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X-ray-sensitive storage phosphors with the optically stable luminescent centres

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Abstract

NaCl, KCl, KBr and LiF crystals doped by In, Tl, Ni, Pd and Ca were investigated as X-ray-sensitive materials. Influence of the way of doping of an impurity and growing of a crystal on such parameters of a material as: sensitivity to ionising radiation; radiative, optical and thermal stability of the image, obtained after an irradiation is investigated. As a result of the work, media for recording of the X-ray images are developed. These allow to reproduce the images in a mode of a photoluminescence. Spatial resolution and the dynamic range of registration of the developed materials concede to similar parameters of commercial storage luminophores like "Image Plates" based on BaFBr : La. At the same time, as distinct from "Image Plates", the developed radiophotoluminophores allow a long storage and multiple readout of the information recorded.

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1. Introduction

Image Plates based on X-ray-sensitive storage phosphors originally described in Ref. [1], now are widely used in the medical and scientific fields for the registration of the images created by ionizing radiation. Along with doubtless advantages, such as high sensitivity, wide dynamic range of registration, Image Plates have also a number of lacks [2]. These do not have sufficiently high spatial resolution, that does not allow effectively to use Image Plates in X-ray microscopy, and partial bleaching of the information at unitary reading because of destruction of the radiation-induced defects. The reduction of colour centre concentration at reading the image can achieve 30%. Besides, Image Plates have large fitting, that does not allow to store the recorded image for long before reading.

The specified lacks are stimuli for development of new materials for recording of the information with the improved characteristics, as is observed now. In the given work the results of study of the characteristics of the materials, offered by us, in which

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radiation-induced luminescent centres are optically and thermally stable, are submitted.

2. Materials for Image Plates

The materials, developed by us, are alkali–halide crystals modified by doping of additional impurities. NaCl, KCl, KBr and LiF single-crystals were studied as a matrix. As activator, the ions In, Tl, Ni, Ga, Pd, and Ca were used. Crystals were grown from the melt by the Stockbarger or Kiropoulos method, the activator either adding into the melt as various compounds or doping by heating of a host crystal in activator salt vapours at 500–700°C.

The mechanism of information recording is based on the known processes of radiative transformation of the colour centres or change of activator defect charge under ionising radiation. The structure of the luminescent centres in various media is different.

In Image Plates at image readout the emission occurs by recombination mechanism. The radiation-induced defects are destroyed under stimulating light. Then the products of destruction recombine with activator centres, forming the luminescent centres in the exited state. Radiating light, the latter transform to ground state of centres existing before ionising irradiation. Owing to recombination character of the process, the image is partial bleaching at readout.

As distinct from this, in materials, offered us, the luminescence have innercentre character, i.e. the radiation arises owing to transitions between energy levels of one centre. At such processes there is no destruction of the image during reading. Besides, innercentre mechanism of a luminescence should essentially allow the higher spatial resolution, as all processes proceed inside one defect having the sizes about the period of a crystal lattice. At recombination luminescence the process occurs in some volume of recombination whose sizes are defined by path length of products of destruction. Thus, the top resolution achieved at recombination luminescence should be lower, than at innercentre luminescence. The top resolution achieved for the image at a luminescence of any type is limited diffraction limit and has a value of the order of 1 μm for visible light.

The nature of the luminescence centres and consequently their properties are various for different types of materials, offered by us.

2.1. LiF with various activators

In LiF crystals the recording is realised on the basis of F_2 centres (aggregates from two F-centres: electron–vacancy complexes), perturbed by an activator ion, taking place in the nearest environment. The activator stabilises the centre [3], i.e. raises its thermal and optical stability, and, besides, raises sensitivity of a material to ionising radiation. At the same time, the presence of perturbation changes optical properties of a material. The absorption and emission bands are slightly displaced to long-wavelength region of spectrum. Before irradiation, the crystal has no ability to exhibit luminescence, therefore the contrast between irradiated and non-irradiated areas of a crystal is maximal. To excite luminescence, it is possible to use a mercury lamp (line of 446 nm) or radiation of He–Cd or Ar^+ laser.

2.2. NaCl, KCl, KBr with nickel

In alkali–halide crystals with nickel occurs a transformation of Ni^{2+}–Ni^+ centres under ionising radiation [4]. The transformation takes place both at interaction of radiation with an activator ion and at destruction initially of the formed F-centres by light or by heating of a crystal. At destruction of the F-centres the intensity of luminescence grows a little, however, crystals are also suitable for registration of the image directly after an exposition [5]. Like LiF crystals, media with nickel do not emit light before ionising irradiation. After irradiation, the crystals emit light in the range of 620–640°C at excitation in ultraviolet region of spectrum. The excitation bands lie at 242 and 360 nm. Despite the large efficiency of excitation, the band near 242 nm is uncomfortable for use in view of the absence of the light sources and the necessity of application of high-quality quartz optics. For excitation near 360 nm, it is possible to use radiation of mercury lamp (line of 365 nm) or N^2 laser.

2.3. *NaCl, KCl, KBr with In, Tl, Ga*

The crystals with an activator of In, Tl, Ga ions are initially able to emit light in the region of spectrum which is characteristic for the given class of activator (400–45 nm). New luminescence centres have been formed in the crystals after ionising irradiation and destruction of F-centres by light or by heating of a crystal [6]. The emission bands of these centres are located in the range 520–570 nm, while the excitation band is located at 340 nm. To excite luminescence, it is possible to use the same sources, as for crystals with nickel. Whereas, the luminescence bands of initial centres, for example In^{+}, and radiation-induced luminescence centres partially overlap, contrast of the image is a little bit worse in such crystals [7].

