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Quantitative evaluation of microimpurity content in lead tungstate initial raw material and scintillation single crystals

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The results of impurity composition determination in lead tungstate raw material and in the scintillation single crystals at various stages of the technological process are presented. Iron content in the samples was determined by extraction photometry after the double-stage sample breakdown. Al, Bi, Cr, Cu, Mg, Mn, Mo, Ni, Si, Sn, and Ti were determined by atomic emission spectroscopy under arc excitation. The revealed differences in the concentration levels of the above-listed impurities in colored and colorless crystals have been demonstrated to be insufficient for make any substantial effect on the crystal light absorption. These differences have been supposed to be caused by formation of intrinsic impurities in the course of the raw material solid-phase synthesis.

Представлены результаты определения примесного состава сырья и монокристаллов вольфрамата свинца на разных стадиях технологического процесса. Содержание железа определяли экстракционно-фотометрическим методом с двухстадийным вскрытием образцов. Содержание Al, Bi, Cr, Cu, Mg, Mn, Mo, Ni, Si, Sn, Ti определяли методом атомно-эмиссионной спектрометрии с дуговым источником возбуждения. Показано, что установленные различия в уровне содержаний перечисленных примесей в окрашенных и неокрашенных кристаллах недостаточны для существенного влияния на их светопоглощение. Высказано предположение, что указанные различия обусловлены появлением собственных примесей в процессе твердофазного синтеза сырья.

The scintillation properties of AWO_4 tungstates (where A = Ca, Cd, Zn, Pb, Mo, Co) are known for a long time. The tungstates were subjected to a intensive studies first in early sixties in connection with the need of the radio industry and electronics for novel laser materials. The practical application of lead tungstate single crystals was started in nineties of 20th century when large-size, optically transparent crystals and scintillation devices based thereon were manufactured.

Lead tungstate (PWO) crystals exhibit a high density, are nonhygroscopic, chemically inert and show a fast action as scintillators, thus being a material of good promise for application in high-energy physics, in particular, in electromagnetic calorimeters. There are numerous works aimed at detailed study of the growing features, optical and scintillation properties of those crystals [1–3]. The impurity composition of the crystals and effect of various technological operations on the impurity content (influencing considerably the scintillator characteristics, such as light transmission, light yield, etc.) are known to a lesser extent.

The properties of the PWO crystal luminophor being a compound containing a transititon *d*-element may be influenced substantially by the presence of impurity ions of elements where the *3d* shell is filled partially, including those from Ti^{3+} to Cu^{2+} [4, 5].

Table 1. Light yield of $PbWO_4$ scintillators made from various single crystals

Single crystal	Light yield, eV/MeV
I	3...5
II	10...12

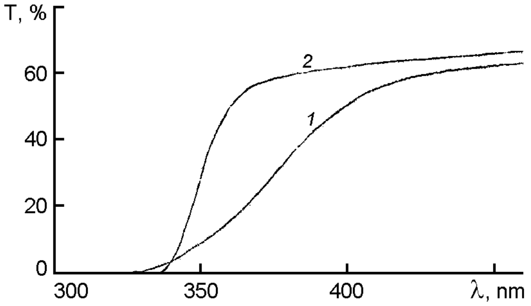

Fig. 1. Transmission spectra of scintillators made from PWO crystals grown from initial raw material (*1*) and recrystallized one (*2*).

Therefore, it is of a scientific and practical interest to study of the concentration levels of the above-mentioned impurities in the material under consideration at various technology stages, starting from the raw material synthesis to the manufacturing of structurally perfect PWO single crystals. Such a study is the aim of this work.

The raw material synthesis for those crystals (being grown by the Czochralski technique) is based on the solid-phase reaction between lead and tungsten oxides. The latter contain various impurities accompanying the main components at all the process stages in a larger or lesser amount. The study objects were the initial mixture of lead and tungsten oxides; the raw material, i.e., the mixture of the same oxides after heat treatment: single crystals I grown directly from the raw material (yellow-colored); and essentially colorless single crystals II grown from ground single crystals I. The light transmission of the $22\times22\times180$ mm^3 scintillators manufactured from the single crystals I and II is presented in Fig. 1; the light yield values for the scintillators differing in transparence are given in Table 1.

As it is noted in [2, 6, 7], the coloration of zinc and cadmium tungstates is observed in the presence of Cr^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Fe^{3+} impurities even at such concentration levels that the single crystal perfection is not deteriorated. The impurity ions located in the regular sites of the crystal seem to form an individual set of energy states, the formation being influenced both by the specific features of the activator itself and its binding with the matrix lattice. A similar situation was observed in the PWO crystals manufactured during this work. Perhaps the coloration of those crystals is due to only one of the mentioned impurities. However, it is difficult to select a model for the possible color center, since the processes occurring in the course of crystal growth are very complex.

