Improvement in Physical Properties of Dispersed Liquid Crystal Thin Films for Storage Display Devices*

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Abstract: In the present work, dispersed liquid crystal thin films have been prepared by dispersion of small amount (0.01, 0.03% wt./wt. ratio) of multiwall carbon nanotube and silica nanoparticle into ferroelectric liquid crystal material and characterized using polarization current technique and dielectric spectroscopy in the frequency range of 50Hz-1MHz. The effect of nanomaterials doping into FLCs on the morphological behaviour, electro-optic switching and dielectric permittivity have been studied and compared with pure FLC material. It is found that MWCNTs doped sample shows better alignment, higher spontaneous polarization and faster switching time which is due to ion trapping of MWCNTs into FLC. The dielectric permittivity decreases with increasing the MWCNTs concentration. In silica doped samples, switching time and spontaneous polarization also decreases with increasing the silica concentration. A decrease in dielectric permittivity (~36%) and transition temperature (5-6°C) was noticed in the silica doped samples. This decrease in permittivity is may be due to the strong anchoring forces develop between higher concentrated silica and FLC molecules. A memory effect has been observed in silica doped FLC samples.

Keywords: Multiwall carbon nanotubes, silica nanoparticle, ferroelectric liquid crystal, polarization, switching time and permittivity

1. Introduction

Dispersed liquid crystal composite materials have received significant attention by research community due to their potential application in electro-optic display[1,2]. Immense work was done on dispersed liquid crystal materials doped with polymers and dyes to understand the liquid crystal

behavior and improve the electro-optic and electrical properties of existing liquid crystals (LCs)[3,4]. Dispersed liquid crystals materials prepared using carbon nanotubes, nanoparticles (NPs) such as MWCNTs, SWCNTs, CdSe[5], BaTiO₃[6], Sn₂P₂S₆[6], Pd[7], MgO[8], SiO₂[9], Au[10] etc. into liquid crystals have shown tremendous interest due to unique thermal, mechanical, electrical properties of nanoparticles. Due to the increasing demand of these novel materials for display applications, the improvement in existing properties of LC materials is highly desirable. The improvement in physical properties of liquid crystals depends on various factors of doping materials. These factors include selection of materials, size, type, concentration, intrinsic characteristic and mutual interaction between guest and host material. Low concentration of NPs are usually preferred to yield a more stable and even distribution on the LCs, which lowers the interaction forces between the LC and NPs[11]. Initially dispersion of NPs into nematic liquid crystals (NLCs) was focused on the dielectric properties[12] and only few results were reported under the influence of aerosol particles on the phase transitions of LCs[13]. The addition of NPs into NLCs results a significant changes in electro-optical, morphological and dielectric properties[14-16].

Recently, much attention has been devoted on the synthesis of new materials of improved properties of ferroelectric liquid crystal (FLCs). In this paper, we study the effect of silica nanoparticle and carbon nanotube concentration on the morphology, electro-optic and dielectric permittivity of FLC and finally results have been compared with pure FLC material.

2. Experimental

2.1 Materials properties

FLC material trade name KCFLC10R (Kingston Chemicals, UK)[17] has been used in present investigations. FLC material has spontaneous polarization 23nC/cm², tilt angle 22°, optical birefringence 0.18 at 25° C and phase sequence as

$$K \xleftrightarrow{5°C} SmC^* \xleftrightarrow{64.5°C} SmA \xleftrightarrow{99.5°C} N^* \xleftrightarrow{112°C} I$$
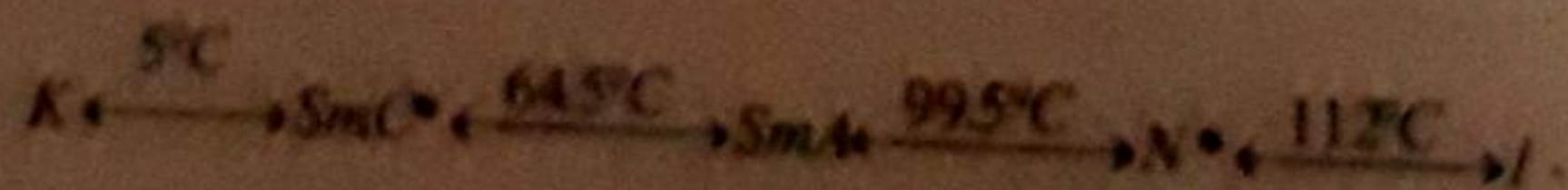
In our experiment MWCNTs and silica nanoparticle (SNP) were purchased from (M/S Sigma Aldrich, India)[18]. The dimension of MWCNTs is 100-170 nm and length 5-9 μm. These spherical silica nanoparticles have particle size 5-15 nm and molecular weight 60.08. SNP in different concentrations (0.01%, 0.03wt./wt.% of FLC) were doped into FLC.

2.2 Preparation of sample cells

To get a completely homogenize mixture, SNP in 0.01%, 0.03% wt./wt. ratio were mixed into FLC at room temperature and than ultrasonication was done at a frequency of 36kHz for one hour. Planar aligned cells made of indium tin oxide (ITO) coated glass substrates of thickness 12μm were used for detailed studies. These glass substrates which were initially spin coated with a solution of nylon 6/6 and m-cresol and then rubbed uni-directionally for planar alignment. The prepared homogenize mixture was filled in empty sample cell by capillary action at the isotropic temperature of FLC. Similar method was adopted to prepare the MWCNT doped in 0.01%, 0.03% wt./wt. ratio into FLC sample cell for detailed measurements.

2.3 Experimental details

Pure FLC and doped sample cells were placed in hot stage (model THMSE 600) attached with temperature controller (model Linkam TP94) for electro-optic and dielectric investigations. Electro-optic studies have been carried out by triangular wave method and output response were seen on a digital storage oscilloscope (model- Tektronix TDS2024B) interfaced with computer.

Phase transition in the samples was observed under cross polarizer at 10x magnification with the help of polarizing microscope (model Olympus BX-51P) interfaced with charge couple device camera. The electric field was applied through function generator (model Philips FG-8002). The output responses were detected using photo multiplier tube (RCA931) attached with a microscope. The dielectric studies have been carried out in the frequency range of 50Hz to 1MHz by LCR meter (model Fluke- PM6306). To avoid the low and high frequency corrections data were calibrated with air and benzene[19].

3.   Results and Discussion

3.1 Morphological analysis

Fig. 1 shows the micro-texture of FLC phases observed in 0.00%, 0.01% and 0.03% MWCNTs-FLC samples at 30^0C & 60^0C under cooling condition. The micro-texture shows that doping of MWCNTs in FLC material slightly enhances the alignment of FLC molecules in the SmC* phase, which are clearly seen in Fig. 1 (b, c). The micro-texture observed for silica doped FLC sample cells at 30^0C and 60^0C are shown in Fig. 2.

30°C   (a)   60°C   30°C   (b)   60°C
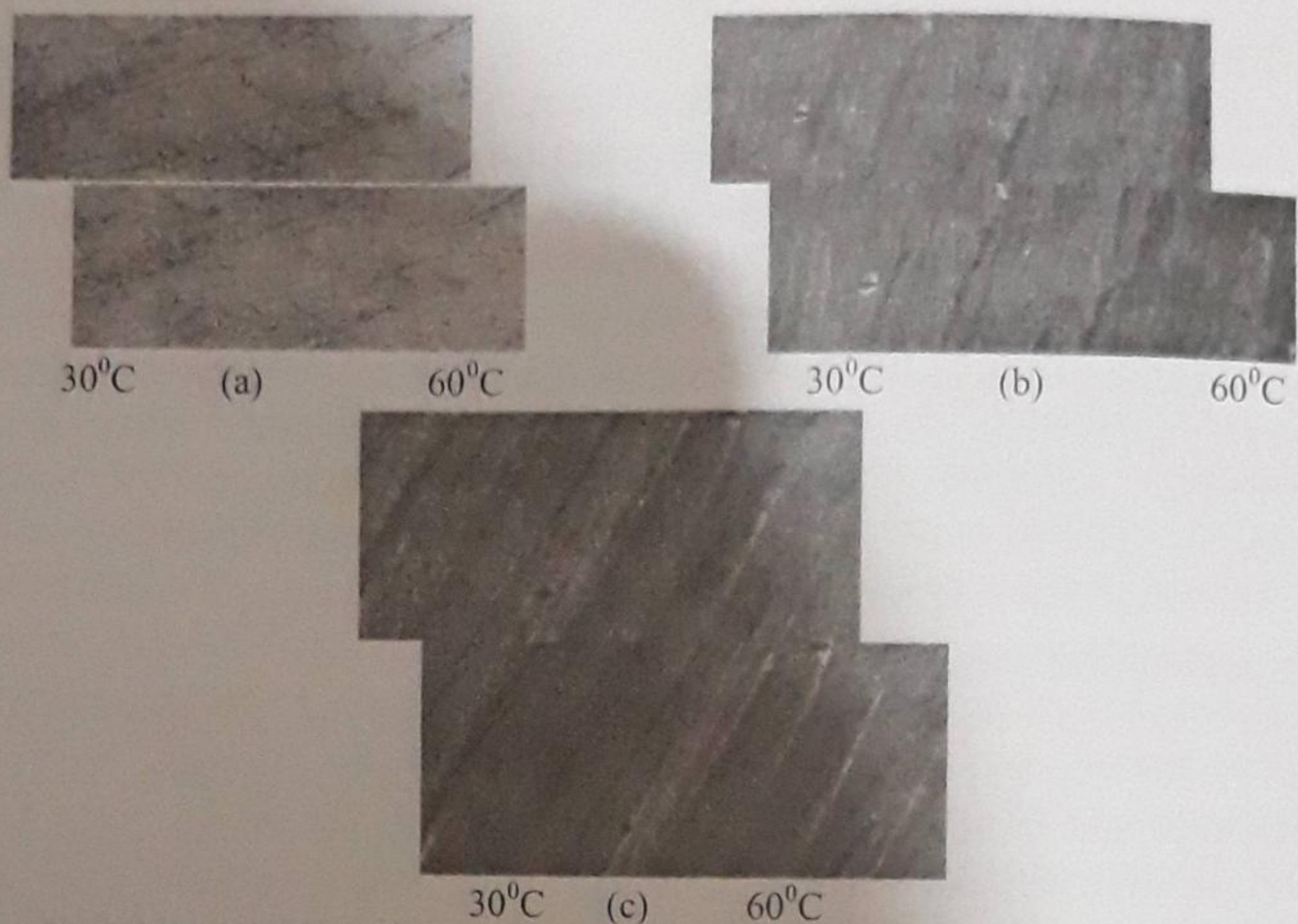
30°C   (c)   60°C

