ABSTRACT

dissertation for the degree of doctor of philosophy (PhD)
specialty 6D071000 – Materials Science
and new materials technology

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«Influence of stimulating modifiers on the optical-mechanical properties of polymer composite materials»

Relevance of the topic

Analysis of the current state of research of high-temperature superconductors (HTS) leads to the conclusion that the oxide superconducting materials will be widely used in the form of thin films, so for further progress is necessary to develop reproducible technologies for their production.

Significant factors limiting the widespread use of htsp are: technological difficulties in the manufacture of ceramic products of complex configuration, the fragility of these products. One of the possible ways to solve the problem is the development of polymer composite materials (PCM) with HTS filler. The creation of filled composites from polymer matrix and high-temperature superconducting connection, allows obtaining a more flexible HTS system. Such systems have structural perfection of polycrystallites and plastic properties of polymers (chemical resistance to aggressive media, mechanical strength, manufacturability in the processing of the product, etc.).

Polymer composites with htsp filler can be widely used in power engineering, electronics and computer engineering, magnetic systems of thermonuclear reactors, electronic systems of space stations, etc. Due to this, devices based on the phenomenon of VSEP during operation can be exposed to various radiation and the environment, which cause changes in physical and chemical properties and structure of materials. High-temperature superconductors are more sensitive to radiation than conventional superconductors. Irradiation in most cases leads to deterioration of the parameters of metal oxide ceramics. In this case, the critical transition temperature is often reduced, although in some cases there is an increase. The reasons for this behavior are still not fully understood.

Currently, there are a large number of theoretical and experimental studies describing the various stages of radiation-physical processes occurring in polymer films and HTS compounds. A significant number of data on the radiation-chemical transformations of these systems under the action of ionizing radiation under different conditions have been accumulated, but both systems have been studied separately. Targeted studies on the effect of radiation exposure on the properties of polymer composites with HTS filler are also important for the development of methods to protect such materials from harmful effects.

In accordance with the above, the study of the regularities of the behavior of PCM with htsp filler under the conditions of exposure to ionizing radiation and the

study of the properties of the structure and the search for possible ways to improve the parameters of the system "Polymer – high-temperature superconductor" is an urgent task.

The aim of the thesis is to study the effect of the filler concentration $YBa_2Cu_3O_{6,7}$, gamma irradiation and low-temperature annealing on the optics-mechanical properties of the Polymer – high-temperature superconductor system.

To achieve the objective the following tasks are set:

- to investigate experimentally the processes of influence of mechanical load on deformation of polymer - composite materials " Polyimide-$YBa_2Cu_3O_{6.7}$;
- to investigate the effect of mechanical load on the deformation of the "Polyimide-$YBa_2Cu_3O_{6.7}$" system after irradiation with different doses of gamma quanta;
- to identify additional absorption bands in IR and Raman absorption spectra of the "Polyimide -$YBa_2Cu_3O_{6.7}$" system irradiated with gamma quanta and to find out their origin;
- on the basis of the analysis of optical transmission spectra, absorption and refractive indices to determine the effect of radiation on the optical properties of the system "Polyimide- $YBa_2Cu_3O_{6.7}$»;
- to investigate the effect of low-temperature annealing on the optical properties of the Polyimide -$YBa_2Cu_3O_{6.7}$ system.

Research methods

- experimental method of research of mechanical load on the deformation "Polyimide-$YBa_2Cu_3O_{6.7}$;
- method of infrared and Raman spectroscopy to determine the change in the structure of the system "Polyimide-$YBa_2Cu_3O_{6.7}$" and the mechanism of radiation exposure;
- optical methods for determining the boundaries of the light transmission, absorption coefficients and the refractive index of the produced samples of the system "Polyimide-$YBa_2Cu_3O_{6.7}$ »;
- study of the structure of the samples by the method of x-ray diffraction using X'pert Pro diffractometer (Philips, PANalytical), CuK_α-radiation ($\lambda_{\alpha Cu}$ = 1.5418 Å).
- electron scanning microscopy using Vega Plus TS 5135 from Tescan Microscope, in high vacuum mode at a typical operating voltage of 30 Kev and atomic force microscopy NT – MDT NTEGRA Therma.

