

electrical properties of PbMoO_4 single crystals



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Introduction

PbMoO_4 crystals are widely used in modern electronics as multifunctional materials. The main areas of applications are acousto-optics, laser technology and cryogenic scintillation systems for detecting rare events in physics of elementary particles. These applications require large-sized crystals of good quality. However, PbMoO_4 crystals grown from a melt on a seed, as a rule, contain characteristic structural imperfections. Among them there are nanometer-sized clusters, including intrinsic point defects and impurities, photoinduced complexes based on anionic MoO_4 groups with trapped photoelectrons, inclusions of foreign phases. Such defects have a strong effect on the electrical and optical properties of crystals. In this work, we study the effect of variations of the initial mixture composition and UV irradiation on polarization and charge transfer processes in PbMoO_4 single crystals.

Experimental details

The single crystals of PbMoO_4 were grown from the melt by conventional Czochralski technique in air by using platinum crucibles. The charge was prepared by solid phase synthesis at 925-975 K for 2 hours from MoO_3 and PbO of α - or β - modifications of "high purity" grade. The reagents were taken both in a stoichiometric ratio and with excess of 0,5 mol% of MoO_3 . The crystals grown in the direction deviated by 30° from a -axis in (001) plane were free from gas bubbles and cracks. The main planes of the samples with dimensions $5 \times 5 \times 1 \text{ mm}^3$ were cut perpendicular to the growth axis. The main faces of the samples were irradiated using light-emitting diode with radiation wavelength $\lambda=365\text{--}370 \text{ nm}$ for 30 – 60 minutes. Then platinum electrodes were deposited by cathode sputtering. Permittivity ϵ and conductivity σ were measured in AC field by the bridge method at fixed frequency ($f=1 \text{ kHz}$) in the temperature interval 290–700 K.