Fig.1. Micro texture of pure and doped sample cells at different temperature at
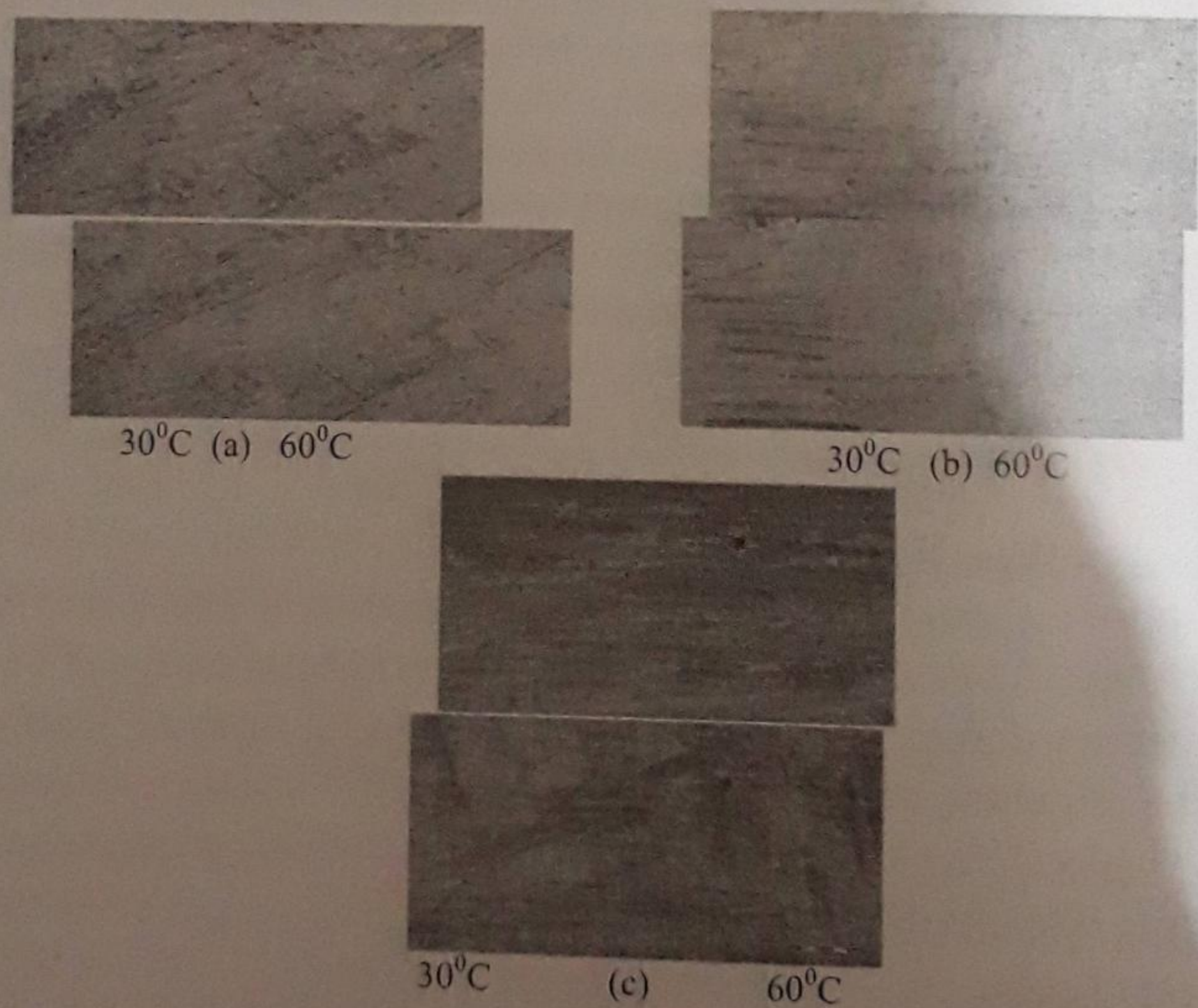magnification of 10x for (a) 0.00% (b) 0.01% and (c) 0.03 % MWCNTs

30°C (a) 60°C   30°C (b) 60°C

30°C   (c)   60°C

Fig 2. Micro texture of pure and silica doped sample cells at different temperature at
magnification of 10x for (a) 0.00% (b) 0.01% and (c) 0.03 %

3.2 Electro-optic properties
3.2.1 Polarization switching

Polarization current technique is one of the most precise methods for the measurement of electro-optic parameters in liquid crystals [20]. In this method, a symmetric triangular wave applied to FLC and doped film reorients the dipoles between two stable polarization states (i.e. UP and DOWN) and molecular realignment in the form of voltage drop was detected on the storage oscilloscope across a standard resistance. For a certain applied voltage the response of current I(t) consist of three components, the capacitive term (I_C) and the ionic conduction term (I_R). The third term is polarization current (I_P) due to the charge induced by the dipole realignment in the form of polarization hump. Thus the contribution to the total current would be

(3.1)
$$I(t) = I_R + I_C + I_P.$$

The area under the polarization hump is a measure of the spontaneous polarization (P_s) is given by[20].

(3.2)
$$P_s = \frac{A(V \times t)}{R(Area\ of\ Sample)},$$

where $A(V \times t)$ is the area under the curve measured by integrating the polarization hump in terms of voltage and time.

Typical temperature dependence on spontaneous polarization (P_s) at 10V (50Hz) in 0.00%, 0.01% and 0.03% MWCNTs doped samples is shown in Fig.3. It can be seen from Fig. 3 that in pure and doped samples polarization decreases with increasing the temperature and follow the first order phase transition behaviour. Doping of MWCNTs in FLC increases the P_s ~30% as compared to pure FLC sample. This increase in P_s might be due to the increase in ion concentration which induces more dipole moment in MWCNTs doped FLC cells. Authors believe that doping of MWCNTs in FLC mixture not only increases the P_s, but also enhances the alignment of FLC molecules and as a result shows more polarization value. The better alignment was confirmed by optical textures as directly reflects in Fig. 1(b-c). Fig. 4 shows the response time (τ_s) behaviour as a function of temperature in pure and doped samples. It is found that response time (i.e.

the time taken by the molecules to switch from ON to OFF state) as represented in Eq. (3.3) [20, 21] decreases with increasing the concentration of MWCNTs in FLC mixture.

$$ (3.3) \qquad \tau_s = \frac{\eta}{P_s E}, $$

where and E are the rotational viscosity and electric field. Fig. 4 infers that the doping of MWCNTs decreases the response time from 2.02 msec to 0.40 msec at 30°C. The fastening of response time in doped sample is explained on the basis on ions trapping mechanism, which are present in any CNTs-LC mixture to some extent. The CNTs makes a double electric layer on the interface between FLC and alignment layer coated on ITO coated glass substrates. The trapping of ions generates a depolarization field (E_{dpol}) on this interface, which is opposite to the external electric field (E_{ext}) applied to the cell. Hence, the effective electric field (E_{eff}) which is equal to $E_{ext} - E_{dpol}$ applied to the FLC layer will be smaller than E_{ext}. As a result, the response time given in Eq. (3.3) is strongly dependent to effective electric field applied to the cell. Because of ion trapping in doped cells, the depolarization electric field is lower as compared to those of pure FLC cell; as a consequence effective electric field in doped cells is higher as in pure FLC cell. As a result, doped sample cells show a shorter response time than pure FLC cell.

