Effect of Illumination on the Dielectric Properties of Lead Molibdate Crystals

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Abstract

The influence of light illumination on the dielectric properties of $PbMoO_4$ crystals is studied. The increase of the permittivity under illumination is revealed. The optical excitation spectrum of the permittivity is practically the same as that of the fluorescence and photoconductivity. The results for dependences of this “photo-dielectric effect” (p.d.e.) on the temperature, the frequency of measuring electric field, the samples thickness and the light intensity are presented. They show a close relation of the p.d.e. to the point defects of crystalline lattice. A possible mechanism for the p.d.e. is suggested.

Key words: lead molibdate, permittivity, photo-dielectric effect

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Introduction

Lead molibdate ($PbMoO_4$) crystallizing in the point group 4/m exhibits a number of remarkable physical properties. A combination of mechanical, electric and optical properties makes this material promising for acoustooptic applications [1]. Another group of possible useful applications of $PbMoO_4$ crystals is associated with such optical properties as a photoluminescence [2] and electrogyration effect [3].

It is known that practically all of the physical properties of $PbMoO_4$ depend on the features of growth technology and post-growing treatments of any type, such as annealing in different ambient atmospheres or excitation with the ultraviolet light or X-rays [4]. Because of different vapour pressures of molybdenum and lead oxides at high temperatures there occurs a stoichiometry violation in the as-grown, even pure, $PbMoO_4$ crystals. The crystals contain many types of lattice defects that influence practically all parameters of the material. So, for instance, a yellow colour of $PbMoO_4$ grown from the melt in air is connected with a complicated absorption band of crystal lattice defects, which is located below the actual fundamental edge [5]. A lot of attention has been paid for a long time to investigations of lattice defects in $PbMoO_4$ crystals [6]. One of the main tasks in the majority of such works has been attempting to improve the optical and the other properties of those crystals by either a selection of growing process parameters or sample annealing under different conditions [6]. The other group of studies has been performed in order to solve a general problem of mechanisms for the lattice defect influence on the physical properties of $PbMoO_4$ crystals. A particular, though important and complicated, problem is a charge transfer with participation of the lattice defects, which defines such properties as a conductivity, photoconductivity, photoluminescence, etc.

It is known that illumination of some photo-luminescent phosphors and photoconductors with a light changes their dielectric constant [7] (a so-called “photo-dielectric effect”, or p.d.e. in abbreviated form). Two mechanisms have been suggested for the p.d.e. The first one is a result of photoconductivity in spatially nonuniform material and the second is related with actual changes in polarizability of some centres forced by the illumination. Studies of the p.d.e. may provide a useful additional information about the properties of localized electronic states in the forbidden zone and the mechanisms for their transformation.

$PbMoO_4$ crystals are both photoconductive and photo-luminescent. As far as we know, there has been no information concerning the influence of illumination on the permittivity of $PbMoO_4$ up to date. The corresponding results are presented in this paper.

Experimental

The investigations were carried out on the as-grown single $PbMoO_4$ crystals. The crystals were grown from the melt using the Czochralsky method (the air atmosphere and the platinum crucible). The raw lead and molybdenum oxides of high purity taken in stoichiometric ratio were used in order to prepare the lead molibdate in a usual way. The crystals obtained were yellowish and transparent. No scattering can be seen with He-Ne laser. Ground and polished plane-parallel crystal slices (the thickness from 1 to 3 mm; the principal plane (001)) with their (001) surfaces covered with platinum electrodes were used for dielectric measurements. One of the electrodes was either semi-transparent (20% transparency in the visible and near-UV regions) or (in some experiments) grid.

The capacity and conductivity of the samples were measured, using the electric bridge technique in low electric fields (less than 5 Vcm^{-1}) and 200Hz–20kHz frequency interval. All the measurements were performed in the temperature range of 300–450 K. White light obtained with the IR-filter or monochromatic light beam were used for the illumination of samples. Except for special experiments, all the measurements were carried out under the illumination density ≈ 5 μW cm^{-2}.

