ANNOTATION

of dissertation for the Philosophy Doctor (PhD) degree in specialty "6D0071000 – materials science and technology of new materials" by

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RELAXATION PROCESSES IN THIN FILMS OF FREON CRYOVACUUM CONDENSATES

The research work is devoted to experimental studies of structural relaxations in thin films of $C_2H_2F_4$ and CCl_4 freons obtained by physical vapor deposition in a wide low-temperature range.

Relevance of the study

It has recently been found that highly stable glasses, characterized by higher kinetic stability and high density, can be obtained by physical vapor deposition (PVD) in the vicinity of the glass transition temperature (T_g), which is determined by a sharp increase in the relaxation time of a supercooled liquid into a solid glassy state. One of the most important properties of stable vapor deposition glasses is that they can be obtained in a thermodynamic state comparable to glasses that have been cooled for hundreds/thousands of years.

A common feature of most stable glass formers is that they have relatively high thermodynamic "fragility" values. The greater the deviation from the time dependence of structural relaxation on the reduced temperature, which obeys the Arrhenius law, the higher the brittleness, i.e., "fragility" is a measure of the non-Arrhenius change in the logarithm of relaxation time versus reduced temperature. For such cases, the temperature dependence of τ is given by the Vogel-Fulcher-Tammann (VFT) expression:

$$\tau = \tau_0 exp\left[\frac{DT_0}{T - T_0}\right]$$

According to recent ideas, glasses with high kinetic stability can only be obtained from very fragile liquids. But it should be noted that it is often extremely difficult to form glass from fragile liquids by cooling their liquid phase.

Typical representatives in this regard are freons (tetrafluoroethane and carbon tetrachloride). They refer to systems that have the above properties and exhibit internal molecular degrees of freedom that can contribute to the creation of stable PVD glasses.

An urgent task is to study freons of carbon tetrachloride and tetrafluoro ethane as model substances, for which no studies have been carried out to date to obtain a glassy state by cooling from a liquid. However, during gas-phase condensation, these substances form highly stable glasses with high fragile index values.

The purpose of the research experimental study of structural relaxations in glassy thin films of tetrafluoroethane ($C_2H_2F_4$) and carbon tetrachloride (CCl_4) freons obtained by physical vapor deposition (PVD) in a wide low temperature range.

The objects of the research are glassy thin films of tetrafluoroethane ($C_2H_2F_4$) and carbon tetrachloride (CCl_4) freons obtained by physical vapor deposition (PVD).

The subject of the research is structural relaxation processes in glasses occurring at low temperatures.

The method of the research PVD thin film condensation; two-beam laser interferometer; IR spectroscopy.

To achieve this purpose, the following tasks were set:

- To study the dependence of the refractive index and density of tetrafluoroethane ($C_2H_2F_4$) and carbon tetrachloride (CCl_4) freon glasses in different structural states on temperature and pressure of cryopreservation.
- Determine the vibrational characteristic absorption bands of freon molecules, which are most sensitive to structural relaxation in samples that occurs during their heating and thermal cycling.
- Determine the temperatures at which structural relaxations occur between different states of the samples by observing changes in the intensity of IR radiation at a fixed frequency of the half-width of the characteristic absorption bands of freon molecules.
- Determine the dependences of the times (τ) of structural relaxation on temperature by observing the transformation of the deposited freon glass into a supercooled liquid under quasi-isothermal conditions using the method of IR spectroscopy.
- Calculate the dependence of relaxation time (τ) on temperature using the Vogel-Fulcher-Tammann equation to parameterize the results obtained.

The novelty and originality of the work lies in the fact that for the first time in it:

The dependence of the refractive index and density of tetrafluoroethane ($C_2H_2F_4$) and carbon tetrachloride (CCl_4) freon glasses on the temperature and pressure of the gas phase of cryopreservation has been established experimentally. It has been found that when freon molecules condense from the gas phase below the glass transition temperature T_g of the samples obtained from the liquid phase, tetrafluoroethane ($C_2H_2F_4$) and carbon tetrachloride (CCl_4) freon glasses of different stability are formed, which, upon their subsequent heating, relax into a supercooled liquid phase.

A shift in the temperature of devitrification T_{onset} of the samples, which characterizes the formation of kinetically stable freon PVD glasses, is revealed. Higher T_{onset} values indicate greater kinetic stability of PVD glasses. It has been found that the substrate temperature T_{sub} has a strong influence on the stability of the vapour-deposited glass. The most stable freon PVD glasses, both in kinetic and thermodynamic terms, are formed during their deposition at a temperature of 0.9 T_g

The main provision for the defense

1. For glasses of tetrafluoroethane ($C_2H_2F_4$) and carbon tetrachloride (CCl_4) freons, obtained by condensation from the gas phase, the dependence of the values of the refractive index and density from temperature T_{sub}=16 K to temperatures corresponding to their glass transition temperatures (T_g=72 K, T_g=78 K ,

respectively) and in the pressure range from $1*10^{-5}$ Torr to $1*10^{-4}$ Torr increase smoothly, reaching saturation above their glass transition temperature.