Fig. 5 shows that the temperature dependence on spontaneous polarization (P_s) for pure and silica doped sample cells at 10V. It can be seen from fig. 5 that polarization decreases with increases the temperature for pure as well as doped samples and decreases with increasing the silica concentration. Approximately 5-6°C decreases in in doped samples have been observed which was confirmed by electro-optic responses. Decrease in T_c, may be due to the change in ordering of FLC molecules and existence of impurity in NPs. Temperature dependence on at different silica concentrations is also shown in fig. 6. Figure 6 shows that 0.01% SNP doped sample have faster switching time than pure FLC and 0.03% doped sample cells. The decrease inand P_s in doped sample cells may be explained on anchoring phenomena. It has been reported that addition of nanoparticle increase the surface anchoring and hence corresponding affects on LC switching time. The LC switching time relation with the anchoring energy for weak and strong anchoring respectively can be expressed as follows [22]

$$(3.4) \qquad \tau_s = \frac{\eta}{K\pi^2}\left(d^2 + \frac{4dk}{W}\right), \qquad \text{for strong anchoring}$$

$$(3.5) \qquad \tau_s = \frac{4\eta d}{W\pi^2}, \qquad \text{for weak anchoring}$$

where d cell thickness, k bend elastic constant and W is anchoring energy coefficient. In both cases (strong and weak anchoring) the switching time is inversely propositional to anchoring energies. It means that if the anchoring energy would have been increased by doping silica particle, the switching time should be lowered. In our results we found similar trends for switching time as predicated from equation 3.4 and 3.5.
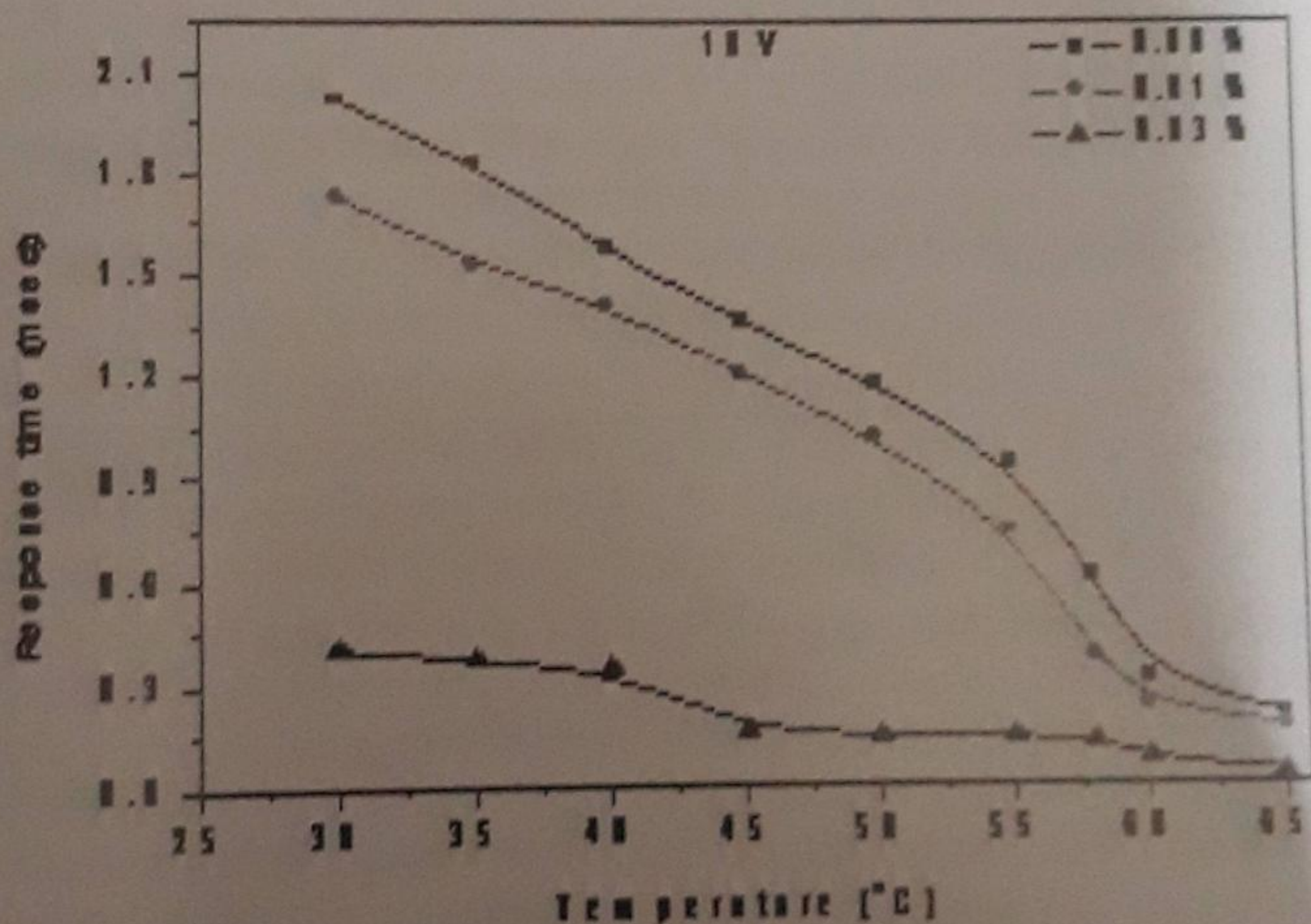
Fig. 3 Typical temperature versus spontaneous polarization with temperature for pure and MWCNTs doped samples at 10 volts ($f = 50$Hz)