Results and Discussion

At first we report the results for electric properties of the lead molibdate crystals derived without any illumination. They evidence that the permittivity ε of $PbMoO_4$ remains practically constant below 370 K and grows slightly with increasing temperature. The ε value for the room temperature is equal to 42, i.e. it is the same as in the study [8]. In the temperature region higher than 370 K, ε decreases with increasing frequency. It is known that frequency dependence of ε may be attributed to spatially nonuniform distribution of conductivity and/or permittivity in the sample. To check out this possibility, the analysis of frequency dependence of the complex impedance may be used [9]. Measurements of the impedance for $PbMoO_4$ crystals have shown neither spatial nonuniformity nor a sufficient influence of the electrodes.

When the temperature is higher than 370 K, the real part of the conductivity ($\sigma=\mathrm{Re}(\sigma`)$) depends on the frequency f according to $\sigma = f^s$, (with s<1). Such the behaviour is typical for the hopping mechanism of charge carrier transport in disordered semiconductors [10]. It can be therefore assumed that the charge transport mechanism in $PbMoO_4$ crystals is hopping. Usually the materials with the hopping conductivity have low values of charge mobility and its exponential temperature dependence. It is difficult to measure charge mobility for high-resistivity materials with the usual methods commonly used for semiconductors. A rough evaluation of the charge mobility may be carried out from a current (I) versus voltage (V) plot in the case of space charge limited current [11]. The I vs V dependence for the $PbMoO_4$ crystals is indeed typical for the space charge limited one. According to the experimental results, the room-temperature value of the carrier charge mobility for $PbMoO_4$ is small (less than 10^{-4} $cm^2V^{-1}s^{-1}$) and increases exponentially with temperature. Thus, both the frequency dependence of conductivity and the temperature dependence of mobility point to the hopping mechanism for the charge transport in $PbMoO_4$.

In addition to the dielectric parameters, we have measured the fluorescent excitation spectrum of the crystals under test. The corresponding maximum located near 360nm is in a good agreement with the earlier data [2].

Now let us present the results for the light illumination influence on the dielectric properties. The temperature dependence of the permittivity change due to the illumination (the photo-permittivity $\Delta\varepsilon=\varepsilon_l - \varepsilon_d$, or the difference between the values for the illuminated sample (ε_l) and that measured in the dark (ε_d)) is shown in Figure 1. The value $\Delta\varepsilon$ at room temperature is negligibly small. When the temperature increases, $\Delta\varepsilon$ grows up and reaches a wide maximum at about 340 K. The maximum value of $\Delta\varepsilon$ depends upon the frequency and is three times higher than ε_d. The effect of illumination takes place only at the frequencies less than $\approx 2\,\text{kHz}$. The conductivity σ depends on the illumination, too. The temperature and frequency dependences of the photoconductivity $\Delta\sigma$ (the difference $\Delta\sigma=\sigma_l-\sigma_d$ between the conductivity values for the illuminated sample (σ_l) and that measured in the dark (σ_d)) correlate with those peculiar for $\Delta\varepsilon$. Both the permittivity and the conductivity increase slowly after switching on the illumination and it takes several minutes for $\Delta\varepsilon$ to achieve its steady-state values (see Figure 2). The increase of temperature leads to increasing rate of the process. It seems interesting that the increase of $\Delta\varepsilon$ with time is comparatively higher than that of the $\Delta\sigma$ parameter.

The dependences of $\Delta\varepsilon$ and $\Delta\sigma$ values on the thickness of samples are shown in Figure 3. It can be seen that the value of $\Delta\varepsilon$ increases with decreasing thickness. We remind that the results presented in Figures 1, 2 and 3 are obtained using the white light.

