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Photoinduced phenomena in Hg films

1. Introduction

The appearance of an interesting phenomenon observed in the photodoping of the high-temperature materials was discussed in our previous publications [1-7]. The measurements in question were carried out first of all on the traditional $YBa_2Cu_3O_{7-\delta}$ single crystals and have shown that during laser photoexcitation the insulating samples of $YBa_2Cu_3O_{7-\delta}$ become highly conductive. Further experiments using the time-resolved methods were performed [8,9] and have indicated unambiguously a linear dependence of photocurrent on irradiated light intensity. Simultaneously for intensities above $6x10^{15}$ photons/cm^2 the superlinear dependence of photoinduced photocurrent was observed. The detected peculiarities were explained by the additional carriers transport mechanism. The values of resistivity decrease were at 50 K by more than 14 orders less and photoinduced conductivity was time delayed due to the absorption. The concepts of phase separation and metallic droplet formation were used to explain the observed phenomena. The similar behaviours of the photoinduced parameters were noticed in work [7] where the analogous photostimulated phenomena were observed under influence of low-power *He-Ne*, *He-Cd*, *He-Se* and nitrogenium lasers.

In the above works all the investigations were carried out on the crystalline samples and no experiments involved either the ceramic samples or the multiphase samples. Recently we have performed measurements of optical second harmonic generation (SHG) in the new superconductors' — Hg-1201 [10]. These samples have phase transition at the temperature of about 125 K.

The research of the photoinduced phenomena plays a vital role in the deeper understanding of high-temperature superconductivity. Some theoretical approaches to understanding of the photodoping in superconductors were done in works [11-13]. In the mentioned papers it was clearly demonstrated that phase-separated droplets inhibit hole mobility initiated by photodoping. Moreover, it was shown beyond doubt that the dilute holes are unstable against phase separation into a hole-rich phase and a pure antiferromagnetic insulating phase. Afterwards it was argued that dynamic separation could lead to BCS pairing.

In the recent work [14,15] it was shown that the SHG methods are sensitive to appearance of superconductivity. Moreover, it was demonstrated that occurrence of SHG signal takes place at the temperatures higher than those at which the resistivity begins to arise. Therefore one can conclude that the SHG methods could prove to be very sensitive methods for investigations of superconducting phase transitions. Simultaneously, a volume origin of SHG was elucidated and in the case of crystals the anisotropy of the observed phenomena was noted.

Our present work aims to widen the field of the previous research by focussing on ceramic samples. We have set out to examine the possibility of detecting SHG in the superconducting component of ceramic samples. These investigations are relevant for the high-resolved time regime in particular. It will be very interesting to investigate the changes of the other physical parameters for example photoresistivity, photoconductivity etc. We shall also check an influence of the oxygen deficiency, photoinduced photon flux as well as other parameters on the time-resolved opto-electronic features. In order to explain the nature of the phenomena, which may be observed in the course of the investigations it is very important to carry out the transient measurements of the photoinduced SHG. Unfortunately the absolute values of the SHG signal both as the corresponding non-linear optical susceptibilities should be very low due to the low contents of the superconducting phase. Therefore all the measurements should be performed at different points of the investigated samples to avoid the possibility of a nonuniform distribution of the superconducting crystalline phase. The time-dependent investigations can give an essential information concerning the nature of the superconductivity in the Hg-1201samples. In the future this data can help in clarifying the role of the electron and phonon subsystems in the phenomena observed. From the material scientist's point of view photoinduced changes can be used to create finely dispersed defects which form pinning centres of the magnetic flux in Hg-1201 materials. There also appears the possibility to design high-time-resolved laser switches.

2. Experimental details

Samples of nominal compositions Hg-1201 were prepared by solid-state reaction at 800°C, 5h from stoichiometric powders of HgO (99% purity), BaO (97%) and CuO (99%). After the annealing in flowing oxygenium at 350°C the material was identified by X-ray method. For defects creation and additional doping by oxygen, samples were reannealed at 600°C for 2.5 h in a flow of oxygen. While heating from 435 to 600°C sample decreased by 12% as the result of loosing Hg.