2. The formation of PVD glasses $C_2H_2F_4$ and CCl4 with different degrees of kinetic stability occurs when their molecules condense below the glass transition temperature T_g. In this case, the most stable PVD glasses are formed during their deposition at a temperature of 0.9Tg.

3. Stable PVD glasses of $C_2H_2F_4$ and CCl_4 freons have high "fragility" index values (m=140, m=112, respectively) and they are considered as systems with non-Arrhenius dependence of relaxation times on temperature.

The theoretical and practical significance of the work.

The results obtained in this work are of value for the theoretical and experimental study of glass transition phenomena, since, despite their translational symmetry, they have orientational disorder.

In the last decade, there has been great progress in manipulating the structure of vapor-deposited glasses. By changing the substrate temperature during deposition, glasses with a wide range of densities and molecular orientations can be obtained from a given molecule. Recent research indicates that the structure of vapor deposited glasses can be tuned to significantly improve the external quantum efficiency and lifetime of organic light emitting diodes (OLEDs). Great research opportunities for improving the physico-chemical properties by controlling the structure of vapor-deposited glasses.

The reliability and validity of the results obtained is determined by the fact that the experimental data obtained in the course of the work are in good agreement with the calculations obtained using the proposed models. In addition, the reliability of the results obtained is confirmed by the presence of three publications in a foreign journal with the Q1 quartile and in publications recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, and in the proceedings of international scientific conferences near and far abroad.

Connection of the topic with the research plan and various State programs.

The work was carried out within the framework of the project of the Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan: "Structural-phase transformations and relaxation processes in thin films of cryo-vacuum condensates of glass-forming organic molecules" for 2020-2022. (AP08855738).

Personal contribution of the lies in the fact that the entire volume of research work, the choice of the research method, the conduct of experiments, the processing of the results obtained, the analysis of the data obtained were carried out by the author independently. In the articles "Structure transformations in thin films of CF_3-CFH_2 cryodeposites. Is there a glass transition and what is the value of Tg?", Investigation of vapor cryodeposited glasses and glass transition of tetrachloromethane films, The study of thermophysical properties of rubber and plastic household waste to determine the temperature conditions of cryoprocessing" Nurmukan A.E. is a writer and correspondent.

The doctoral student participated in all the experiments and interpretation of the results and prepared the first versions of the articles describing the introduction, methodology, results, conclusions, and graphics. In addition, Nurmukan A.E. participated in the design of articles in accordance with the requirements of the journal and in improving the article after each stage of peer review. The setting of tasks and discussion of the results were carried out jointly with the supervisors.

Publications. Based on the materials of the research work, 20 printed works were published: 4 in journals from the list of CQASHEMS RK for the publication of the main results of the work for the PhD degree and 10 articles in journals near and far abroad with an impact factor included in the international information resources Web of Science (Clarivate Analytics, USA) and Scopus (Elsevier, Netherlands); 5 works in the materials of international scientific conferences, 1 patent for a utility model.

Approbation testing of thesis. The results obtained in the research work were reported and discussed: at the International Conference 15th International Conference on the Physics of Non-Crystalline Solids & 14th European Society of Glass Conference (PNCS-ESG). – 2018, at the 3rd International Conference on Applied Surface Science (ICASS2019). – 2019, at the International Conference on Cryocrystals and Quantum Crystals 2019. – 2019, at The Online 10th International Colloids Conference. – 2020, at the International Scientific Conference 5th International Conference on Applied Surface Science (ICASS2022). – 2022.

The results obtained in the dissertation work were published:

– A. Drobyshev, A. Aldiyarov, D. Sokolov, **A. Nurmukan**, A. Shinbayeva, Structure transformations in thin films of CF_3-CFH_2 cryodeposites. Is there a glass transition and what is the value of Tg? // Applied Surface Science. – 2018. – Vol. 446. – P. 196-200. **(Q1 WoS)**

– A. Drobyshev, A. Aldiyarov, D. Sokolov, **A. Nurmukan**, A. Shinbayeva. IR studies of thermally stimulated structural phase transformations in cryovacuum condensates of Freon 134a // Fizika Nizkikh Temperatur. – 2018. – Vol. 44. – No. 8. – P.1062-1072.

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Patent

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