The objects of the study are PCM samples based on polyimide with different concentrations of filler ($C = 0{,}05\,\text{mass.}\%$, $C = 0{,}1\,\text{mass.}\%$, $C = 0{,}5\,\text{mass.}\%$) powder form , obtained at the Institute of Chemistry of NAS RK named after Bekturov.

Subject of study are the radiation effects, changes in optical and mechanical properties under the influence of temperature, static mechanical load and irradiation with gamma quanta on the system "Polyimide – high-temperature superconductor ".

Scientific novelty of the study

- the influence of the filler content on the optical and mechanical properties of composite materials based on polyimide is revealed;
- the influence of mechanical load on the processes of simultaneous reduction of plasticity and hardening of polymer composites irradiated with gamma quanta is revealed;
- in the IR spectra of the Polyimide system, absorption bands appear due to the formation of radicals and the flow of radiation-stimulated competing processes in the structures of the polyimide, as well as the phase transition of the system from orthorhombic-I to orthorhombic-II associated with the filling of the oxygen position by oxygen atoms, the migration of which is due to radiation-stimulated diffusion.
- the regularities of the decrease in optical transmittance, absorption coefficients and refractive index of polymer materials, depending on the dose of gamma irradiation and composition of the fillers due to diffusion of oxygen from the structure PI in nodes oxygen O(4) O(5) of the YBCO system, which causes the process of restructuring, which consists in displacement or orientation of the optical centers of the matrix of the polyimide.

Practical significance

The practical significance of the work – due to the fact that the results can be used to create a flexible HTS compound in a polymer matrix and the ability to use them to control the formation of the structure of the system.

Approbation of the work.

The main provisions of the thesis were presented and discussed at domestic and foreign international conferences: IV International Farabi readings "Farabi Alemi", Almaty, 2017; international scientific forum nuclear science and technology, dedicated to the 60th anniversary of the Institute of nuclear physics, Almaty, 2017; Conference "Chaos and structures in nonlinear systems. theory and experiment: Proceedings of the 10th International scientific conference, Almaty 2017; Conference "International Conference on Advanced Structural and Functional Materials 2018", Poland, 2018.

Main results.

- relationship between structural-phase transitions and physical-mechanical properties of the Polyimide - system from the filler content.
- the dependence of the tensile strength and elongation of the samples of the "Polyimide-$YBa_2Cu_3O_{6.7}$" system on the dose of irradiation and on the filler content is associated with the migration of oxygen atoms, which slows down or completely suppresses the formation of a spatial grid in the PI matrix;
- the dependence of IR and Raman spectra of Polyimide - $YBa_2Cu_3O_{6.7}$ system samples on the radiation dose is related by the structural-phase transition from orthorhombic-I to orthorhombic-II;

- the appearance of new absorption bands in the transmission and absorption spectra of the "Polyimide-$YBa_2Cu_3O_{6.7}$" system after irradiation with quanta is associated with the formation of diene structures and a sharp decrease in the content of oxygen atoms in the structures of the polyimide matrix.

Personal contribution of the author. Review and analysis of scientific literature on the topic of the dissertation, the direct execution of the experimental part of the work. Processing, interpretation and generalization of the results obtained, as well as active participation in the writing and design of articles, abstracts, reports of republican and international conferences.

Publications.

The results of researches were reported in 10 scientific publications including: - 3 articles issued in the journal recommended by the committee on control in the field of education and science of the Ministry of education and science of the Republic of Kazakhstan. - 3 articles issued in international scientific editions entering the data based Scopus, non-zero impact factor. - 4 articles and theses issued in international scientific conferences.

Content and structure of the dissertation.

The dissertation comprises Introduction, 4 sections, conclusion, the list of the used sources. The total volume of the dissertation makes up 103 pages, 7 tables, 49 figures, and the list of 187 references.

