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Heterogeneous structure of glassy benzophenone

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Raman scattering and photoluminescence techniques were applied in the study of structural changes in benzophenone recorded during benzophenone's transit between glass and crystalline phases. It has been found that the structure of glassy benzophenone is essentially heterogeneous: consists of ''structured clusters'' with the structure of unstable β-crystalline modification of benzophenone.

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INTRODUCTION

Benzophenone is known in its glass phase and in two crystalline modifications: stable α-modification (orthorhombic structure) and unstable β-modification (monoclinic structure). The β-modification is stable only at temperatures lower than 240 K. At $T>250\,\mathrm{K}$ it transforms into α-modification.[1] The glass phase can be obtained by quenching its liquid. There is extensive literature about the optical properties of benzophenone in both its glass and crystalline phases.[1,2] But there is no study that considers the benzophenone's transit between glass and crystalline phases via changes in its optical properties.

The aim of the present work is to investigate the change in the structure in benzophenone recorded during benzophenone's transit between glass and crystalline phases using Raman scattering technique. Special attention is devoted to the study of the Raman scattering in the dependence on the direction of the temperature change, i.e., when heating the glass phase to melt, or when cooling liquid benzophenone. In this paper we also have used the luminescence technique to identify the different phases of benzophenone.

EXPERIMENT

Raman measurements were carried out in a 90° scattering configuration. The spectra were recorded with a Jobin-Yvon Ramanor U 1000 spectrometer (double monochromator with two plane holographic gratings, additive mounting in an asymmetric Czerny-Turner configuration) equipped with a standard photon-counting detector controlled by the SPECTRA MAX software. The dispersion was 9.2 cm^{-1}/mm at 514.5 nm and the stray light rejection was 10^{-14} at 20 cm^{-1} from the Rayleigh line. The spectral slit width was 2 cm^{-1}. The excitation source was the 514.5 nm line of an Ar^{+} laser and its power was about 200 mW on the sample, which was contained in a capillary and fixed in a cryostat providing for temperature variation.

Luminescence spectra were recorded using a 1000-W Hg lamp for excitation. The lamp had been filtered of visible and IR components using a bandpass filter. The dispersion and detection of the light were accomplished using a spectrometer and photomultiplier tube.

RESULTS

Low-frequency Raman spectra of glasses have two characteristic features: the so-called boson peak and quasielastic scattering (QS). It is believed that these features, which are commonly observed for glasses, arise from a density of low-energy vibrational states, given by the contributions of extended states, the usual phonons, and additional localized modes, which arise from disorder.[3–5]

Figure 1 shows a set of the low-frequency Raman spectra when heating glassy benzophenone over the glass transition ($T_g=217\,\mathrm{K}$). At 190 K (Fig. 1, curve 1) the wide band is seen at about 17 cm^{-1}. This is the so-called boson peak. With increasing temperature (Fig. 1, curve 2) the contribution to the spectrum from the QS line appears. This line has a form of a wide peak reaching its maximum at zero-shift frequency.[6] It is seen that at the temperature 210 K the boson peak is hidden under the envelope of significantly broadened QS line. At the temperature of about 217 K glassy benzophenone transforms to a supercooled liquid state, and at a little higher temperature than the glass-transition temperature a remarkable change becomes evident in the Raman spectrum (Fig. 2, curve 3). At $T=225\,\mathrm{K}$ the QS line disappears and a new structure appears, corresponding to a crystalline modi-

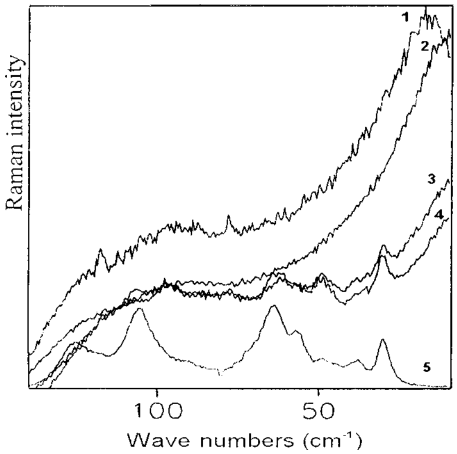

FIG. 1. Evolution of low-frequency Raman spectra of benzophenone with increasing temperature from 190 to 230 K. The initial state is glassy benzophenone. Temperatures are 190 K (1); 210 K (2); 225 K (3); 225 K (4) −15 min after recording (3); 230 K (5).

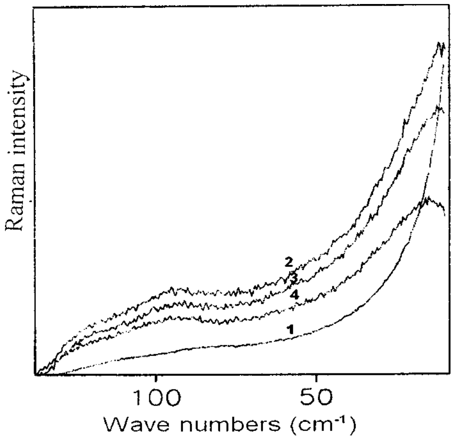

FIG. 2. Evolution of low-frequency Raman spectra of benzophenone with decreasing temperature from 330 to 190 K. The initial state is liquid benzophenone. Temperatures are 330 K (1); 220 K (2); 210 K (3); 190 K (4).

