Chapter 8

Summary and scope for further work

8.1: Summary of the work

As pointed out by various researchers working on glass transition phenomena, the relaxation in supercooled plastic crystalline (PC) phase is found to be very similar in characteristics to that of supercooled liquids. However, the number of PC materials that can be supercooled easily to reach the glassy state is not large enough to get a clear picture about the factors that determine the glass formation in these materials. For example as shown in chapters 3 and 4, the OD crystals like cis-1,2-dimethylcyclohexane, cyanocyclohexane, isocyanocyclohexane, pentachloronitrobenzene, cyanoadamantane, cyclohexanol, cyclooctanol, cycloheptanol and caffeine etc. can be supercooled easily to reach the glassy state, whereas in some plastic crystals viz. t-butylchloride, carbontetrachloride, neopentanol and neopentylglycol etc., the supercooling is not so easy to form a glassy crystal. This happens because during the time of supercooling the plastic phase-I transforms to a more ordered phase-II. This collapse to a more ordered phase can be prevented to some extent by choosing a second component that forms a solid solution for the OD phase as shown in chapters 5-7. These OD crystals are of significant practical interest as these materials have potentially a large role to play in emerging energy technologies, with the applications ranging from lithium batteries to photovoltaic and fuel cells. These materials have the ability to reversibly absorb or release a

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huge amount of heat at the solid–solid phase transition temperature. This property makes them attractive for use as solid state thermal energy storage materials. Apart from the primary relaxation process, a faster dynamic process is also exhibited by plastic crystals below their glass transition temperature. Unfortunately, this so called $\beta$–relaxation is not well understood in the past prior to this work. Besides, dielectric strength of some of plastic crystals is found to be very sensitive to the amount of dopant (chapter 3). Some flexible plastic crystals exhibit multiple relaxation process. In addition, some plastic crystals are found to exhibit more than one glass transition event (chapter 4). In this context dielectric relaxation measurements above 77 K in a number of pure plastic crystals as well as two-component plastic crystals over a frequency range of $10^6 - 10^{-3}$ were performed. Differential scanning calorimeter has been used as supportive technique. All the measurements reported here, are at atmospheric pressure. X-ray measurements at room temperature were also performed wherever possible.

From dielectric study we have obtained the information about the spectral shape, relaxation rate, magnitude of relaxation and their temperature dependence for the $\alpha$– and $\beta$– processes. We have also obtained information about the phase changes by monitoring the dielectric behaviour during the slowing heating of the sample over the transition zone. From DSC study, we have obtained the transition temperatures including the $T_g$s, the associated thermodynamic parameters like enthalpy of transition $\Delta H$ and the necessary information regarding the stability of the supercooled phase. Apart from that, we have also obtained the necessary information regarding the solid to liquid phase diagrams in the case of two-component plastic crystals. Chapterwise details of the results are furnished below.

Chapter 3 deals with the effect of dopants on the relaxation in plastic crystalline phase of some of hexasubstituted benzenes viz. pentachloronitrobenzene (PCNB), dichlorotetramethylbenzene (DCTMB), trichlorotrimethylbenzene (TCTMB) along with some of their deuterated samples, and 1-cyanoadamantane (CNADM). Only one relaxation process similar
to that of the primary (or $\alpha$-) relaxation characteristic of glass-forming materials is found, but there is no indication of any observable secondary relaxation within the resolution of our experimental setup. However, in the case of PCNB the dielectric strength ($\Delta\varepsilon$) of the above said $\alpha$-process does not change appreciably with temperature, though interestingly, a small addition of a dopant such as pentachlorobenzene (PCB), trichlorobenzene (TCB), and chloroadamantane (CLADM) to the molten state of PCNB drastically lowers the dielectric strength by a factor of 4 to 8. Powder X-ray diffraction measurements at room temperature and DSC data do not indicate any appreciable change in the crystalline structure. It is noticed that the effect of PCB as a dopant on the magnitude of $\alpha$-process of CNADM is moderate, whereas both PCB and TCB as dopants show a much reduced effect on the relaxation in DCTMB and TCTMB. It is suggested that the drastic changes in the dielectric strength of the $\alpha$-process is due to the rotational hindrance caused by the presence of a small number of dopant molecules in the host crystalline lattice. In the above context, the possibility of a certain degree of antiparallel ordering of dipoles is also discussed.