The choice of this HTS material as a filler was due to the fact that it has the vast majority of local States associated with charged defects. The concentration of defects in it can be controlled by the introduction of oxygen atoms. They will appear as charged centers, which significantly affect the electronic structural state of the PCM. On the other hand, in YBa2Cu3O6+x at positions O4 and O5, the content of labile oxygen can vary as widely as possible: from x = 0 to x = 1. At x = 1, an orthorhombic O−I structure of this compound is formed in the form of a metal phase, which is a superconductor with a superconducting transition temperature Tc ∼ 90 K. in this state, it has O4 oxygen positions along the b axis in the chains . . . - Cu1−O4-Cu1− . . . almost all are filled, and along the a axis positions O5 in chains . . - Cu1–O5-Cu1–. . . almost all are vacant. Htsp has a tetragonal structure T, at x = 0, and it is a dielectric. In this state, it is characterized by the fact that the oxygen positions O4 and O5 are vacant, including the orthorhombic O-II-phase (x ∼ 6, 5) with a superconducting transition temperature Tc ∼ 60 K

The first section presents a literature review on the various properties of polyimide composite materials and the effect of irradiation on their properties and structures.

The second section of the work shows the experimental results obtained for the study of structural changes in the "Polyimide -" system by IR and Raman spectroscopy. It is shown that Raman and IR spectroscopy methods are more sensitive and reliable in the study of structural changes in polymer composites compared to other methods. A method for studying the optical characteristics of

the "Polyimide -$YBa_2Cu_3O_{6.7}$" system in the ultraviolet region has been developed. On the basis of the obtained data, calculations were made and data on the absorption and refractive index were obtained.

he third section presents the results and analysis of changes in the optical properties of the "Polyimide -$YBa_2Cu_3O_{6.7}$" system as a result of low-temperature annealing. Treatment with liquid nitrogen does not affect the structure of the matrix of the polymer composite material (PCM) and the polyimide film, and the decrease in the amplitude in the region of 4200-1750cm-1 is due to a decrease in the concentration of free oxygen ions in the polyimide structure. The appearance of new peaks in the spectrum for a sample with a concentration of 0.5% mass. it is characterized by a deformation oscillation of the Cu-O bond in the chains and the formation of oxygen vacancies and the oscillation of the Cu(1) – O(1) chain near one or more oxygen vacancies O (4). The absence of the absorption band of other isolated hydroxyl groups is explained by the high degree of coating the surface of the htsp ceramic atoms with a polymer matrix. The change in the main IR spectra, and the appearance of new peaks for all samples after treatment with liquid nitrogen is due to the embedding of nitrogen molecules in the PCM lattice, this changes the energy state of the lattice and as a result, increases the energy of interaction between free ions.

The fourth section compares the results of the study of changes in the optical-mechanical properties of gamma irradiated composite material. Gamma irradiation of polyimide films with a dose of up to 600 kGr does not affect their transparency in the range of 550-1100 nm. Irradiation of polyimide films with doses of 250 and 600 kGr creates signs of a weakly expressed thin structure in the range of 220-300 nm, due to the contribution to optical transmission from the formed diene structures and an increase in the content of oxygen atoms. Increasing the radiation dose to 600 kGr does not lead to a significant change in the content of carbon, hydrogen and oxygen in the films. Gamma irradiation of samples of polyimide composite materials causes a decrease in their transparency, which increases significantly with increasing filler concentration. In the range of 600-1100 nm, these polyimide composite materials retain the achieved transparency. The introduction of different filler concentrations causes the same displacement of the absorption boundary from ~2.3 to ~3.9 eV in all polyimide composite materials, and shifts in the range from ~3.7 to ~4.1 eV lead to a sharp jump in the absorption coefficient from ~1.0 · 10^4 to ~11.0 · 10^4 cm^{-1}. The achieved value of the absorption coefficient for all polyimide composite materials remains unchanged, which cannot be said for an unradiated pure polyimide film. The YBaCuO filler and gamma irradiation cause the transition of the polyimide from the amorphous state to the crystallite state, which leads to a decrease in the content of oxygen and carbon atoms in the matrix and the creation of active boundary layers around the YBaCuO particles that cause this transition. Introduction of filler with concentrations C = 0.05 and 0.10 wt.% leads to a decrease in the extinction coefficient to ~50 %, and at C = 0.50 mass.% its values increase sharply by ~200 % at the same doses of gamma irradiation in comparison with a pure polyimide

film. This is due to the formation of a thin oriented adsorption layer of the polymer adjacent to the surface of the filler particles. A sharp increase in the extinction coefficient of polyimide composite materials with a filler concentration of 0.50 wt. this is due to the fact that the radius of influence of structurally active fillers on the macromolecules of the matrix increases sharply and reaches 10 microns.