3. Methods of readout of the images

The materials for recording of the images cannot be considered separately from ways and devices of luminescent picture registration. The results achieved by one or other way as a rule characterise not the best achievable parameters of the medium, but the characteristic of a medium–readout system complex. It is necessary to take into account the allowable resolution of the reading device, dynamic range of the photodetector and amplify-recording part of the device, speed of reading and other parameters. Therefore, we carried out researches of an opportunity of image registration in our objects by various methods. We, basically used supervision of the image by an eye, registration on a photographic film and through the photomultiplier in a mode of the photon account.

At supervision the eye requires rather high brightness of the image. As a result, doses at registration of the images are ($0.003-300\,\mathrm{mJ/cm^2}$) for reception of the seen image in a rather wide dynamic range. The best resolution is 1–2 μm. Owing to the high degree of adaptation of the eye, the supervision of half tones in a wide range of intensities of a luminescence is possible.

The luminescence image fixed on a photographic film loses the dynamic range (10^2 instead of 10^5). Besides, the relation between the size of a grain on a film, i.e. best resolution, and its sensitivity is essential. At registration of the images with a high resolution the photographic film on all parameters loses to the eye. X-ray doses, that are necessary to readout the image by photofilm in the case of a resolution of 1–2 μm are 100–1000 $\mathrm{mJ/cm^2}$.

The photons account is one of the best both on the resolution, and on a dynamic range. The minimal dose registered by us through the given method was at least 10 times smaller than through supervision by the eye. Dynamic range is not less than 10^4. The spatial sanction is 2 μm. The basic lack of the given method is point-by-point readout that results in great increase of time of process in comparison with other ways of registration.

4. Experiment

The creation of the image was carried out by us with ionised radiation in the range 1–30 keV. Sources of radiation were: the ring VEPP-3 and X-ray tube target by various cathodes. In the field of soft (1–5 keV) radiation, the station X-ray lithography

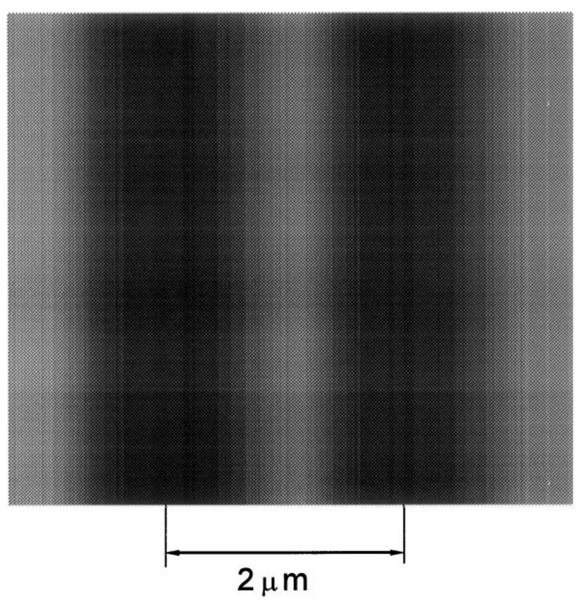

Fig. 1. Examples of image: 2 μm test-structure (gold). The luminescence was read out by point-to-point scanning and registration in the photon account mode.

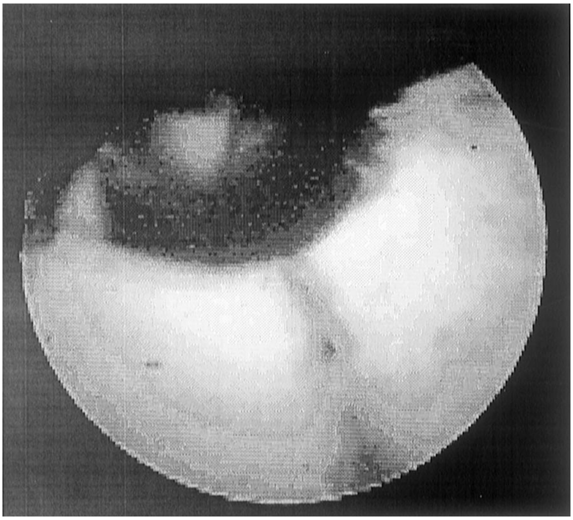

Fig. 2. Examples of image: Fragment of head of mosquito. Registration by DS-20 camera.

VEPP-3 was used, in the field of hard (6–30 keV)–station EXAFS – and X-ray tomography. Especially, the test - object with 2 μm size of structure [8], and various biological objects [9,10] were investigated.

An exposition dose varied both with time, and current of the store ring. Besides, in a number of cases, the radiation was weakened with the help of absorbers (lavsan in soft area of a spectrum or metal foil in rigid). The exposure dose changed in the range 2×10^{-6}–1 J/cm^2.

The luminescence image was observed through microscope by the eye, or was registered by electron-optical detectors.

At heating of a crystal up to a temperature of the order of 500–600°C the image is erased. Also, crystals are ready for a reuse. In our experiments the record-readout bleaching was spent not less than 30 cycles, thus the loss of sensitivity was no more than 5% (Figs. 1 and 2).

5. Conclusions

The received results show that the stirage phosphors, developed by us, can be applied to registration of the X-ray images in various experiments. Their spatial resolution is not less than 2 μm, dynamic range of registration more than 10 000. The bottom limit of sensitivity determined as properties of a material, and reception system, has a size not less than 3 mm J/cm^2. Despite smaller sensitivity in comparison with Image Plates the developed media are of interest owing to high resolution, opportunity of repeated reading without destruction of the image and opportunity of a long storage of the image (till 10 years in separate experiments).

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