The influence of BaF_2 on scintillation properties of $PbWO_4$ crystal

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$PbWO_4$ crystals doped with BaF_2 was grown up by using modified temperature-grads technique. The crystal defects were investigated by chemical etching. The XRD of the sample has shown that the peaks were at normal sites, but the lattice parameters was slightly larger than that of pure $PbWO_4$ crystal. The transmittance spectrum along *c* axis of the $PbWO_4$:BaF_2 crystal has evidenced a higher transmittance than that of pure $PbWO_4$ crystal. The luminescence intensity of the 400–450 nm peak in X-ray excited luminescence spectrum of the $PbWO_4$:BaF_2 crystal is increased significantly, about twice than that of pure $PbWO_4$ crystal. The light yield of BaF_2 doped $PbWO_4$ crystal was enhanced up to 2.5 times. These results show that BaF_2 doping of $PbWO_4$ can improve scintillation properties of the crystal for medium-energy particle detection.

Выращена партия кристаллов $PbWO_4$, легированных BaF_2, с применением модифицированного способа температурных градиентов. Дефекты в кристаллах исследованы методом химического травления. Рентгенография образцов показала, что пики имели обычное расположение, однако параметры решетки несколько превышали параметры для кристалла чистого $PbWO_4$. Спектр пропускания вдоль оси *c* кристалла $PbWO_4$: BaF_2свидетельствовал о повышении коэффициента пропускания по сравнению с кристаллом чистого $PbWO_4$. Интенсивность пика люминесценции с максимумом в области 400–450 нм в спектре рентгенолюминесценции увеличивалась почти вдвое по сравнению с кристаллом чистого $PbWO_4$. Световыход кристалла $PbWO_4$, легированного BaF_2, повышался в 2,5 раза. Эти результаты показывают, что легирование $PbWO_4$: BaF_2 может улучшить сцинтилляционные характеристики кристалла. Кристалл может рассматриваться как перспективный материал для детекторов частиц средней энергии.

Because of its remarkable scintillation character with short decay time, high density and high radiation resistance, $PbWO_4$ (PWO) crystal was chosen as scintillator in high energy physics experiments such as LHC and ALICE at CERN, BTEV at Fermi Lab, PANDA at Darmstadt and so on [1–6]. But the application of this crystal in the quickly growing market of X-ray transmission devices for medical diagnostics (CT) and various fields such as in PET and medium-energy particle detectors, is rather problematic due to low scintillation light yield (LY), which is more than two orders of magnitude less than that of NaI (Tl). The increase of LY of PWO by several times would open up a wide field of practical applications for this material [7]. In order to improve its LY, many works had been done to dope PWO with some special impurities.

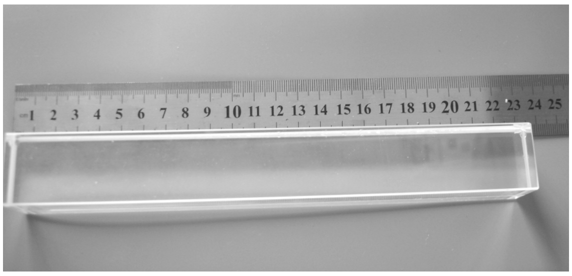

Fig. 1.

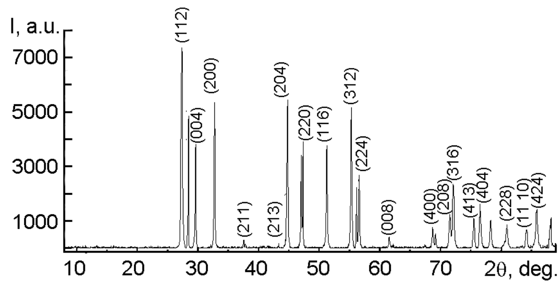

Fig. 2. X-ray diffraction pattern of $PbWO_4$: BaF_2 crystal powder.

