

Effect of growth atmosphere on Ce^{3+} incorporation in Gd_2SiO_5 single crystals

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Peculiarities of oxide crystal growth by the Czochralski technique have been discussed in the present paper. A correlation between oxygen content in the growth atmosphere and the Ce^{3+} incorporation coefficient at growing the GSO:Ce crystals has been revealed in experiment. Possible mechanisms of the oxygen concentration influence on the cerium ion incorporation coefficient are discussed. The studies performed have shown an important part played by the growth atmosphere in the growing of oxide crystals with reproducible performance characteristics.

Обсуждаются особенности выращивания оксидных кристаллов методом Чохральского. Экспериментально обнаружена корреляция между концентрацией кислорода в газовой среде и коэффициентом вхождения ионов Ce^{3+} при получении кристаллов GSO. Обсуждаются возможные механизмы влияния концентрации кислорода на коэффициент вхождения ионов церия в кристалл. Проведенные исследования показали важную роль состава среды выращивания при получении оксидных кристаллов с воспроизводимыми функциональными характеристиками.

The composition and pressure of growth atmosphere are of a great importance in the growing of oxide crystals. This effect appears as variations in structure-sensitive properties of melts [1] (viscosity and surface tension) caused by internal structure transformations there. The gas medium influences the melting temperature (T_m) of substances being crystallized. In particular, the T_m difference for SrAl_2O_4 [2] and YAlO_3 [3] grown under normal pressure of gaseous atmosphere and in vacuum may attain 200°C and 70°C respectively. Partial pressure of oxygen (P_{O_2}) in the growth atmosphere influences also the structure transformations in oxide melts and possibility of existence of differently coordinated cations therein. It was shown [2, 4] that at oxygen partial pressure less than $1 \cdot 10^{-10}$ atm., all

the Ce^{2+} cations in $\text{CaO-Al}_2\text{O}_3$ system for compositions containing 52 % of Al_2O_3 have the octahedral coordination resulting in $\text{Ca}_5\text{Al}_6\text{O}_{14}$ compound formation at crystallization. At $P_{\text{O}_2} > 1 \cdot 10^{-10}$ atm., the ratio of oxygen and aluminum ions in melt provides $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ formation with the six- and seven-coordinated calcium polyhedrons. The structure changes caused by influence of growth medium redox potential are inherent in the great majority of binary oxide melts [1], however, the basic mechanism of the structure changes is connected with completeness of thermal dissociation processes in dependence on thermochemical stability of these melts.

Optimal growth conditions are usually set by a special crystallization assembly construction and growth regime selection.

However, the developed technology based on growth conditions optimization does not solve the problem of reproducible crystal production, because the probability of intrinsic defects formation (especially, on industrial scale growth) are rather high, and scintillator performance characteristics of many crystals are unsatisfactory. This is because a temperature range corresponding to the experimentally chosen optimum growth conditions is connected with degree and direction of the melt internal structure variations during the growth cycle. In the case when the structure transformations in melt take place, there exists a trend to narrowing of the optimal temperature conditions range. As a result, the probability of crystallization out of the optimal thermal conditions range increases, and thus, the probability of intrinsic structure defects in crystals increases as well. The typical intrinsic defects are light scattering centers and color centers. Formation of these centers is promoted mostly by stoichiometric disordering of melt caused by its temperature and by the mass transfer in the "melt — growth atmosphere" system. Moreover, under temperature action, clusters in melt can be formed with a coordination not corresponding to one in the crystalline matrix.

In accordance with the above, it seems to be expedient to study the factors influencing the physicochemical properties of multi-component oxide systems, and constitute a big danger of defect formation and destabilization of crystal scintillation characteristics. These are the follows: the oxide melts are open thermodynamic systems; incongruent melt evaporation is characteristic for most of them; high anisotropy of oxide crystal properties (thermal conductivity, preferential growth direction, oxygen diffusion, as well as anisotropy of optical and luminescent properties).

