

Photoinduced Effects in Single Crystals of PbO–MoO₃ System

T.M. BOCHKOVA^a, D.S. BONDAR^{a,*}, M.P. TRUBITSYN^a,
M.D. VOLNIANSKII^a AND D.M. VOLNYANSKII^b

^a*Oles' Honchar Dnipro National University, prosp. Gagarina 72, 49010 Dnipro, Ukraine*

^b*Dnipro National University of Railway Transport named after academician V. Lazaryan, Lazaryan str. 2, 49010 Dnipro, Ukraine*

Doi: [10.12693/APhysPolA.141.400](https://doi.org/10.12693/APhysPolA.141.400)

*e-mail: dima_bondar@ua.fm

Photoinduced changes in the optical absorption and dielectric properties of PbMoO₄ and Pb₂MoO₅ crystals are considered. Differences in the manifestation of the photochromic effect in both crystals are associated with differences in their crystal structure. It is assumed that the photodielectric effect in the PbMoO₄ and Pb₂MoO₅ crystals is due to the presence of the same anionic complexes. The nature of the structural defects in the crystal lattice and their transformation under the heat treatment of PbMoO₄ and Pb₂MoO₅ crystals in various atmospheres and ultraviolet irradiation was analyzed.

topics: optical absorption, dielectric relaxation, lead molybdate, double lead molybdate

1. Introduction

The phase diagram of the PbO–MoO₃ system contains two congruently melting compounds: PbMoO₄ with a melting point at 1343 K, and Pb₂MoO₅ with a melting point at 1223 K [1]. Crystalline lead molybdate (PbMoO₄) is widely used in acousto-optical devices for controlling the parameters of light and optical data processing. Besides, these crystals doped with rare-earth elements are recognized as the most perspective materials for creating solid Raman lasers for LIDAR systems, in which lead molybdate is used as an active laser medium and Raman converter [2]. Lead molybdate is also a promising cryogenic scintillator in neutrino-free double β decay experiments [3, 4]. Great demand for the PbMoO₄ crystals of acceptable quality has stimulated the development of the crystal growth technology [5–11].

Two-lead molybdate (Pb₂MoO₅) has not yet been widely used in acousto-optics, mainly owing to the lack of an affordable technology for growing high-quality crystals. Nevertheless, Pb₂MoO₅ is an optically biaxial crystal with large and strongly anisotropic acousto-optical parameters, which opens up the perspectives of its applications in fundamentally new acousto-optical devices [12, 13].

The structure of the considered crystals is different. Lead molybdate PbMoO₄ possesses a scheelite-type structure with a tetragonal space symmetry group $I4_1/a$ and lattice constants $a = b = 0.54312$ nm, $c = 1.21065$ nm. The unit cell contains $Z = 4$ formula units. In the PbMoO₄ lattice, Pb

atoms are positioned within the PbO₈ dodecahedra, which are linked with each other by the edges. The PbO₈ dodecahedra and MoO₄ tetrahedra are linked via common vertices. Each O atom is coordinated, in turn, by two Pb atoms and one Mo atom [14–16].

The lattice of Pb₂MoO₅ belongs to a monoclinic system with the space symmetry group C_{2h}^3-C2/m [17]. The unit cell contains four formula units $Z = 4$, the lattice parameters are $a = 1.4225$ nm, $b = 0.5789$ nm, $c = 0.7336$ nm ($\beta = 114.0^\circ$), where the b -axis is directed along the C_2 symmetry axis. The Pb₂MoO₅ structure is characterized by a cleavage plane with indices $(\bar{2}01)$. Also Pb–O zigzag-like chains are along the z -axis, the existence of which is a specific distinctive feature of the Pb₂MoO₅ crystal structure.

The effectiveness of the applications strongly depends on the quality of the grown crystal. A significant drawback of these acousto-optical materials is light yellow coloration and the dependence of optical absorption on external influences (UV irradiation, annealing in various atmospheres).