The spectral dependences of $\Delta\varepsilon$ and $\Delta\sigma$ are presented in Figure 4. It is seen that the influence of illumination on the dielectric properties of $PbMoO_4$ occurs only in a relatively narrow spectral range below the actual band edge. The excitation spectra of the photoluminescence, photoconductivity and the so-called photo-permittivity are very similar. Nevertheless, there are some qualitative differences, e.g., the $\Delta\varepsilon(\lambda)$ curve has a slightly

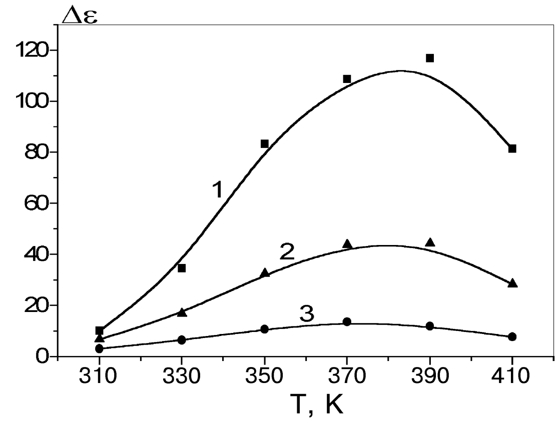

Fig. 1. Temperature dependence of the permittivity change $\Delta\varepsilon$ in $PbMoO_4$ single crystal for the sample thickness of 0.80 mm and the white light: 1 - 300, 2 - 500 and 3 - 1000Hz.

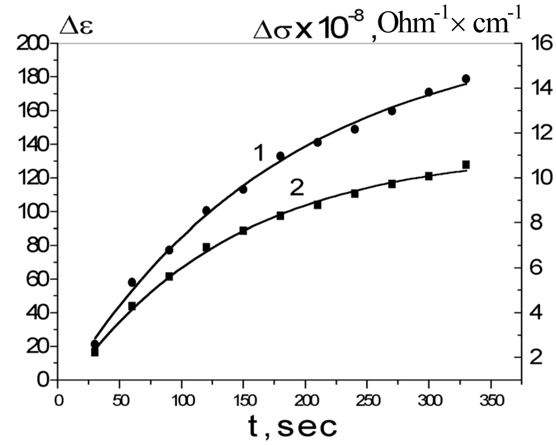

Fig. 2. Dependence of the permittivity $\Delta\varepsilon$ (1) and conductivity $\Delta\sigma$ (2) variations on the illumination duration for $PbMoO_4$ single crystals (T=370 K, F=1000Hz, the sample thickness 0.80mm, the white light).

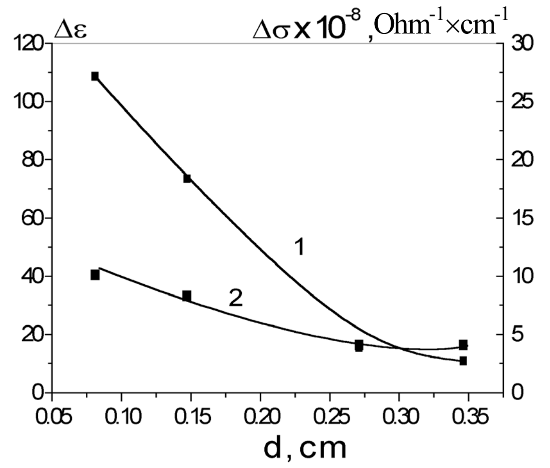

Fig. 3. Dependences of the permittivity Δε (1) and the conductivity Δσ (2) variations on the sample thickness for $PbMoO_4$ single crystals (T = 370 K, F = 300Hz, the white light).

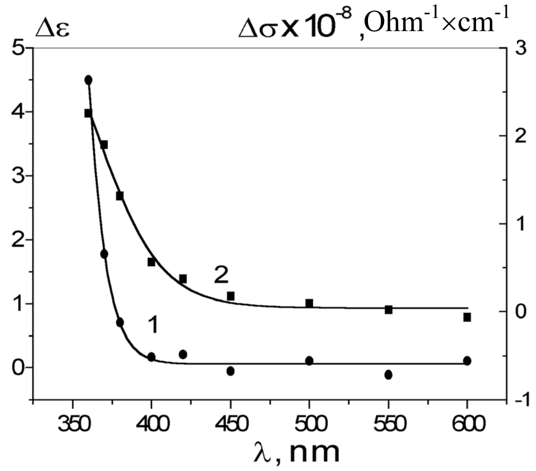

Fig. 4. Spectral dependences of the permittivity Δε (1) and the conductivity Δσ (2) variations (T = 350 K, F = 500Hz, the sample thickness 1.44 mm).

larger slope than the Δσ(λ) one.

