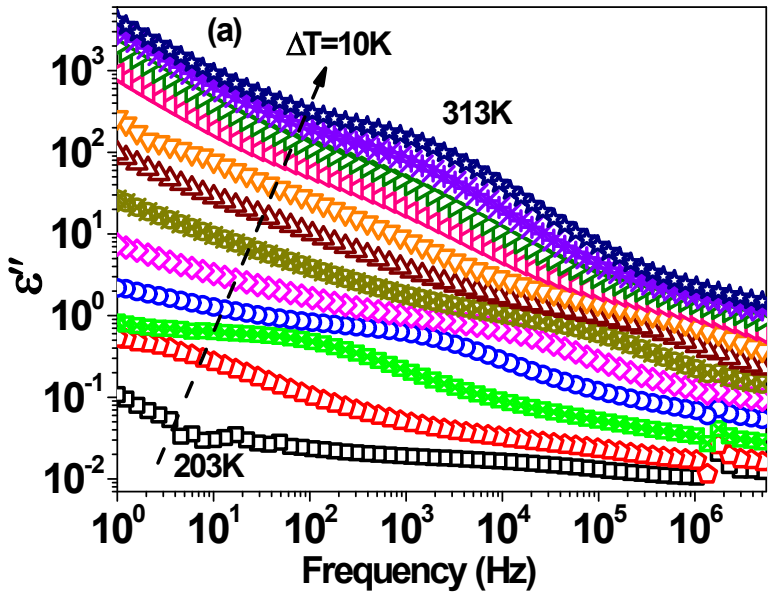
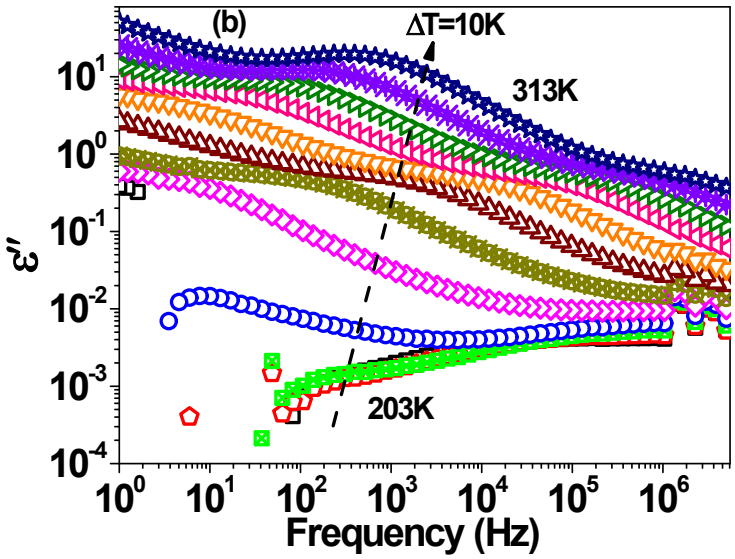
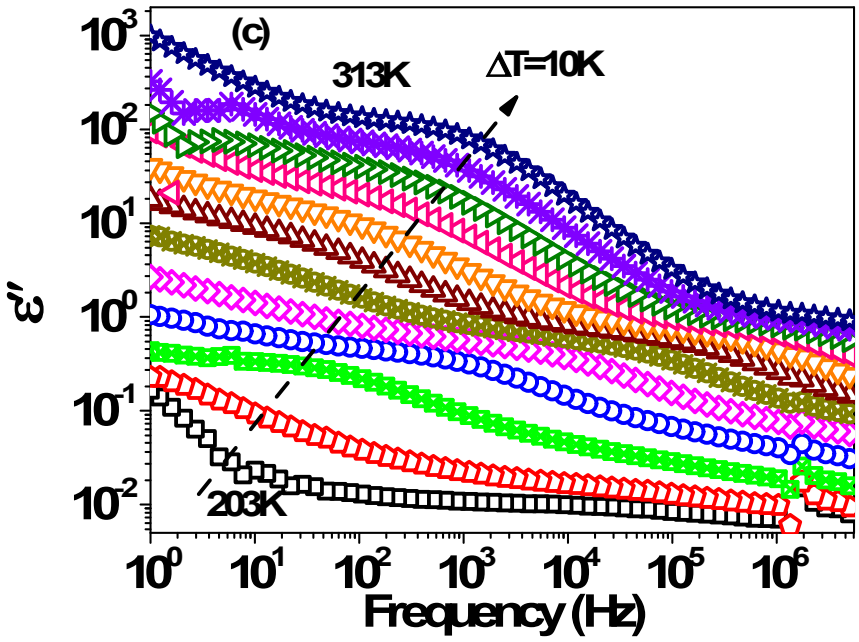


Figure S6: Real part (ε') of the complex permittivity of (*a*) 0.0-SiO_2 (*b*) 0.5-SiO_2 (*c*) 2.0-SiO_2 (*d*) 10.0-SiO_2 SPEs.