All structure calculations were performed using complex programme CSD [12]. Starting structure for Hg-1201 was chosen according to Ref. 12 (space group P4/mmm). Thermal parameters and sites occupations differ from the model Hg-1201. Structural parameters of superconducting phase with content by X-ray method as $(Hg_{0.89}Pb_{0.17}Ba_{0.11})Ba_2CuO_{4+\delta}$ annealing at 3500C) and $(Hg_{0.83}Pb_{0.17})Ba_2CuO_{4+\delta}$ (reannealing at 6000C) are shown in the Table 1. Lattice parameters, refined using full profile data for these phases are: a=b=3.8760(2)A, c=9.5189(9) (6.8533(2) g/cm^3 and a=b=3.8760(2)A, c=9.5189(1) (7.0003(2) g/cm^3), respectively.

Tab. 1. Structural parameters of superconducting phase with content by X-ray method as ($Hg_{0.89}Pb_{0.17}Ba_{0.11})Ba_2CuO_{4+\delta}$ annealing at 3500C) and ($(Hg_{0.83}Pb_{0.17})Ba_2CuO_{4+\delta}$ (reannealing at 6000C)

ATOM (x=0.11)	N	x/a	y/b	z/c (x=0,17)	N	x/a	y/b	z/c
Hg	1*	0	0	0	1**	0	0	0
Ba	2	1/2	1/2	0,2966(1)	2	1/2	1/2	0,2937(6)
Cu	1	0	0	1/2	1	0	0	1/2
O(1)	2	1/2	0	1/2	2**	1/2	0	1/2
O(2)	2	0	0	0,209(1)	2	0	0	0,220(8)
O(3)	1*	1/2	1/2	0	2**	1/2	0	0

Sites occupations * Hg: 0.89(1)Hg+).11(1)Cu; O93): 0.12(34)0
**Hg: 0.83(1)Hg+0.17(1)Cu; O91): 0.78(9)0; O93): 0.24(9)0

An experimental investigation of the photostimulated changes caused by nitrogen laser (λ=337 nm) UV irradiation with a pulse width of about 650 ps will be presented. The instrumental resolution was about 120 ps. The investigated films were irradiated using focused pulsed nitrogen laser UV light with a photon flux less than $6x10^{18}$ phot./cm ^{2}. This power restriction was caused by the necessity of avoiding sample heating.

The traditional Auston-switch configuration was used to check the transient photocurrent. All the specimens were placed on a 75 μm stripling transmission line formed by evaporated Ag. The voltage of the DC bias sources was varied from 0 to 7 V and the corresponding line was connected to a boxcar detector. The corresponding device allowed obtaining a high-frequency response of up to 180 GHz. The gate width of the boxcar was chosen as 35 ps for the PC at times less than 15 ns, and for time evolution measurements in the range from 20 ns to 1000 ns the gate width was selected to be from 8 to 25 ns.

The intensity of the nitrogen laser was varied using a commercial fast-response joulemeter (Genetic, Inc., model ED-200). To avoid the bolometric effect or thermal effect a relatively weak laser intensity of 5 to 9 mJ cm^{-2} was used. A quantitative--evaluation based on standard heat transfer calculations shows that the surface temperature rises by a few Kelvin and is dissipated within 80...120 ns. Our evaluations have shown that the thermal equilibrium was established within the 80...120 ns.

To measure the photoconductivity and resistivity, indium contacts were soldered onto two opposite faces of the sample to determine the photoconductivity in the two-probe geometry An apparatus for SHG was set up with an unfocused beam from a single-mode picosecond YAG-Nd laser (W=30 MW; λ=1.06 μm). The angle of incidence was varied from 20 to 48^0 to the surface normal. A pair of Fresnel rhombus (Nicol prism) rotated the plane of polarization of the pump light. The separation between the SHG and the pump light was achieved using a SMR-12 grating monochromator. The SHG intensity was measured using an FEU-79 photomultiplier. The measurements were performed in the single-pulse regime, with a pulse frequency repetition of 12 Hz. As an intensity standard we used a quartz single-crystal cell in the optic axis plane. The crystal was mounted in a temperature-regulated cryostat for smooth variations of temperature in the range from 4.2 to 300 K.