Study of the electrical and optical properties of both crystals revealed a number of photoinduced phenomena. In particular, the photochromic and photodielectric effects were observed in [18–21]. Photochromism consists in changing the optical absorption spectra and, as a consequence, changing the color of crystals irradiated with UV light. The photodielectric effect is manifested by the appearance of anomalies on the temperature dependences of permittivity ε and conductivity σ after UV light irradiation.

In this article, we analyze similar features and differences in the manifestation of these phenomena in single crystals of the PbO–MoO₃ system.

2. Experimental

Single crystals of PbMoO₄ and Pb₂MoO₅ were grown in air from melt by the Czochralskii method. The charge was prepared from the lead and molybdenum oxides of “high purity” grade using ceramic technology. Both reagents were taken in the stoichiometric ratio. The obtained PbMoO₄ crystals had a diameter of up to 35 mm and a length of about 50–60 mm; Pb₂MoO₅ crystals were up to 20 mm in diameter and up to 40 mm in length. Both types of the crystals were free from macroscopic inclusions (gas bubbles, cracks) and had a light yellowish color [22]. High-temperature treatment of the PbMoO₄ crystals in air was carried out in a muffle furnace at 1200 K. The annealing time in the experiments varied from 2 to 90 h. Annealing of Pb₂MoO₅ crystals in vacuum was carried out at 1000 K during 1–2 h.

The optical transmission spectra were measured at 295 K on the crystal doubly polished plates using a “Specord M-40” spectrophotometer. The polished planes were oriented parallel to (001) for PbMoO₄ and (010) for Pb₂MoO₅. The thickness of the samples was 10–13 mm for PbMoO₄ and 5.3 mm for Pb₂MoO₅.

The photochromic coloration was observed after irradiation by light of Hg lamp during 2–5 h. Colored samples were returned to the initial state by annealing at 700–800 K in air for 2 h.

Permittivity ε was measured in the AC field by the four-wire method using a Keysight E4980AL LCR Meter at different frequencies ($f = 1\text{--}10$ kHz) in the temperature interval 290–700 K. Samples were prepared as plane-parallel plates with dimensions $5 \times 5 \times 1$ mm³. The main planes of the samples were cut as for optical experiments. Platinum electrodes were used. Before each measuring cycle, the short-circuited samples were heat treated in air at 700 K for 10 min. Such procedure was used in order to eliminate the dependence of the electrical properties on the sample pre-history. After thermal treatment, the samples were cooled to room temperature and irradiated for 40 min through the polished side faces with UV light of Hg lamp. Permittivity was measured on a heating run with a rate of 8 K/min.

3. Results and discussion

3.1. Color centers in PbMoO₄, Pb₂MoO₅ single crystals

The problem of obtaining colorless PbMoO₄ crystals is very important for optical applications. Because, as a rule, PbMoO₄ crystals grown in different laboratories using the Czochralski method in air have yellow color and exhibit a photochromic effect

due to the presence of intrinsic and/or impurity defects. Great efforts have been made to develop technology for the growth of high quality PbMoO₄ crystals [2, 5–11, 18, 21–23]. Particular attention was paid to the purity of the initial reagents, evaporation of components, and determination of the optimal directions of crystal pulling. In a number of works [6, 24–27], the color of PbMoO₄ crystals was attributed to the existence of impurities of the iron group (Mn, Cr). In [28–31] it was suggested that the dominant type of point defects in PbMoO₄ are cationic vacancies. Authors assumed that evaporation of the components from the melt led to the appearance of molybdenum ions vacancies (V_{Mo}) which changed the structure locally and resulted in the formation of hole color centers.

Colorless PbMoO₄ crystals were obtained for the first time by high-temperature annealing in an atmosphere with a low partial pressure of oxygen [23]. The author suggested that the interaction with the environment during the growth and annealing of PbMoO₄ crystals leads to the formation of Pb³⁺ and Mo⁵⁺ defects. The optical absorption in the area of 23000 cm⁻¹ (435 nm) was attributed to the oxidation of Pb²⁺ ions to Pb³⁺. Unfortunately, the crystals discolored by annealing in a vacuum were colored under the action of high-energy radiation. Broad absorption bands with maxima at 26300 cm⁻¹ (380 nm) and 17400 cm⁻¹ (575 nm) at 80 K were attributed to intrinsic transitions in the Mo⁵⁺ ion.

