Pressure- and temperature- driven phase transitions in pyridine

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Abstract. Studies of aromatic and heteroaromatic compounds under high pressure in recent years have attracted great attention to the possibility of the synthesis of amorphous hydrogenated materials with attractive technological properties. In this context, pyridine is of particular interest in terms of its rich polymorphism. We studied the liquid and solid phases of pyridine by dielectric spectroscopy and pulsed ultrasonic methods in the pressure and temperature range P < 4.2 GPa and 78 < T < 350 K. It is shown that up to 20% of the sample passes into the glassy state during crystallization from the melt to the low-pressure phase. Disordered phase has a high dielectric constant and a high absorption coefficient of ultrasound. All these features are absent in the high pressure phase.

1. Introduction
Pyridine (C5H5N) is a heterocyclic compound resembling benzene in which one of the CH groups is replaced by nitrogen. Numerous articles are devoted to the study of this compound at high pressures [1-7]. Moreover, in the pressure range of 7–9 GPa and P > 20 GPa, pyridine polymerization leads to the formation of two different covalently bonded compounds with a crystalline structure of graphane and nanotreads [8, 9]. At the same time, polymorphism of the molecular phases of pyridine at high pressures has not been sufficiently studied. Such studies could clarify the polymerization mechanism of both pyridine itself and its close analogue of benzene.

At low pressures up to 7 GPa, X-ray and spectroscopic studies suggest that there are two phases of pyridine I and II. The normal pressure phase (phase I) has an orthorhombic structure with Pna21 symmetry [10]. Phase II with symmetry P212121 has a specific volume practically identical to that of phase I. Phase II is apparently stable under pressure P > 1.2 GPa and is observed at normal pressures in deuterated pyridine (thus, pyridine has a rare property of isotopic polymorphism [2]). However, the boundary between phases I and II remains unknown. Various studies [2, 3] demonstrate the existence of both phase I and phase II at room temperature and pressures of ≈1.2 GPa. According to the authors of [5], this indicates the metastability of the observed crystal structures and dependence on the thermobaric history of the sample. Taking into account the similarity of the optical spectra of these phases and the proximity of their crystal structures, fundamentally different experimental methods are required to clarify the polymorphism of pyridine at pressures up to 2 GPa. To this end, we provided dielectric spectroscopy measurements and ultrasonic studies of pyridine.
2. Experimental methods

The ultrasonic experiments were carried out using a low-temperature ultrasonic piezometer in the pressure range up to 1.1 GPa in the temperature range 78–295 K. Measurements of the velocity and absorption of ultrasound at frequencies of 5–10 MHz were carried out using an original setup based on the National Instruments PXI system [11]. We used piezoceramic plates made of lithium niobate LiNbO$_3$ to generate and receive ultrasonic waves with resonant frequencies of 5 MHz for transverse and 10 MHz for longitudinal waves. The sample was placed into a high pressure cell in a Teflon capsule with copper caps. During the experiment, we measured the transit time of the ultrasonic pulse and the change in the length of the sample. The accuracy of measuring the transit time of an ultrasonic pulse was ~ 1 ns, and for the length of the sample was 5 μm. In addition to pressure studies at room temperature and $T=77$ K, we provided isobaric experiments during the heating of the apparatus from 77K to 295K at fixed pressures.

Dielectric spectroscopy was performed in a Toroid chamber using a Novocontrol Alpha spectrum analyzer. The measuring cell was a Teflon capsule with a copper capacitor placed inside it with a Teflon spacer with the holes. The electric capacitance of the empty capacitor was 5 μF. We used the chromel-alumel thermocouple as temperature sensor and the manganin wire as pressure sensor. The accuracy of the pressure and temperature measurements was ± 0.1 GPa and ± 0.5 K, respectively.

In order to take into account the phenomena associated with the stability of the liquid and crystalline phases of pyridine, we used the standard procedure for changing temperature and pressure, accompanied by an isothermal pressure increase in the liquid phase and subsequent isobaric cooling and heating of the sample. The data presented in the article were collected at the stage of temperature rise, after the transition of the sample to the solid phase.

3. Results and discussion

Pyridine crystallizes at 1.2 GPa at room temperature, based on dielectric spectroscopy data. Crystallization is accompanied by a drop in permittivity from values of the order of 10, typical for the liquid phase, to 2.5. The transition pressure turns out to be higher than the pressure of equilibrium crystallization of pyridine at 295 K equal to 0.55 GPa, but is consistent with the known literature data [5] and is caused by metastability of pyridine at high pressure. Subsequent isothermal compression up to 4.2 GPa did not reveal changes in dielectric constant, which indicates the absence of phase transitions in this pressure and temperature range. The glass transition of pyridine mentioned in the literature [5] was not observed in our experiments, and each isothermal compression led to crystallization of the sample.