Results and discussion

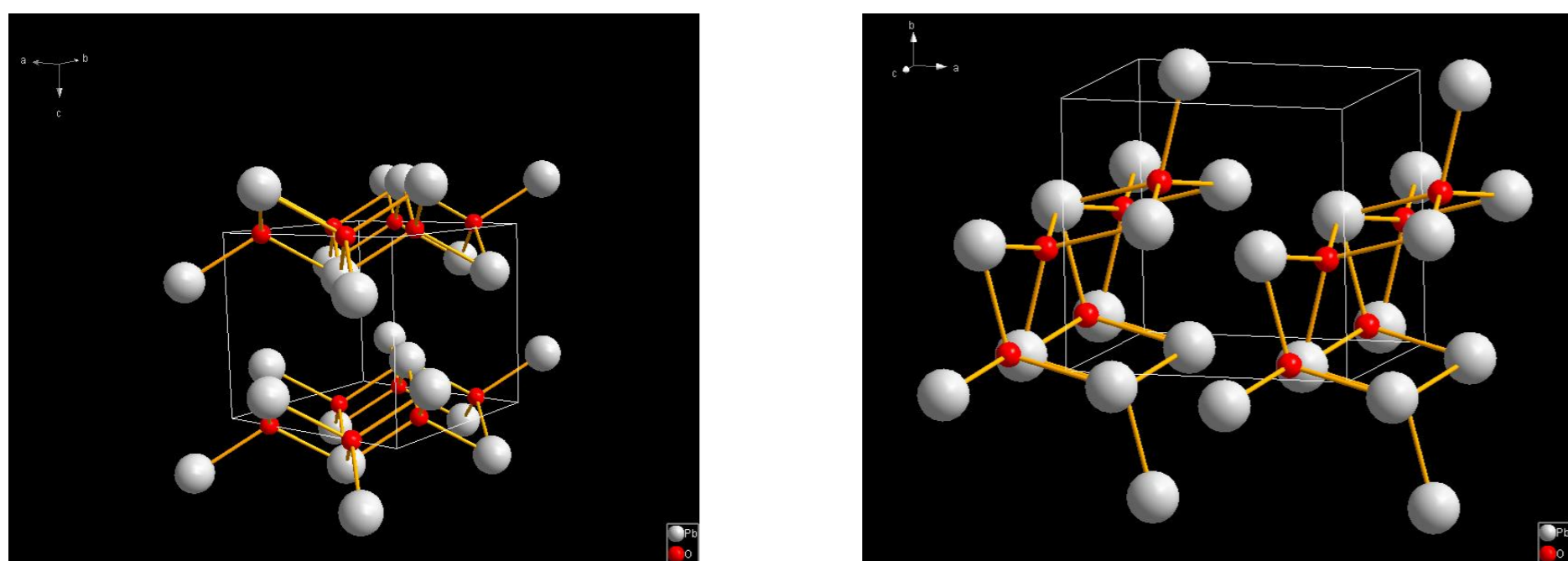


Fig.1. PbO can exist in two polymorphic forms. This is an α -modification (lead litharge), which has a red color and belongs to the tetragonal syngony (symmetry space group $P 4/nmm$, $Z=4$, unit cell parameters: $a=0.3976 \text{ nm}$; $c=0.5023 \text{ nm}$, figure on the left). And β -modification (massicot), the crystals of which are yellow in color and are characterized by rhombic symmetry (space group $P bcm$, $Z=2$, unit cell parameters: $a=0.5489 \text{ nm}$; $b=0.4755 \text{ nm}$; $c=0.5891 \text{ nm}$, figure on the right).

