

The IR photoinduced changes in the Y-Ba-Cu-O thin films

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The Y-Ba-Cu-O thin films are promising materials because they have not only superconducting properties but also good optical properties, particularly in the IR spectral range. We investigate the photoinduced optical changes in the IR region for oriented Y-Ba-Cu-O thin films deposited on <110> surface of ZnSe single crystals, using differential IR spectroscopy Fourier technique in the spectral region between 100 cm^{-1} and 450 cm^{-1} . We have also found the photoinduced photodarkening effect under the influence of the CO₂ pulse laser ($\lambda = 10.6\text{ }\mu\text{m}$). The possibility of using the above-mentioned materials as promising materials for IR optoelectronics and nonlinear optics is discussed.

1. Introduction

Recently, we have revealed that the Y-Ba-Cu-O thin films are promising materials not only for the exclusive superconductor devices, but also as media for the photoinduced changes [1]–[3]. The latter indicates the possibility of uncontrolled factors influencing the observed effects. Concerning the photoinduced effects in superconductors and in solid films particularly, one can say that up to date there no exact explanation of the observed phenomena. Moreover, the existing experimental work [4], [5] are substantially empirical.

The reversible photoinduced changes are very weak as they embrace less than 1% of the total numbers of atoms. The usual optical spectroscopy methods (containing information about their integral spectral signals) are less useful for that purpose. The necessary knowledge concerning phototransformation can be actually obtained by differential IR spectroscopy Fourier technique in a long-wave IR spectral region (below 400 cm^{-1}). The essence of this technique consists in using a differential signal (instead of the integral one) obtained as a result of subtracting the IR spectra registered before and after the influence of an external factor and then renormalized due to a proper superposition in the next steps. This technique was fruitfully applied for

different kinds of disordered semiconducting films. The main aim of the experiment mentioned was to identify the reversible short-range phototransformation induced by the external IR light beam.

The Y-Ba-Cu-O superconducting films have a wide range of spectral transparency (0.65–50 μm) with the absolute values of transparency belonging to 38–60%. Optimal thickness of the films lies within 0.8–1.3 μm . The experimental arrangement is shown in Fig. 1. We have used CO laser ($\lambda = 5.5 \mu\text{m}$) as a source of the photoinduced changes. The control of the photoinduced phototransparency was performed for the CO₂ laser at a wavelength of 10.6 μm and the spectral lines in the region 5–11 μm . The control of energy in the photoinduced beam was performed using a joulemeter (Gentic, Inc., model ED-200).

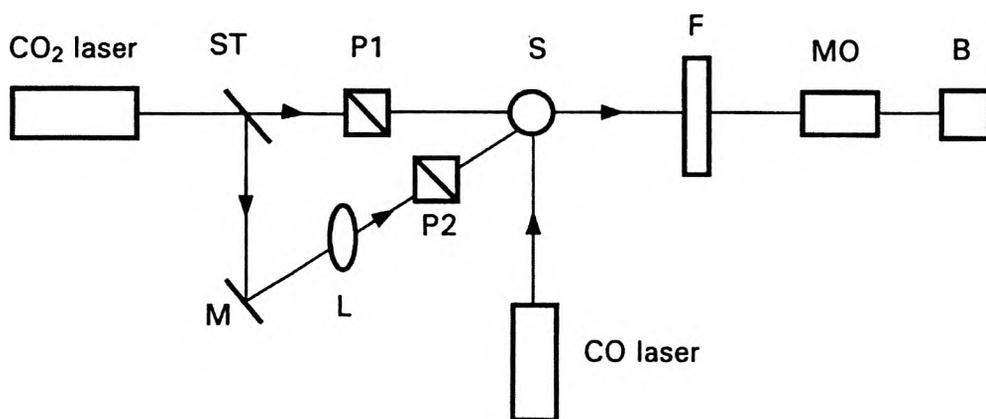


Fig. 1. Experimental equipment for performing the photoinduced changes. ST – semitransparent ZnSe beam-splitter, P1, P2 – polarizers, S – sample, F – filter, MO – monochromator, B – bolometer, M – mirror L – wavelength parametric generator.

In this work, we study the influence of external illumination on optical constants of the superconducting Y-Ba-Cu-O thin films. One of our main goals is to find a correlation between the IR photoinduced changes and the optical constants, particularly optical phototransparency, photodarkening and superconducting appearance. In this article, we also investigate the possibility of using the films under study as materials for recording optical information in IR spectral region. Up-to-day, to our knowledge, there were only single works devoted to photoinduced properties of high temperature superconductor thin films [6].

2. Sample preparation

The Y-Ba-Cu-O thin films were sputtered onto a ZnSe <110> substrate kept at 923 K during deposition in a dc magnetron source with $p_{\text{base}} \sim 10^{-9}$ Tr in a UHV stainless steel system. A single target of Y-Ba-Cu-O thin films was used with a 1:1.5 mixture of

oxygen and argon at a total pressure of 360 mTr. *In situ* annealing was carried out during 30 min at 1.2 atm oxygen atmosphere at 683 K. Optical-polarized measurements have shown that the transmitted light in the specimens has no preferred polarization direction.