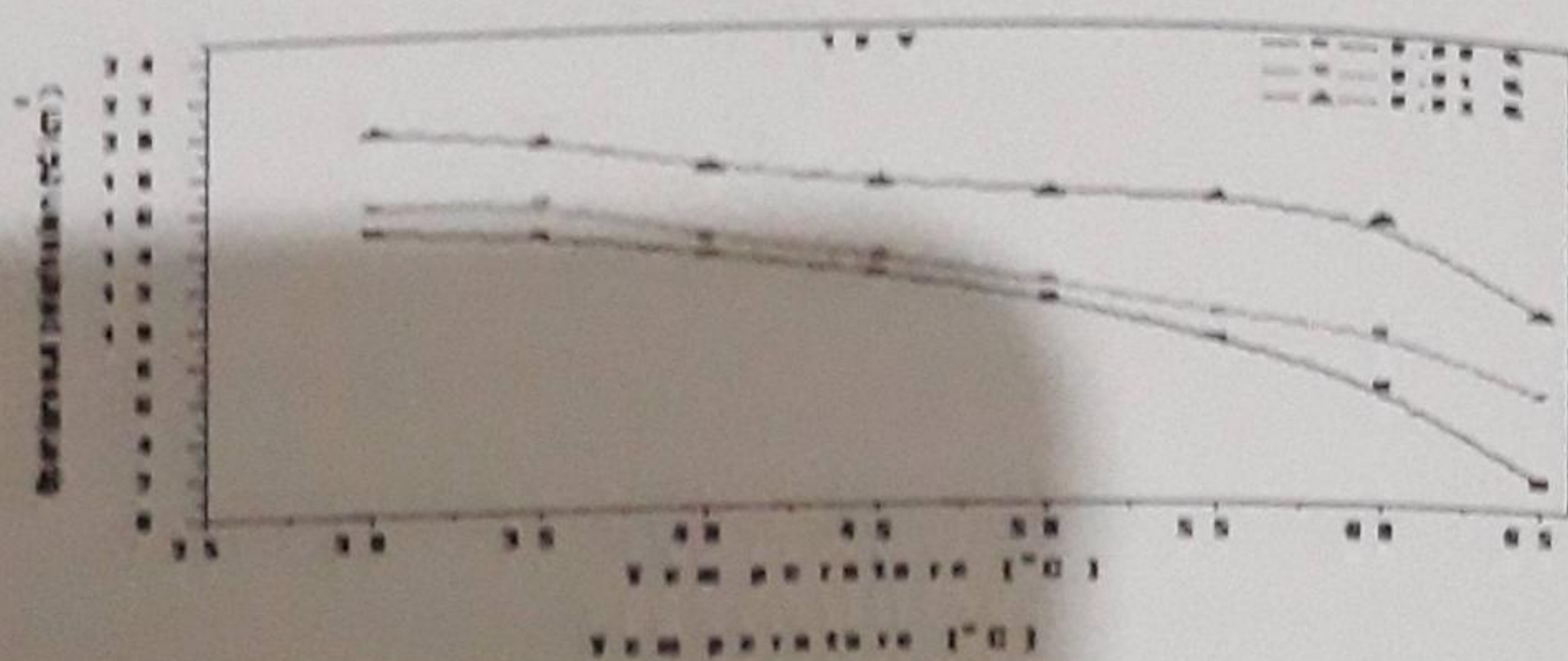Praveen Malik and K. K. Raina

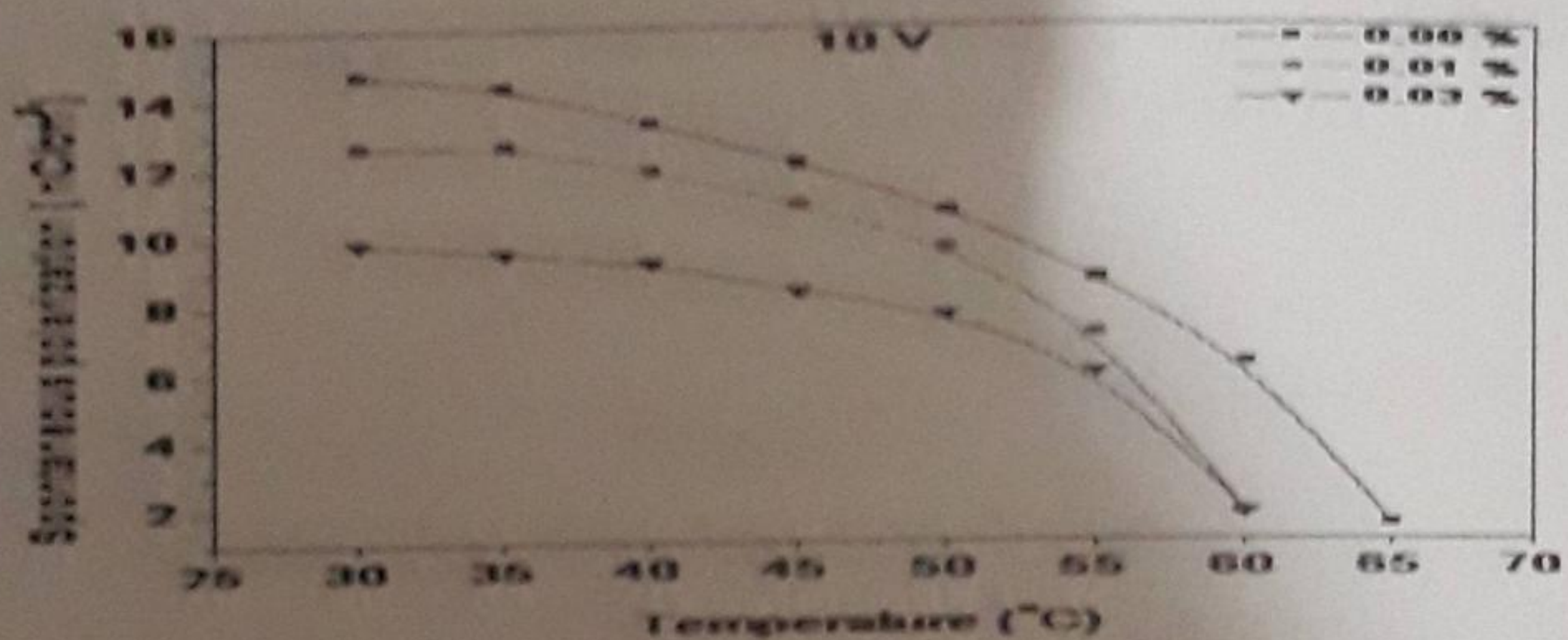Fig. 4 Temperature dependence on response time for pure and MWCNTs doped samples

Fig. 5. Temperature dependence on spontaneous polarization (P_s) for pure and silica doped
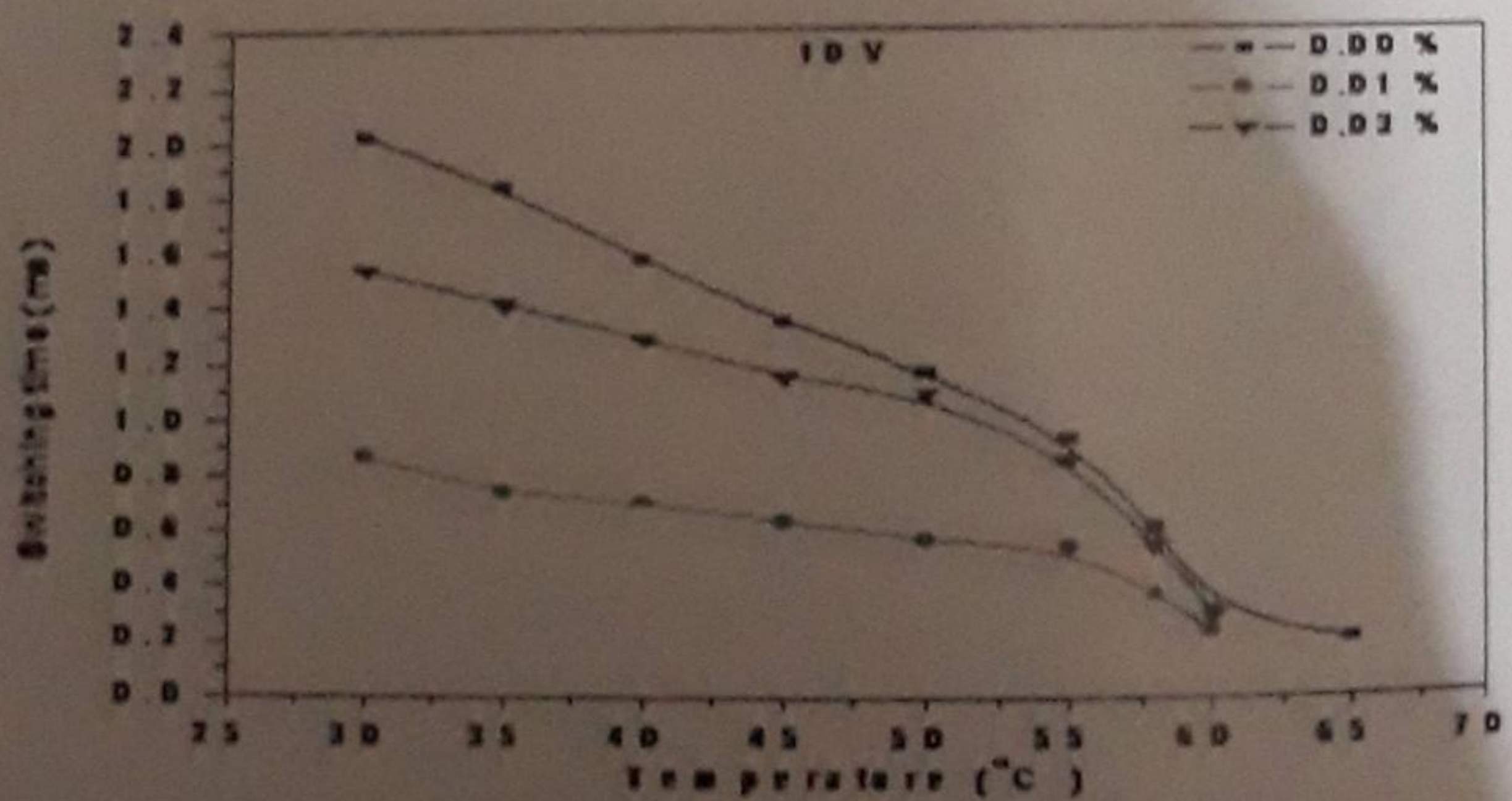
cells at 10V

Fig. 6. Temperature dependence on switching time () for pure and silica doped

sample cells

3.2.2 Frequency dependence on dielectric permittivity

Dielectric spectroscopy is an important tool to understand the molecular relaxation process in liquid crystals. The complex dielectric permittivity (ε^*) in terms of real (ε') and imaginary parts (ε'') is given by the relation[23]

$$(3.6) \qquad \varepsilon^*(\omega,\tau) = \varepsilon'(\omega,\tau) - i\varepsilon''(\omega,\tau),$$

Where $\omega = 2\pi f$ is the angular frequency of the applied electric field and τ is the relaxation time. The dielectric response consists of goldstone mode (GM) and soft mode (SM) in the SmC* phase which arise due to azimuthal and tilt angle fluctuations. The relaxation process for GM is given by

$$(3.7) \qquad \varepsilon^*(\omega,\tau) = \varepsilon_\infty + \frac{\Delta\varepsilon_{GM}}{(1+i\omega\tau)^{1-\alpha_{GM}}} + \frac{\sigma}{i\epsilon_o\omega},$$

where ε_∞ is the high frequency dielectric permittivity, $\Delta\varepsilon_{GM}$ and are dielectric strength and distribution parameter for GM mode respectively. ϵ_o is electric permittivity of free space and σ is electric conductivity.