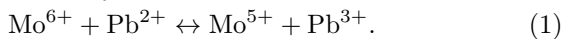
We have carried out comprehensive studies of optical absorption in PbMoO₄ crystals grown in Laboratory of Active Dielectric Crystals of Dnipro National University. We considered the effects of composition variations, high-temperature treatment in air, UV irradiation and doping on the optical properties of PbMoO₄ single crystals [18, 19, 21, 32]. According to our results the optical transmission of the crystals in the visible region of the spectrum is strongly influenced by local centers. Cationic and oxygen vacancies can be considered the most typical defects arising during crystal growth. The impurity content can be controlled by charge purification and doping. A charge with an excess of MoO₃ up to 0.5 mol.% was used to compensate the non-stoichiometry of the composition due to evaporation of the components of the melt. This reduces the likelihood of complex defects as Mo⁶⁺ ion vacancies. The presence of Pb²⁺ ion vacancies apparently plays an essential role in the formation of color centers in the crystal lattice of PbMoO₄, as well as the substitution of Pb²⁺ with by Ba²⁺, Bi³⁺ ions [18, 21, 32, 33]. Annealing in different atmospheres, changing the number of oxygen vacancies, leads to a change in the charge state of a certain fraction of cations. According to the model developed in [23], the optical absorption in the region of 23000 cm⁻¹ is caused by the oxidation of Pb²⁺ ions to the Pb³⁺ state. The Pb³⁺ paramagnetic centers in scheelites (CaWO₄–Pb) were observed

by EPR [34] earlier. Perhaps, the lack of the evidence for the existence of Pb^{3+} in lead molybdate is due to the low concentration of these centers. In as-grown yellow PbMoO_4 crystals the concentration of Pb^{3+} was estimated to be $1.4 \times 10^{15} \text{ cm}^{-3}$ in [23].

A thorough study [16] of the crystal structure of PbMoO_4 by X-ray and neutron diffraction methods showed the absence of Mo^{6+} ions vacancies and the presence of a significant number of Pb^{2+} ions vacancies in the crystals grown in air. It is believed that the charge misfit introduced by such defects can be compensated by both the oxygen vacancies V_{O} and by the $\text{Pb}^{2+} \rightarrow \text{Pb}^{3+}$ transition.

We have annealed PbMoO_4 crystals in air at 1200 K. In the case of a relatively short-term (2–7 h) annealing, a significant decrease in optical transmission near 23000 cm^{-1} was observed. We believe that filling the oxygen vacancies should stimulate the transition of some Pb^{2+} ions to the Pb^{3+} state to provide charge compensation for the lead vacancies. After prolonged heat treatment (85–90 h), the transmission near 23000 cm^{-1} dropped to zero. In addition, a noticeable increase in transmission of the light in the optical spectra was observed near 25000 cm^{-1} and in the area of $16000\text{--}17000 \text{ cm}^{-1}$. These optical absorption bands were attributed in [23] to internal transitions in the Mo^{5+} ion. The presence of Mo^{5+} ions is not unusual for scheelites. Such centers were found in CaWO_4 [35], CaMoO_4 [23], PbMoO_4 [23, 36]. Recently published low-temperature experiments of EPR in PbMoO_4 crystals showed the existence of several types of photoinduced centers, including Mo^{5+} [33, 37]. In [35] it was pointed out that the presence of oxygen vacancies near Mo^{6+} ions favored the capture of electrons and the formation of Mo^{5+} . Since high-temperature annealing in air decreases the concentration of oxygen vacancies, as a result, the number of Mo^{5+} ions also decreases.