3. Results and discussion

The temperature dependencies of SHG and resistivity respectively for the different kinds of Hg-1201superconductors are shown in Fig.1. One can clearly see that the beginning of the SHG is shifted towards the resistivity or magnetical susceptibility from 8 to 12 K in the high temperature region. One can say that the optical SHG senses the nearing of the superconducting transitions or shows the presence of the asymmetric modulation earlier than the traditional methods. Comparing the temperature dependence of the magnetic susceptibilities and resistivity one can suggest a similar behaviour.

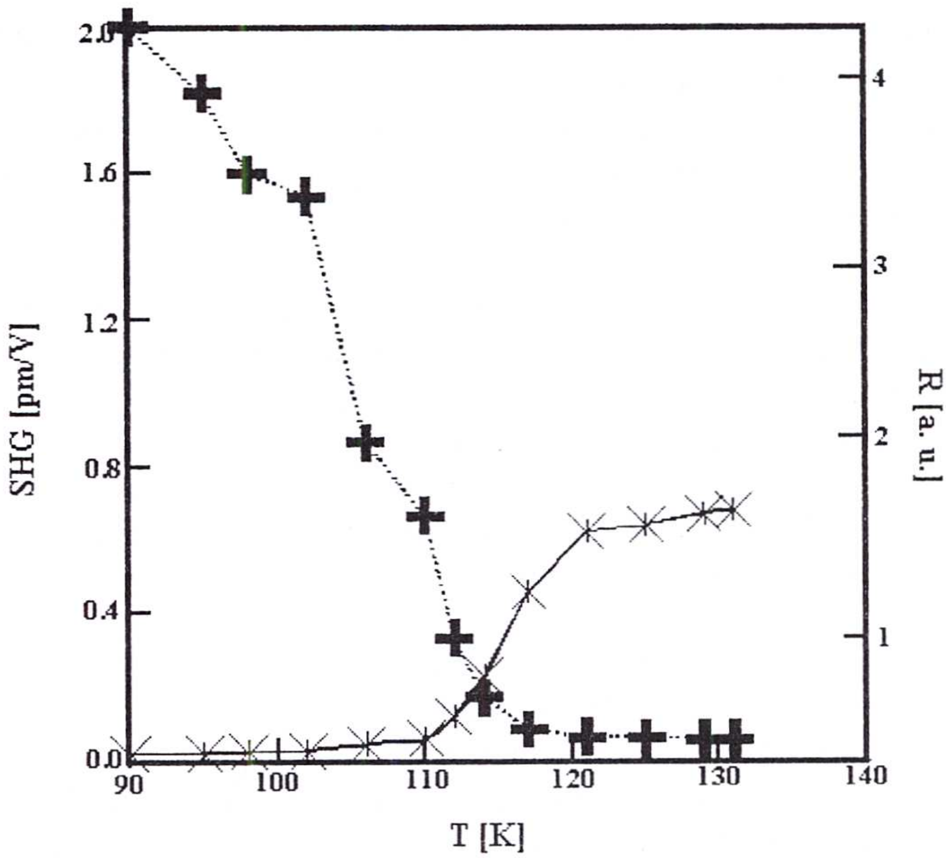

Fig. 1. Temperature dependence of the SHG (+) and resistivity (x)

It is a known fact that the SHG effects can occur only in noncentrosymmetry media, however single crystalline components in both phases (normal and superconducting) are centrosymmetric. Therefore the non-linear optical phenomena described by third rank polar tensor components should be forbidden by symmetry. However, due to the existence of the specific electron-phonon coupling in such kinds of crystals the corresponding effects can be allowed. Generally speaking the non-linear response of the surface layer of a centrosymmetric crystal at the frequency of SHG is usually described as the sum of the quadrupole polarization and the dipole polarization. The first term is caused by the spatial dispersion and by the discontinuity in the normal component of the optical electromagnetic field at the interface. The second term arises from the surface layer of the semiconductor with broken inversion symmetry with a thickness of a few lattice constants.

