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Investigation of optical and electro-physical properties of heterogeneous ferroelectric materials

Abstract of PhD Thesis

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Abstract

The present PhD study had been carried out at the Institute of Solid State Physics (ISSP) of Latvian University and Atomic Institute of Austrian Universities (Vienna) during the period from 1983-2005. The thesis as a collection of papers and summary has been written in English and includes abstracts in English and Latvian. Head of scientific work: **Dr.hab.phys., Prof. Guntis Liberts**, scientific adviser: **Dr.hab.phys., Prof. Andris Krumins**.

In this work complex experimental investigations on optical and electrophysical properties of heterogeneous ferroelectric (FE) materials, where binary compounds had been chosen with respect to one strong polar, and second – paraelectric or antiferroelectric (AFE) material, as for multicomponent systems mainly layered thin film FE heterostructures had been investigated. **Main tasks of research** consists of the development of research methodology, that may offer a link between application and properties, design of nonlinear-optical methods of mapping of physical fields, and experiments on different types of FE thin films and related layer structures.

During the years 1982-2005 following experimental equipment for dielectric, optical and nonlinear-optical research have been developed: dual channel gated photon counting system for the measurements of very small second harmonic generation (SHG) signals; dual channel boxcar averaging of SHG signals, including normalization compare to reference; time resolved (*ns*) SHG measurements system; SHG polarization measurements; SHG thermography system; electric field-induced SHG (EFISHG) techniques for static and pulse fields; optical thermostat for the measurements of SH temperature dependence (77 – 800 K); simultaneous SHG, dielectric etc. hysteresis loop determination; computer controlled Hewlett Packard precision LRC meter 4284A (60 Hz - 200 MHz); equipment based on Michelson laser interferometer with lock-in data processing tools (Stanford Research Systems SR 530) for detecting piezoelectric and electrostriction effect.

Complex dielectric and optical measurements and methodology have been developed to characterize main properties of heterogeneous FE materials and devices. Universal character of thermoactivated local cluster polarization of disordered FE perovskites has been detected in the absence of external electric static field during thermally cycling of depolarized and electrically poled samples. Characteristic relaxor/dipole glass behavior has been determinated in the wide region of temperatures and field strength of PLZT X/70/30. Detailed research of relaxation properties gives two consequences: 1) polarization decay after the change of field has a much smaller time constant compare to the decay after the change of temperature, 2) decay due to the change of temperature is not affected by electric field at least if applied within the time intervals used in the experiment, the existing polar state is not destroyed by the field $E < E_{cr}$. In the thin films of relaxor FE glass-like behavior was evidenced by: Vögel-Fulcher relationship, deviation from the Curie-Weiss behavior, temperature evolution of the local order parameter, temperature evolution of the relaxation-time spectrum, maximum in the third-order nonlinear dielectric permittivity, increase in the scaled third-order nonlinear dielectric permittivity.

Internal bias field strong influence on the shape of hysteresis loops has been established after neutron and gamma rays irradiation of sol-gel PZT films. Observed effects may be related to capture of mobile charge carriers on defects (grain

boundaries, interfaces). Electron and gamma radiation induced defects in PLZT ceramics are restored at 420 - 570 K, the activation energy of radiation induced polar properties is estimated to be 0.1-0.3 eV.

Macroscopic laser radiation induced thermooptical bias tuning effect has been applied to control parameters of PLZT EO laser interactive elements, particularly – Fabri-Perot interferometer. A new method of SHG thermography has been developed.

SHG thermography has been verified on the surface of FE coated model. Composite FE-polymer based SHG thermosensitive coatings have been synthesized for wide temperature region (77 - 800 K) applications. Active FE fillers on the basis of perovskite solid solutions of lead-strontium titanate and barium-strontium titanate has been proposed for use as SHG visualization and retina safety tools in *ps* and *fs* laser systems.

Actuality of thesis and goals of research

Novel trends in the field of applications of ferroelectrics (FE) show that single crystalline FE materials have been replaced by nanosize FE systems, composites, ceramics and great variety of so called smart FE materials mainly with heterogeneous structure. Old question focused on the stability of spontaneous polarization have surprising answers in nanosize FE, stability of polar properties has been reexamined in both time and spatial dimensions. At the early period of FE a heterogenity of FE material had been related to defects, grains, domains or concentration fluctuations. Now an interface or surface influence on manifestation of polar properties are under discussion as well as properties of glassy-like FE (analogy to spin glasses and dipole glasses). Theoreticians have developed calculations of nanosize FE properties (contrary to classic Kenzig limit for stable FE) while thousands of experimental works devoted to disordered or heterogeneous FE are more empiric, often new simply using new nanoscopic equipment has carried out experiments.