Chapter 4 deals with the dielectric relaxation investigations on three interesting super-cooled plastic crystalline substances i.e. isocyanocyclohexane (ICNCH), cyanocyclohexane (CNCH) and 1-cyanoadamantane (CNADM). All of these have the main dipole moment situated in their side group -C≡N or -N≡C. Differential scanning calorimetry (DSC) was also employed as a supporting technique. Glassy crystal were easily formed in the first two samples by slowly cooling the plastic phase, but in CNADM it was formed by rapidly quenching the room temperature plastic phase. In addition to the so called $\alpha$-process that can reasonably be described by a Havriliak-Negami (HN) shape function, a secondary (or $\beta$-) relaxation process is found in all the materials. The $\beta$-process in CNADM has an activation energy ($\Delta E_\beta$) of about $13.8 \pm 1$ kJ/mol, and is present even in the corresponding ordered crystalline phase i.e. in its monoclinic phase. On the other hand, the magnitude of $\Delta E_\beta$ in both the isomers of cyanocyclohexane i.e., ICNCH and CNCH is similar and is about 21.1
and 23.4 kJ/mol respectively. Unlike CNADM, the cyclohexane derivatives are capable of exhibiting additional intra-molecular process due to chair-chair conversion (i.e. in addition to the rotational motion of the side group -C≡N or -N≡C). Therefore, the secondary process of these systems is compared to that occurring in the binary liquid glass formed by dispersing a small quantity of these dipolar liquids in nearly non-polar ortho-terphenyl (OTP). Measurements were also made in the supercooled binary mixtures of other cyclohexyl derivatives like cyclohexylchloride and cyclohexylbromide with OTP which lack a flexible side group. The sub-$T_g$ relaxation process exhibited in all these cases have almost similar activation energy as in case of pure ICNCH and CNCH. These observations together with the fact that the activation energy for this process is much below that of chair-chair conversion which is about 43 kJ/mol leads us to the conclusion that sub-$T_g$ relaxation process in the binary mixtures is JG type, and perhaps $\beta$- relaxation process in phase I of ICNCH and CNCH is also similar. With the help of semi-empirical calculations of the dipole moments for the axial- and equitorial confirmers, it is concluded that the process associated with the chair-chair may not be dielectrically very active and hence, should be relatively weaker in magnitude. The $\beta$-process in CNADM has an activation energy ($\Delta E_\beta$) of about 13.8 ± 1 kJ/mol, and is present even in the corresponding ordered crystalline phase indicating that it may not be characteristic of the glass formation of phase I. The molecular structure of CNADM is such that it does not possess other intra-molecular degrees of freedom of the type equatorial to axial- (or chair-chair) transformation. Our experimental finding that JG relaxation for CNADM dispersed in glassy OTP matrix is about 31 kJ/mol. indicates that the well resolved sub-$T_g$ process in CNADM is due to the small side group i.e. -C≡N and JG relaxation in phase I of CNADM is perhaps not resolvable or too small to be detected.

Chapter 5 deals with the investigations of two interesting (two-component) solid solutions, where one is a hydrogen (H-) bonded pair and the other is a non-H-bonded pair. The former is the two component system cyclooctanol (COOL) + cycloheptanol (CHOL), which
forms a simple cubic phase. This solid phase has been investigated at low temperatures and for several concentrations by means of low-frequency dielectric spectroscopy and differential scanning calorimetry (DSC). Depending upon the concentration, this phase reveals a glass transition in the temperature range of 138-172 K and a pronounced relaxation process identifiable with the so-called α-process characteristic of a single component orientationally disordered crystal. The dielectric spectra are found to follow the Havriliak-Negami (HN) equation. The analysis of the various parameters obtained show an isomorphic relationship between the simple cubic phases of both pure components through a continuous change of parameters. In addition, a sub-$T_g$ process, which is Arrhenius, is found. The kinetic freezing of the various dielectric processes has been critically examined in relation to the $T_g$ found in the DSC experiments. The non-H-bonded pair that has been studied is cis-1,2-dimethylcyclohexane (DMCH) and cyclohexylchloride (CHC). The liquid mixture of DMCH and CHC upon lowering the temperature forms a solid solution on the DMCH-rich side, which is an orientationally disordered crystal. This phase demonstrates a pronounced process in the dielectric measurements that follows the HN equation. The results are discussed in the context of the solid-liquid phase diagram of this binary system.