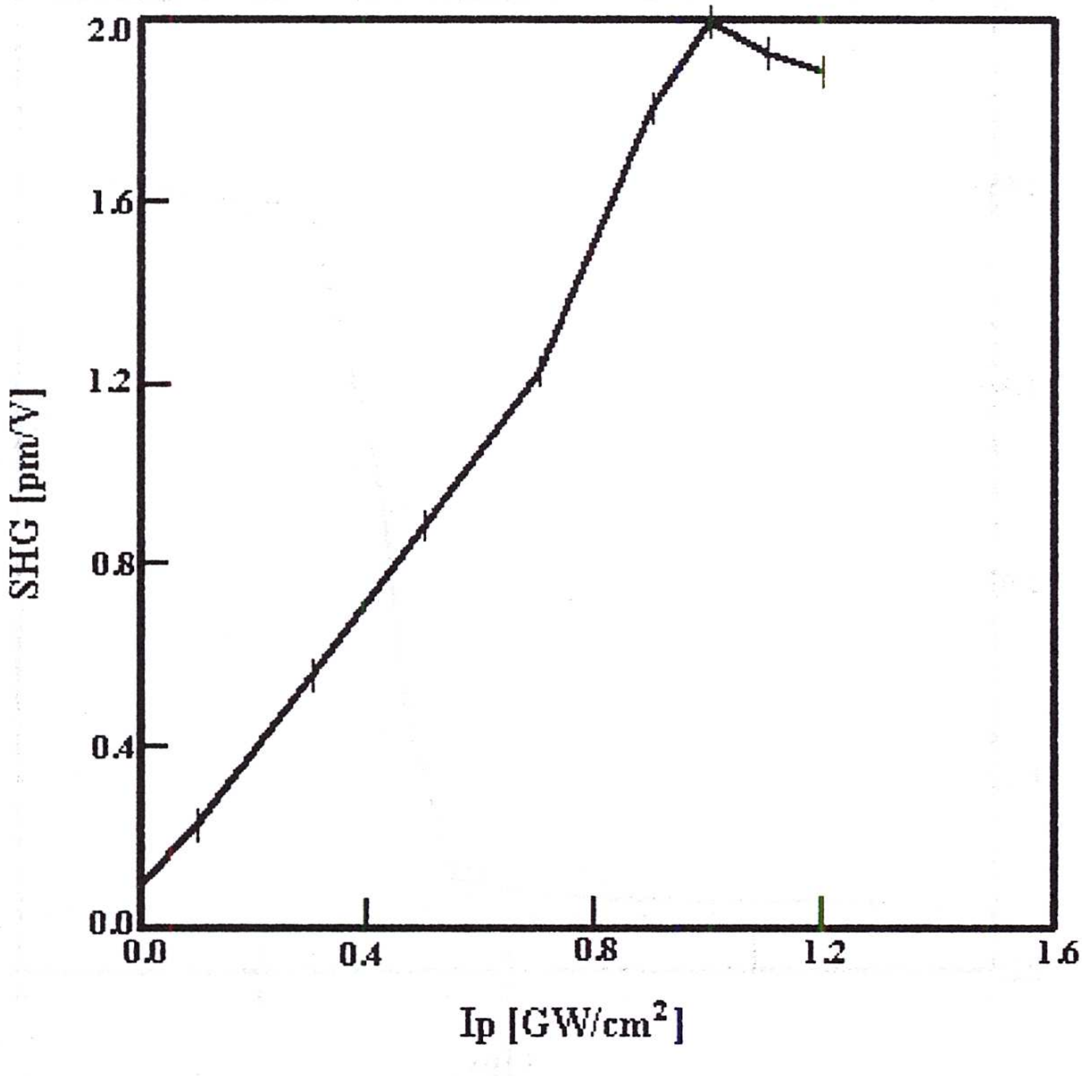

Fig. 2. Pumping-power dependence of the SHG

Fig. 2. depicts the behaviour of the photoinduced SHG with increasing of the nitrogen laser photon flux. There is an apparent sublinear dependence of the corresponding behaviours. For the samples with the higher Tc the absolute signal value increases. Simultaneously at the photon fluxes near $6*10^{15}$ photons/cm^{2} there is also a noticeable kink, which indicates the possibility of involving the new types of free carriers to the corresponding non-linear optical susceptibilities. On the other hand, such optical nonlinearity reflects the intrinsic role of the electronic subsystem, which is disturbed by the non-linear electron-phonon interaction.

The SHG, photocurrent (PC), photoresistivity (PR) and photovoltaic (PV) temperature dependencies were measured as the temperatures below the critical as the function of time. Moreover, the measurements were performed within the temperature range of 4.2...250 K. The shift between the SHG and PC remains almost unchanged within this temperature region but when the temperature nears to the the SHG maximum smoothly vanishes.

