

Growing and study of optical and luminescence properties of scintillation oxide crystals

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Discussed are the peculiarities of the oxide crystal growing by Czochralski technique, the effects of the growth atmosphere on the structure transformation extent and direction, stoichiometric disordering of the oxide melts, the various defect formation nature in the crystals. It is just the redox potential of the growth atmosphere defining the oxygen thermochemical activity in the oxide melts that has been shown to influence considerably the extent and direction of the processes mentioned. The resulting effect of factors influencing the internal structure has been found to define the coordination of clusters of the crystal-forming components and the melt ability of single-phase crystallization.

Обсуждаются особенности выращивания оксидных кристаллов методом Чохральского, влияние газовой среды выращивания на глубину и направление структурных преобразований, стехиометрическую разупорядоченность оксидных расплавов, природу образования в кристаллах различных дефектов. Показано, что существенное влияние на глубину и направления этих процессов, в том числе термохимическую устойчивость расплава, оказывает окислительно-восстановительный потенциал газовой среды выращивания, предопределяющий термохимическую активность кислорода в оксидных расплавах. Результирующее действие факторов, влияющих на внутреннюю структуру, определяет координацию кластеров кристаллообразующих компонентов и способность расплава к монофазной кристаллизации.

The high-efficiency scintillation oxide crystals (tungstates, silicates, and aluminates of alkali-earth metals and rare-earth elements) are used widely in apparatus and equipment for nuclear and high-energy physics, tomography, ecological environment monitoring, etc. Such a wide use of those crystals is due to the unique physical properties thereof (short radiation length, high density and scintillation efficiency, radiation and temperature resistance). The new generation of radiation monitoring equipment makes high demands to scintillation materials. The specific applications of the above-mentioned scintillators as components of modern instruments in mass production require a great number of crystals characterized not only by a high structure perfection but also by a minimum scatter in optical, luminescence, and scintillation

characteristics. Thus, it is necessary to develop a production technology of the crystals providing a high homogeneity over the crystal volume and a high reproducibility of properties for numerous crystals.

The crystals of complex oxide compounds were grown Czochralski by method with induction heating from corresponding raw oxides of 99.995 purity grade. In our previous works [1, 2], a special attention was given to investigations in thermal conditions and regimes of the crystal growth. Those studies have demonstrated the production possibility of optically homogeneous and structurally perfect crystals with pre-specified scintillation characteristics. The growth conditions were optimized by designing a special crystallization assembly and by selecting the growing regime depending on the crystal nature, physical parameters, and size.

The technology basing on optimization of the growth thermal conditions did not provide the crystal reproducibility, since a formation possibility of intrinsic structure defects (ISD) therein was not excluded, especially in mass production. Those defects are known to deteriorate the scintillator performances. This is due to the fact that the temperature range width providing the experimentally selected optimal thermal conditions (OTC) is related functionally to the directionality and depth of the melt internal structure indification in the course of growing. When the structure transformations in the melt are within the kinetic region, the OTC tend to narrowing, thus resulting in an increasing crystallization probability beyond the region of optimal thermal conditions and in appearance of intrinsic structure defects in the crystals.

It is just the light scattering centers (LSC) and color centers (CC) that we consider to belong to typical ISD. The formation of those centers is favored considerably by the melt stoichiometric disordering that is caused by its temperature and the mass transfer within the melt/growing atmosphere system during the growing cycle. Moreover, depending on the melt temperature, clusters may be generated therein where coordination differs from that in the crystal matrix. An incoherent incorporation of such clusters into the crystal results in formation of macroscale inclusions and blocks. Hence, in our opinion, it is expedient and topical to study the factors influencing the chemical properties of multicomponent oxide melts and being most dangerous in defect formation and deterioration of scintillation characteristics in the grown crystals. The following circumstances belong to those factors: (i) the molten oxide mixtures are open thermodynamic systems; (ii) incongruent evaporation is typical of most such systems; (iii) the oxide crystals show a heavy anisotropy of properties (heat conductance, preferred growth direction, oxygen diffusion, optical and luminescence characteristics).

