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Optimization of thermal conditions in growing of GSO:Ce crystals by Czochralski technique

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Crystallization conditions of gadolinium silicate Gd_2SiO_5:Ce have been studied depending on the crystallographic direction of the crystal growing in various thermal conditions. For the developed crystallization assembly, it is just the crucible position relative to the inductor 5 to 7 mm higher than the inductor upper turn that has been shown to be the optimum one. Determined have been the growing parameters and regimes providing the obtaining of high spectrometric quality crystals of up to 50 mm in diameter and up to 150 mm length. The ∅40×40 mm^2 scintillators prepared from those crystals show the energy resolution 10.4 % under γ irradiation with ^{137}Cs (662 keV).

Исследованы условия кристаллизации силиката гадолиния Gd_2SiO_5:Ce в зависимости от кристаллографического направления их выращивания в различных тепловых условиях. Показано, что для разработанного кристаллизационного узла оптимальным является расположение тигля относительно индуктора на 5–7 мм выше верхнего витка индуктора. Определены параметры и режимы роста, позволяющие получать кристаллы диаметром до 50 мм и длиной до 150 мм высокого спектрометрического качества. Сцинтилляторы ∅40×40 мм^2, изготовленные из этих кристаллов, показали энергетическое разрешение 10,4 % при облучении γ-излучением ^{137}Cs энергией 662 кэВ.

Gadolinium oxyorthosilicate (Gd_2SiO_5) single crystals activated with cerium (GSO:Ce) are known to be crystal luminophors showing a high conversion efficiency of ionizing radiation and a short (30 to 60 ns) decay time, thus being a material suitable for fast-action detecting systems. However, the wide use of GSO:Ce is hindered by its high cost that is due not only to the production costs of the raw materials but mainly to difficulties in production of crystals with a low optical density that, in addition, should not fail during the growing and machining.

This failure is connected with the fact that GSO:Ce crystals show a perfect cleavage along the (100) plane. Thus, the crystal may be stratified up to complete splitting both in the course of growth and under mechanical treatment. Moreover, GSO:Ce belongs to monoclinic syngony (the space symmetry group $P2_1/C$) that predetermines a pronounced anisotropy of its phusical properties. In particular, the thermal expansion coefficient of GSO:Ce in the [010] direction exceeds by a factor of 2 or 3 that for [100] one, thus increasing also the crystal failure probability along the (010) plane [1]. The failure probability increases sharply when macro-inclusions are present in the crystal that are a typical structure defects in GSO:Ce. These macro-inclusions have been established to be ordered and to form chains extended along the [001] direction that may be localized in the crystal volume as a growth column or alternating transversal bands of inherent impurity [2].

In [1–6], the GSO:Ce growing process has been studied comprehensively and, basing on the experimental results, it has be

concluded that it is necessary to grow GSO:Ce under a low temperature gradient (about 10 K/cm). Also, it is reasonable to orient the crystal in such a manner that the crystallographic direction [010] would coincide with the lowest temperature gradient in the crystallizer temperature field and the [100] one would be perpendicular to the growing axis. Moreover, the growth gas medium should contain oxygen (3000 ppm) to provide the crystal strengthening. To reduce the macro- and micro-defects content in the crystal, it has been recommended to the ratio between the crystal rotation speed and its diameter in a manner providing the flattened crystallization front shape during the growing. In particular, the rotation speed should amount 35 rpm if the growing crystal diameter is to be of 50 mm.

Having no doubts about the experimental results obtained in the works cited above, we believe that the quantitative estimations therein are related to specific variants of the procedures developed to grow the GSO:Ce crystals by Czochralski technique. As a whole, the experimental findings point to the necessity of further investigations to improve the reliability of the perfect GSO:Ce crystals technology.

The optimum of the single-phase crystallization and the crystal macro-structure in the course of growth from the binary oxide melt is attained when the clusters of the components forming the crystal are stereochemically matched with the growth surface structure and crystallization centers misoriented in relation to the crystallographic growth direction are absent on the surface [7]. Technologically, this task is attained by proper selection of thermal conditions providing the melt overheating near the crucible wall by rendering additional energy and its removal into environment due to radiant exitance of emitting surfaces and convective heat transfer.