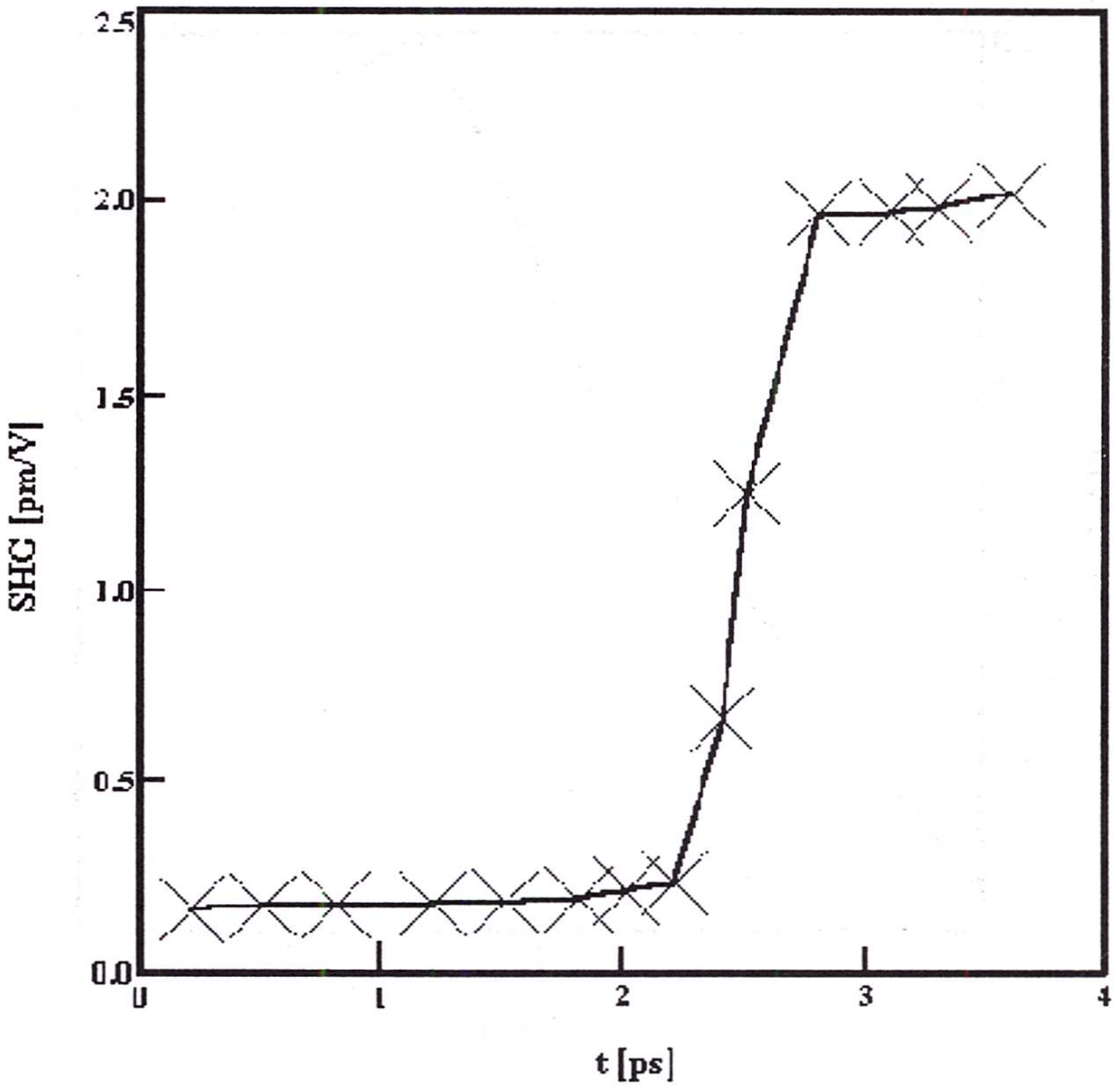

Fig. 3. Time-delaying dependence of the SHG

The most interesting from our point of view are the pump-probe SHG measurements performed at 95 K for the samples with x=0.11. These results are depicted in the Fig. 3. In Fig. 3 especially it is evident that PC maximum increases with the time and reaches its maximum value at times within 2.2...2.4 nsec. Another very important aspect is the asymmetry behaviour of the dependence's observed. Comparing this dependence with the one for the PV one can suggest an essential shift between the PV and PC maxima. These maxima are shifted in time from 0.5 to 0.9 nsec. Simultaneously one can clearly see the delay in the appearing of SHG maxima with respect to the pump nitrogen laser light up to 1...1.5 ps.

It is necessary to stress that all the data were obtained after there over 8000 - 13500 pulses. The asymmetry behaviours of the time dependence seem very interesting are quite significant. In all such experiments the PV signals serve as the internal detector of the pump pulse with the same instrumental resolution. From the time evolution dependencies of the SHG and corresponding PC, one can clearly see the delay in the SHG signal relative to the PV dependence, which indicates that the SHG tail is delayed by up to 15 ps.

To explain the appearance of superconductivity in work [15] it was shown that one of the main causes of the occurrence of superconductivity is the strong interaction between the electrons and the local anharmonic vibrations. Following this line of thought the interaction of electrons with anharmonic vibration mode leads to the appearance of two subbands and causes their additional narrowing with the simultaneous frustration of the exchange interaction. The electron contribution to the non-linear optical susceptibilities described by the third-rank polar tensor and is caused by