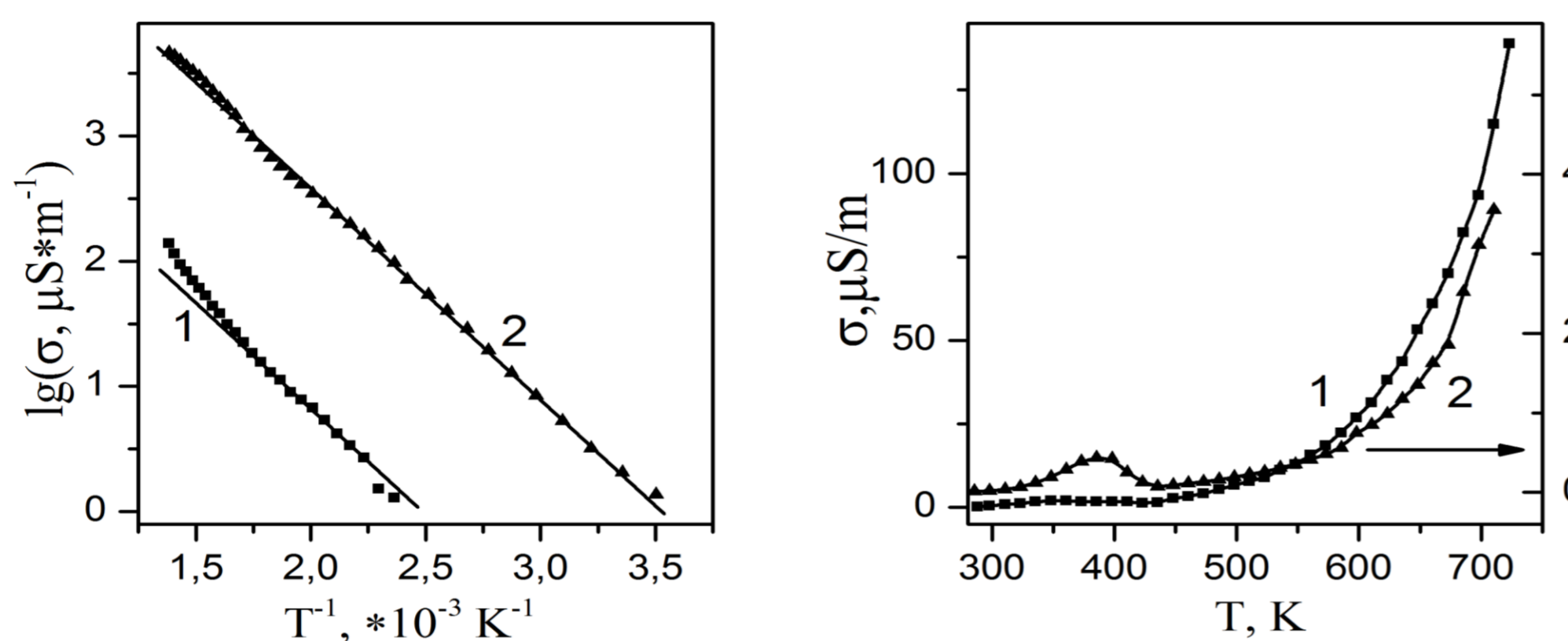


Fig. 2. The temperature dependences of AC conductivity of PbMoO_4 crystals before (left) and after UV irradiation (right): 1 – crystals were grown using β - PbO ; 2 - crystals were grown using α - PbO .

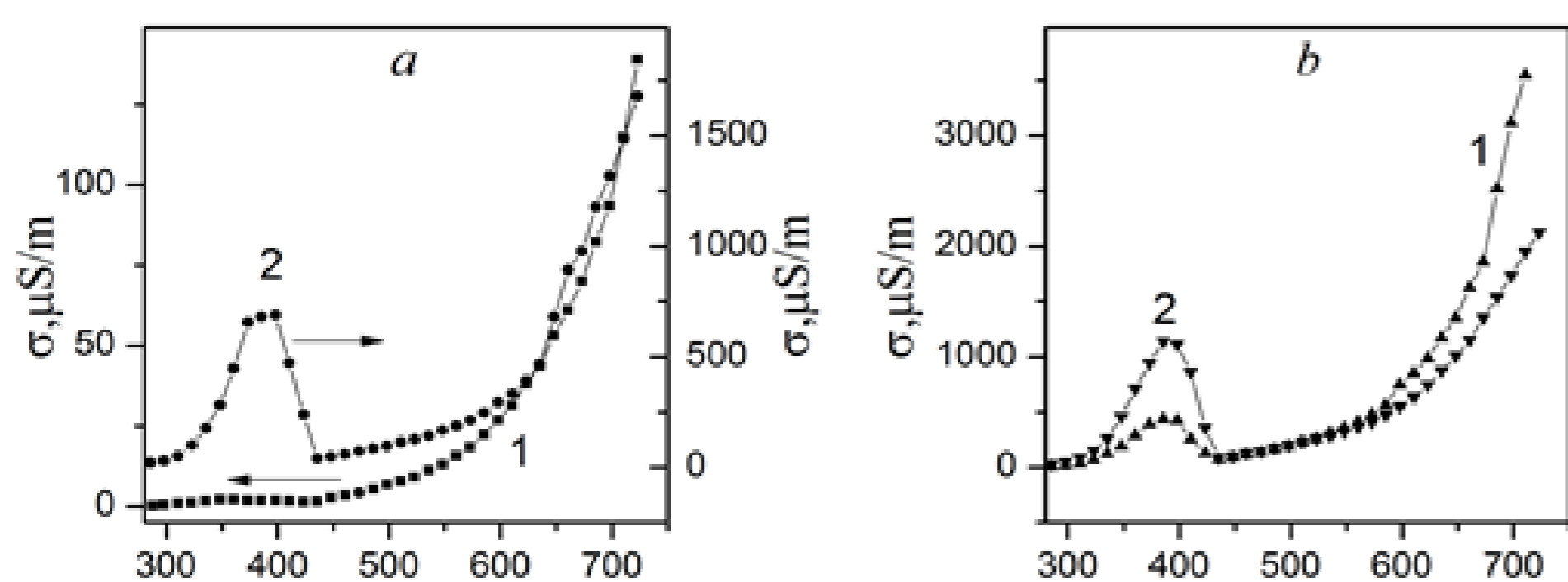


Fig.4. The temperature dependence of AC conductivity ($f=1 \text{ kHz}$) of pre-illuminated with UV light PbMoO_4 crystals: the crystals grown using β -modification (a) and α -modification of PbO (b) (1 – the charge of stoichiometric composition, 2 – the charge with 0.5 mol% MoO_3 excess).