(b)
ΔT=10K
313K
203K
ε''
Frequency (Hz)


(c)
313K
ΔT=10K
203K
ε''
Frequency (Hz)

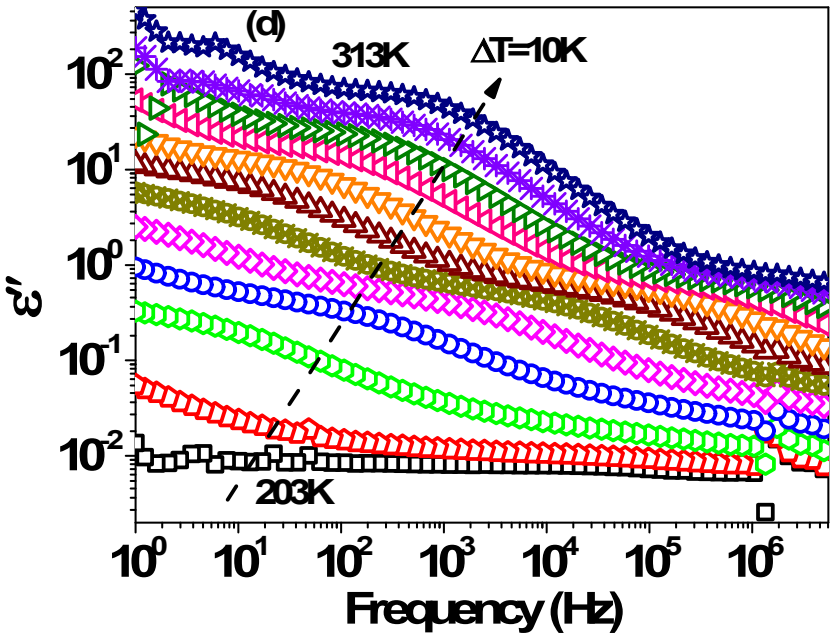
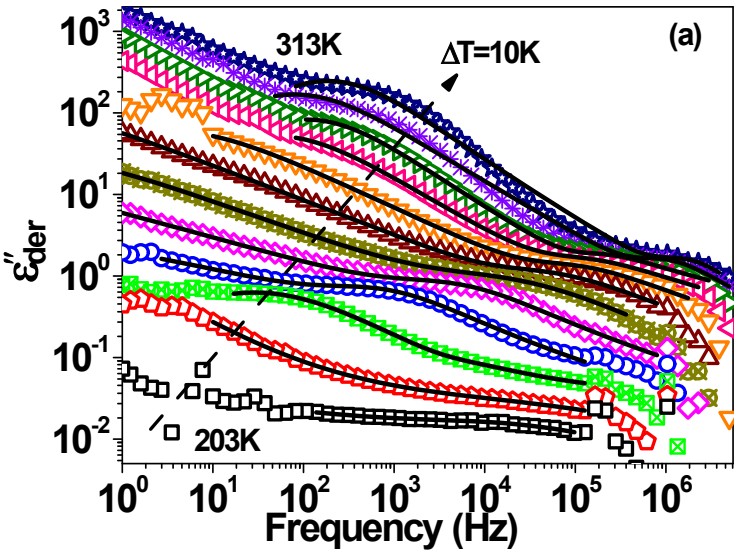
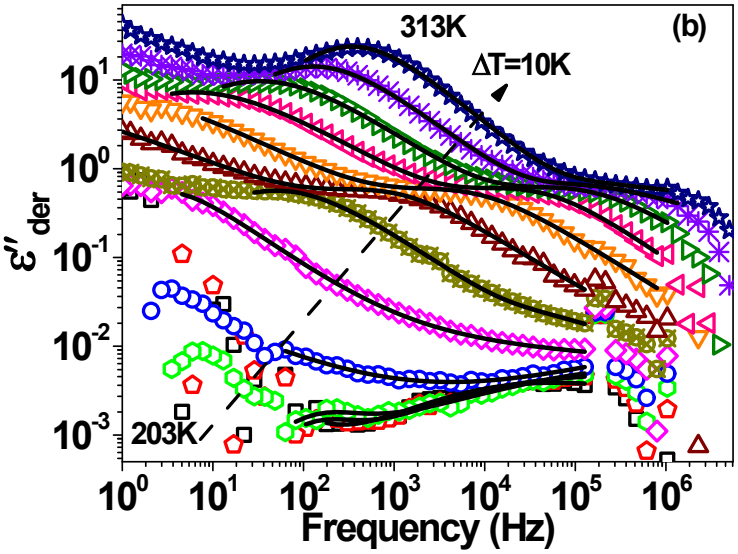
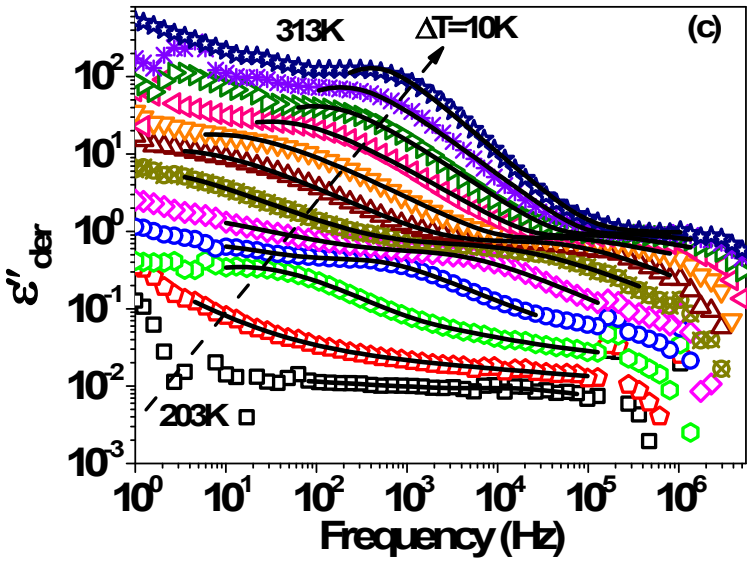
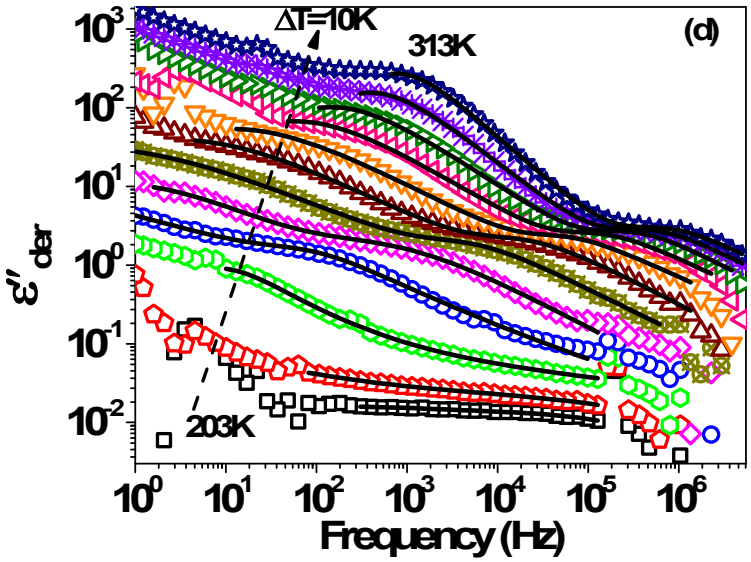