the electron charge transfer from the CuO layer, more probably, plays an intrinsic role in the appearance of the non-linear optical response. The data obtained in this work suggest that the above theoretical approach can help to clarify the origin of the high-temperature superconductivity and the problems of the critical temperature increasing. It is also necessary to stress that in work [4] the observed delaying in the PC was explained by low mobility of free carriers due to their self-localisation in disordered antiferromagnetic phase.

Photoexcitation with the great fluxes creates a large number of carriers, which shifts the Fermi energy and causes screening, leading to the shift of Fermi level relative to van Hove singularities which are responsible for the appearing of the superconducting pairing state [14]. At the same time the fast non-radiative recombination rate in superconductors may be understood when electron-hole pair forms a transient local bonding arrangement which constitute a self-trapped exciton and may be presented as a transient in time pair of valence alteration defects. This transient bonding arrangement can return either to its original state or to other bonding configurations. By applying the external electromagnetic field of the high intensity the material is divided into small anisotropic microvolumes such that they can be grouped into three different categories having, respectively, the largest projection of their dielectric tensor and hence a large absorption cross sections polarisation in three different directions. If we sum up these microvolumes belonging to each category separately we obtain three absorption contributions. The structural change is possibly caused by the recombination, which changes the anisotropy of this microvolume or leaves it intact. The latter case leads to the redistribution between the several electron-hole pairs.