The iron impurity determination in most tungsten-containing materials is rather easy as a rule. However, in the case of PWO, it is somewhat difficult to dissolve the substance prior to analysis due to differences in acid-base properties of the oxides constituting it. The traditional breakdown methods of low-soluble oxides using fluxes are unsuitable for subsequent determination of iron traces; heating of lead tungstate with mineral acids results in formation of poorly soluble tungstic acid. The authors have proposed an original two-stage method to break down PWO including formation of hydrated tungstic acid by treatment in HCl followed by its dissolution in the presence of EDTA and citrate ion. The iron content in the samples was determined using the extraction photometric method [8] that was not used before to determine iron in the material under study. The iron content value in each sample was averaged from 6 experiments.

To determine Al, Bi, Cr, Cu, Mg, Mn, Mo, Ni, Sn, Ti, V, and Mo in PWO single crystals, the atomic emission spectroscopy with arc excitation source was used. The fractional distillation conditions for the elements to be analyzed were optimized for the matrix carbidization occurring directy in the craters of sample-carrying carbon electrodes (the lower electrode having a 3 mm deep crater of 4.5 mm in diameter, the upper one, with a 5 mm deep crater of 2 mm in diameter). The sample was mixed preliminarily with graphite powder in 2:1 ratio and evaporated into the arc plasma at the arc current of 16 A and 40 s exposure. The spectrum was recorded using a DFS-8 spectrograph. The calibrating samples were prepared on the basis of graphite powder standard reference material mixing it with the $PbWO_4$ raw material in the mass ratio 2:1.

In Table 2, presented are the determination results of the impurity composition for lead tungstate raw material and single crystals. From these data a trend is seen to increase of the impurity content in the material after each subsequent technological

Table 2. Impurity composition of lead tungstate raw material and single crystals (p.c. by mass)

Element	Initial oxide mixture	Re-melted oxide mixture	Single crystal I		Single crystal II	
			Sample 1	Sample 2	Sample 1	Sample 2
Fe($\pm0.3\cdot10^{-4}$)	$2.8\cdot10^{-4}$	$2.9\cdot10^{-4}$	$4.0\cdot10^{-4}$	$4.6\cdot10^{-4}$	$6.6\cdot10^{-4}$	$7.3\cdot10^{-4}$
Ni($\pm0.5\cdot10^{-4}$)	$<5\cdot10^{-5}$	$1\cdot10^{-4}$	$<5\cdot10^{-5}$	$<5\cdot10^{-5}$	$5\cdot10^{-5}$)	$<5\cdot10^{-5}$
Cu($\pm0.5\cdot10^{-4}$)	$2\cdot10^{-4}$	$2\cdot10^{-4}$	$1\cdot10^{-4}$	$5\cdot10^{-5}$	$3\cdot10^{-4}$	$1\cdot10^{-4}$
Al($\pm0.5\cdot10^{-4}$)	$2\cdot10^{-4}$	$1\cdot10^{-4}$	$2\cdot10^{-4}$	$1\cdot10^{-4}$	$1\cdot10^{-3}$	$1\cdot10^{-4}$
Mg($\pm0.5\cdot10^{-4}$)	$2\cdot10^{-4}$	$2\cdot10^{-4}$	$1\cdot10^{-4}$	$1\cdot10^{-4}$	$2\cdot10^{-4}$	$1\cdot10^{-4}$
Bi, Cr, Ti, Sn	$<5\cdot10^{-5}$					
Mn	$<2\cdot10^{-5}$					
Si, Mo	$<2\cdot10^{-5}$					

operation, the trend is most pronounced for iron. However, the crystals I that contain less impurities are colored and characterized by a rather low light yield while the crystals II are colorless and show a higher light yield. Batenchuk et al. [9], who studied the quenching action mechanism of iron ions on the cadmium tungstate luminescence, has noted that the absorption spectra of $CdWO_4$ single crystals containing $3.3\cdot10^{-4}$ and $8.3\cdot10^{-4}$ % (mass) of Fe^{3+} were almost identical while the crystal light absorption was increased appreciably at iron content of $5.5\cdot10^{-3}$ % (mass). The differences in the impurity content between crystals I and II found by us seem to be insufficient to influence substantially the light absorption. The absorption characteristics of those crystals can be supposed to be defined in first turn not by concentrations of the foreign impurities being considered but by appearance of intrinsic impurities in the course of $PbWO_4$ solid-phase synthesis due to partial loss of oxygen bound with W atoms [10] as well as of PbO (by analogy with the CdO loss under heat treatment of $CdWO_4$ revealed before [11]).

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Кількісна оцінка вмісту мікродомішок у вихідній сировині та сцинтиляційних монокристалах вольфрамату свинцю

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Наведено результати визначення домішкового вмісту у сировині та монокристалах вольфрамату свинцю на різних стадіях технологічного процесу. Вміст заліза визначали екстракційно-фотометричним методом з двостадійним розкриттям зразків. Вміст Al, Bi, Cr, Cu, Mg, Mn, Mo, Ni, Si, Sn, Ti визначали методом атомно-емісійної спектрометрії з дуговим джерелом збудження. Показано, що різниці, що встановлено, на рівні вмісту перелічених домішок у забарвлених та незабарвлених кристалах недостатньо для суттєвого впливу на їх світопоглинання. Висловлено припущення, що вказані відмінності обумовлені появою власних домішок у процесі твердофазного синтезу сировини.