To reduce the stoichiometric disordering of the melt internal structure caused by the incongruent evaporation, the intensity of the latter can be reduced by selecting the optimum thermal conditions and controlling the oxygen partial pressure in the growth atmosphere. An optimum amount of a volatile component can also be used to maintain the melt stoichiometry. In particular, when growing the cadmium tungstate (CWO)

crystals, where the melt is subjected to an intense incongruent evaporation, we have used the raw charge containing an excess (0.1 mass %) of cadmium oxide. To study the redistribution of main components over the CWO single crystal length during its growth, the non-destructive X-ray fluorescence analysis was used [3]. At the initial growing stage, the crystal contains an excess of cadmium. As the crystal grows, the cadmium mass fraction decreases monotonously, the crystal color changing its color over its length from yellowish through colorless to greenish. This is explained by the fact that cadmium ion is removed from the crystal during growth due to its incongruent evaporation of the melt. However, by optimizing the thermal growing conditions, we succeeded in growing of colorless crystals in air from stoichiometric raw charge, while the CdO excess as low as about 0.1 mass % causes the yellowish coloration of the crystal.

A method for manufacturing colorless CdWO₄ crystals by growing under excess oxygen pressure is known [4]. To that end, it is necessary to increase the overstoichiometric CdO excess up to 1 mass % at the oxygen pressure about 1.5 at. In our opinion, such a considerable required CdO excess is due to the excess oxygen pressure that favors the formation of [CdO] type clusters in the melt. The coordination of those clusters is inconsistent with the tungstate (P2/c) crystal structure of CWO, therefore, the clusters are driven away by the growth surface as an intrinsic impurity.

It is impossible to estimate quantitatively the change of the melt internal structure. In contrast, changes in its structure-sensitive properties associated directly with the structure changes can be determined and used, in particular, to optimize the growing thermal conditions. The structure-sensitive properties were studied in experiments for Gd₂SiO₅ (GSO), PbWO₄ (PWO), CdWO₄ (CWO), Y₃Al₅O₁₂ (YAG), and YAlO₃ (YAP) oxide melts. The running structure transformations were monitored by measuring the viscosity changes and the melt mass loss (due to evaporation) as functions of the growth atmosphere pressure and composition. In particular, Fig. 1a shows the viscosity (η) isotherms of YAG melt as functions of the growth atmosphere pressure and composition [5]. In nitrogen atmosphere, the melt viscosity may attain 90 cP while it drops down to 20 cP in argon containing about 2 vol. % vol. of hydrogen.

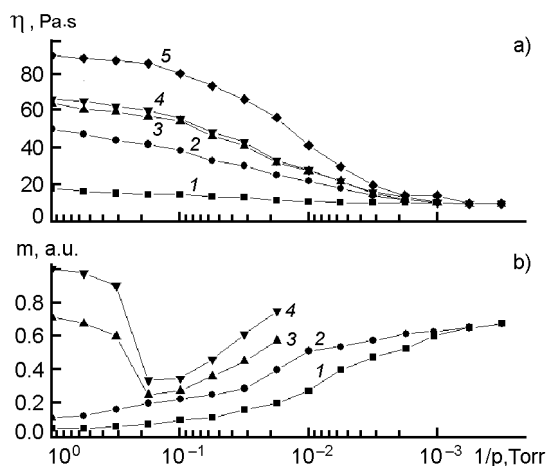


Fig. 1. Variation of melt structure-sensitive properties depending on the growth atmosphere pressure: (a) dynamic viscosity of YAG melt in Ar(H) (1), Ar(O) (2), N₂(O) (3), Ar (4), N₂ (5); (b) melt mass loss (rel. units) for YAP (1), YAG (2), PWO (3), CWO (4).

Introduction of oxygen (up to 1.5 vol. %) causes also the melt viscosity decrease. As the growth atmosphere pressure is decreased, the viscosity drops dramatically in the 10^{-2} to $5 \cdot 10^{-3}$ Torr range. This evidences the starting profound structure transformations in the melt till its decomposition which result in a drastic intensification of its incongruent evaporation.