In our experiments, the irradiation with UV-light of the as-grown crystals changed the yellow color of crystals to dark gray. This photochromic effect was reversible. Heating in air up to 700–800 K eliminated the absorption induced by UV irradiation. Three wide absorption bands with maxima 25000, 23500 and 17000 cm^{-1} appeared in the optical absorption spectra. Based on the adopted model [23], the photochromic effect in PbMoO_4 crystals most likely is caused by the charge exchange between cations by means of the redox reactions. It can be described by



Among the most studied phenomena induced by UV excitation is the luminescence of PbMoO_4 crystals [15, 38–40]. It is suggested there that photoluminescence is caused by radiative transitions in $(\text{MoO}_4)^{2-}$ complexes and transfer of an electron from Pb^{2+} ions to the adjacent molybdenum groups. The formation of $\text{Pb}^{3+}\text{--}\text{Mo}^{5+}$ glow centers generated by UV irradiation was considered in [39].

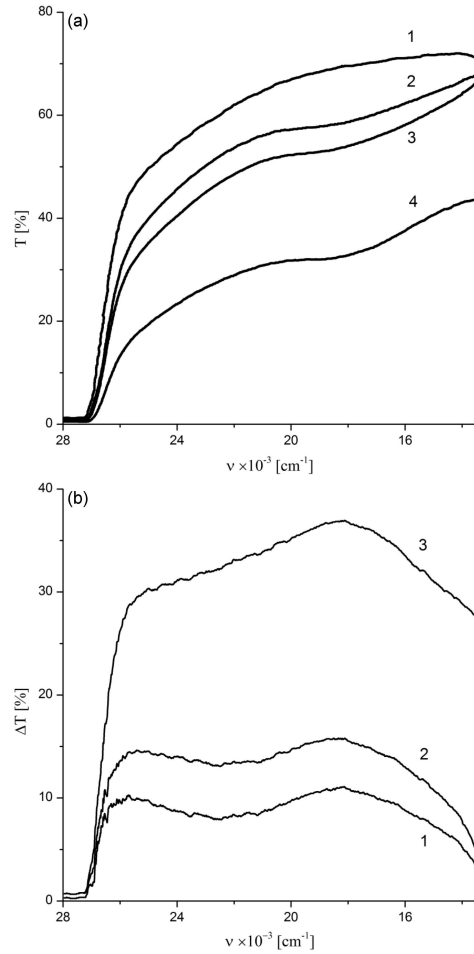


Fig. 1. The effect of isothermal treatment in vacuum ($T = 1000 \text{ K}$) and UV irradiation on the optical transmission of Pb_2MoO_5 crystals grown in air (a): 1 — initial state; 2 — after heat treatment for 1 h; 3 — after UV irradiation of annealed sample for 2 h; 4 — after additional heat treatment for 1 h and repeated UV irradiation. The spectral differences (b) are shown by the curves: 1 = 1 – 2; 2 = 1 – 3; 3 = 1 – 4. The thickness of the samples was 5.3 mm.

The authors of [40] also suggested that the electronic states of lead participated in the formation of emission centers or took part in the transfer of energy to the centers responsible for the photoluminescence in PbMoO_4 . This conclusion was confirmed in [37], where mixing of lead orbitals in the ground state of the MoO_4 complex was found to be about 40%. These results correlate well with our model of cation charge exchange that includes in the photochromic effect in PbMoO_4 crystal.

We also studied the influence of UV irradiation and high-temperature treatment on the optical transmission of Pb_2MoO_5 single crystals. The results of the experiments are given in Fig. 1. The effects of the external influences on the PbMoO_4 and Pb_2MoO_5 optical properties are quite different, and the following features can be mentioned.

First, there is no appreciable photochromic effect in the as-grown Pb_2MoO_5 crystals. The changes in the crystal optical transmission spectrum after UV irradiation for 2 h are about 1–2%, which is within the experimental error.

Second, high-treatment of Pb_2MoO_5 single crystals in a vacuum led to a significant decrease in the optical transmission (Fig. 1a). The curves of the difference between the spectra of the as-grown and annealed Pb_2MoO_5 crystals show two wide absorption bands near 25500 and 17000 cm^{-1} (Fig. 1b). These bands, as we noted in the case of PbMoO_4 , are typical of internal transitions in the Mo^{5+} ions, so that we can conclude that the Mo^{5+} ions concentration in Pb_2MoO_5 increases as a result of annealing in vacuum. This does not contradict the results obtained for PbMoO_4 , however, no discoloration of the crystals due to the reduction of Pb^{3+} ions to Pb^{2+} is observed.