The measurements of photoinduced changes are performed using the pulse CO laser with the photon flux changing from 10^{13} to 10^{17} photons/cm² per pulse. We have measured phototransparency (PT) as a difference between the transparency after and before photoexcitation.

The Y-Ba-Cu-O films were amorphous-like. Their critical temperature was equal to 91 K. All the measurements were done at 77 K.

3. Results and discussion

Figure 2 present data for the dependences of the photoreversible PT as a function of the film thickness. All the data are presented in arbitrary units due to the high surface non-uniformity (more than 24%) of the films considered. One can clearly see that there appears an additional PT due to increasing film thickness about 1000 nm. This unexpected fact seems to be related to essential contribution of the interface between the substrate and films. One can also clearly see, at least, two maxima: at 1350 and 1800 nm. The appearance of a step-like structure indicates the essential role of the so-called long-lived metastable trapping state due to the irreversible photostructural changes [7]. Moreover, one can predict the occurrence of the metastable long-lived localized states essentially changing the averaged life times of the levels. In order to understand the nature of the dependences observed, we have performed measurements of the differentiated Fourier spectra in the spectral range 80–400 cm⁻¹.

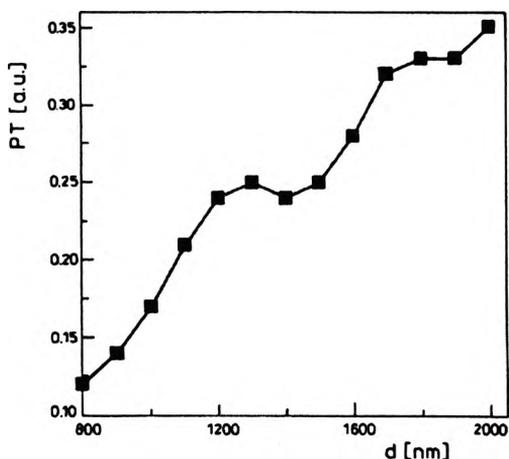


Fig. 2. Dependence of the maximal reversible PT as a function of film thickness for the wavelength 10.6 μm for the CO laser ($\lambda = 5.5 \mu\text{m}$) photoinduced photon fluxes about the 18×10^{13} photon/cm² per pulse after 30 min of illumination.

Therefore, one can speak about an increase of growing destructivity of crystallization reaction because the corresponding modes are indicated as complex clusters stimulating the appearance of the above mentioned structural fragments defining optical photoinduced changes [8].

The data obtained, together with the next quantum chemical estimations, show the essential role of Cu–O optical phonons in formation of metastable IR photoinduced states, because the CO photoexposure light strikes exactly into the main spectral peak of the observed vibrations. Simultaneously, one can assume that these bonds cause low-temperature ordering of the Cu–O bonds in the films and favour the appearance of bounded electron–electron pairs. The nature of the phenomena observed is not fully explained. Therefore, it requires additional theoretical and experimental investigations. These phenomena could be explained by the irreversible IR photoinduced changes and by the contributions of the dynamic subsystems which essentially redisturb the systems.

The incident radiation of CO laser for the films of different thickness causes simultaneous creation of the metastable trapping states, which are frozen due to the electron–phonon anharmonic interactions.

Spectral distributions of optical density D as functions of a wave number f in the Y-Ba-Cu-O thin films induced by photoexposure and thermoannealing cycles are illustrated in Fig. 3. One can clearly see the essentially different behaviour of the optical density for the different photon fluxes, especially at frequencies between 275 and 300 cm^{-1} . Such behaviour confirms the essential effect of the photoinduced flux on optical properties of the films. A full process of the reversible photostructural

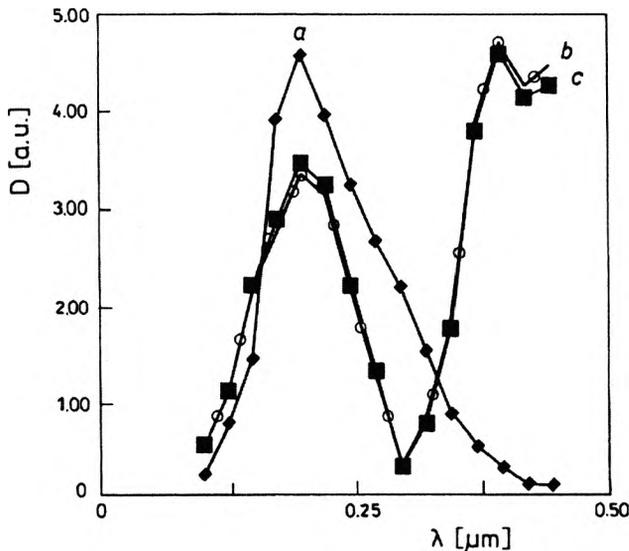


Fig. 3. Spectral dependence of the optical density D (in arbitrary units) for the photoexposed (a), thermoannealed (b) and unexposed samples (c).

transformation (PhST) in the Y-Ba-Cu-O thin film may be described by the following destructive crystallization reaction:



where the expressions in brackets denote chemical bonds destroyed or formed due to sample photoexposure.