Figure S7: Imaginary part (ε'') of the complex permittivity of (*a*) 0.0-SiO_2 (*b*) 0.5-SiO_2 (*c*) 2.0-SiO_2 (*d*) 10.0-SiO_2 SPEs.


313K
ΔT=10K
(a)
203K
ε''_{der}
Frequency (Hz)


313K
ΔT=10K
(b)
203K
ε''_{der}
Frequency (Hz)


313K
ΔT=10K
(c)
203K
ε''_{der}
Frequency (Hz)


ΔT=10K
313K
(d)
203K
ε''_{der}
Frequency (Hz)

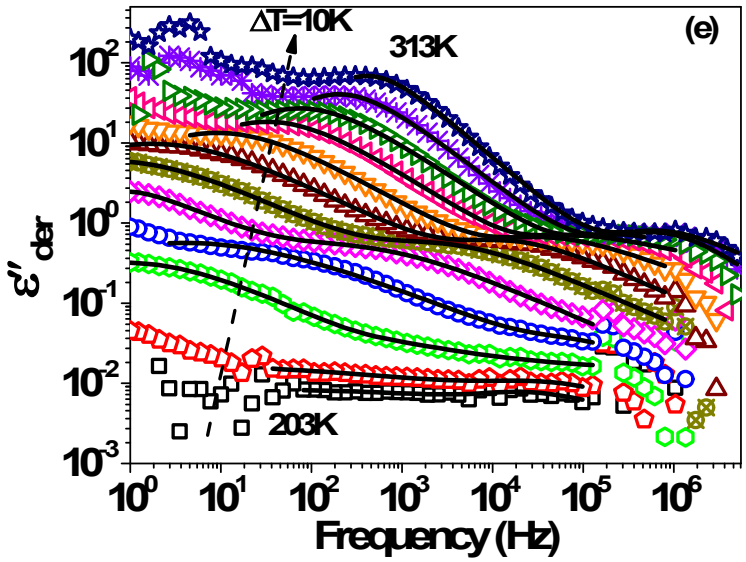
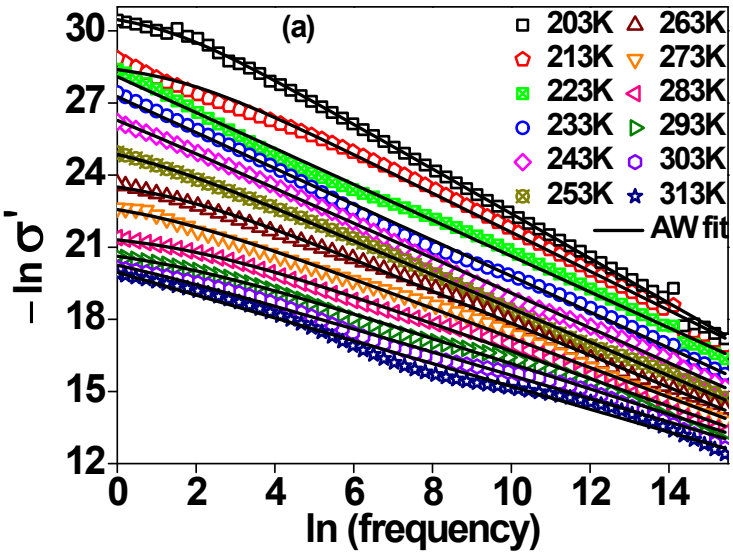
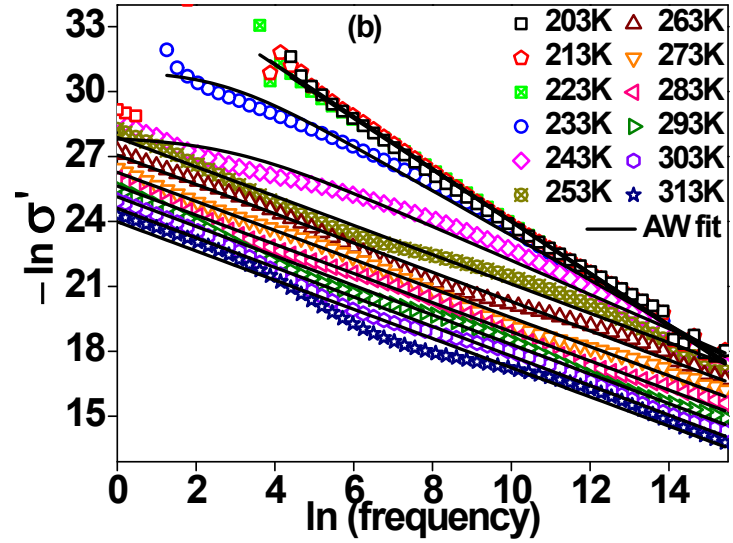
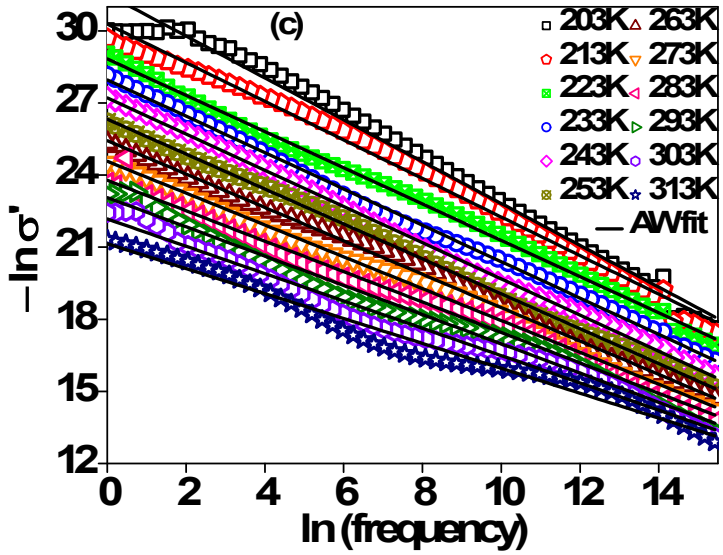
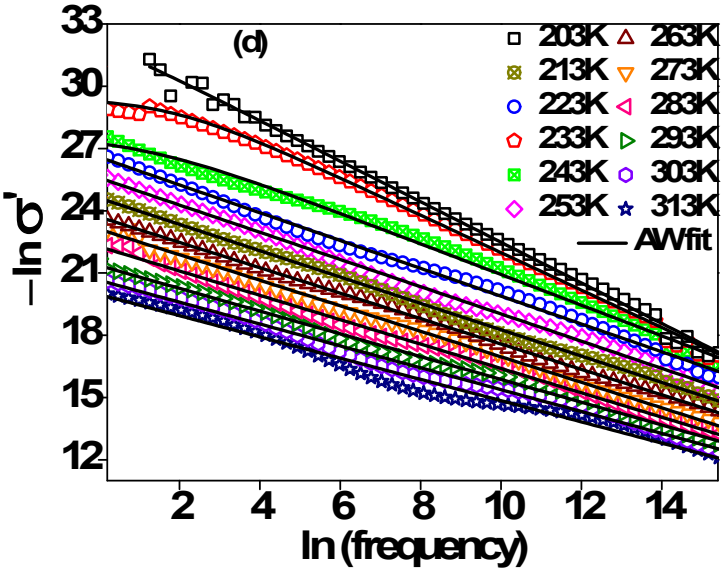


Figure S8: ε''_{der} curves of (*a*) 0.0-SiO_2 (*b*) 0.5-SiO_2 (*c*) 2.0-SiO_2 (*d*) 5.0-SiO_2 (*e*) 10.0-SiO_2 SPEs.