Third, UV irradiation of Pb_2MoO_5 crystals annealed in a vacuum led to a slight decrease in transmission (4–5%) in a wide range of wavelengths (Fig. 1a). Most likely, this was due to the formation of F-centers on oxygen vacancies, the number of which increased as a result of annealing.

Fourth, heat treatment in air at 800 K for 2 h of samples annealed in vacuum and irradiated with UV light restored the optical transmission to its original state. No additional coloration was observed.

It is obvious that the differences in the processes of defect formation and their evolution under the external influences in the considered crystals depend on the differences in their crystal structure. At the same time, both crystals contain the characteristic molecular anionic tetrahedra $(\text{MoO}_4)^{2-}$ with almost the same Mo–O distance (0.177 nm) [16]. One can suppose that these coordination complexes are responsible for the photodielectric effect inherent in both crystals. The photodielectric effect is considered in the next section.

3.2. Photodielectric effect in PbMoO_4 and Pb_2MoO_5 single crystals

It was previously reported that UV irradiation caused anomalies of the temperature dependences of permittivity ε and conductivity σ of PbMoO_4 and Pb_2MoO_5 crystals [17, 19–21]. Such effect was attributed to the dipole defects formation induced by UV light. It was shown that $\varepsilon(T)$ and $\sigma(T)$ maxima increased in amplitude for higher exposure time. The anomalies $\varepsilon(T)$ and $\sigma(T)$ could be detected only on the first heating run and disappeared after heating up to 500 K for PbMoO_4 and 700 K for Pb_2MoO_5 . Obviously, disappearance of the $\varepsilon(T)$ and $\sigma(T)$ maxima can be ascribed to thermal destruction of the dipole centers. These centers can be regenerated by subsequent UV light irradiation of the sample at room temperature.

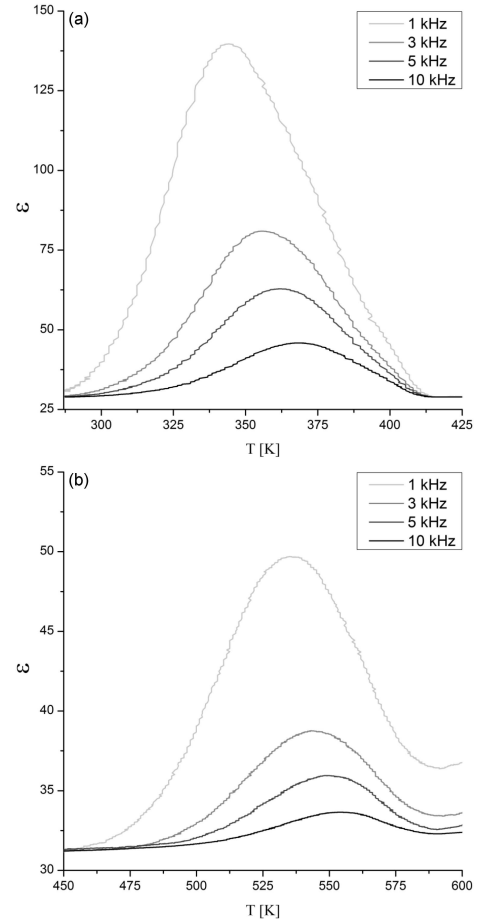


Fig. 2. Dependencies of permittivity $\varepsilon(T)$ for PbMoO_4 (a) and Pb_2MoO_5 (b) crystals irradiated with UV light. Irradiation was performed on annealed samples at $T = 290$ K for 40 min.