Other ions do not contribute to the resulting output of the photoinduced changes of optical constants because their frequencies are out of the measured spectral photoinduced region. In multiple photoexposure-thermoannealing cycles these changes of optical density ΔD may be repeated with a small irreversible component (of 0.8–1.3%).

Let us consider all possible cases of the photoinduced coordination defects formation (CDF) [5] in the Y-Ba-Cu-O films described by Eq. (1). Eight D^+ and D^- oxygen defects of the generation schemes accompanied by destruction of the heteropolar chemical bonds must be considered to be the essence of this analysis. These schemes were made complete taking into account the various possible initial conditions (heteropolar Ba–O bonds) and essential features of the charge defect formation (CDF). The thermoannealing displaces the equilibrium of these configurations in opposite sides. On the other hand, the probability of the defects being annihilated and of the heteropolar (Ba–O) bonds appearing in the Y-Ba-Cu-O increases at higher temperatures. It is difficult to explain why the transformed bond concentration is actually less than 1–2% for such structural states. Factors determining the oxygen defect formation efficiency are not usually considered in the self-trapped exciton model. Therefore, the existing coordination defects represent quasi-atomic centres, which contain an electric charge excess and are characterized by a negative electron correlation energy. A strong polaron effect appears in this model due to the interaction between the positive centres and the lone-pair electrons of a neighbouring atom (*i.e.*, a donor–acceptor interaction). First of all, the intermolecular Cu–O interaction constants are reduced in comparison to the ones initially existing in the Y-Ba-Cu-O structural network. Therefore, these complexes can be classified as the soft atomic configurations having a double-well potential and a negative electron correlation energy. Such a coincidence of the reversibly transformed bond concentration and the soft atomic configurations serves as an additional argument in favour of the assumptions proposed above. A rigidity network and relaxation effects in the nearest neighbour coordination centres are commonly accepted in the CDF model as major factors governing their behaviour. Their quantitative description is usually given by a local atomic density δ [6] defined as:

$$\delta = \frac{\sum_i A_i / \rho_i - \sum_i A_i x_i / \rho}{\sum_i A_i x_i} \quad (2)$$

where A_i , x_i and ρ_i are atomic mass, atomic weight and density of the i -th structural fragment arising after the bond switching, respectively. The average density of the sample is denoted by ρ .

The existence of the photoinduced state is conveniently connected with a defect pair stability. Let us introduce an ε_i energy parameter which is equal to a difference between bond dissociation energies before and after the photoexposure. If we denote the (Cu–Cu⁺⁺) and (O⁻–O⁻) pair concentration by x_1 and x_2 , then the activation energy barrier can be written in the following way:

$$\Delta E = \frac{\varepsilon_1 x_1 + \varepsilon_2 x_2}{x_1 + x_2} \quad (3)$$

Supposing that the probabilities of the two reversible PhST channels are equal (*i.e.* $x_1 = x_2$) the values ΔE for the specimens mentioned can be easily calculated leading to the following results: Cu–O (17 kJ/mole), Y–O (14 kJ/mole) and Ba–O (3.4 kJ/mole).

The photoinduced changes also decrease in such a magnitude order [9]. The photodarkening efficiency in the nonstoichiometric samples can be estimated taking into account a difference between the values ε_i for the various schemes of CDF. We are able to construct a mechanism of reversible phototransformation in the investigated glasses under investigation, comprising the following photoinduced stages:

1) the excitation of an electron or/and a hole pair that is auto-localized at the soft atomic configurations (as an initial microscopic process),

2) the weakening of the inter-molecular bonds resulting in displacements of the atomic groups,

3) the metastable state formation due to structural changes at the short-range ordering (redistribution of chemical bonds or a CDF) and at the intermediate-range ordering levels (*i.e.* rearrangements of atomic blocks and displacements of non-bonded atoms).

These stages are mutually connected and they depend on the chemical-technological properties of the thin films under investigation as well as temperature and spectral distribution of absorbed light.

The intra- and intermolecular bond-breaking processes are therefore involved in the present model of reversible PhST in the Y–Ba–Cu–O as was initially described in [10]. A real scheme of the bonds switching associated with the photodarkening can be obtained considering all possible cases of the local coordination changes.

4. Conclusions

We have shown that with the increasing film thickness about 1000 nm there appears the additional phototransparency. This fact seems to be related to essential contributions of the interface layer between the substrate and films. We have revealed that there exist, at least, two maxima of phototransparency, at 1350 and 1800 nm film thicknesses. The appearance of the step-like structure indicates the essential role of

the so-called long-lived metastable trapping state due to the irreversible photostructural changes. Moreover, one can predict the appearance of the metastable long-lived localized states essentially changing the averaged living times of the levels. We have revealed an essentially different behaviour of the photoinduced optical density, especially at frequencies between 275 and 300 cm^{-1} .

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