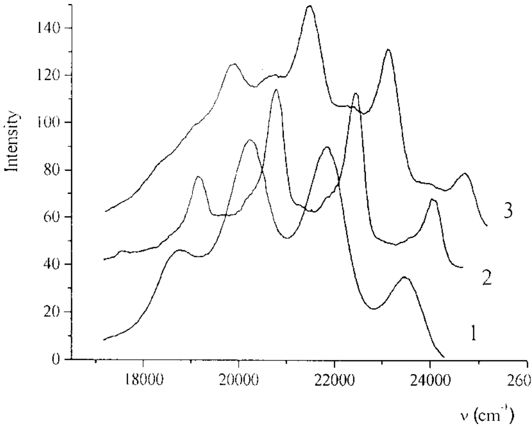

FIG. 3. Luminescence spectra of benzophenone at 120 K. Glassy benzophenone (1), α-benzophenone (2), and microcrystals that are formed from the liquid phase (3).

fication. The curve 4 was obtained at the same temperature 225 K but after 15 min since recording the curve 3. The crystalline structure becomes more pronounced. It should be noted that the recording time was also 15 min. So, the real delay between two spectra 3 and 4 was 30 min. Spectrum at $T=230\,\mathrm{K}$ (Fig. 1, curve 5) corresponds to the crystalline phase: neither the boson peak, nor quasielastic scattering contribute to the spectrum.

Figure 2 shows the evolution of Raman spectra when cooling liquid benzophenone down to the low temperature. At the $T=330\,\mathrm{K}$ the crystalline modification of benzophenone melts and we see the only QS line (Fig. 2, curve 1). With a decreasing temperature there appears a shoulder in the QS line at $T=220\,\mathrm{K}$ (Fig. 2, curve 2), which turns into a pronounced peak with further cooling, while the QS intensity falls off substantially in the range of 20–10 cm^{-1} (Fig. 2, curve 3). At $T=190\,\mathrm{K}$ only the boson peak is seen in the spectrum (Fig. 2, curve 4).

A comparison of these two cases shows that crystallization can only be obtained by heating the glass phase to the melt but not by cooling the liquid down to the glass phase in the time scale of experiment.

As mentioned above, benzophenone has two crystalline modifications: α and β. However, the type of crystalline structure that is formed from the liquid phase remains uncertain from the Raman spectra. In order to understand this structure the spectra of the luminescence have been investigated. Figure 3 shows the luminescence spectra of benzophenone recorded at 120 K. Curve 1 is the luminescence of the glass phase. Curve 2 is the luminescence of the α phase. Curve 3 is the luminescence measured after the cooling of the crystalline phase, which was crystallized from the liquid phase at 225 K. The Raman spectrum of this crystalline phase corresponds to the curve 5 in Fig. 1. It is seen that the luminescence spectra of the different phases of benzophenone exhibit a progression of broad bands, whose intervals correspond to the frequency of the carbonyl stretching vibration and are distinguished only by the spectral position of the first emission band. The luminescence of α, β, and glass phases of benzophenone has been studied in detail,[1] therefore, we can identify each modification of benzophenone according to the peak position of their first emission band. The position of the first peak in curve 3 is located at 24 700 cm^{-1}. Based on this, we can say that the crystalline structure of the phase that is formed during crystallization from the supercooled liquid phase corresponds to the unstable β-phase.

DISCUSSION

Over the past few years there has been an enormous effort to try to understand the properties of amorphous materials in terms of their microscopic structure.[5,7–10] It is supposed that the arrangement of structural units is not completely random (homogeneous model) but has nonhomogeneous structure on intermediate-range order. These include work on soft-potential model (SP) (Ref. 9) and "free-volume model."[10] Up to now only a few studies have been carried out in order to ascertain whether the supercooled liquid has nonhomogeneous structure on an intermediate-range order.[11] An extensive thermodynamic treatment of heterophase fluctuations in glass-forming liquids can be found in Ref. 12, and references therein.

Our results could be explained from the heterogeneous point of view on the structure of the glassy benzophenone. Heterogeneous structure suggests the coexistence of solidlike configurations with rigid structure and regions with flexible structure. Judging from the Raman spectra in Figs. 1 and 2, it is clear that we could not produce crystallization as a liquid is cooled, but crystallization is observed when reheated through the glass-transition region. This result means that the structure of the glassy benzophenone contains the nucleus of the crystalline phase (structured clusters). The process of nucleation and growth of the crystalline nucleus begins in the supercooled liquid. Thus, the homogeneous disorder changes to heterogeneous. The rate of the crystal nucleation increases quickly if the temperature is lowered, while their growth decreases, and at temperatures below T_g the system is essentially frozen. As a result, in the glassy state there coexists regions where benzophenone's molecules are packed very closely together (structured cluster) and the regions with flexible structure. In the course of heating the glassy state through the glass transition, these nuclei have a possibility of moving around to undergo growth of their radii and when the radii of the nuclei become larger than the critical radius, the process of crystallization occurs (Fig. 1, curves 3–5). In contrast, when a liquid is cooled from the melt, its structure is characterized by homogeneous disorder and does not contain the nucleus of crystalline phase. Thus the process of crystallization is such a slow process that it cannot be observed during the measurements. We consider this experimental observation as an evidence for the presence of structured clusters in the glassy and supercooled liquid state. Moreover, from the measurement of the luminescence it has been found that the clusters have the crystalline structure, which corresponds to the structure of the unstable β modification of benzophenone.

CONCLUSION

On the basis of Raman and luminescence spectra of benzophenone we have shown that the structure of the glassy benzophenone is essentially heterogeneous and consists of the ‘‘structured clusters’’ with structure of unstable crystalline modification. Further investigations of the structure of benzophenone are in progress.

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