Figure 2a shows $\varepsilon(T)$ dependence for the PbMoO_4 crystals irradiated previously with UV light at room temperature, measured at different frequencies. One can see that as the AC field frequency increases, the well detected $\varepsilon(T)$ peak shifts to high temperatures and its amplitude decreases. Figure 2b shows a similar behavior for Pb_2MoO_5 but the photodielectric peak for double lead molybdate is observed at 200 K higher as compared with PbMoO_4 (Fig. 2a). One can note that the frequency dispersion observed is typical of thermal relaxation processes. Nevertheless, the $\varepsilon(T)$ peaks are quite symmetrical, which is markedly different from usual step-like dielectric relaxation anomalies.

To discuss the nature of the dipole centers responsible for the photodielectric effect, consider available experimental data. In recent EPR and TSL experiments [33, 37] three types of the photoinduced centers were found in PbMoO_4 crystals. All of them represented $(\text{MoO}_4)^{3-}$ complexes with trapped electrons and with different surroundings in the nearest Pb sites. All these centers were stable only at low temperatures and were destroyed by heating in the interval 40–120 K. However, these

models show the possibility of capturing the photoexcited electron by the complex $(\text{MoO}_4)^{2-}$ and transforming of it into $(\text{MoO}_4)^{3-}$. Our optical data confirmed the appearance of Mo^{5+} ions under the action of UV irradiation. Taking into account the EPR data in PbMoO_4 and other scheelites [33, 37, 41–43], we associate the formation of dipole defects induced by UV light and causing anomalies in $\varepsilon(T)$ and $\sigma(T)$, with the capture of photoelectrons by molybdenum ions located inside a tetrahedron distorted by oxygen vacancies $(\text{MoO}_3)^-$. An additional neighbouring defects in lead sublattice could stabilize such complexes similarly to the situation in PbWO_4 [42]. The electric dipole moment of a distorted $(\text{MoO}_3)^-$ tetrahedron is created by excess charges of a photoelectron captured by molybdenum and oxygen vacancy. In an external AC field, reorientations of the dipole moment caused by thermally activated hopping of oxygen vacancy lead to the appearance of the anomalies in the electrical properties of PbMoO_4 .

The photodielectric effect is observed in both PbMoO_4 and Pb_2MoO_5 and displays similar behaviour. Thus one can assume that the mechanism of these effects may be similar and attribute the photodielectric effect to common structural complexes, i.e., $(\text{MoO}_4)^{2-}$ anionic groups. Obviously, the temperature differences of the $\varepsilon(T)$ maxima in PbMoO_4 and Pb_2MoO_5 crystals can be related to different structural surroundings of $(\text{MoO}_4)^{2-}$ tetrahedra.

It should be noted that only one of the possible models was considered here. There are other possible traps for photoelectrons and, for instance, $\text{Pb}^{2+}\text{-V}_\text{O}$ dipole centers found earlier in PbWO_4 [42].

4. Conclusions

A comparative analysis of the photoinduced effects in PbMoO_4 and Pb_2MoO_5 single crystals subjected to heat treatment in different atmospheres and irradiated with UV light was carried out. Significant differences between the phenomena caused by external influences on the optical properties of PbMoO_4 and Pb_2MoO_5 were found.

It is assumed that in PbMoO_4 , Pb^{2+} vacancies play an important role and make for the appearance of Pb^{3+} centers. These defects cause optical absorption in the region of 23000 cm^{-1} , which is responsible for the yellow color of the crystals. Heat treatment in air of the crystals at 1200 K leads to filling the oxygen vacancies, which results in oxidation of Pb^{2+} to Pb^{3+} and Mo^{5+} ions to Mo^{6+} . The optical absorption of the annealed crystal sharply decreases in the area of 23000 cm^{-1} and increases in the region $16000\text{--}17000\text{ cm}^{-1}$. A reversible photochromic effect was observed after UV irradiation. The absorption in the area of 23000 and 17000 cm^{-1} increases due to a recharge of the cations in the crystal lattice.

Annealing in vacuum does not discolor Pb_2MoO_5 crystals similarly to PbMoO_4 , but, on the contrary, leads to additional optical absorption in the area of 25500 and 17000 cm^{-1} due to an increase in the concentration of Mo^{5+} ions. A noticeable photochromic effect is observed only for Pb_2MoO_5 crystals annealed in vacuum. It is assumed that this is due to the formation of F centers on oxygen vacancies, the number of which increases as a result of annealing.

