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Physical principles of industrial growing technology of lead tungstate (PWO) for high-energy physics applications

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A new model is proposed describing defects responsible for optical properties and radiation hardness of PWO single crystals. The model clarifies origins of optical properties important for application of PWO as a scintillator in high-energy physics experiments and provides a base for purposeful optimization of growth and annealing processes to achieve reliable reproducibility of specified parameters in production of PWO scintillators on industrial scale. The model is based on assumption that the optical properties of nominally pure PWO are determined mainly by inherent inclusions of tungsten oxides with variable tungsten valence WO_{3-x} that are formed during the crystal growth and may be modified by thermal treatment or irradiation. The new concept enabled development of industrial technology at "North Crystals" company, where scintillation blocks with parameters specified for CERN ALICE and CMS projects are being produced now with reproducibility of about 100 %.

Предложена новая модель для описания дефектов, ответственных за оптические свойства и радиационную стойкость монокристаллов PWO. Модель поясняет происхождение оптических характеристик, имеющих важное значение для применения PWO в качестве сцинтиллятора в экспериментах по физике высоких энергий, и обеспечивает основу для направленной оптимизации процессов роста и отжига с целью достижения надежной воспроизводимости заданных параметров при промышленном производстве сцинтилляторов на основе PWO. Модель основывается на допущении, что оптические свойства номинально чистого PWO определяются, в основном, неизбежными включениями оксидов вольфрама с различной валентностью вольфрама WO_{3-x}, образующимися в процессе роста кристалла, и могут быть модифицированы путем термообработки или облучения. Новая концепция обеспечила возможность разработки промышленной технологии в фирме "Северные Кристаллы", где сцинтилляционные блоки с параметрами, соответствующими требованиям проектов CERN "ALICE" и "CMS", в настоящее время изготовляются с воспроизводимостью, близкой к 100 %.

Development of industrial production of lead tungstate (PWO) single crystals for high energy physics experiments is impossible without clear understanding of mechanisms responsible for optical properties and radiation hardness of PWO. The approach to these problems has to be aimed not only at interpretation of all experimental data available, but also, and predominantly, at practical application of this basic knowledge to produce crystals with properties purposefully designed by selection of necessary technological conditions for growth and annealing of PWO. Intense study of fundamental processes responsible for optical and scintillation properties and radiation hardness has been stimulated in 1994 by choice of PWO as a scintillation material for CMS and ALICE projects at CERN.

Now it is generally accepted that ionizing radiation does not affect the emission spectrum of PWO. The recombination mechanisms in PWO are not influenced by irradiation, and the decreased quantum yield in irradiated crystals is caused mainly by irradiation-induced absorption in the spectral region of PWO emission [1, 2]. In certain circumstances, exposure to ionizing radiation may also result in bleaching of the crystal [3]. Fast scintillations are observed only in the crystals with emission in the blue region (420–440 nm). The decay time of the green luminescence component is considerably longer than that of the blue component, and application of the crystals with the green component in emission spectrum is rather limited [4].

A relationship between absorption of as-grown PWO in near UV region (~350 nm) and value of optical absorption change induced by irradiation has been established, and the absorption near 350 nm is now accepted at CERN as a figure of merit for radiation hardness [5].

Recent studies have unexpectedly revealed that all nominally pure PWO crystals, irrespective of growth and annealing technologies used, contain internal defects. The defects result in increased UV absorption and trend to coloration under intense irradiation. Doping with trivalent lanthanides was found to increase the crystal transparency and to improve radiation hardness of PWO [6]. Thus, the doping seems to inhibit formation of the defects deteriorating the PWO optical quality. Defects containing Pb^{3+} ions and O^- centers have been put forward as the main cause of poor radiation hardness and increased optical absorption in the 350–370 nm and 420 nm regions, respectively [7]. Improvement of optical properties and radiation hardness in the doped crystals is explained by an excessive positive charge introduced into the lead sublattice due to doping and inhibiting formation of Pb^{3+} and O^- defects, which are more favorable in undoped crystals to compensate the charge of natural lead vacancies [6]. It is well established now that defect formation in PWO depends strongly on the amount and composition of impurities contained in the melt. The requirements for optimal melt are elaborated in [8], and the influence of the impurities on the PWO properties are extensively studied in [6, 8–11].

However, analysis of published results shows that the concept of Pb^{3+} and O^- centers fails to interpret the whole variety of experimental data on PWO [10]. Recently, a new approach capable of explanation of the experimental results quite well has been proposed [12–14]. The approach is based on assumption that the optical properties and radiation hardness of PWO are due mainly to inclusions of tungsten oxides with variable valence WO_{3-x}. These inclusions are formed by atoms inherent in the PWO crystal and enter the crystal during its growth. The concept has been developed in [15, 16], where the influence of the defects on the PWO crystal properties and the relation between the defect formation and the technological conditions of growth and annealing has been revealed.