Frequency dependence of dielectric permittivity (ε' and ε'') for pure FLC and MWCNT doped sample at 30°C is demonstrated in Fig.7. Fig. 7(a) shows that, at the lower frequency (50Hz-1kHz), ε' decreases from ~80-44% with increasing the MWCNTs concentration as compared to pure FLC sample. This continuous decrease in ε' is found up to 1kHz, however above 1-2 kHz no significant variation in ε' was noticed. This decrease in permittivity with the doping of MWCNTs may be due to the high electron affinity of the nanotubes leading to the ions trapping [24]. Fig. 7(b) also shows that in the low frequency limit, ε'' also decreases from ~53 (pure FLC sample) to ~10 in doped cell. A single relaxation mode at the frequency of ~200Hz is clearly reflected. The frequency dependence behaviour on and for pure and silica doped sample at 30°C are also given in fig. 8. Fig. 8(a) infers that in higher doped sample cells decreases with increasing the silica concentration. While at frequencies ($\geq 1kHz$) no much variation in was notice. Fig. 8(b) follows a typical absorption behaviour observed for liquid crystal samples. It can be seen from fig. 8(b) that permittivity continuously decreases with increasing silica amount. A relaxation mode which appears at ~100Hz in pure FLC cell slightly shifts to ~200Hz for silica doped samples. The observed Cole - Cole behaviour for pure FLC, multiwall doped and silica doped samples at 30°C are shown in figure 9 and 10.
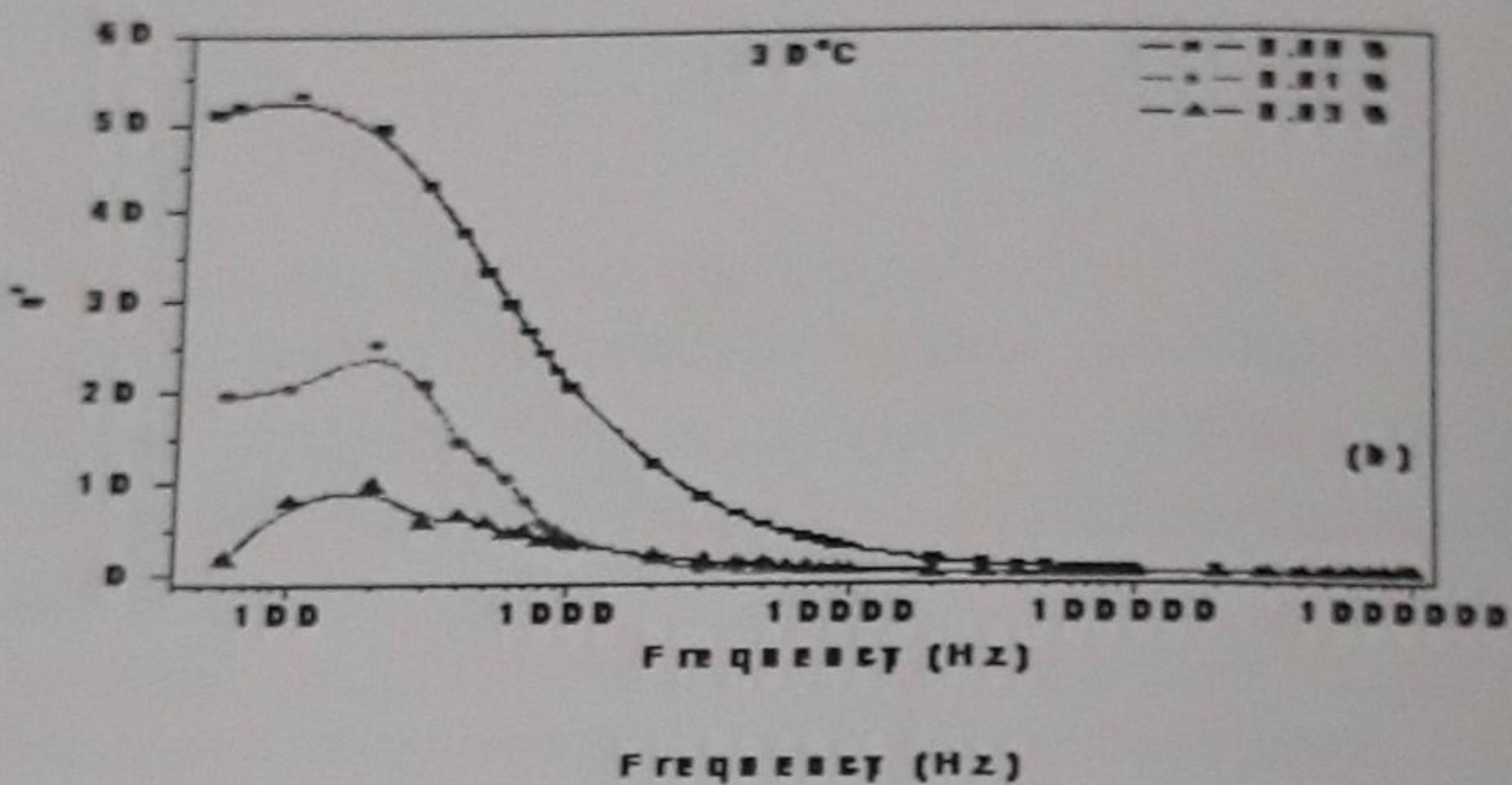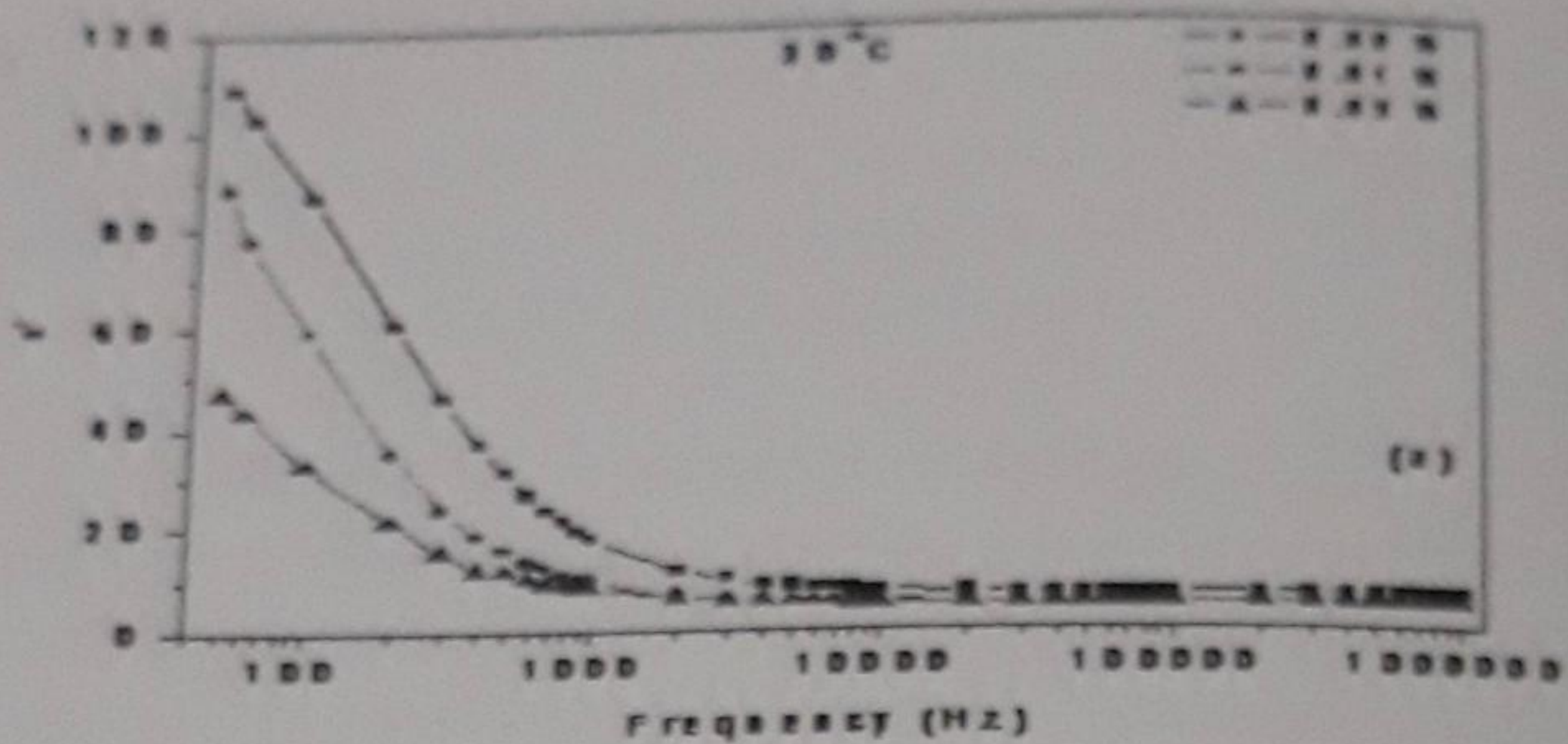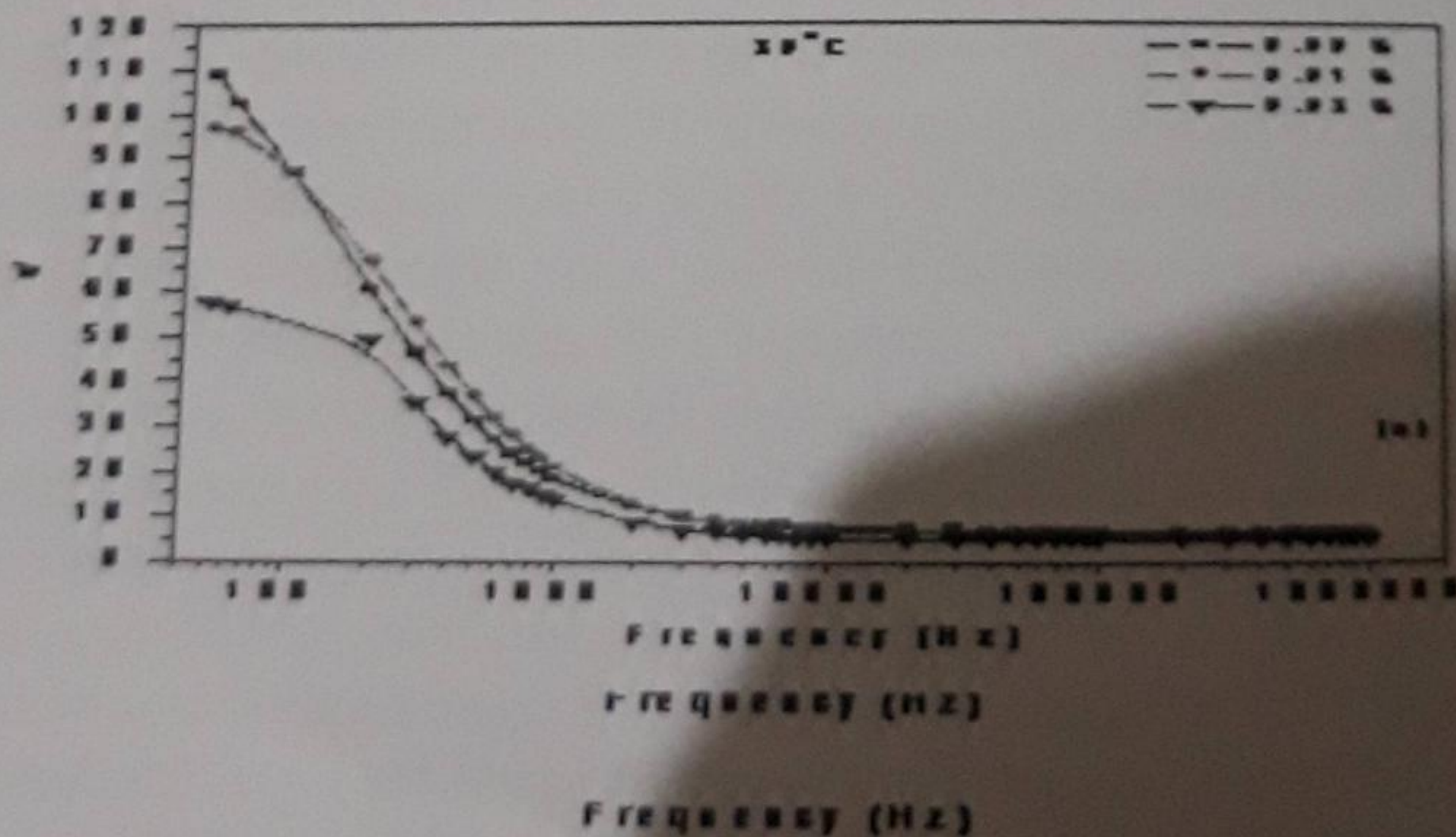
Fig.-7 Frequency dependence on dielectric permittivity in pure and MWCNTs doped samples at 30°C for (a) ε' and (b) ε''
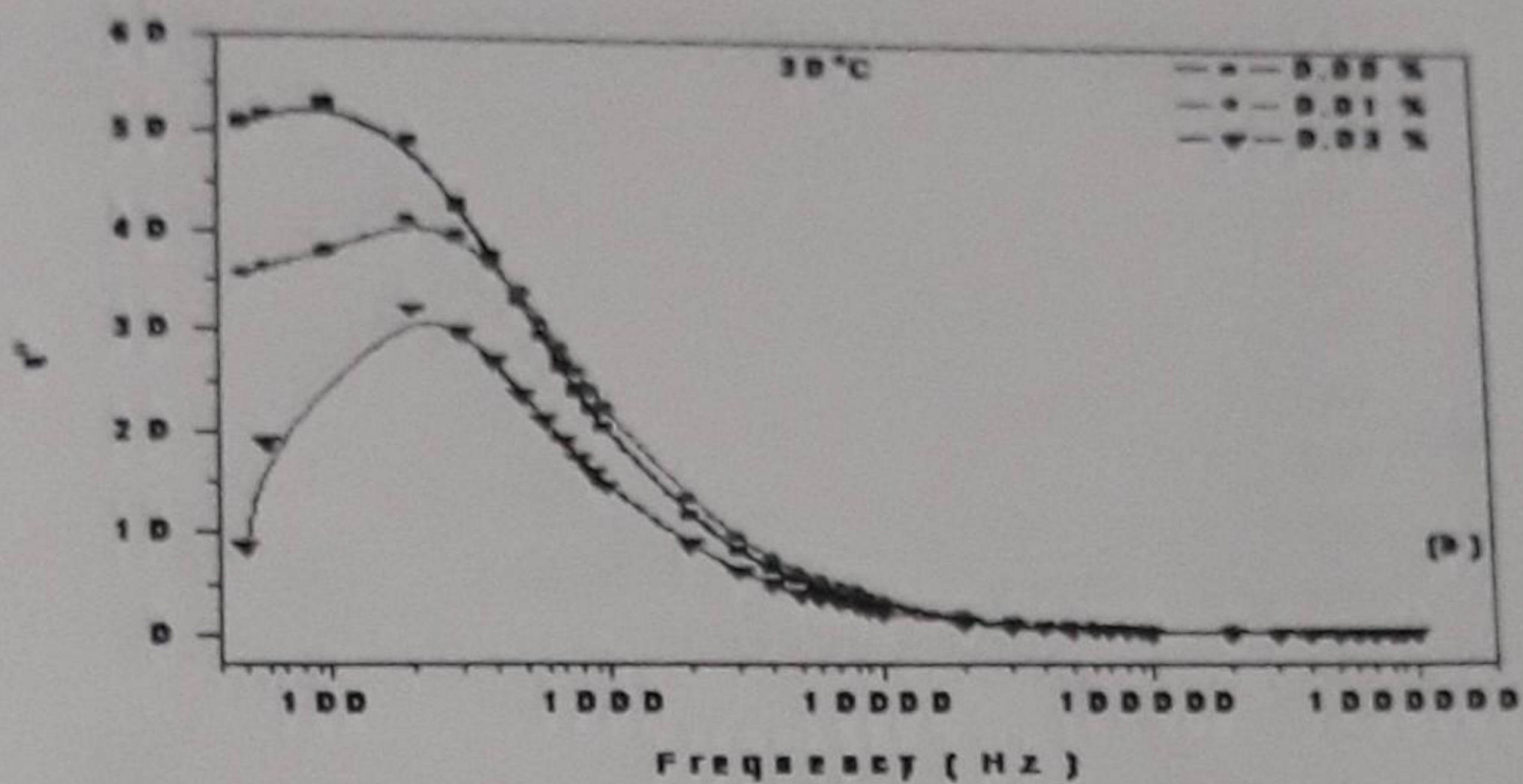
Fig. 8 Frequency dependence on dielectric permittivity (a) real part (b) imaginary part for pure and silica doped samples at 30°C
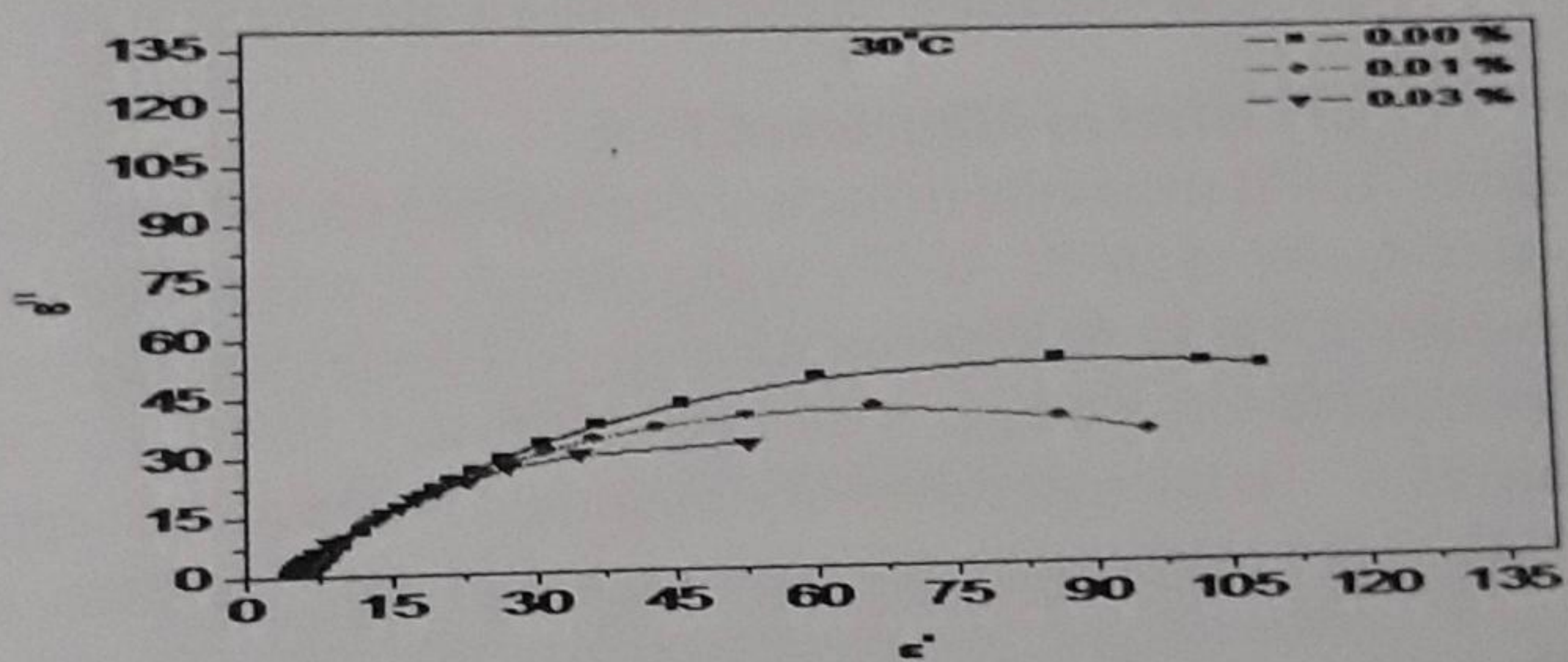