UV irradiation of PbMoO_4 and Pb_2MoO_5 crystals also leads to the appearance of $\varepsilon(T)$ permittivity relaxation peaks. One can assume that the photodielectric effect has the same nature and can be attributed for the common for both PbMoO_4 and Pb_2MoO_5 crystals coordination complexes, i.e., molybdenum–oxygen tetrahedra. The dipole defects contributed to the photodielectric effect can be associated with Mo–O tetrahedra distorted by oxygen vacancy and photoelectrons capture. Hopping of V_O through Mo–O tetrahedra vertices is accompanied by re-orientations of dipole moments of $(\text{MoO}_3)^-$ complexes. For the used frequencies of the AC field, $\varepsilon(T)$ anomalies are detected in the temperature interval where thermally activated destruction of the dipole centers becomes sufficient. This fact determines the specific character of the ε dependence on temperature and frequency.

References

- [1] T. Namikata, S. Esashi, *Jpn. J. Appl. Phys.* **11**, 772 (1972).
- [2] M.B. Kosmyna, B.P. Nazarenko, V.M. Puzikov, A.N. Shekhovtsov, *Acta Phys. Pol. A* **124**, 305 (2013).
- [3] M. Minowa, K. Itakura, S. Moriyama, W. Ootani, *Nucl. Instrum. Methods Phys. Res. A* **320**, 500 (1992).
- [4] F.A. Danevich, B.V. Grinyov, S. Henry et al., *Nucl. Instrum. Methods Phys. Res. A* **622**, 608 (2010).
- [5] E. Pfeifer, P. Rudolph, *Crystal Res. Technol.* **25**, 3 (1990).
- [6] G.M. Loiacono, J.F. Balascio, R. Bonner, A. Savage, *J. Cryst. Growth* **21**, 1 (1974).
- [7] N. Senguttuvan, S. Morthy Babu, C. Subramanian, *Mater. Sci. Eng. D* **47**, 269 (1997).
- [8] S.C. Sabharwal, Sangeeta, D.G. Desai, *Cryst. Growth Des.* **6**, 58 (2006).
- [9] Sangeeta, D.G. Desai, A.K. Singh, M. Tyagi, S.C. Sabharwal, *J. Cryst. Growth* **296**, 81 (2009).
- [10] M. Tyagi, S.G. Singh, A.K. Singh, S.C. Gadkari, *Phys. Status Solidi A* **207**, 1802 (2010).
- [11] S. Takano, S. Esashi, K. Mori, T. Namikata, *J. Cryst. Growth* **24**, 437 (1974).