(a)
203K
213K
223K
233K
243K
253K
263K
273K
283K
293K
303K
313K
AW fit
– ln σ'
ln (frequency)
30
27
24
21
18
15
12
0
2
4
6
8
10
12
14


(b)
203K
213K
223K
233K
243K
253K
263K
273K
283K
293K
303K
313K
AW fit
– ln σ'
ln (frequency)
33
30
27
24
21
18
15
0
2
4
6
8
10
12
14


(c)
203K
213K
223K
233K
243K
253K
263K
273K
283K
293K
303K
313K
AWfit
-ln σ'
ln (frequency)
30
27
24
21
18
15
12
0
2
4
6
8
10
12
14


(d)
203K
213K
223K
233K
243K
253K
263K
273K
283K
293K
303K
313K
AWfit
-ln σ'
ln (frequency)
33
30
27
24
21
18
15
12
2
4
6
8
10
12
14

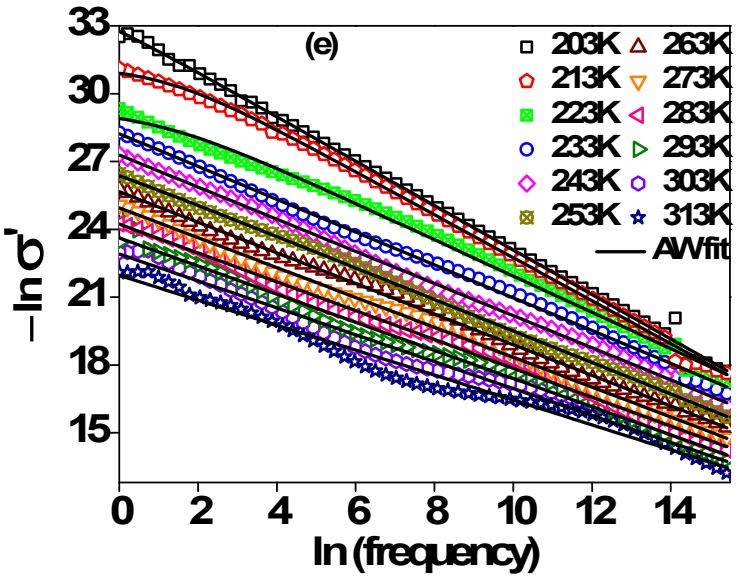


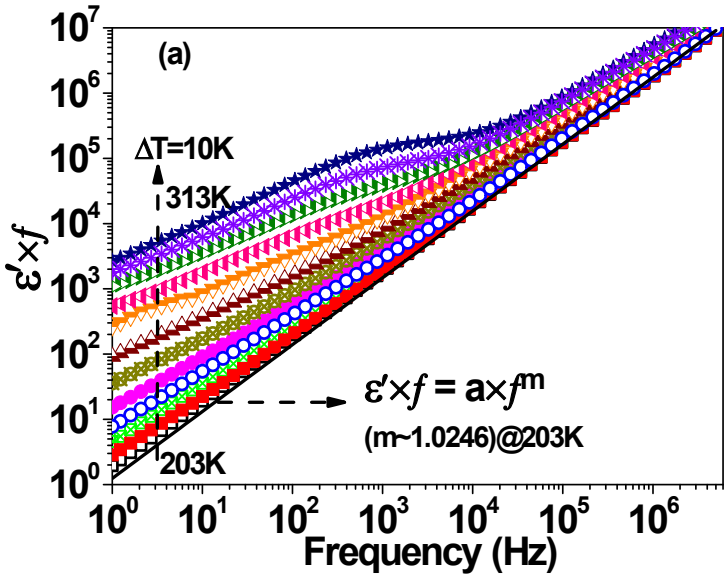
Figure S9: Negative log-log plot of ac conductivity (σ') for (*a*) 0.0-SiO_2 (*b*) 0.5-SiO_2 (*c*) 2.0-SiO_2 (*d*) 5.0-SiO_2 (*e*) 10.0-SiO_2 SPEs. Solid line shows fit using Almond-West (AW) formalism.