In this work, we have shown that choice of PbO crystal modification type for charge preparation and the excess amount of MoO_3 affect the processes of polarization and charge transfer in PbMoO_4 crystals. The use of the α -modification of PbO as the initial reagent increases AC electrical conductivity ($f = 1 \text{ kHz}$) in a wide temperature range. Preliminary illumination of the samples with UV light leads to the appearance of a maximum in the temperature dependences of the permittivity and conductivity. The introduction of excess of molybdenum oxide in the amount of 0.5 mol% into the mixture for growing PbMoO_4 crystals gives the similar results.

Within the framework of the hopping conductivity model, we suppose that the observed changes in electrical properties are associated with a redistribution of the density of localized states in the bandgap of PbMoO_4 crystals, caused by the appearance of the structural and the photoinduced nanometer-sized defects in the crystal lattice.

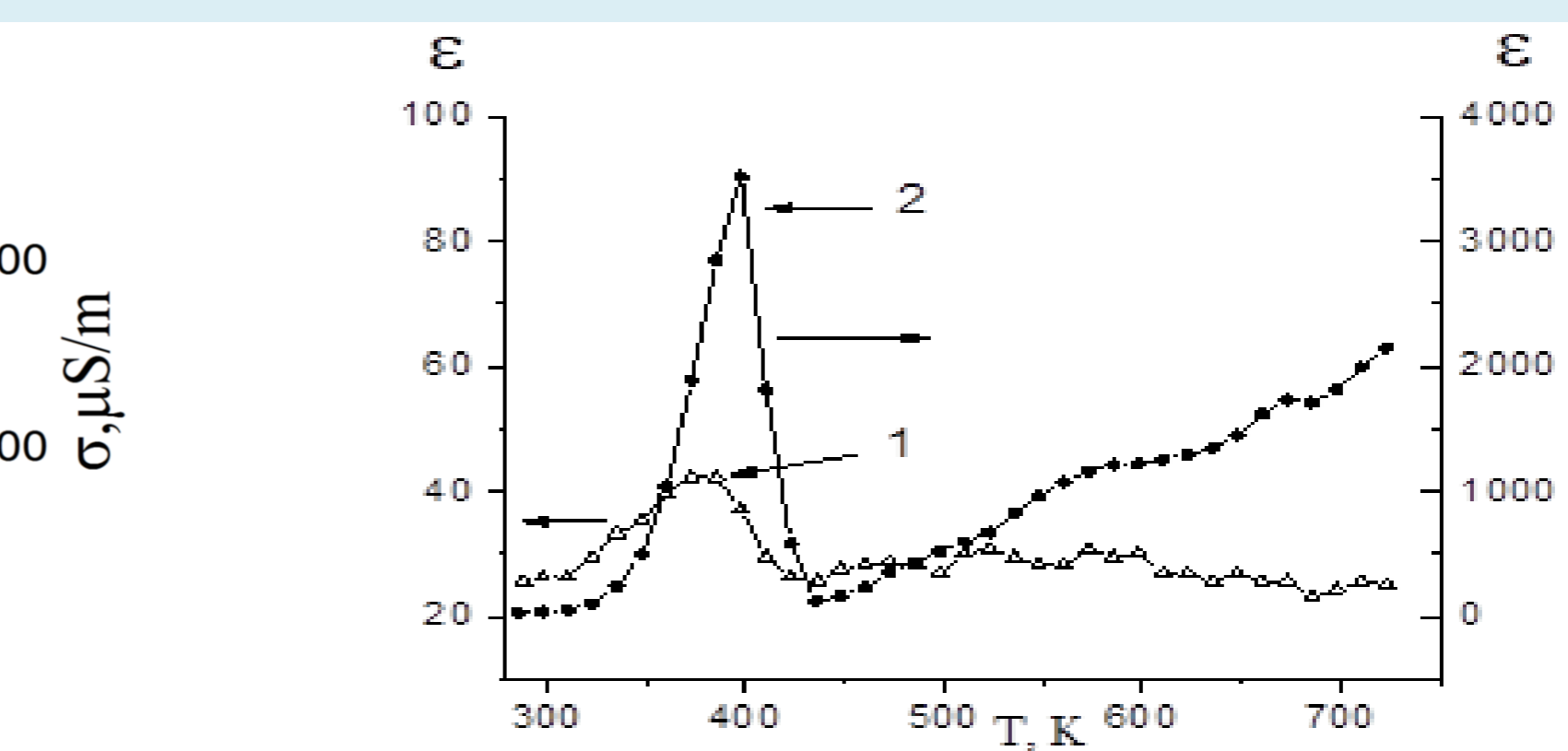


Fig. 3. Permittivity dependencies $\epsilon(T)$ for PbMoO_4 crystals of stoichiometric composition: 1 – crystals were grown using β - PbO ; 2 - crystals were grown using α - PbO . The measurements were carried out after irradiation of the samples with UV light.

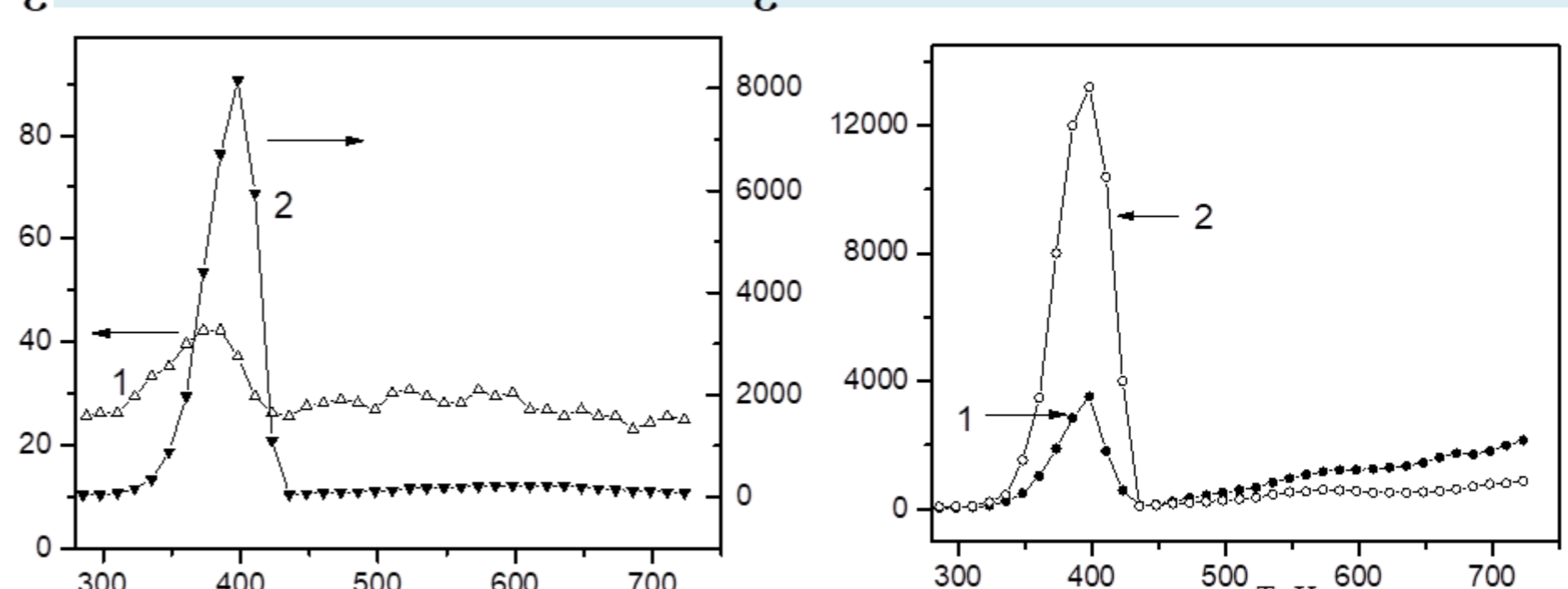


Fig.5. Permittivity dependencies $\epsilon(T)$ for PbMoO_4 crystals grown using β - PbO (left) and α - PbO (right): 1 – stoichiometric composition, 2 – composition with excess of 0,5 mol % MoO_3 . The measurements were carried out after irradiation of the samples with UV light.