Here we present ***complex experimental investigations*** **on optical and electrophysical properties of heterogeneous FE materials,** where binary compounds had been chosen with respect to one strong polar, and second – paraelectric or antiferroelectric material, as for multicomponent systems mainly layered thin film FE heterostructures had been investigated.

We have chosen electrooptical and nonlinear optical effects as more coupled to the nature of spontaneous polarization (for example - Burns model approbation) phenomena from the one side, while more pronounced unstable or relaxor properties on the another side have been determined by using low frequency piezoelectric and dielectric and other effects, related to main applications of novel FE materials. Nonlinear optical (SHG) measurements clearly detects local cluster polarization, thermooptical properties reveals close to critical behavior of local polarization under laser-induced heating of FE sample, irradiation effects strongly affects and freezes-in local electric fields, low-frequency external electric fields and mechanical stress induces processes of ordering mainly of non-ergodic nature. **The goal** of presented work is an experimental research of joint electrophysical and nonlinear-optical phenomena in modern heterogeneous perovskite structure materials (composites, ferroelectrics, high-temperature superconductors). **Main tasks of research** consists of the development of research methodology, that may offer a link between application and properties, design of nonlinear-optical methods of mapping of physical fields, and experiments on different types of FE thin films and related layer structures.

Structure of PhD Thesis

The thesis consists of**: introduction**, detailed **characterization of the samples** under investigation (disordered ferroelectrics (FE) of the perovskite type oxygen octahedral structure, high-temperature cuprate superconductors (HTSC), tryglicinesulphate (TGS) crystals with dopants, lithium tetraborate single crystals, artificial composites containing FE component, thin films. **Experimental equipment** for characterization of heterogeneous FE samples developed during 1983-2005 has been shortly described.

Main results concerns with nonlinear optical (second harmonic generation – SHG) measurements of local FE properties, electrooptical and thermooptical effects in PLZT ceramics, dielectric spectroscopy in PLZT and thin film relaxor FE, description of unique SHG thermographic system. There are **6 general conclusions** of PhD thesis summarized at the end of paper, references to 15 SCI journals and 37 other related publications and acknowledgements.

Main objects of research

Oxygen octahedral type **perovskite structure ferroelectrics (FE)** have been of interest as research objects in the **Division of Ferroelectricity (founded by Prof. Voldemars Fritsberg (1926-1982) of the Institute of Solid State Physics at University of Latvia for many years (1962-2005).** The perovskite compounds are an extremely important group of FE materials, their importance stems not only from technological considerations to produce wide spectrum of FE active solid solutions, but also from a fundamental interest in understanding the structural phase transitions and symmetry breaking involved. Such a symmetry breaking in the centrosymmetric paraelectric phase due to lattice defects and /or fluctuations of the spontaneous polarization gives rise to enhanced thermo-optical, dielectric nonlinear and piezoelectric properties and so called **symmetry forbidden second harmonic generation (SHG***).* All the complex FE systems presented here were based on chemical engineering of complex FE solid solutions and compounds (mainly binary and lead titanate based) exhibiting extreme sensitivity to external fields, for example, applied external electric field strength of some V/cm gives rise to remarkable dielectric, piezoelectric etc. response sometimes with enhanced hysteresis and wide spectrum of relaxation times of polarization. Today terms -FE with diffuse phase transition or compositional fluctuations being in action 30 years ago are currently replaced by so called ***relaxor FE,*** dipole glasses and at lower temperatures quantum physics phenomena takes place.

Polar clusters or fluctuations of spontaneous polarization are responsible for large electrooptical, piezoelectric, nonlinear-optical, pyroelectric and dielectric response in these materials. We have chosen four following types of FE: 1) classic **FE single crystals**, 2) **disordered FE single crystals** exhibiting diffuse phase transitions (PT), 3**) lanthanum modified lead zirconate-titanate (PLZT)** transparent ceramics, and 4) **composites and layered thin film structures** containing FE or perovskite type cuprate HTSC. Special efforts were devoted to investigate electrophysical properties of following lead titanate (PT) substituted heterogeneous FE: $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), $PbSc_{0.5}Nb_{0.5}O_3$ (PSN), $PbSc_{0.5}Ta_{0.5}O_3$ (PST), and $PbLu_{0.5}Nb_{0.5}O_3$ (PLN).