As mentioned above, the increase in the dielectric constant due to the illumination (the p.d.e. effect) has been observed and studied for a long period on the phosphor materials. The two main mechanisms of this effect are described in the literature. The first one deals with the p.d.e. in nonuniform media, such as, e.g., ceramics or pressed powders with the photoconductive boundary between crystallites. Those media may be represented as double-slice dielectrics [7]. The increase in conductivity of one of the slices (the boundary) under the illumination would increase the measuring capacity of the sample and, hence, the permittivity of the material. The second mechanism considers the p.d.e. as a real change in the permittivity of material through a photo-excitation of some local electronic states in the forbidden zone and, in that way, the increase in their polarizability. This kind of mechanism has been viewed theoretically for the case of disordered semiconductors [12]. Since the properties of materials with qualitatively different p.d.e. mechanisms are similar, these two mechanisms are rather difficult to separate.

Now we consider if is it possible to apply the first mechanism of p.d.e. to the results presented above. As shown above, the investigated samples do not reveal spatial non-uniformity. However, since the samples are illuminated through semitransparent electrodes, the conductivity along the direction perpendicular to the crystal plate could be nonuniform because of a nonuniform light absorption. In order to check up a possibility for this mechanism of p.d.e., specially aimed measurements have been carried out. Namely, the sample has been illuminated through its side edge, with the light beam being directed parallel to the electrodes. The permittivity and the conductivity have demonstrated qualitatively similar behaviours for the light beam directions parallel and perpendicular to the electrodes. This testifies that the p.d.e and photoconductivity are not related to one another as direct cause and effect.

We have already mentioned that the p.d.e might originate from changing the polarizability of some electronic states, as a result of the light excitation. As a matter of fact, these states and the fluorescent centres may be referred to the same crystalline lattice defects. The experiments show that the photo-excitation spectra for both the fluorescence and the p.d.e. in $PbMoO_4$ are alike. The luminescent and the p.d.e centres in these crystals may be therefore the same, too. However, a comparison of durations of these two processes shows their considerable difference [13]. This gives reasons to guess that there is no direct connection between the p.d.e.

and the fluorescence centre photo-excitation mechanisms.

Finally, we elucidate in a more detail the possible mechanism for the p.d.e in $PbMoO_4$ crystals. As mentioned above, the electron transport in this material is hopping. It would be hardly reasonable to suppose that the mechanism of the charge transport changes under influence of illumination. Instead, photo-excitation can change both the concentration of charge carriers and their mobility. The ordinary transport mechanisms in uniform media, including the hopping mechanism, involve neither the associated permittivity nor the imaginary part of the conductivity. Nevertheless, according to [14], the associated permittivity can take place in the media that consist of some groups of local electronic states with intrinsic barriers separated by extrinsic ones. To produce the associated permittivity in crystal, the extrinsic barrier must be higher than the intrinsic one. One can imagine that the local electronic states in the gap are formed by the lattice defects and, in case of their spatially nonuniform distribution, these states are united in some groups (clusters). The local states inside a cluster are separated by intrinsic barriers. Meanwhile, the clusters themselves are parted by the extrinsic barriers. Complete information about the electronic spectrum of $PbMoO_4$ crystal is needed in order to get a more detailed idea of the clusters. However, the information about the lattice defects (e.g., the concentration distribution, structure, electronic states, etc.) in the lead molibdate is very limited. However, many studies show that the features of light absorption, fluorescence, photoconductivity, UV- and X-ray colouration of $PbMoO_4$ can be explained on the basis of existence of wide band of localized electronic states of different nature near the edges of the gap. The local state density is higher at the edges of the gap. It is known that these electronic states are associated with non-stoichiometry and/or impurities. Some experimental results may be explained only when the availability of complicated associated defects is supposed. So, according to [15], the yellow colour of the as-grown crystals is related to the associated coupled defects. The pairs of oxygen and lead vacancies bound by electrostatic forces in $PbWO_4$ crystal represent peculiar dipoles that take part in forming the electret state [16]. Moreover, the existence of complicated elongated defects in $PbMoO_4$ crystal has been assumed in [17]. The similar elongated defects represent in fact the clusters mentioned above.