The mass loss of PWO and CWO melts with decreasing growth atmosphere pressure (Fig. 1b) is decreases first due to weakened intensity of the upward gas flow that transfers the evaporation products out of the melt surface. As the pressure decreases further, the melt mass loss starts to rise sharply at certain pressure values characteristic for each melt, depending on thermochemical stability of the latter. This evidences the starting profound thermochemical dissociation in the melts resulting in starting decomposition of the PWO and CWO melts that tend to incongruent evaporation already at temperatures near the crystallization point. Thus, the experimental results evidence the structure transformation in oxide melts that can be activated or suppressed by varying the oxygen partial pressure in the growth atmosphere [6].

The oxygen mass exchange occurs between the melt and the growth atmosphere. The reversion of the oxygen mass exchange vector in the growth atmosphere-melt system and variation of the oxygen stoichiometry in the melt take place within the whole cycle of the crystal growing.

Since the Czochralsky technique involves repeated overheating and overcooling of the melt, a crystal grown using that technique can be stated to be inhomogeneous in the oxygen stoichiometry. This is confirmed by the local coloration of upper and lower crystal parts observed sometimes in PWO crystals that are grown, due to the method specific features, from overcooled melt with increased oxygen content. Our experiments have shown that the oxygen partial fraction in the growth atmosphere varies also during the GSO growing cycle (Fig. 2). In the Figure, presented is the variation of the oxygen diffusion vector in the growth atmosphere-melt system as a function of the heating power (P) being applied to the melt.

It is to take into account that most oxide scintillation crystals require a limited oxygen content in the growth atmosphere when being grown. This is true, in particular, for Ce-doped scintillators as well as for crystals (PWO) where the charge state of activator ions or the crystal-forming cations may change resulting in formation of color centers. The oxygen concentration should be limited by both maximum and minimum admissible values. In particular, the PWO crystals, when approaching to stoichiometry in oxygen, take coloration due to change in the lead cation charge state, while at a deficiency in oxygen (less than 0.3 vol. %), the coloration is caused by a partial reduction of tungsten cations. Thus, by selecting optimum composition and pressure of the growth atmosphere, the crystals can be obtained with a low optical density in the intrinsic luminescence spectral region. When growing the GSO crystals, the oxygen partial fraction in the growth atmosphere should be controlled thoroughly. The oxygen allowable amount in the specific technology developed at our organization cannot exceed 0.3 vol. %, since as that limit is exceeded, the crystals take coloration due to charge state change of the activator ions (Ce³⁺).

In this work, a series of grown crystals was subjected to X-ray structure investigation using a SIEMENS D500 diffractometer under copper emission with graphite monochromator. GSO samples were studied cut out of the same crystal (top and bottom parts) as well as a crystal with defect inclusion in the bottom part. The X-ray structure data are presented in Table 1. A trend to increase of the unit cell parameters from top to bottom of the Table columns is seen, that is most pronounced for the unit cell volume. The data over the crystal length