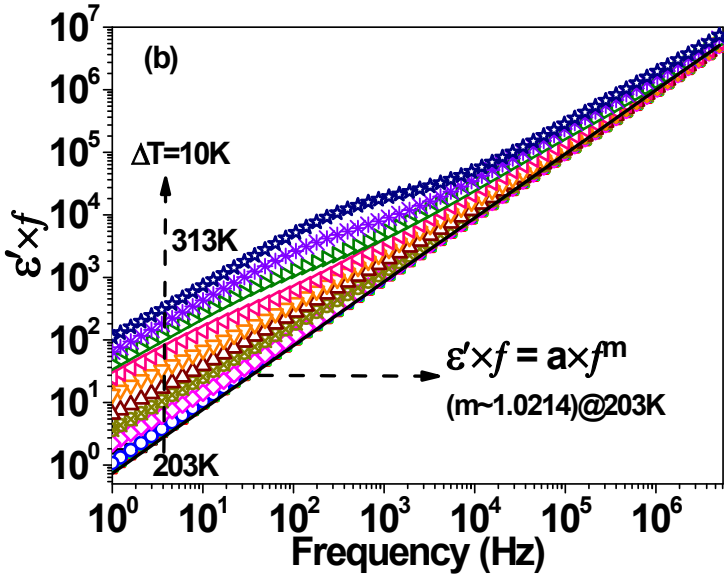
Kramer-Krönig approach [S1]:

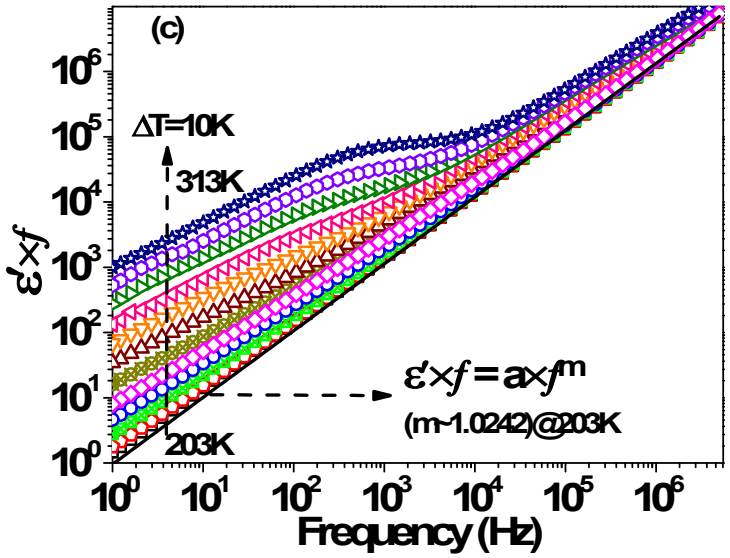
The mathematical expression for Kramer-Krönig approach is given by eq. S1.

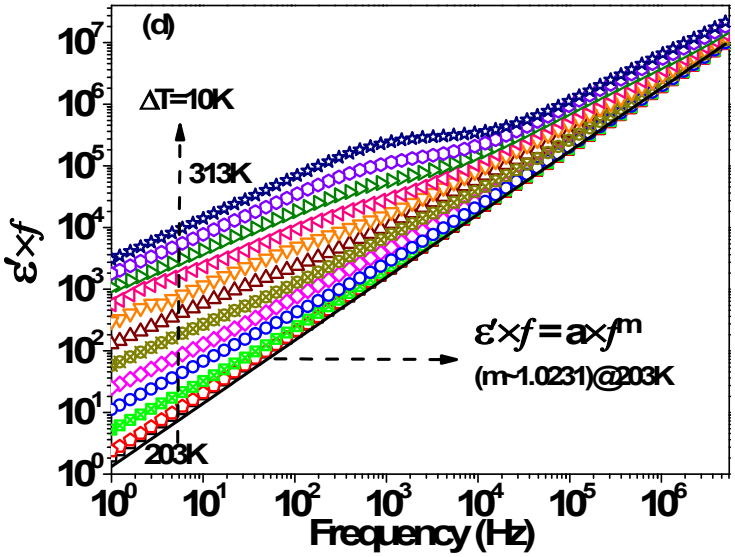
$$\varepsilon' f = a f^{m} \quad \text{(S1)}$$

The exponent 'm' is weak temperature dependent parameter. Nearly unity value of the exponent shows NCL behaviour and fractional values shows dominance of UDR. Figure S8 shows the variation of ($\varepsilon' f$) with frequency. Fitting the spectra as per eq.S1 results in approximate unity values in and around lower temperatures ~203 K showing the dominance of NCL in low temperature range. The exponent 'm' decreases with increasing temperature indicating the dominance of UDR in high temperature range. It may also be noted that 'm' values is almost similar for different silica loading showing that it is only temperature dependent irrespective of the filler concentration. Considering the frequency dependence, the linear region showing NCL extends over entire frequency region at lower temperature while this linear region shifts to higher frequencies on increasing temperature.