In this work, we generalize the new concept of defect formation in PWO. Origins of optical absorption and radiation hardness of PWO as well as the relation between the properties and the technological measures to optimize the growth and annealing processes are especially addressed. The problem is treated from the viewpoint of implementation of the new approach into industrial production of PWO single crystals used as scintillator material for radiation detectors in high energy physics experiments.

The most important experimental results relevant to defect formation can be summarized as follows. An ideal PWO crystal is colorless and does not oxidize or reduce under heat treatment or irradiation. Exposure to ionizing radiation results neither in coloration nor in increased absorption in the near UV region. Modification of optical properties of nominally pure PWO single crystals under external influence is caused by structural defects, which are "the weakest link" in applications of the single crystals. Modification of the defects in PWO under irradiation can be treated as a solid-phase reaction resulting in formation of new chemical compounds.

We have tested sets of undoped and doped samples grown and annealed in different conditions. It was revealed that the melt gets enriched in tungsten during the growth process. This is explained by predominant evaporation of lead in the form of Pb_2WO_5. The excess tungsten is favorable for formation of tungsten oxides WO_{3-x} entering the $PbWO_4$ crystal during the growth [13].

The crystal color is defined mainly by light absorption in these inclusions and depends the x value in the formula WO_{3-x}. The color change of a PWO crystal under heat treatment is consistent with the color change of WO_{3-x} under the corresponding treatment. The color of WO_3 is yellow; $WO_{2.96}$, green, $WO_{2.8-2.88}$, blue; $WO_{2.7-2.75}$, violet; and WO_2, brown. Under reductive annealing, the color of a PWO crystal changes gradually in the sequence from yellow to green to colorless to blue to violet to brown. Under annealing of the crystal in oxidizing conditions (when partial oxygen pressure in the environment exceeds the equilibrium value), the transformation proceeds in the opposite direction. A similar color transformation of PWO takes place under ionizing irradiation [14]. Under extended reductive annealing or high irradiation dose, the undoped crystal turns black while the lanthanide doped crystal acquires a violet shade [12, 14]. Finally, it has been demonstrated that the green component in radioluminescence spectrum of PWO is emitted only from the crystal surface layers [15, 16].

Analysis of the experimental data on PWO optical properties and their modifications under annealing and irradiation enabled us to bring together the experimental evidences and experience in technology development and to formulate the main features of defects responsible for PWO properties under consideration in view of application of PWO crystals as scintillators in high energy physics experiments. Thus, the color and its modifications under external influences are defined mainly by inclusions of WO_{3-x} $(0 < x < 1)$, the composition (x) thereof depending on conditions of growth and annealing. WO_{3-x} inclusions are inherent defects in PWO. These inclusions are responsible for the crystal color and absorption in the near UV region. Tungsten valence in the clusters changes during the crystal growth, under annealing and irradiation, thus causing changes in the crystal color. Under reductive annealing, transformation of the inclusions proceeds in the sequence: WO_3–$WO_{2.96}$–$WO_{2.8-2.88}$–$WO_{2.7-2.75}$–WO_2 as the tungsten valence in the WO_{3-x} inclusions changes from 6 to 4. This process results in the color change in the sequence: yellow-transparent-blue-violet-black. At $x = 0$, the crystal has absorption in the range of 350 to 450 nm and is yellow. Increase in x results in increasing absorption at the long-wavelength side from this absorption band. At $x = 0.3$, the crystal acquires an intense violet coloration. In this range of x values, an optimal value x_{opt} corresponding to a transparent crystal is to be attained to provide good crystal quality. The quantum yield of such crystals also attains the maximum value.

Doping of PWO melt by oxides L_2O_3 (L = Y, La, Gd etc.) prevents formation of inclusions WO_{3-x}. Instead, clusters $W_{1-y}L_yO_{3-x}$ $(0 < x < 0.3)$ enter the PWO crystal. Influence of these clusters on PWO optical properties is weaker than that caused by WO_{3-x}. Moreover, binding of oxygen in $W_{1-y}L_yO_{3-x}$ is stronger than that in WO_{3-x}. Consequently, tungsten valence in the doped PWO crystals is less vulnerable to external influence. Amount of the doping oxide L_2O_3 should be sufficient to substitute the undesirable clusters WO_{3-x} by more favorable inclusions $W_{1-y}L_yO_{3-x}$. On the other hand, excessive inclusion of $W_{1-y}L_yO_{3-x}$ into the crystal deteriorates its optical transparency. The optimal doping level also results in minimal absorption in the near UV region.