Layered perovskites in the role of superconductors as pioneered by Sleight 15 K T_c Bi-Ba-Pb-O material had been investigated also in the Division of Ferroelectricity (DF) by A.Gajevskis and L.Shebanov for many years. So, the switching of research to HTSC area in DF ISSP had been made immediately with specialization to composites, electroding and irradiation (lasers, neutrons, gamma-rays). We have

chosen Y-Ba-Cu-O and Bi, Tl etc. containing HTSC ceramic platelets or thin films as the conducting electrode materials for piezoelectric, nonvolatile FE memory and related devices. Compatibility with FE materials and lack of high frequency dispersion of HTSC strip lines are useful for perspective THz applications.

Heterogeneity of perovskite type FE has been related to common lattice defects coupled to polar displacement of FE active ions, chemical disorder like compositional fluctuations, classical FE fluctuations, superstructures in solid solutions, grain boundaries and domain walls. Our research is focused on both single crystal and disordered FE, however, we have separated two cases: materials with ***intrinsic defect*** /disorder structure and ***artificially created structures***.

PMN and KTL single crystals are so called *model crystals* to characterize and understand polar properties related to structure imperfections of various kinds. PMN crystal is well known in the studies of diffuse FE phase transitions and now is characterized as a ***relaxor type FE***. KTL and KNT system had been introduced to study systematically phase transitions due to introduction of Li and Nb ions in lattice. Li of-center and ***dipole glass physics*** has been developed for last 20 years, particularly by SHG technique used also in our experiments. Transfer of local polar clustering to medium size (nm) submicron FE domains is a main problem in FE nanophysics today, were stability of polar properties and vice versa – switchability is of great practical interest. Great difference of polar properties in the case of external static fields and for different thermal prehistory of samples mainly has been interpreted due to non-ergodic behavior of dipolar subsystem. As a consequence we have a spurious situation with all available experimental data, especially under external field and for various heating or cooling rate.

Ceramic structure of FE species seems to be with highest performance in the case of transparent PLZT ceramics, being developed by hot-pressing technology in ISSP. Another ceramic compounds additionally needs oxygen or vacuum thermal treatment to obtain definite grain and compositional parameters.

Due to enhancement of light transparency of La- doped PZT system, well known in piezoelectric applications, PLZT with 7-12 La % content and variations in Zr/Ti ratio are perspective in electrooptical, pyroelectrical and electrostrictive actuator devices. PLZT as a model material for research of diffuse phase transition has been used with respect to high quality of such ceramics, which allow using highly informative Raman scattering, SHG and acoustic techniques. Compositional tuning of electrostrictive, EO and thermo-optical properties of some PLZT compositions has been used in our experiments with PLZT modulators. We have focused our attention to composition PLZT X/70/30 where more determinate polar/antipolar properties manifestation takes place compare to classical diffuse phase transition and morphotrope phase boundary dictated behavior of PLZT X/65/35 system.

Composites FE-polymers have been synthesized for the needs of nonlinear-optical thermography developed in our laboratory. By using FE fillers exhibiting high spontaneous polarization characteristics and its dependence from the temperature, it is possible to obtain thermo sensitive coatings and paints suitable for contactless laser-assisted SHG thermography. We have chosen perovskite type FE solid solutions $Ba_xSr_{1-x}\ TiO_3$ and $Pb_xSr_{1-x}TiO_3$ characterized by sharp phase transitions in the temperature region from 77K up to 800 K. Epoxy and PMMA (also PMB (butyl)A polymers serves as transparent and SHG inactive binders.