(a)
ΔT=10K
313K
203K
ε′×f = a×f^m
(m~1.0246)@203K
ε′×f
Frequency (Hz)


(b)
ΔT=10K
313K
203K
ε′×f = a×f^m
(m~1.0214)@203K
ε′×f
Frequency (Hz)


(c)
ΔT=10K
313K
203K
ε′×f = a×f^m
(m~1.0242)@203K
ε′×f
Frequency (Hz)


(d)
ΔT=10K
313K
203K
ε′×f = a×f^m
(m~1.0231)@203K
ε′×f
Frequency (Hz)

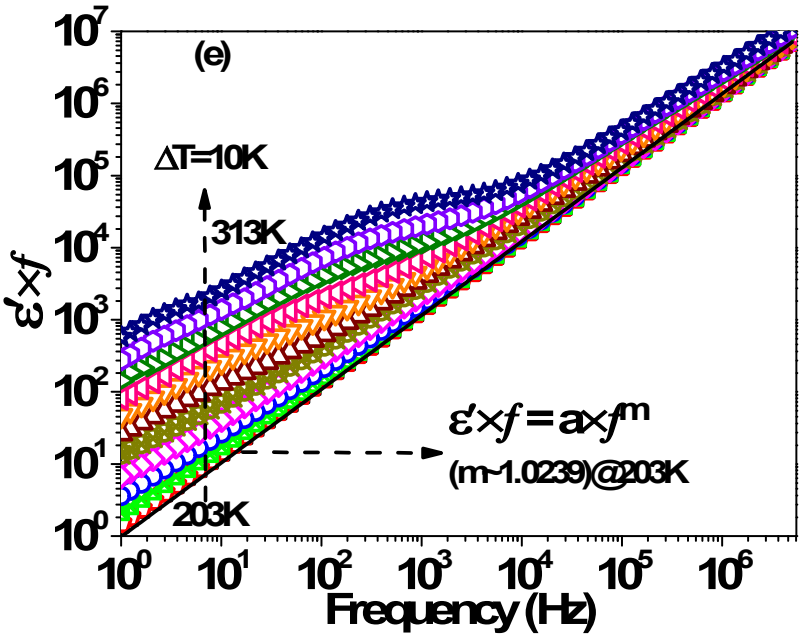
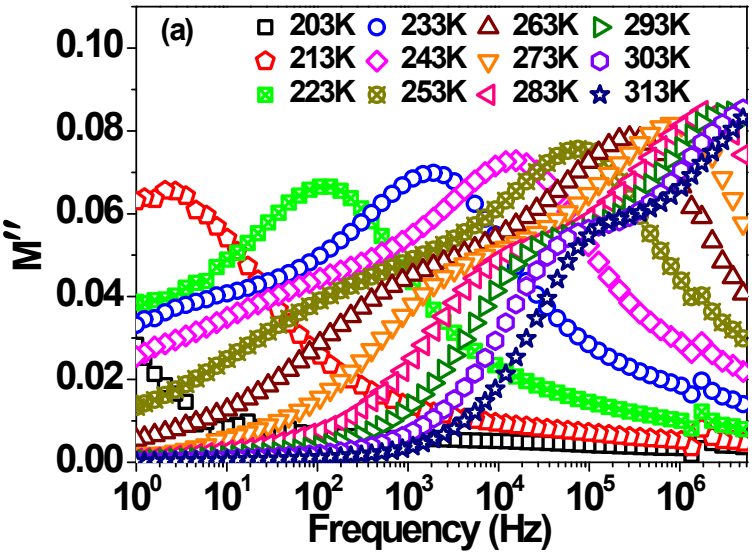
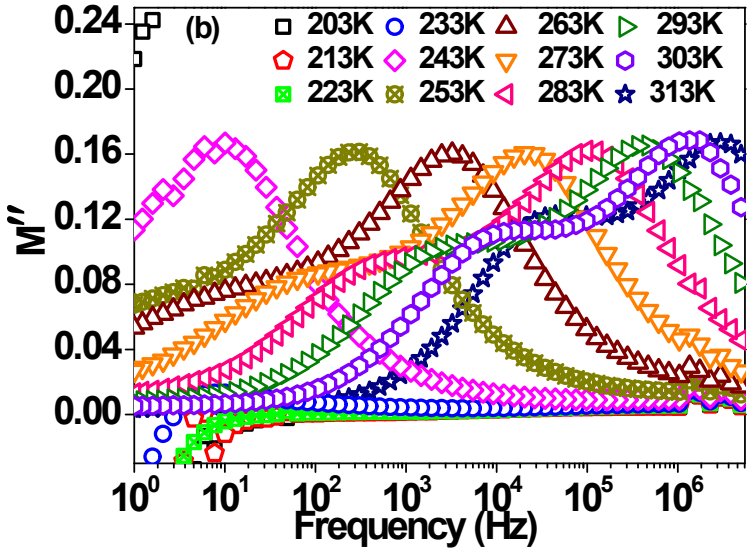
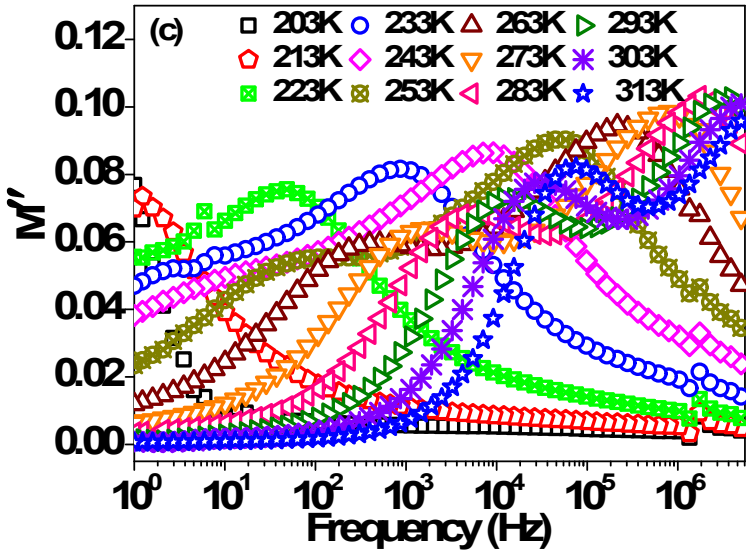