- [12] A.Yu. Tchernyatin, *Proc. SPIE* **5953**, 59530U-1 (2005).
- [13] M.G. Mil'kov, M.D. Volnianskii, A.I. Antonenko, V.B. Voloshinov, *Akusticheskij Zhurnal* **58**, 206 (2012).
- [14] W. Sleight, *Acta Cryst. B* **28**, 2899 (1972).
- [15] S. Nedilko, V. Chornii, Yu. Hizhnyi, M. Trubitsyn, I. Volnyanskaya, *Opt. Mater.* **36**, 1754 (2014).
- [16] I.A. Kaurova, G.M. Kuz'micheva, A.A. Brykovskiy, V.B. Rybakov, Yu.N. Gorobets, A.N. Shekhovtsov, A. Cousson, *Mater. Des.* **97**, 56 (2016).
- [17] S. Miyazawa, H. Iwasaki, *J. Cryst. Growth* **8**, 359 (1971).
- [18] T.M. Bochkova, M.D. Volnyanskii, D.M. Volnyanskii, V.S. Shchetinkin, *Phys. Solid State* **45**, 244 (2003).
- [19] T.M. Bochkova, M.P. Trubitsyn, M.D. Volnyanskii, D.S. Bondar, D.M. Volnyanskii, *Mol. Cryst. Liq. Cryst.* **699**, 111 (2020).
- [20] I.P. Volnyanskaya, M.P. Trubitsyn, D.M. Volnyanskii, D.S. Bondar, *J. Phys. Electron.* **26**, 63 (2018).
- [21] T. Bochkova, D. Bondar, M. Trubitsyn, M. Volnianskii, *Springer Proc. Phys.* **264**, 11 (2021).
- [22] K.V. Agarkov, T.M. Bochkova, M.D. Volnyanskiy, *Crystals of Active Dielectrics. Growth Experience*, Akcent PP Dnipro, Ukraine 2020.
- [23] W. Ballmann *Kristall Technik.* **15**, 367 (1980).
- [24] H.J. Bernhardt, *Phys. Status Solidi A* **45**, 353 (1978).
- [25] J. Chen, Q. Zhang, T. Liu, Z. Shao, *Physica B* **403**, 555 (2008).
- [26] J.P. Parant, G. Villela, D. Gourier, C. le Sergent, J.P. Dumas, *J. Cryst. Growth* **52**, 576 (1981).
- [27] D. Gourier, J.P. Parant, D. Vivien, *Phys. Status Solidi B* **113**, 509 (1982).
- [28] Yu.N. Gorobets, I.A. Kaurova, G.M. Kuz'micheva, A.N. Shekhovtsov, V.B. Rybakov, A. Cousson, *J. Surf. Investig.: X-ray Synchrotron Neutron Tech.* **8**, 734 (2014).
- [29] A.Ya. Neiman, A.A. Afanasiev, L.M. Feodorova, V.T. Gabrielian, S.M. Karagezian, *Phys. Status Solidi A* **83**, 153 (1984).
- [30] A.Ya. Neiman, L.M. Fedorova, A.A. Afanasyev, *Rus. Inorg. Mater.* **23**, 811 (1986).
- [31] A.Y. Neiman, E.V. Tkachenko, L.M. Fedorova et al., *Rus. Inorg. Mater.* **16**, 11, 2025 (1980).
- [32] T.M. Bochkova, M.D. Volnyanskii, D.M. Volnyanskii, V.S. Shchetinkin, *Ukr. J. Phys.* **48**, 128 (2003) (in Ukrainian).
- [33] M. Buryi, V. Laguta, M. Fasoli et al., *J. Lumin.* **205**, 457 (2019).
- [34] G. Born, A. Hofstaetter, A. Schermann, *Phys. Status Solidi B* **37**, 255 (1970).
- [35] G.H. Azerbayejani, A. Merlo, *Phys. Rev. A* **137**, 489 (1965).
- [36] E.G. Reut, A.I. Ryskin, *Opt. Spektrosk.* **35**, 862 (1973) (in Russian).
- [37] M. Buryi, V. Laguta, M. Fasoli, F. Moretti, M. Trubitsyn, M. Volnianskii, A. Vedda, M. Nikl, *J. Lumin.* **192**, 767 (2017).
- [38] M.R.D. Bomio, L.S. Cavalcante, M.A.P. Almeida, R.L. Tranquilin, N.C. Batista, P.S. Pizani, M. Siu Li, J. Andres, E. Longo, *Polyhedron* **50**, 532 (2013).
- [39] W. Van Loo, *Phys. Status Solidi A* **28**, 227 (1975).
- [40] D.A. Spassky, S.N. Ivanov, V.N. Kolobanov, V.V. Mikhailin, V.N. Zemskov, B.I. Zadneprovski, L.I. Potkin, *Radiat. Meas.* **38**, 607 (2004).
- [41] V.V. Laguta, J. Rosa, M.I. Zaritskii, M. Nikl, Y. Usuki, *J. Phys. Condens. Matter* **10**, 7293 (1998).
- [42] V.V. Laguta, M. Martini, A. Vedda, E. Rosetta, M. Nikl, E. Mihokova, J. Rosa, Y. Usuki, *Phys. Rev. B* **67**, 205102 (2003).
- [43] V.V. Laguta, A. Vedda, D. Di Martino, M. Martini, M. Nikl, E. Mihokova, J. Rosa, Y. Usuki, *Phys. Rev. B* **71**, 235108 (2005).