There are *two original ideas to create composites FE-HTSC*. First one, FE ambient of HTSC component seems to be as the self-sustained deformable enhancer of critical current in an isostructural cuprate HTSC component. Essentially, the

tuning and matching of both Curie temperatures (ferroelectric phase transitions (PT) and superconductive PT seems to be very important. Second, it will be very perspective to embedd isostructural (perovskite) cuprate electrodes in the volume of regular FE devices. It is necessary to point out , that superconductive electrodes are frequency dispersion free , giving chance for low jitter ultrafast (THz) switching and sampling devices. For both application of such a composites it is very important to identify FE or HTSC components during the thermal treatment processes, because both (FE and HTSC) properties are sensitive to oxygen concentration and oxygen vacancies topology in perovskite lattice.

Experimental techniques

During the years 1982-2005 we have developed following experimental equipment for dielectric,optical and nonlinear-optical research:

1) dual channel gated photon counting system for the measurements of very small SHG signals;
2) dual channel boxcar averaging of SHG signals, including normalization compare to reference;
3) time resolved (ns) SHG measurements system;
4) SHG polarization measurements;
5) SHG thermography system;
6) electric field-induced second harmonic generation (EFISH) techniques for static and pulse fields;
7) optical thermostat for the measurements of SH temperature dependence (77K - 800 K).
8) simultaneous SHG , dielectric etc. hysteresis loop determination
9) Computer controlled Hewlett Packard precision LRC meter 4284A (60 Hz- 200 MHz)
10)Piezoelectric and electrostriction effect measuring equipment based on Michelson laser interferometer with lock-in data processing tools (Stanford Research Systems SR 530)

In order to compare single crystal data with the properties of disordered FE materials, we have chosen for research some samples of single crystals being used for pyroelectric (TGS derivatives) and non-linear optical (borate family)devices. In some extent they serves as reference objects for testing of very complex experimental equipment.

Determination of local polarization in heterogeneous FE and paraelectrics

Understanding of an origin of the local polarization of macroscopically isotropic paraelectric (PE) phases of ferroelectric materials near phase transitions (PT) is very important. Earlier optical properties of FE (photoelasticity, electro-optical effects, temperature dependence of refractive index, Raman scattering etc.) have been interpreted on the framework of classical fluctuations of spontaneous polarization SHG examination of the symmetry forbidden SH signals in the PE phases of FE and data, reported by several researchers have revealed thermoactivation like character of local cluster polarization. Such a cluster polarization seems to be related to defect induced relaxation of hypotethical local dipole moments. As for classical FE model crystals, like $BaTiO_3$, the equilibrium concentration of defects for nominaly pure crystals has been evaluated about 10^{18} cm^{-3}, which is of the same order of magnitude as an inverse volume of classical mean size of polarization fluctuations in perovskite FE. Temperature dependence of SHG signals in barium titanate single crystals has

been reexamined by more correct hyper-Rayleigh SH light scattering technique. Arhenius type thermoactivation relationships for the SH signals with characteristic values of polarization cluster activation energies 0,2 - 0,5 eV had been established.

The first model crystal of disordered FE chosen for our research was $K_{1-x}Li_xTaO_3$ (KTL) with Li concentration 3,8 at.%, which determines the place of the crystal in so called ***region of crossower of classic FE ordering ($LiTaO_3$) and dipole glass*** like behaviour. The discussion about polar ordering in KTL and *identification of Li ion off-center in the KTL lattice* introduces new ideas of short range polar ordering contrary to classic long range FE phenomena. It is necessary to point out, that many experimental data reported earlier have been measured in the presence of external electric field, therefore, so called ***zero field*** techniques (including SHG acentricity test, Raman scattering, NMR) would be reasonable to study short-range dipole ordering processes also under low strength external fields and essentially for the determination of so called random fields, exceeding, for example in PLZT value about 10 kV/cm.

Our SHG experiments on KTL have been performed in the absence of external electric field. Approximation of the temperature dependence of SH signal by thermoactivation relationship gives values of polarization activation energy ~0,6 eV, which is close to the corresponding values of Li of- center potential bariers, reported by other groups.

The ***second disordered FE model crystal*** under SHG test was $PbMg_{1/3}Nb_{2/3}O_3$ ***(PMN).*** We have at first measured SHG intensity as a function of temperature, external electric field and orientation of crystal. These experiments have shown low temperature phase transitions and switching (relaxing)of thermoactivated local polarization at definite temperature(170K) with two characteristic values of activation energy 0,02 eV and 0,04 eV . Polarization sensitive SHG measurements have revealed changes between two noncentrosymmetric structures in PMN also without external electric field .