Radiation hardness of undoped PWO is defined mainly by WO_{3-x} inclusions; in doped PWO, by $W_{1-y}L_yO_{3-x}$ ones. Influence of ionizing radiation is similar to that of oxidizing-reducing annealing. In both cases, tungsten oxidation level in the clusters is changed. As a result, the crystal color changes. Irradiation of PWO crystal containing WO_{3-x} ($W_{1-y}L_yO_{3-x}$) inclusions with oxygen content lower than optimal ($x < x_{opt}$, yellow color) results in bleaching of the crystal. In lanthanide-doped PWO crystals, the WO_{3-x} inclusions are substituted by $W_{1-y}L_yO_{3-x}$ ones, which are more resistive to change the tungsten valence under irradiation.

The green emission component from the bulk of the crystal is observed only in PWO grown from melt containing MoO and some other oxides resulting in formation of clusters $PbMoO_4$, etc. The green component is absent in the luminescence spectrum of nominally pure PWO crystal. The green luminescence may be emitted only from the crystal surface containing relevant structural defects.

Thus, the features discussed above can be summarized into a general conclusion that changes in physical properties of PWO are due to chemical or structural transformations in the crystal. On the other hand, if external factors affect the crystal chemical composition or structure, this is reflected in its physical properties. This approach was implemented in development of PWO growth and annealing technology on industrial scale at "North Crystals" Company, Apatity. The PWO crystals meeting specifications of the CERN project ALICE are being produced with about 100 % reproducibility at the rate of 125 to 135 pieces per year for each growth facility. More than 10000 crystals for the ALICE project are already produced. Production of scintillation blocks for the CERN project CMS is started this year.

References

1. E.Auffray, P.Lecoq, A.Annenkov, M.Nikl et al., *CMS NOTE 97/54*, July 8, 1997, CMS CERN, CH-1211, Geneva 23, Switzerland.
2. Ren-Yuan Zhu, *IEEE Trans.Nucl. Sc.*, **44**, 468 (1997).
3. S.Baccaro, P.Bohacek, B.Borgia et al., *Phys. Stat. Solid. (a)*, **164**, R9 (1997).
4. G.Tamulaitis, S.Burachas, V.P.Martinov et al., *Phys.Stat. Solid. (a)*, **157**, 187 (1996).
5. E.Auffray, M.Lebeau, P.Lecoq, M.Schneegans, *CMS Note*, May 19, 1998.
6. M.Kobayashi, Y.Usuki, M.Nikl, K.Nitsh, *Nucl.Instr.Meth.Phys.Res.*, **A 399**, 261 (1997).
7. M.Nikl, *J.Appl.Phys.*, **82**, 5758 (1997).
8. A.Annenkov, M.V.Korzhik, P.Lecoq, *Nucl. Instr.Meth.Phys.Res.*, **A 490**, 30 (2002).
9. M.Kobayashi, Y.Usuki, M.Ishi et al., *Nucl. Instr.and Meth.Phys.Res.*, **A 465**, 428 (2001).
10. M.Nikl, *Phys.Stat.Solid., (a)*, **178**, 595 (2000).
11. S.Burachas, A.Apanasenko, B.Grinyov et al., *Intr.J.Inorg. Mater.*, **3**, 1101 (2001).
12. S.Burachas, S.Beloglovski, I.Makov et al., *Nucl.Instr.Meth.Phys.Res.*, **A486**, 83 (2002).
13. S.Burachas, S.Beloglovski, I.Makov et al., *J. Cryst.Growth*, **243**, 367 (2002).
14. S.Burachas, S.Beloglovski, I.Makov et al., *Nucl.Instr.Meth.Phys.Res.*, **A505**, 656 (2003).
15. S.Burachas, S.Beloglovsky, D.Elizarov et al., *Radiat. Meas.*, **38**, 367 (2004).
16. S.Burachas, S.Beloglovsky, D.Elizarov et al. to be published in *Nucl. Instr. Meth.Phys.Res.* **A 537**, (2005).

Фізичні основи промислової технології вирощування кристалів вольфрамату свинцю для застосування у фізиці високих енергій

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Запропоновано нову модель для опису дефектів, відповідальних за оптичні властивості та радіаційну стійкість монокристалів PWO. Модель пояснює походження оптичних характеристик, що мають важливе значення для застосування PWO як сцинтилятора в експериментах з фізики високих энергій та забезпечує основу для цілеспрямованої оптимізації процесів росту та відпалу з метою досягнення надійної відтворюваності заданих параметрів за умов промислового виробництва сцинтиляторів на основі PWO. Модель базується на припущенні, що оптичні властивості номінально чистого PWO визначаються, головним чином, неминучими включеннями оксидів вольфраму з різною валентністю вольфраму WO_{3-x}, які утворюються у процесі росту кристала, та можуть бути модифіковані шляхом термообробки або опромінення. Нова концепція забезпечила можливість розробки промислової технології у фірмі "Северные Кристаллы", де сцинтиляційні блоки з параметрами, які відповідають вимогам проектів CERN "ALICE" и "CMS", на даний час виготовляються з відтворюваністю, близькою до 100 %.