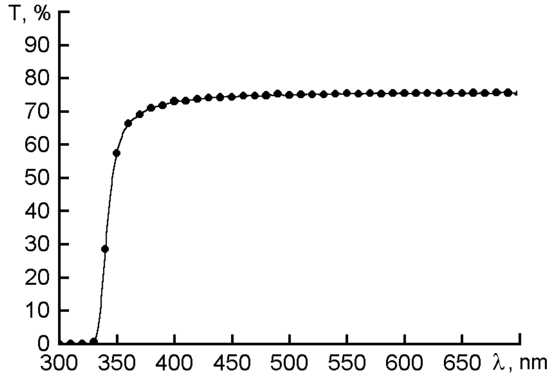

Fig. 3. Transmittance of a $PbWO_4$: BaF_2 crystal along *c* axis (sample size 20×20×25 mm^3).

The PWO doped or co-doped with Mo, Cd, Ca, Nb, Sb were found to have higher light yields than pure PWO crystal in finite extent, and their decay times are increased, respectively [8–9]. In this work, a new attempt to use BaF_2 as a dopant in PWO crystal is reported. The significant LY increase and improved transmittance evidence the excellent scintillation properties of the $PbWO_4$: BaF_2 crystal. Hence, $PbWO_4$: BaF_2 crystal may be of promise for medium-energy particle detector.

PWO doped with BaF_2 was grown along <001> orientation using modified Czochralski technique. The BaF_2 content in the melt was about 2000 ppm. The growth rate was 0.6 mm/h. The axial temperature gradient at the growing solid-melt boundary was about 30 deg/cm. The crystals are all colorless and fully transparent as is seen in Fig. 1. Using Si crystal as a reference, the crystal structure was investigated at room tempreture X-ray diffraction technique, the results being shown in Fig. 2. One of the crystals was cut into 20×20×25 mm^3 samples to measure its transmittance spectrum while the others were cut into 25×25×200 mm^3 samples. All of the samples were finely polished. The transmittance was measured using a SHIMADZU UV2501(PC)S spectrometer. The results obtained are shown in Fig. 3. The X-ray excited luminescence was measured using a X-ray Excited Luminescence Spectrometer, and the results were shown in Fig. 4. The light yield at room temperature was measured using a HAMAMATSU Photomultiplier Tube (R2059PMT) which has a bialkali photocathode and quartz window. A collimated γ-ray source, such as ^{60}Co or ^{137}Cs, was used to excite the sample. The results are shown in Table.

Fig. 2 presents an X-ray diffraction pattern of $PbWO_4$: BaF_2 crystal powder at room temperature. All the peaks in this Figure agree with those of the pure PWO crystal. From the Figure, the lattice parameters of this crystal were calculate. Those are: $a = b = 5.4638$ Å, and $c = 12.043$ Å, thus coincident with the characteristics of PWO crystal belonging to the C_{4h}^{6}–$I_{41/\alpha}$ space group. The unit cell volume is 359.53 Å^3, which is slightly larger than that of pure PWO crystal. Thus, the Ba^{2+} and F^- ions expand the PWO crystal cell. This result should be ascribed to the facts that the bond value of F^- ions is equal to one O^{2-} ion, thus, more ions are pulled into the cell by the Coulomb forces to maintain the equal bond value in the cell, and so cause the cell expansion.

Fig. 3 is a transmittance spectrum of a 20×20×25 mm^3 $PbWO_4$: BaF_2 crystal sample along *c* axis. The absorption edge is at 330 nm. Transmittance is 65 % at 360 nm, 70 % at 420 nm, and up to 76 % at 650 nm, what is slightly higher than that of pure PWO crystal and exceeds the requirement of CERN [10]. The improved transmittance is favorable for the scintillation properties of the crystal. There is no absorption peaks in the wavelength range from 330 to 700 nm.

Fig. 4 presents an X-ray excited luminescence spectrum of a $PbWO_4$: BaF_2 crystal at room temperature. There is a luminescence

Table. Light yield of pure PWO and PWO:BaF_2 crystals

Light yield	Pure PWO	BaF_2:PWO	Sample size, mm
L.Y./200 ns (p.e./MeV)	21	52	20×20×25
% □BGO as 100□	2.8 %	~6.9 %	20×6×6

band peaked at 400–450 nm, which agrees with that of pure PWO crystal, but the wavelength is shorter than that of the respective peak of PWO crystal in this wavelength range. However, the luminescence intensity is increased significantly (up to 2 times) as compared to that of pure PWO. There is no luminescence peak in the wavelength range from 500 to 600 nm that is one of the characteristic peaks of pure PWO crystal in green wavelength range. The three facts, the shorter peak wavelength, the sharply increased luminescence intensity and the disappearance of characteristic peak at green wavelength range, show the evident improvement of luminescence properties of PWO crystal.