As for ***lanthanum modified lead titanate- zirconate (PLZT)*** ceramics with Zr/Ti ratio 70/30 we have also determined thermoactivated local polarization For the examination of mixed (FE, AFE, PE) states of PLZT ,we have specially chosen PLZT La/70/30 samples. SHG experiments for these samples also have revealed glassy like properties, like freezing of dipole configurations at low temperatures, the irreversible origin of randomly oriented frozen local dipoles, and thermoactivation behaviour of local polarization characterizable by activation energy. Higher activation energies have been interpreted by coarsening of polarization clusters. We have continued dielectric experiments in this system under external electric field in the wide frequency region. Relaxor properties have been explained by memory model of relaxors, where prehistory field/temperature/storage time was analyzed without individualizing the relaxing dipole in real lattice space.

We have performed additional qualitative SHG test in centrosymmetric crystal with determined large scale defects - NaCl:Na colloids. Earlier studies of temperature dependence of SH intensity in these crystals containing large Na (50 nm) particles suggests rexamination of SHG data. Our experiments have shown direct correlation between peaks on the SH intensity curve vs temperature and characteristic temperatures of colour center formation (i.e. transformation of colloidal centres) studied in details by thermostimulated current technique earlier by Ziraps. So, we have established once more qualitative agreement with thermoactivation approach to explain forbidden SH signals in solids.

Summary, we have shown universal character of thermoactivated cluster polarization for a wide class of heterogeneous FE materials (KTL, PMN, PLZT, thin FE films, NaCl :Na, ceramics).

Dielectric properties of relaxor FE

$Pb(B'B'')O_3$ perovskites and lead titanate based binary system $(Pb(B'B'')O_3)_{1-x}$-$(PbTiO_3)_x$, $x<x_c$, are known as more pronounced relaxor ferroelectrics (RFE). We have studied these materials in details with respect to following substitutions in B' and B'' sites:
(B′ = Mg, Zn, Ni, Sc, In …, B″ = Nb, Ta, W …)
Excellent properties of this RFE family has been determined: linear electro-optic coefficient

$r_{51} \sim 460$ pm/V
piezo-optical coefficient $\pi_{33} \sim 20 \cdot 10^{12}$ m^2/N
dielectric permittivity $\varepsilon \sim 10^4 - 10^5$,
effective piezoelectric coefficient $d_{33} \sim 2500$ pm/V,
electro-mechanical coupling $k \sim 90\text{-}97\%$,

For comparison the former generation best ferroelectric $Pb(Zr,Ti)O_3$ ceramics exhibit $\varepsilon \sim 10^2 - 10^3$, $d_{33} \sim 200$ pm/V.
In the films of relaxor FE **glass-like behavior** was evidenced by :

Vögel-Fulcher relationship
deviation from the Curie-Weiss behavior
temperature evolution of the local order parameter
temperature evolution of the relaxation-time spectrum
maximum in the third-order nonlinear dielectric permittivity
increase in the scaled third-order nonlinear dielectric permittivity

Internal bias field strong influence on the shape of hysteresis loops has been established after neutron and gamma rays irradiation of sol-gel PZT films. Observed effects may be related to capture of mobile charge carriers on defects (grain boundaries,interfaces). Electron and gamma radiation induced defects in PLZT ceramics are restored at 420-570 K, the activation energy of radiation induced polar properties is estimated to be 0,1-0,3 eV.

Macroscopic laser radiation induced thermooptical bias tuning effect has been applied to control parameters of PLZT EO laser intracavity elements, particularly – Fabri-Perot interferometer.

Laser-writting of electrode structures in PLZT ceramics and indium trioxide layers

In order to optimize and enhance electrooptic characteristics of bulk PLZT EO modulators and thin film FE devices, we have produced complicated configurations of volume electrodes in PLZT ceramics by direct laser writing method.Laser ablation in PLZT has been performed by using CW Q-switched YAG:Nd laser (1064 nm). Electrode groves produced with the changing of the depth along electrode axis have been of interest to achieve homogeneous distribution of the electric field in the active volume of electro-optical modulator. The same technique of laser ablation has been used to obtain gas sensitive gaps on the surface of In_2O_3 located on the glass (K-80) substrate. A sensor based on a laser ablated gap in indium trioxide on glass substrate was made a a long serpent-type gap exhibiting enhanced sensitivity of humidity.