In the Czochralski method with inductive heating, the melt free volume can be overheated either by increasing the radiant exitance of the crystal or by changing the crucible position along the inductor axis [1] when the crucible upper part is shifted out of the inductor towards the region of the inductor edge effect where the magnetic flux density drops sharply.

The raw material to grow the GSO:Ce crystals was synthesized in solid phase from gadolinium and silicon oxides (Gd_2O_3, SiO_2) of industrial purity grade. Cerium oxide CeO_2 of the same purity grade was used as the activator. The initial oxides were calcined previously to remove moisture and volatile impurity.

The GSO:Ce crystals were grown from iridium crucibles of 90 mm diameter in nitrogen (argon) medium with oxygen additive up to 1.5 % by volume. The pulling speed was 1.5 to 3.0 mm/h, the rotation one, 30 to 40 rpm. An iridium diaphragm was placed above the crucible at a distance 2 to 3 mm from the upper edge. The melt level prior to growing was 4 to 5 mm lower than the upper crucible edge. To control the temperature gradient above the melt surface, an additional heater was mounted in the upper part of the crystallization assembly. Its working regime was controlled by differential thermocouples T_1 (10 mm above the initial melt level) and T_2 (200 mm above the same level).

The initial stage of the growth process, namely, introduction of the seed crystal into contact with the melt and formation of the growth cone up to the pre-specified diameter, is among the technologic stages of importance. This stage is the most critical one when the GSO:Ce crystal is grown along the [010]. This is connected with the fact it if just the [001] that predominating growth direction of a GSO:Ce crystal in the thermal symmetry typical of the Czochralski technique. Therefore, if the growth start along [010] is not preceded by the melt overheating, formation of blocks and spontaneous crystal reorientation to a direction near to [001] are highly probable [2]. Such crystal fail already at the initial stage of post-growth annealing. The situation is complicated because there are no any signs of the spontaneous crystal reorientation, including the visual ones. The GSO:Ce crystals grown along [001] are less disposed to the formation of blocks. It is just this fact that has predetermined the selection of the GSO:Ce growing direction. In the course of growing, the melt is evaporated at a rate increasing with the overheat level. The composition analysis of crystalline condensate has shown a Gd_2O_3:SiO_2 ratio close to 1:1. This fact evidences the azeotropic character of the melt evaporation, thus, the melt stoichiometric composition is not to be corrected at repeated growing.

Our measurements on the melt thermo-e.m.f. have shown that as the crucible is shifted down by 10 or 15 mm as compared to the inductor, the melt temperature becomes lowered and 20–25 mm above the crucible bottom, the temperature gradient changes its sign. This is confirmed by

thermo-e.m.f. measurements over the melt depth that changes its polarity in this region. This phenomenon results in a reduction of the effective melt volume involved in the crystal formation, since the melt part adjacent to the bottom is not involved in the total melt convection. In these conditions, we did not obtain the crystals of a satisfactory quality. A strong light scattering and a column of macro-inclusions were observed in those crystals which, in addition, become stratified under machining.

In [2], the macro-defects have been shown to be arranged asymmetrically over the crystal cross section. In our opinion, this is due to nonequivalence of the crystallization pressure (CP) that is defined by the following relationship [8]

$$\pi = \frac{\Delta T \cdot Q}{T_0 \cdot V_1}, \qquad (1)$$

where ΔT is the crystal overcooling; Q, the molar crystallization heat; T_0, the substance melting temperature; V_1, the molar volume of the crystal. For each growing form involved in the crystal formation, there is a certain limiting CP value; below of that value, the growing form is capable of hindering the impurity entering into the crystal being grown. The limiting CP is attained due to accumulation of the inherent impurity near the growth surface. The inherent impurity is the aggregated melt particles where the gadolinium cations forming the crystal are coordinated in a different fashion than in the growing form(s). Taking into account that the $Gd_2Si_2O_7$ phase exists in the Gd_2O_3–SiO_2 phase diagram along with the $GdSi_2O_5$ one, it is just the $Gd_2Si_2O_7$ phase (rhombic syngony) where Gd ions have the coordination number 7 only that can be assumed to be the inherent impurity, by analogy with other oxide systems. In addition, the pseudo-gaseous structure complexes being formed in the melt under overheating may also give rise to the "inherent impurity".