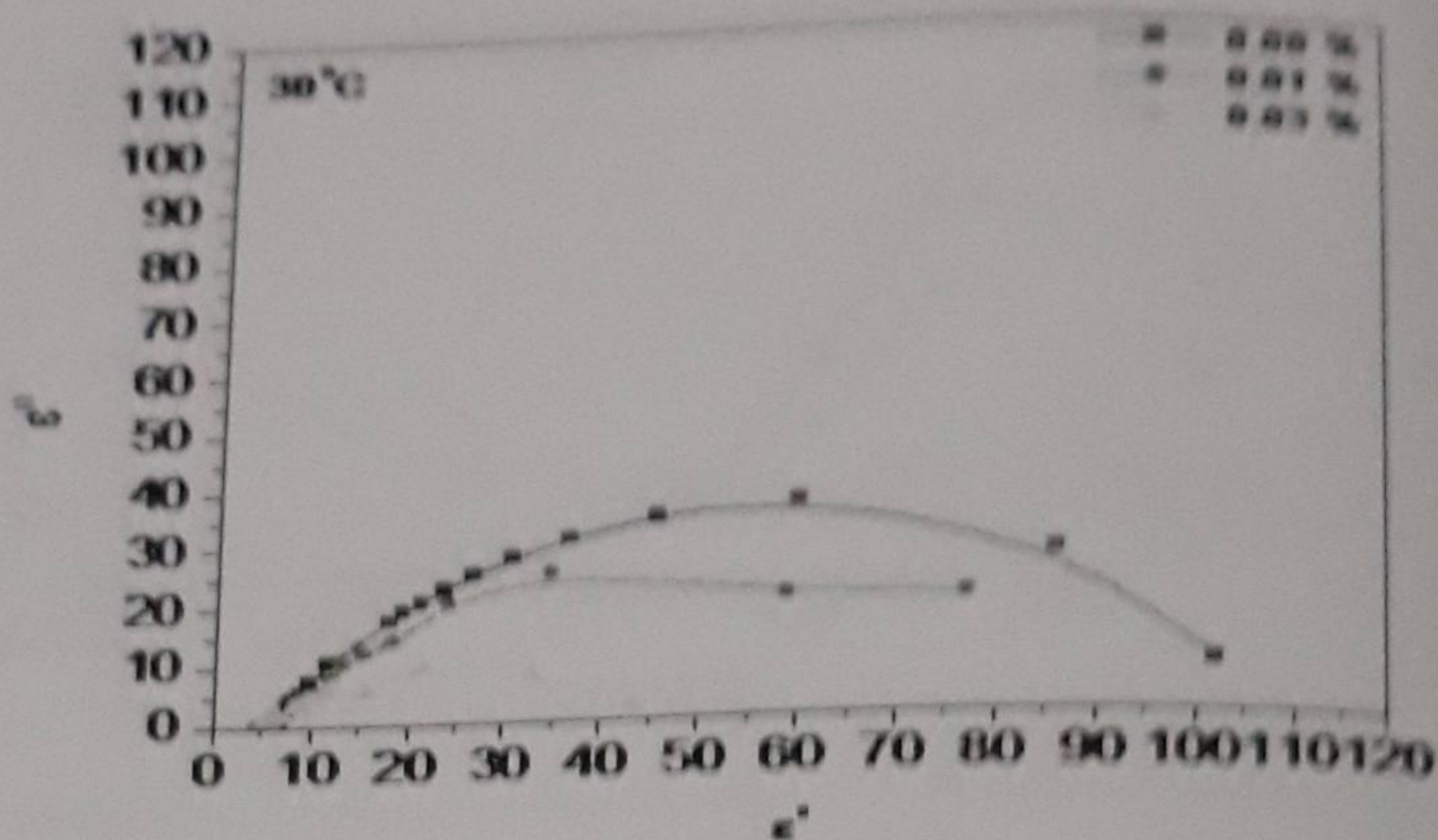Fig.9 Cole – Cole plots for pure and silica doped samples at 30°C