Laser assisted SHG thermography

There is currently much interest in the development of an optical tomography, including mapping of scalar thermal and vectorial electric fields in various materials and devices.

Nonlinear optical methods, particularly, spatial and time resolved SHG analysis of the surface (or special SHG active coatings), would be applied for 2D thermal mapping using optical contact free approaches: intrinsic optical response of the object under investigation, for example- nonlinear optical response of the coated FE surface .

Nonlinear optical group in ISSP LU (head G.Liberts) have developed at 1985-87 a novel SHG based thermosensing method, which embraces wide temperature range and good accuracy together with common origins of classical thermometry : use of reference phase transition points (temperatures) of the thermosensitive coating material.

In the classical measurements of the surface temperature T by using pyroelectric imagers (Forward looking infrared –FLIR) the information about temperature has been transformed in to the electric signals due to pyroelectric effect in the thin ferroelectric (FE) target plate of vidicon tube. Despite of the good sensitivity of pyroelectric or cooled semiconductive detectors such a technique has principal limitations and cut-off in the region of low temperatures where Planck formula gives miserable number of light quanta to detect, and principially fails in the presence of radiation from the sources beside. To eliminate such a crucial question of the FLIR remote thermal sensing an active optical coating is necessary. Active properties imply here significant and definite changes of SHG response vs temperature in the localized coating volume, surface, or boundary layer of the ambient. According to the classical principles of thermometry, where a temperature dependence of magnetic susceptibility has been used as a thermometer , we transfer such an approach to the nonlinear optical susceptibility of coatings, exhibiting the most intensive up-conversation and thermosensing properties , based on the well known SHG effect in ferroelectrics.

Compare to the FLIR configuration , the ferroelectric or nonlinear optical element is displaced on to the surface of the thermal object giving additional possibilities of direct visualisation of thermal fields. It is necessary to point out extremaly high spectral brightness of laser induced SHG sources compare to black-body radiation of thermal scenes even at high temperatures. In comparison with laser-induced fluorescence (luminescence) based thermography, SHG approach is inertionless (possible excitation with fs laser pulses)and, as has been mentioned above, has the same spectral brighteness as laser sources.

SHG active ferroelectric (FE) thin film located on the surface under test serves as the laser activated thermosensing element itself. There are different reasons for the temperature dependence of SHG response, which could be interpreted on the basis of reversal structural changes of the coating, changes of resonant conditions of the SHG process, interference and coherence length effects. Typically the SHG effect in FE shows a simple relation between the spontaneous polarization P_{sp} of the material and SHG intensity $I_{2\omega}$. In the first approximation, a proportionality between an SHG intensity $I_{2\omega}$ and the square of P_{sp} has been established for a wide range of FE materials. For the second order phase transition in FE and below Curie temperature T_c

a square of spontaneous polarization and SHG intensity $I_{2\omega}$ follows to a simple (linear) rule:

$$I_{2\omega} \sim (P_{sp})^2 \sim T - T_c \qquad (1)$$

This relationship has been verified for many FE with second order phase transition (PT) without significant differences in the case of single crystal, powder or polycrystalline samples. In the case of the first order FE PT a temperature hysteresis of the SHG signal takes place. Really many ferroelectric materials manifests a PT behaviour near the second type one. Another important factor seems to be a diffusiness of the PT, because for the diffuse PT a slope of SHG signal temperature dependence decreases.

In the first approximation, SHG in two-component coating consisting of FE pigment and SHG passive binder (centrosymmetric or weakly nonlinear) could be understood on the framework of SHG analysis of powders. The stability of FE properties in the coarse grains of powder has been observed down to submicron sizes of the particles , which are many times smaller as optimal dimensions of SHG pigments (g = 1 - 10 μm). There exists a possibility of mechanical mixing different SHG pigments with nonoverlapping thermosensing regions in the same coating. Thin FE plate coated with ultrathin absorber of thermal radiation could serve as an optical analogue of pyrovidicon when replacing an electron beam scanning with fs pulsed laser beam scanning respectively. Novel trends in granular,glassy and ceramic nonlinear optical materials for ultrashort pulse applications show that such a materials are useful at least as visualization tools for laser beam adjustment and laser user safety. Special interest arises in the field of integrated nonlinear optics after the nanosize $LiIO_3$ cystals embedding in the laponite nanodisc matrix for production of low cost SHG waveguides.