Table presents the LY of $PbWO_4$: BaF_2 crystal and pure PWO crystal at 200 ns at room temperature. It is seen that the LY of $PbWO_4$: BaF_2 crystal is increased up to 52 p.e./MeV, which is about 2.5 times higher than the LY of pure PWO crystal. It attains 6.9 % as compared to the LY of BGO crystal, but the percentage LY value pure PWO crystal is only 2.8 % as shown in the Table. The LY increase in doped with BaF_2 is effective and significant. Since the LY of PWO crystal reaches 8 % of that of BGO crystal, it can be used as scintillator in medical CT instrument, PET et al.

Basing on the above facts, it can be stated that BaF_2 is successfully doped into PWO crystal, and Ba^{2+} and F^- ions, especially the F^- ions, effect considerably the luminescence intensity and LY of PWO crystal. For the facts that there are no remarkably differences on the bond value and ion radii comparing with Ba^{2+} and Pb^{2+} ions, but they are markedly different comparing with one O^{2-} and two F^- ions, we presumed that the significant differences are mainly induced by the fact that about two F^- ions occupying one O^{2-} site in PWO crystal. A.Borisevich et al. [3] also found similar effects on the scintillation properties in PbF_2 doped PWO crystal, but the effect is weaker than that in $PbWO_4$: BaF_2

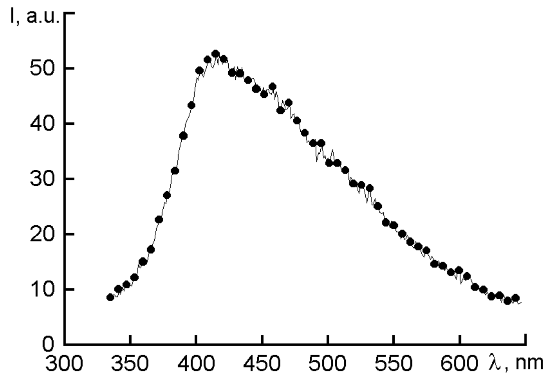

Fig. 4. X-ray excited luminescence spectrum of a $PbWO_4$: BaF_2 crystal at room temperature.

crystal. Those authors believe also that the main reason should come from the fact that F^- occupying O^{2-} site.

Thus the large-size PWO crystals doped with BaF_2 were successfully grown up by modified Czochralski technique. The lattice parameters of $PbWO_4$: BaF_2 are larger than those of pure PWO. This phenomenon may be attributed to Ba^{2+} and F^-, which cause the PWO lattice distortion. The preliminary measurement results show that PWO crystal doping with BaF_2 can improve the spectroscopic and scintillation properties. Perhaps the scintillation properties of $PbWO_4$: BaF_2 will be further improved by the optimization of growth parameters.

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Вплив BaF_2 на сцинтиляційні властивості кристалів $PbWO_4$

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Кристали $PbWO_4$, леговані BaF_2, вирощені з застосуванням модифікованого способу температурних градієнтів. Дефекти у кристалах досліджено методом хімічного травлення. Рентгенографія зразків показала, що піки мали звичайне розташування, однак параметри гратки дещо перевищували параметри для кристала чистого $PbWO_4$. Спектр пропускання вздовж осі *c* кристала $PbWO_4$: BaF_2 свідчив про підвищення коефіцієнта пропускання у порівнянні з кристалом чистого $PbWO_4$. Інтенсивність піка люмінесценції з максимумом у межах 400–450 нм у спектрі рентгенолюмінесценції збільшувалася майже удвічі у порівнянні з кристалом чистого $PbWO_4$. Світловихід кристала $PbWO_4$, легованого BaF_2, підвищувався у 2,5 рази. Ці результати свідчать, что легування $PbWO_4$ BaF_2 може покращити сцинтиляційні характеристики кристала для детектування частинок середньої енергії.