Chapter 6 deals with the investigation is to see how various relaxation processes including the chair-chair transformation (as found by earlier researchers at room temperature in the mechanical relaxation spectroscopy) in cyclohexane derivatives evolve as the temperature is lowered. For this purpose, two remarkable (two-component) solid solutions that are orientationally disordered are investigated, where one is a hydrogen (H-) bonded pair, and the other is non-H bonded pair. The former is the two-component system of cyclohexanol (CHXOL) and 2,2-dimethyl-1-propanol or neopentanol (NPOL), where the liquid mixture on cooling forms an orientationally disordered phase which is probably a face centered cubic phase and is a solid solution of the corresponding pure phases. This solid phase has been investigated at low temperatures and for several concentrations, by means of dielectric spectroscopy and
differential scanning calorimetry (DSC). Depending upon the concentration, this phase reveals a glass transition in the temperature range 135 - 150 K and associated with this is a pronounced relaxation process identifiable with the so called \( \alpha \)-process. The dielectric spectra of this process is found to follow the Havriliak-Negami (HN) equation. The analysis of the various parameters obtained show an isomorphic relationship between the face centered cubic phases of both the pure components through a continuous change of parameters. Another process of much smaller magnitude designated as \( \alpha' \)-process was found above the glass transition temperature \( T_g \) which kinetically freezes around 170 K. This process interestingly, is also non-arrhenius in nature, becomes increasingly weaker with increase in the second component, and may be identified with (axial) chair- (equitorial) chair transformation. In addition, a weak high frequency process (whose origin could not be ascertained), and a clear sub-\( T_g \) process identifiable as Johari-Goldstein (JG) or \( \beta_{JG} \) process are found. The kinetic freezing of the various dielectric processes have been critically examined in relation to the Tg found in the DSC experiments. The non H-bonded pair that has been studied is cyanocyclohexane (CNCH) and cyclohexylchloride (CHC). The liquid mixture of CNCH and CHC on lowering the temperature also forms a solid solution for the entire concentration range which is orientationally disordered. This phase is stable for the concentration range \( 0 \leq x_m \leq 0.4 \) (without transition to any other phase) which allowed us to study all the relaxations by extending the measurements to lower temperatures. The solid solution demonstrates a pronounced \( \alpha \)-process that follows HN-equation and a sub-\( T_g \) identifiable with the \( \beta_{JG} \) process which is Arrhenius. There is also an indication of yet another process designated as \( \alpha' \)-process above \( T_g \) as in the case of CHXOL-NPOL system discussed above.

Chapter 7 deals with the investigations on an extraordinary two-component (H-) bonded pair i.e., CHXOL-CHPOL. Where in CHXOL-CHPOL, the phase I/II(?) of cyclohexanol (CHXOL) beyond \( x_m \geq 0.075 \) forms a solid solution with the phase I of cycloheptanol (CHPOL). This solid phases has been investigated at low temperatures and for several
concentrations, by means of dielectric spectroscopy and differential scanning calorimetry (DSC). Depending upon the concentration, this phase reveals a glass transition in the temperature range 135 - 150 K and a pronounced relaxation process identifiable with the so-called $\alpha$-process characteristic of single component orientationally disordered crystal. The dielectric spectra is found to follow the Havriliak-Negami (HN) equation. The analysis of the various parameters obtained show an isomorphic relationship between the phases of both the pure components through a continuous change of parameters. In addition, two sub-$T_g$ processes which is Arrhenius is found. The kinetic freezing of the various dielectric processes have been critically examined in relation to the $T_g$ found in the DSC experiments.

8.2: Scope for further work

(i) The main problem with the time domain measurements is the considerable (10 %) uncertainty in the measured dielectric strength ($\Delta\varepsilon$) value. This is because we are using a linear amplifier for sampling the data, whereas a logarithmic amplifier will serve the purpose much better, as the loss currents vary by several decades of current.

(ii) Measurements on the higher frequency side above 1 MHz., will improve the analysis of the data and hence understanding of the mechanism concerned.

(iii) Temperature variation of the X-ray pattern of the hexasubstituted benzenes will give a much wider scope for understanding these materials, especially if one can make measurements on single crystals grown instead of the powder samples used in the present study.

(iv) Low temperature X-ray analysis of the binary solid solutions are expected to throw more light on the structure and nature of these samples.