When the crucible is shifted up (10 to 12 mm above the upper inductor turn), the convention vector in the surface melt layer changes its direction. In this case, visually observable crystals are formed near the crucible wall. The melt surface heating by means of the upper heater results in disappearance of the crystallites and reduction of the axial temperature gradient behind of the diaphragm from 30–50 K/cm to 10 K/cm that is recommended in [4]. Nevertheless, good quality crystals are not obtainable in these conditions, too. Macro-inclusions in the upper and lower parts of the GSO:Ce crystals grown in the "warmed" crystallization assembly are characteristic defects. Those flaws make it impossible to produce bulk scintillators of a size comparable with that of the grown crystal. The dynamics of temperature field variation in a crystallization assembly provided with an additional heater during the full growing cycle is shown in Fig. 1a.

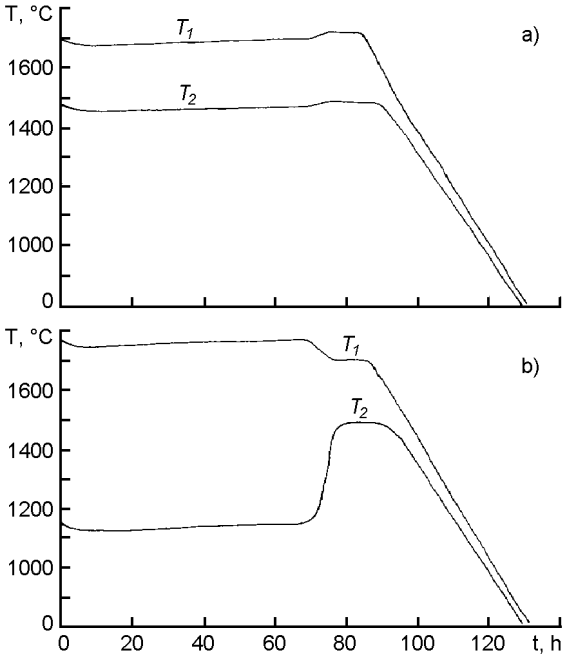

Fig. 1. Dynamics of thermal condition variations at various stages of the crystal formation during its automated growing with additional heating. T_1, temperature variation at 10 mm distance from the initial melt level; T_2, the same at 200 mm from the initial melt level. (a) the additional heating during the full growing cycle (starting from seeding); (b) the additional heating used during the final stage (the lower cone formation).

The optimum crucible position in relation to the inductor in the specific crystallization assembly design was found to be 5 to 7 mm above the upper inductor turn. The thermal field distribution for this case was selected so that at the initial growth stage, the temperature gradient at a distance of 10 mm from the melt to the diaphragm was about 150 K/cm, while that in the space between the diaphragm and the furnace upper butt, about 30 to 50 K/cm. The addi-

tional heater in the upper part of the crystallization assembly was switched on starting from the initial moment of the lower cone of the crystal, when the crystal upper part attained the temperature zone corresponding to its elastic strain. At the same time, the chamber at this stage was evacuated, thus enabling to finish the crystal growing and cooling process at an axial temperature gradient not exceeding 3 to 5 K/cm [9]. The dynamics of temperature field variation in a crystallization assembly for the above regime of the GSO:Ce crystal growing is shown in Fig. 1b.

In manufacturing of high optical perfection GSO:Ce crystals with stable scintillation characteristics, one of problems is associated with cerium dopant, the efficient distribution coefficient (α) thereof capable of variation within a wide range (from 0.5 to 0.9 [3]). The actual α value is defined as [10]

$$\alpha = \frac{\alpha^*}{\alpha^* + (1 - \alpha^*) \cdot e^{-v\delta/D}}, \qquad (2)$$

where α^* is the equilibrium distribution coefficient of cerium ions; ν, the crystal growth speed; δ, the diffusion layer thickness; D, diffusion coefficient of cerium ions in the melt. The δ value depends on the growth process parameters (ν and ω, being the crystal growth and rotation speeds) as well as on the factors defining the melt physical properties, namely, its viscosity (η) and D. Due to specific features of the Czochralski technique defining the temperature variation in the course of growth, η and D are variable parameters with the instant values depending on the variation of the growth thermal conditions. If ν and ω are constant process parameters, then $\alpha = f(\delta/D)_T$. At a low growth speed and a constant rotation speed, we can write $\delta = (D_T^{1/3} \cdot \eta_T^{1/6}) \cdot 1.6\omega^{-1/2}$ where D_T is the instant value of thermal convective diffusivity and η_T, the melt kinematic viscosity, both being functions of temperature.