Fig. 10 Cole – Cole plots for pure and silica doped samples at 30°C

3.2.3   Memory effect in silica doped FLC

Figure 11(a-b) shows the frequency dependence on dielectric permittivity (ε') at 0, 5, 10V at 30°C. At 0V, high value of ε' was notice in the SmC* phase which is due to the GM contribution. It is found that the value of ε' decreases as the bias voltage is changed from 0 V to 10 V. This sudden decrease in ε' on the application of strong field is due to the suppression of GM mode and corresponding molecules reach in unstable state. It is found that again switch off the bias voltage (0V) and hold the sample in off condition for ☐few 1-2 minutes, the ε' value does not much change and remained as it was in the presence of bias of 10V. This confirms that FLC molecules did not come back in their stable state as they were before applying the bias and hence doped sample shows a memory state. Similar type of memory effect was also observed at (0, 5 and again 0V) at 35°C as shown in figure 12(a-b).
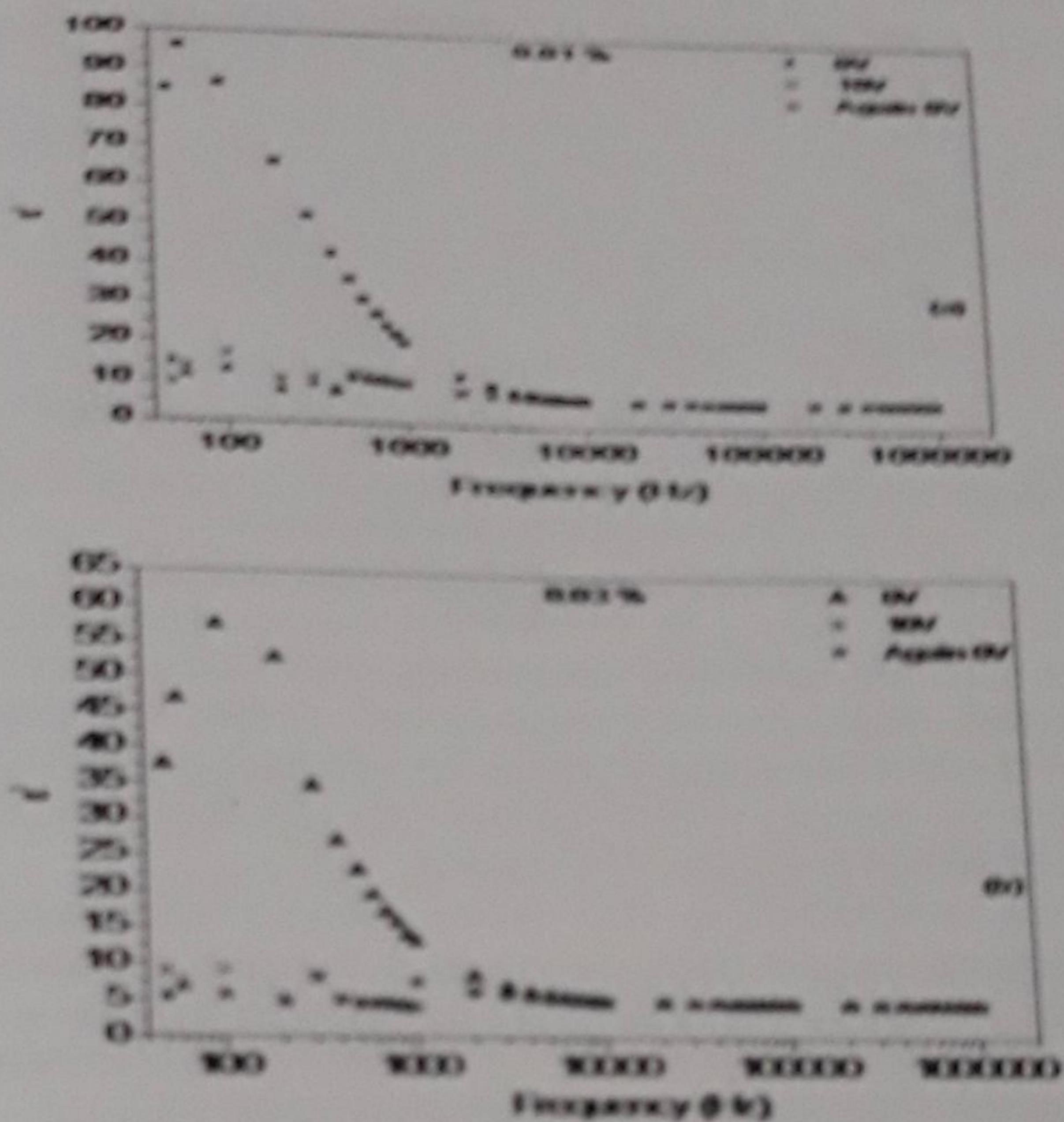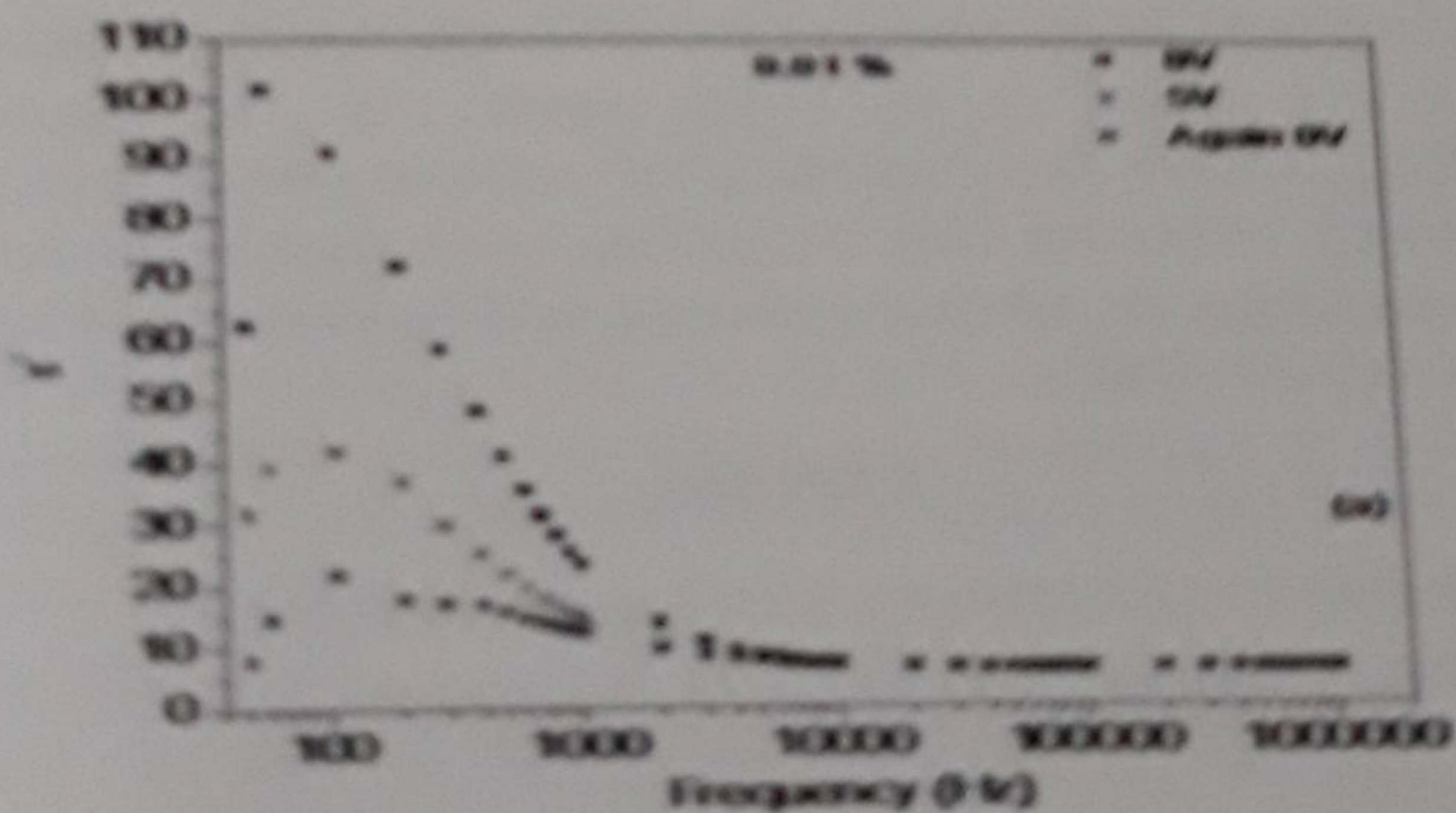
Fig-11 Dielectric permittivity as a function of frequency at 0V, 10V and again 0V at 30°C for (a) 0.01% and (b) 0.03% silica doped samples
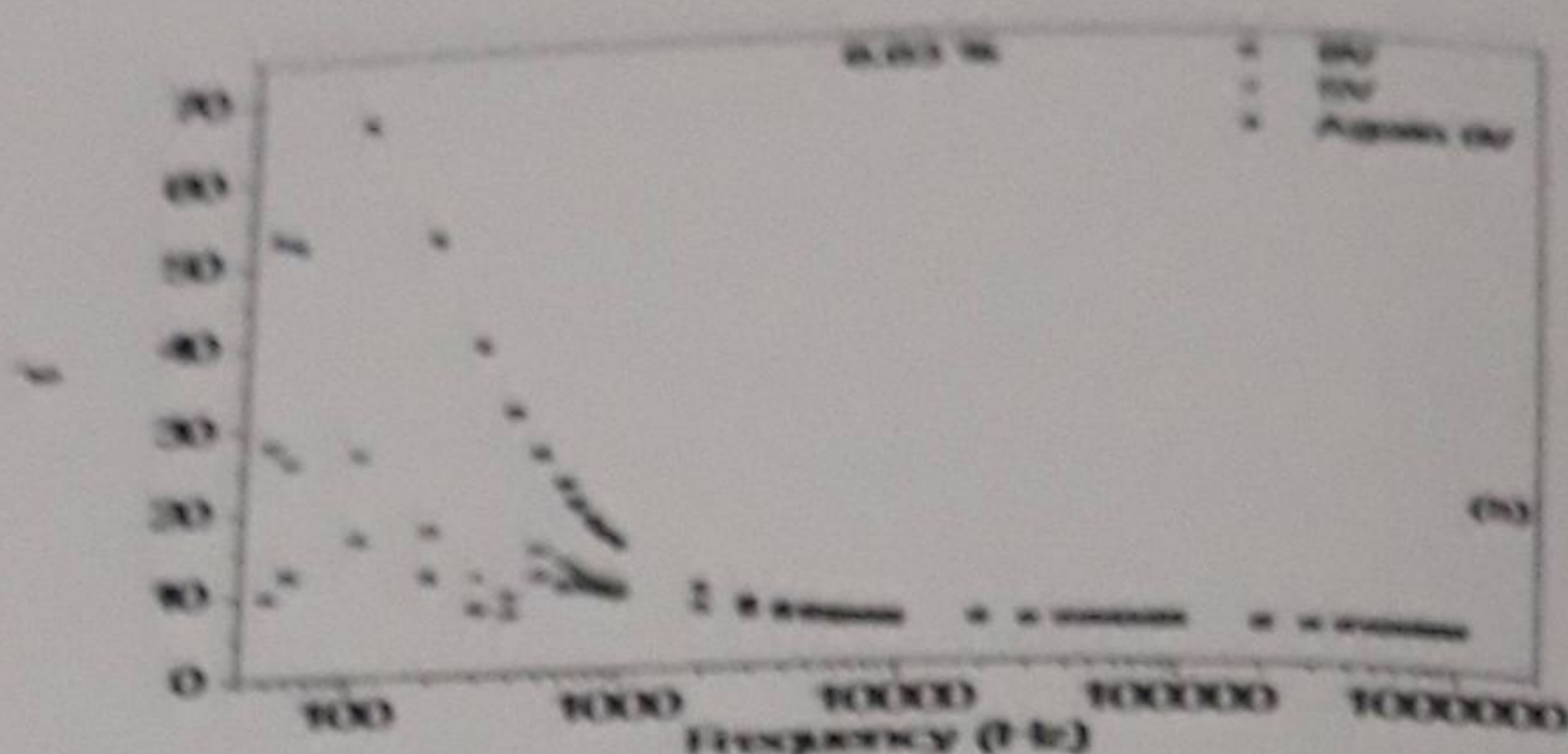
Fig. 12 Dielectric permittivity as a function of frequency at 0V, 5V and again 0V at 35°C for (a) 0.01% and (b) 0.03% silica doped samples

4. Conclusions

- Carbon nanotubes and silica nanoparticles doped ferroelectric liquid crystal thin films have been prepared and studied. The effect of MWCNTs and silica particles doping on the morphological, electro-optic properties and dielectric permittivity have been investigated and results have been compared with pure FLC material.

- Dispersion of MWCNTs in FLC material shows a better alignment, faster response time and higher spontaneous polarization than pure FLC cell. This increase is due to the ion trapping of MWCNTs in FLC material. A reduction in permittivity with increasing the MWCNTs has been observed, which is more pronounced below 1 kHz.

- The switching time and spontaneous polarization decreases with increasing the silica concentration which is due to increase in anchoring energies between silica nanoparticle and FLC molecules.

- A decrease in dielectric permittivity (~36%) and transition temperature (5-6°C) was noticed in the doped sample cell. The decrease in permittivity is due to the strong anchoring forces develop between higher concentrated silica and FLC molecules. The reduction in dielectric permittivity under the influence of the bias field in silica doped FLC cells shows a memory effect.

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