When electrons and holes diffuse over distances larger than the scale of the anisotropy microvolumes before recombining then any resulting local structural changes will appear not in the original absorbing microvolume but in more distant microvolumes that have different orientations from the original one. Such diffusive recombination will not produce a net anisotropy because the anisotropy of the more distant microvolumes is not correlated with that in which the absorption occurred. At moderate light intensities these recombinations are most likely geminate. These conditions can explain major differences between the scalar and vector effect. The cumulative effect of redistribution events will reduce the absorption for polarization direction of the inducing light and enhance equally the absorption in the two perpendicular directions.

The induced anisotropy is optically reversible when bleaching and creation processes are negligible. The optical axis will change with the polarization direction of the induced light. This model leads to an interesting prediction; that an illumination even with a polarised light produces an optical anisotropy in superconductors. This is the consequence of redistribution. Unpolarised light travelling in the defined direction is absorbed only by microvolumes responding to orthogonal polarization. Recombination, local structure changes and redistribution should then yield a decrease in absorption for orthogonal polarization and an increase in absorption for parallel polarization:

As explained earlier [9], an accumulation of photo-structural events tends to produce a so-called light-saturated state that is characterised by having less medium-range order than the annealed state. When the disordered state is established the changes in macroscopic properties such as density, hardness and optical absorption come to saturation. To explain continuing changes in optical anisotropy it is important to realise that recombination-induced bond rearrangements continue as long as the material is exposed to electron-hole pair producing light .In the light-saturated state recombination processes continue to produce local bonding changes during illumination and these in turn compete with local thermal relaxation processes to establish a dynamic equilibrium or steady state. Most measured scalar properties are macroscopic averages over local configurations and thus are insensitive to these continuing local changes.

At the same time the excitation at 3.7 eV tends to partly shifts of the oxygen atoms, which is revealed in the metastable states with a long relaxation time. Such a specific behaviour of the electron and defective subsystem lead to time-dependent changes in the mixed wave functions, which determine the peculiarities of the SHG and corresponding electric parameters. In our opinion the difference between the relaxation times for the atomic and electronic states is caused by the non-homogeneity of the system At the same time phase separation between disconnected hole-rich regions separated by the insulating regions plays a very significant role in the processes mentioned. Afterwards these electrons will be quickly trapped at oxygen vacancies on adjacent partially oxidised CuO chains and will tend to enhance the orthorhombic distortion locally.

However, the antiferromagnetic long-range spin ordering restricts the hole mobility. Therefore the observed insulator-metal transition can be explained by the intrinsic phase separation of the photogenerated carriers and metallic droplet formation in the antiferromagnetic insulators. We can observe a coexistence of metastability with the phase separation in the metallic region.

4. Conclusion

The results obtained unambiguously indicate the possibility of detecting the superconductivity in the high temperature superconducting ceramics by using the methods of the non-linear optics. It was clearly shown in particular that the possibility exists to use the photoinduced SHG to determine a degree of the superconducting phase appearance. A good correlation with the photocurrent, photovoltage and photoresistance data was obtained. The time-resolved measurements show an existence of the shift between the mentioned parameters that indicates the different contributions of the electronic and phonon subsystems to the corresponding non-linear optical susceptibilities, which reflects the complicated features of the electron-phonon interactions. Similarly to the crystals a magnetic field plays an important role in the suppression of the superconductivity. The phenomena observed for the ceramics can be used for the creation of the short-time switches.

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Summary

Investigations of the photoinduced phenomena in Hg-1201 polycrystalline films coated on the MgO surface have been performed using time-resolved measurements of the photovoltage, photocurrent, photoresistivity, and optical second harmonic generation. A time delay shift between the non-linear optical response and photocurrent was revealed. Applying the external magnetic fields of up to 1 T lead to an essential decrease of the second harmonic generation response. Several different approaches to explain the observed data are discussed.