Bearing in mind that the D values for vast majority of impurities differ by several decimal orders from η for melted oxides (the Schmidt factor exceeds 1), the diffusion layer thickness can be assumed to be defined mainly by the melt viscosity. The melt overheating during the growing provides a viscosity reduction and the attained overheating value defines in the end the actual α value.

A reduction of α due to oxygen introduction to the gas medium (nitrogen) at GSO crystal growing has been reported [3]. This is confirmed in our experiments where a cerium content increased by 10 to 15 % has been found over the crystal length of 180 mm. It is known [13] that a common feature of melted oxides obtained in an inert gas medium consist in a stoichiometric disordering in oxygen that is rather high, in particular, in nitrogen atmosphere. This is due to the fact that under oxygen deficiency in the melt, nitrogen particles interact with the cations and form rigid directed nitride bonds that result in an increased melt viscosity. An increased partial oxygen pressure in the gas medium and its diffusion into the melt cause a reduced nitrogen solubility and the nitride bond destabilization, thus reducing the melt viscosity. This finding is confirmed, in particular, by the viscosity study of $Y_3Al_5O_{12}$ depending on the gas medium pressure and composition [13]. In that work, the increase of oxygen concentration in nitrogen atmosphere up to 2 % (vol.) causes a reduction of the melt dynamic viscosity by about 25 %.

It can be assumed basing on the above that the cerium distribution coefficient at GSO growing in nitrogen atmosphere containing oxygen is due to a great extent to reduced melt viscosity and resulting decreased thickness of the diffusion layer through which cerium ions are transported. At the same time, our experiments have shown that the oxygen partial fraction of 0.25 to 0.30 % (vol.) (introduced initially into the gas medium and being controlled during the whole growing cycle using a "Zirkon" gas analyzer) is not a constant parameter of the growing process due to oxidation of the iridium crucible resulting in a reduction of the oxygen concentration introduced into the initial static gas atmosphere by 5.0 to 7.0 %. This contributes additionally to the multifactor dependence of the diffusion layer thickness that can be smoothened in part by selecting the thermal conditions favoring the melt overheating as the crystal is pulled.

The single-phase, crack-free, optically homogeneous GSO:Ce crystals containing no macro-defects and light scattering centers up to 40 mm in diameter and up to 150 mm length were grown in such thermal conditions, although the crystallization assembly of the above design makes it possible to obtain the crystals of up to 50 mm in dia (see Fig. 2). The $\varnothing 40 \times 40$ mm^2 scintillators manufactured from those crystals have shown the energy resolution of 10.4 % under

Fig. 2. GSO crystal grown using the additional heating during the final stage of the crystal formation.

the ^{137}Cs γ radiation (662 keV). To compare, the scintillators from the crystals grown using other technology variances exhibited the average energy resolution of 13 to 15 %.

Thus, in this work, the features of GSO:Ce crystal growth have been studied in various thermal conditions influencing the crystal quality. The formation of an inherent impurity in the melt has been found to be the decisive factor that deteriorates the optical perfection of GSO:Ce crystals. The oxygen partial fraction on the gas medium has been found to be not a constant parameter of the GSO:Ce crystal growing process. This fact results in an increased inhomogeneity of cerium distribution over the crystal length. Basing on the determined growth parameters and regimes, a technology has been developed providing the crack-free 150 mm long GSO:Ce crystals of 40 mm in diameter. The bulk scintillators made from those crystals have exhibited a high spectrometric quality thereof.

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Оптимізація теплових умов вирощування кристалів GSO:Ce методом Чохральського

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Досліджені умови кристалізації силікату гадолінію Gd_2SiO_5:Ce залежно від кристалографічного напрямку їхнього вирощування у різних теплових умовах. Показано, що для розробленого кристалізаційного вузла оптимальним є розташування тигля щодо індуктора на 5–7 мм вище верхнього витка індуктора. Визначено параметри й режими росту, що дозволяють одержувати кристали діаметром до 50 мм і довжиною до 150 мм високої спектрометричної якості. Сцинтилятори ∅40×40 мм^2, виготовлені із цих кристалів, показали енергетичну роздільну здатність 10,4 % при опроміненні γ-випромінюванням ^{137}Cs енергією 662 кеВ.