Figure S10: Kramer-Krönig formalism applied to (a) 0.0-SiO_2 (b) 0.5-SiO_2 (c) 2.0-SiO_2 (d) 5.0-SiO_2 (e) 10.0-SiO_2 SPEs.




(b)
203K
213K
223K
233K
243K
253K
263K
273K
283K
293K
303K
313K
M''
0.24
0.20
0.16
0.12
0.08
0.04
0.00
10^0
10^1
10^2
10^3
10^4
10^5
10^6
Frequency (Hz)


(c)
203K
213K
223K
233K
243K
253K
263K
273K
283K
293K
303K
313K
M''
0.12
0.10
0.08
0.06
0.04
0.02
0.00
10^0
10^1
10^2
10^3
10^4
10^5
10^6
Frequency (Hz)

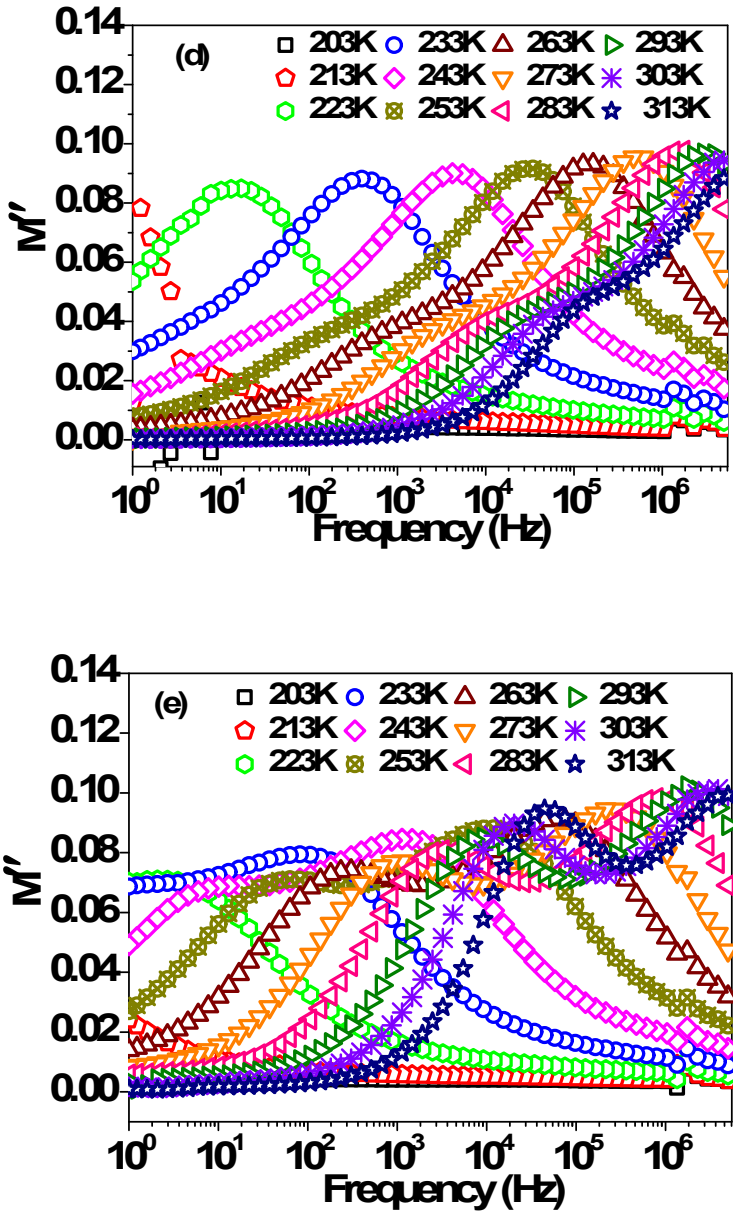


Figure S11: Imaginary part of the Modulus, M″(*f*) of (a) 0.0-SiO_2 (b) 0.5-SiO_2 (c) 2.0-SiO_2 (d) 5.0-SiO_2 (e) 10.0-SiO_2 SPEs.

REFERENCES

S1. T. Dam, S. S. Jena and D. K. Pradhan, *Phys. Chem. Chem. Phys*., 2016, **18**, 19955-19965.