The temperature dependence of the dielectric constant at a frequency of 2 MHz at pressures $P \leq 0.6$ GPa (see figure 1) exhibits a complex behavior with three characteristic features. The low-temperature broad maximum is due to the low-frequency relaxation process and cold crystallization. Two other kinks are associated with the melting of pyridine (a high-temperature kink) and the transition from an orientationally ordered state (characterized by low dielectric permittivity) to a state with orientational disordering (with higher dielectric permittivity). The temperature range where high values of dielectric constant are recorded precedes the melting of pyridine and its boundary approximately coincides with the range where the maximum absorption of longitudinal ultrasonic waves is observed. It should be noted that the increase in pressure leads to the expansion of this range from 15 K at zero pressure to 35 K at a pressure of 0.6 GPa.

During isobaric cooling from the melt in the pressure range from 0 to 0.6 GPa, pyridine transforms into a mixed crystalline and glassy state. Evidence for it is the presence of a characteristic low-frequency relaxation process with an amplitude of the order of 2, observed during subsequent heating of the sample. From the comparison with the dielectric constant of liquid pyridine (equal to 10), we can conclude that approximately 20% of the sample is in the glassy state. The glassy state is unstable and, with a further increase in temperature, crystallization occurs (the cold crystallization), accompanied by a decrease in the amplitude of the relaxation process with a subsequent decrease to zero. It is interesting to note that
the glassy state is metastable and the joint observation of the glassy and crystalline phases is an infrequent phenomenon, since the presence of the crystalline phase in contact with the glassy one should lead to crystallization of the entire sample. The cold crystallization also manifests itself in ultrasonic measurements as an anomaly in dependence of shear moduli and absorption of ultrasound (see figure 2 and figure 3). Melting of the crystalline phase is accompanied by a huge absorption of longitudinal and transverse ultrasonic waves. In the same temperature range, we observed a decrease in the bulk modulus and the disappearance of the shear modulus.

Figure 1. Temperature dependence of the dielectric constant at a frequency of 2 MHz at three different pressures.

Figure 2. Temperature dependences of bulk B and shear G elastic moduli at P = 0.5 GPa.

Figure 3. Temperature dependences of transmission coefficients of longitudinal (circles) and transverse (squares) ultrasonic waves at P = 0.5 GPa.
At higher pressures $P > 0.6$ GPa, the temperature dependence of the dielectric constant and ultrasound velocities changes. At $P = 1$ GPa, isobaric cooling leads to the complete crystallization of pyridine, which is manifested in the disappearance of the low-frequency relaxation process and the associated peak in the temperature dependence of the dielectric constant (see figure 1). The absence of a glassy phase, as a result, leads to the disappearance of the anomaly caused by cold crystallization in the temperature dependences of the elastic moduli and the absorption of ultrasound. Another important difference between high pressure and low pressure temperature dependence of permittivity is the absence of a kink associated with the disordering of the crystalline phase before melting. Thus, the only feature observed on the figure 1 is associated with the melting of pyridine.

The marked anomalies are shown in the pyridine phase diagram, where the literature data were also used (see figure 4). Pressure $P = 0.9$ GPa is the boundary below which effects related to disordering are observed in pyridine: vitrification and softening of the crystalline phase before melting. We associate disappearance of anomalies with increasing pressure with a transition from the low pressure phase (phase I) to the high pressure phase (phase II). Note that the transition pressure $P = 0.9$ GPa turns out to be relatively lower than the previously proposed values of $P = 1$ GPa [5] and $P = 2$ GPa [4], obtained on the basis of optical measurements.

![Phase diagram of pyridine](image)

**Figure 4.** Phase diagram of pyridine. Circles indicate the phase transformations in pyridine obtained as a result of ultrasonic measurements, rhombs – results of dielectric spectroscopy. Squares – literary data from the work [3]. The solid line shows the melting curve, and the dashed lines show the phase boundaries in solid pyridine.

4. Conclusion

Thus, the joint measurements by dielectric spectroscopy and ultrasonic method revealed a difference in the properties of the solid phases of pyridine and clarified the phase boundary between them. It was found that upon cooling from the melt to the low pressure phase (phase I) in the pressure range $0 < P < 0.6$ GPa glass forms together with the crystalline phase. The glassy state is unstable and crystallizes upon heating. Before melting, phase I transforms into a state characterized by high values of permittivity and high absorption of ultrasonic waves. In our opinion, this behavior is associated with the disordering of crystal molecules at temperatures preceding melting. These anomalies disappear when the pressure rises above 0.9 GPa, which we associate with the transition to the high-pressure phase pyridine II.
Acknowledgments
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