Composites FE-polymers have been synthesized for the needs of nonlinear-optical thermography developed in our laboratory. By using FE fillers exhibiting high spontaneous polarization characteristics and its dependence from the temperature, it is possible to obtain thermosensitive coatings and paints suitable for contactless laser-assisted SHG thermography. We have chosen perovskite type FE solid solutions $Ba_xSr_{1-x}TiO_3$ and $Pb_xSr_{1-x}TiO_3$ characterized by sharp phase transitions in the temperature region from 77K up to 800 K. Typical grain sizes of such a separated powders lies in the micrometer range close to the mean values of coherence length of SHG effect, which, for example for pure lead titanate has a value of 1,6 micrometers.

Different methods has been applied to coat the surfaces under investigation. The *first* one was a casting of polymer-ferroelectric composite onto the surface. The *second* was aerosol spray or brush painting of the surface. The first method used for the producing thermosensitive SHG counting involves the casting of the film from a solution containing inorganic FE filler and a polymer in a solvent. Film thickness from 20 to 200 micrometers were obtained up till 50 per cent volume fraction filled with FE pigment. Several binders have been used: epoxy resin (upper temperature of operation (T < 450K), polybutilmetaacrylate PBMA (T < 400K) and silicon resin (T < 500 K).

Both components of the coatings were transparent for laser (1064 nm) and SHG light. Due to large differences of the refraction indexes of the pigment (n = 2,5) and polymer (n = 1,6) an influence of the temperature dependence of refractive index mismatch seems to be negligible, just resulting SHG emission is close to Lambert scatterer in the wide region of temperatures. Angular dependencies of SHG intensity for thin opaque films obtained by casting technique are like to two equally sized lobes in the forward and reverse directions. As for the SHG backscattered light in the

reflection mode from the coated surface the same lobe like scattering indicatrix has been observed.

Assuming that there exists some another systematic errors such as deviations of an angle of incidence of laser beam during scanning, nonuniform distribution of thickness and filler concentration of real coating etc., an additional normalization of collected SHG maps relative to reference steady state thermal pattern of the coated surface before heating has been performed. SHG active coatings are well suited for thermal imaging and direct visualisation of thermal profiles in the green light (determined by most popular Nd laser line) acceptable for eye.Use of sapphire:Ti laser as an fs pulsed excitatation source displaces registration to the blue region of spectrum. Two -dimensional temperature distributions with submilimeter spatial resolution have been performed with accuracy better than 1 K. The prototype of unique SHG thermovision system "Harmoscan" had been approved in supersonic wind tube in CAGI (Zhukovsk, Russia). Up to now there are no analogs for such a system at all.

Novelty of thesis

It is necessary to point out that author had at first investigated in details SHG signals in basic model materials for disordered FE : PLZT, PMN, KTL. Author certificates related to complex spatial configuration electrodes in PLZT modulators and unique SHG thermographic system had been also approbated in practice. Authors contribution was dominating to perform presented here dielectric spectroscopy experiments on PLZT and relaxor FE thin films.

Summary of PhD Thesis

1. Complex dielectric and optical measurements and methodology have been developed to characterize main properties of heterogeneous FE materials and devices.

2. By using high sensitive non-linear optical methods (SHG), an universal character of thermoactivated local cluster polarization of disordered perovskite type ferroelectrics (FE) has been detected in the absence of external electric static field during thermally cycling of depolarized (virgin) and electrically poled samples.

3. Internal bias field strong influence on the shape of hysteresis loops has been established after neutron and gamma rays irradiation of sol-gel PZT films. Observed effects may be related to capture of mobile charge carriers on defects (grain boundaries, interfaces). Electron and gamma radiation induced defects in PZT films are restored at 420-570 K, the activation energy of radiation induced polar properties is estimated to be in 0,1-0,3 eV range.

4. A new method of SHG thermography has been developed. The principle of SHG thermography has been verified on the surface of FE coated model. Composite FE-polymer based SHG thermosensitive coatings have been created for wide temperature region (77 K - 800 K) applications. Active FE fillers synthesized on the basis of perovskite solid solutions of lead-strontium titanate and barium-strontium titanate have been proposed for use as SHG visualizators and safety tools in ps and fs laser systems.

Inventions

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