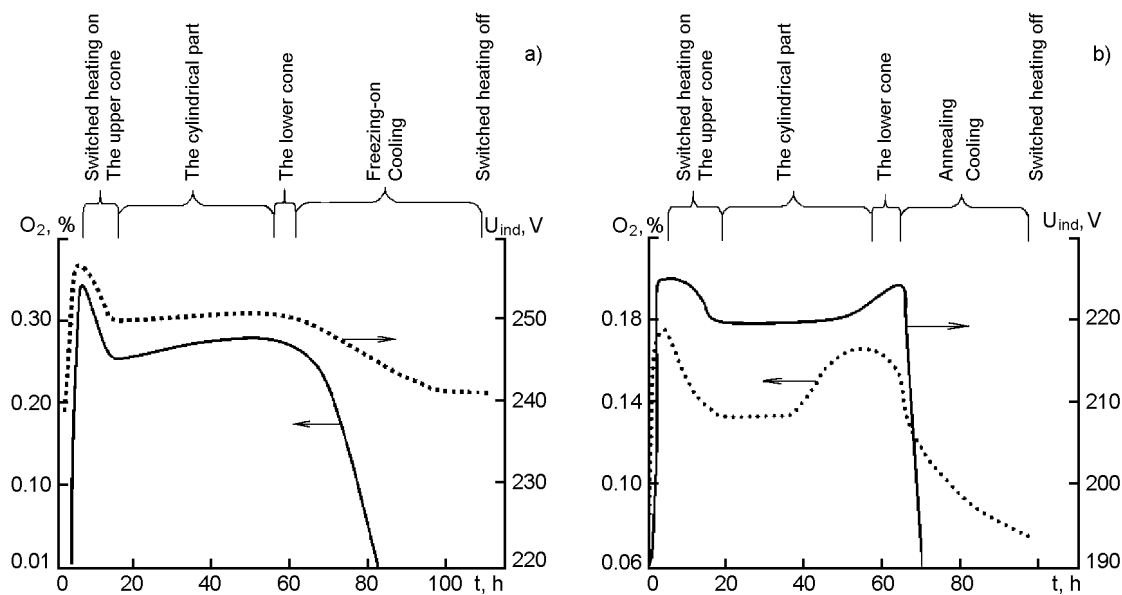


Fig. 2. Variation of oxygen partial fraction in Ar atmosphere and the crucible heating power in the course of a GSO crystal growing: (a) the crystal is frozen into the melt, (b) the crystal is torn-off from the melt.

Table 1. Unit cell parameters and volume for GSO crystals

Crystal No.	Features	a , Å	b , Å	c , Å	α , °	V , Å ³
1	Top	9.13551(4)	7.05776(6)	6.75051(6)	107.5312(5)	415.032(6)
1	Bottom	9.13569(5)	7.05784(6)	6.75037(6)	107.5290(5)	415.040(7)
2	Knot	9.13632(6)	7.05828(7)	6.75113(7)	107.5363(7)	415.125(7)

show a certain increase of the unit cell volume towards the crystal bottom that seems to be associated with changes in the stoichiometry and impurity composition.

The CWO, GSO, and PWO crystals belong to lower syngonies and exhibit therefore several anisotropic properties. Among those, the following are of importance from the standpoint of technology and performance of scintillators made therefrom: heat conductance, thermal expansion, thermal diffusion of oxygen into the crystal volume, crystallographic orientation of the scintillator planes across which the emitted light exits.

We have studied the anisotropy of oxygen thermal diffusion in the course of CWO sample annealing in air. The colored samples have been shown to lose the color most actively along the [001] direction. The oxygen diffusion is slowest in the [010] direction perpendicular to the (010) cleavage plane [7]. The CWO, PWO, and GSO scintillators have been studied to determine the preferred light exit direction at various crystallographic orientations. The

Table 2. Light yield under ¹³⁷Cs γ source, per cent

Crystal	Size, mm ³	(001)	(010)	(100)
CWO-1	10×10×10	39.4	39.9	37
CWO-2	10×10×10	43.4	44.7	43.8
PWO-3	10×10×10	5.7	5.4	5.4
PWO-4	10×10×10	5.6	5.3	5.4

X-ray ($E \sim 30$ keV) luminescence intensity in the CWO and PWO samples has been found to be about 40 % higher in the [001] and [010] crystallographic directions (Fig. 3). Under high-energy (0.5 to 1 MeV) irradiation, the exiting light fraction across the (010) plane for CWO and across the (001) for PWO exceeds by 5 to 7 % that for other planes (see Table 2) [8].

The CC formation due to the stoichiometric disordering in oxygen is reversible. The quality of crystals showing a post-growth coloration within the intrinsic luminescence

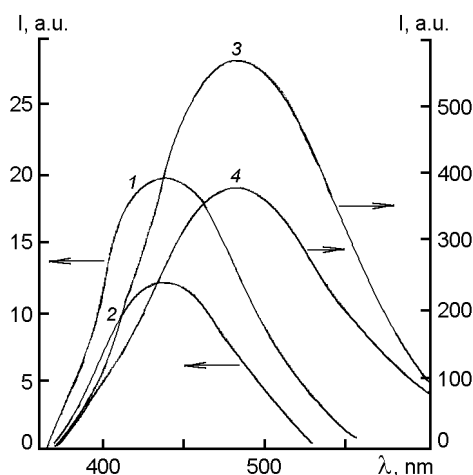


Fig. 3. X-ray luminescence spectra of PbWO_4 (1, 2) and CdWO_4 (3, 4) crystals for directions (001) (1), (100) (2), (010) (3), (100) (4).