Since the material under study is dielectric, the Fermi level must be located in the middle of the gap. It means that localized electronic states near the upper edge of the gap are empty, while those near the lower edge are occupied. The light with the energy close to the gap excites electrons from the lower to upper state. The electrons in the upper and the holes in the lower parts of the gap can move by hopping along the clusters. The displacement of these charges in external electric field gives rise to appearance of dipoles. It seems reasonable that such the mechanism can qualitatively explain the p.d.e. The photo-excitation of charges (electrons and/or holes) may be considered as increase in polarizability of the local electronic states. According to [12], polarizability (or permittivity) in the disordered semiconductors should have a linear dependence on the light intensity.

The results for the influence of light intensity (J) on the permittivity and conductivity in $PbMoO_4$ crystals are presented in Figure 5. One can see that the plot of $\Delta\varepsilon$ vs. J is super-linear and the approximation gives $\Delta\varepsilon = cJ^2$. This disagrees with the result [12]. The conductivity behaviour differs essentially from that of $\Delta\varepsilon(J)$. The dependence $\Delta\sigma(J)$ is linear. It seems that this result gives a ground for assuming that the photoconductivity and the f.d.e. mechanisms are, at least partly, connected with different defects. The $\Delta\varepsilon(J)$ behaviour may be explained by the influence of light on both the

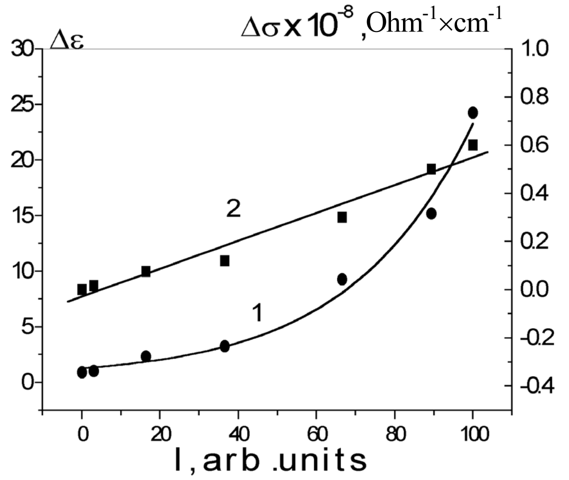

Fig. 5. Dependences of the permittivity Δε (1) and the conductivity Δσ (2) variations on the light intensity (T = 350 K, F = 100Hz, the sample thickness 2.4 mm).

concentration and polarizability of the local centres. But the details of such the mechanism is not quite clear.

Conclusions

Summing up, the as-grown lead molibdate crystals represent a partially disordered system, which contains randomly distributed defects of different nature. Some of these defects are ordered in the associations (clusters). The electronic energy levels inside the clusters are separated by intrinsic barriers. Within the clusters, the electrons (holes) are transferred by hopping through these barriers. The clusters are located at some distance one from another and are separated with higher (extrinsic) barriers. One can imagine the existence of the two types of clusters: the first one is localized near the upper (the “electronic cluster”) and the second near the lower (the “hole cluster”) edge of the gap. The displacement, by external electric field, of charges (both electrons and holes) excited inside the clusters with the illumination or thermally should induce a dipole moment and so increase the permittivity at low frequencies.

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