spectral region can be improved considerably by annealing (Table 3). The CC in PWO have been shown to be removable by annealing at submelting temperatures under oxygen partial pressure about 10^{-5} atm. We have developed a combined annealing procedure [9] providing a more efficient improvement of the PWO crystal optical parameters. The increase of optical transmission is due to transformation of color centers $\text{Pb}^{3+} \rightarrow \text{Pb}^{2+}$ resulting in an enhanced transparency in the 360 nm band and $\text{O}^- \rightarrow \text{O}^{2-}$ causing a transparency increase in the 420 nm one (see Fig. 4). The colored GSO crystals can be decolored by annealing under reduced atmosphere pressure at the atmosphere chemical potential about 38 kJ. The properly selected regimes provide the absorption reduced down to 10^{-2} cm^{-1} [10]. The optical and scintillation properties of CWO crystals are enhanced considerably by high-temperature annealing in oxygen-containing atmosphere [11], thus providing the light yield increase by 15 to 20 %.

To conclude, the studies have shown an important part played by oxygen to provide the production of a crystal with reproducible performance characteristics. The melt evaporation intensity has been shown to depend on the growth atmosphere pressure. Changes in oxygen diffusion in the melt-atmosphere system have been revealed in the course of oxide crystal growing. The mass fraction of the disordered phase in the GSO melt has been found to depend on the melt temperature and the oxygen partial pressure in the growth atmosphere. Optimum oxygen partial pressure values have been

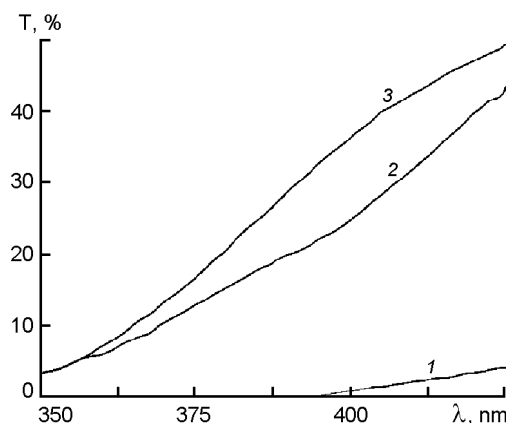


Fig. 4. Optical transparency spectra of a PWO single crystal prior to anneal (1) and after 1st (2) and 2nd (3) annealing stages.

Table 3. Effect of annealing on GSO crystal performance characteristics

Annealing atmosphere	Light yield I , rel. units	Afterglow level η (%) after 20 ms
unannealed	1.00	0.003
Air	0.89	0.002
Vacuum	1.20	0.086
Reducing atmosphere	–	0.061

found for CWO, PWO, and GSO crystal growth. Optical and performance properties of the crystal have been studied as functions of the growing and heat treatment conditions, and crystallographic orientation.

Basing on the results obtained, the technologies have been developed providing the reproducible production of crystals with minimum scatter in optical, luminescence, and scintillation characteristics. As a result, crystals providing the light yield (photons per MeV) 20,000 for CWO, 11,500 for GSO, and 200 for PWO. The tomographic elements as well as various 1D and 2D assemblies made of those crystals provided high light yields, low afterglow levels, high-temperature stability and the performance homogeneity. The high yield of effective products has been attained at a high perfection degree (absence of blocks, inclusions, mosaic, thermoelastic stresses).

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Вирощування і дослідження оптико-люмінесцентних властивостей сцинтиляційних оксидних кристалів

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Обговорюються особливості вирощування оксидних кристалів методом Чохральського, вплив газового середовища вирощування на глибину і напрям структурних перетворень, стехіометричної розупорядкованості оксидних розплавів, природу створення у кристалах різних дефектів. Показано, що істотний вплив на глибину і напрями цих процесів, у тому числі термохімічну стійкість розплаву, надає окислювально-відновний потенціал газового середовища вирощування, що зумовлює термохімічну активність кисню в оксидних розплавах. Результуюча дія чинників, що впливають на внутрішню структуру, визначає координацію кластерів кристалостворюючих компонентів і здатність розплаву до монофазної кристалізації.