The Gd_2SiO_5 (GSO) melt possesses a rather high thermochemical stability and low evaporation rate of pseudo-gaseous suboxides. Results of X-ray fluorescence studies, and real possibility to carry out a series of GSO growths with intermediate loading the crucibles with raw material without correction of stoichiometric compositions suggest that the evaporation products and the melt are equimolar.

An active oxygen mass transfer between melt GSO growing by the Czochralski method because the melt is an open thermodynamic system. Hence, it appears that under conditions of a real non-stationary

crystallization process, the partial pressure of oxygen and its thermochemical activity (chemical potential) in the melt must also vary continuously. The features of the Czochralski method are that the melt during the growth cycle repeatedly imposed to both overheating and overcooling. So, any crystal grown by Czochralski method can be stated to be non-homogeneous in oxygen stoichiometry. This fact is confirmed by local coloration appearing sometimes in upper and lower parts of GSO crystals grown from melt with an oxygen excess.

It is worth to note that majority of oxide scintillation crystals require limitations of oxygen content in the growth atmosphere. This concerns to cerium (Ce) doped scintillators, where changes of charged state of activator ion or lattice basic cations are possible. This results in formation of color centers. Moreover, the iridium oxidation reaction $O_2 + Ir \rightarrow IrO_2$ also takes place during the growth with the IrO_2 solid compound formation [8].

The oxygen content value should be limited both from maximum and minimum sides. In particular, at GSO:Ce growth, the acceptable oxygen partial pressure for our technology should not exceed 0.3 vol. %, because the crystal coloration takes place at higher values due to increase of Ce^{3+} ion charged state. Moreover, increase of oxygen content in the melt due to diffusion from the gaseous medium promotes formation of defects in the form of accompanying phases (according to the phase diagram) [5]. Thus, choosing the optimal growth atmosphere content and pressure, we can obtain crystals with low optical density in the GSO luminescence band.

In [6], it is reported that Ce^{3+} effective incorporation coefficient (k_0) at GSO growing increases with decreasing P_{O_2} in growth atmosphere. The k_0 drops from about 0.7 to 0.9 in pure nitrogen atmosphere down to 0.56 at introduction of 3000 ppm of oxygen into the gaseous medium. This is explained by the fact that Ce^{4+} with small ionic radius (0.88) is not capable to substitute Gd^{3+} in sevenfold polyhedrons, and is rejected from the growth surface [7]. Thus, the study of oxygen concentration dynamics in the "growth atmosphere — melt" system during the GSO growth cycle is of a great practical interest.

In our experiments on GSO growth, we used the raw material obtained by solid state synthesis from Gd_2O_3 and SiO_2 of 99,995 purity grade. Cerium oxide (CeO_2)

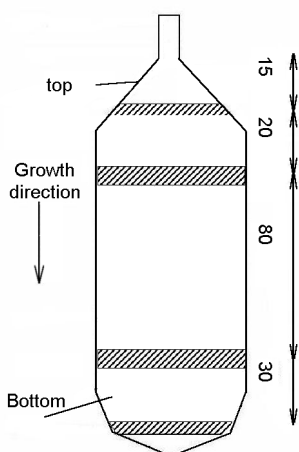


Fig. 1. Sampling scheme for concentration measurements of GSO crystal doped with Ce^{3+} .

of the same purity was used as activator. The starting components were preliminary calcined to remove moisture and volatile impurities. The GSO crystals were grown in iridium crucibles of 90 mm dia. in $N(Ar)$ atmosphere with addition of 0.1–0.3 vol % of oxygen. The pulling rate was 1.5 to 3.0 mm/h, and the rotation speed was 30 to 40 rpm. An additional heater in the upper part of growth assembly was installed to control the temperature gradient above the melt surface.

The experiments [10] showed the P_{O_2} variations in atmosphere during the GSO growth cycle. Measurements of P_{O_2} in gaseous medium during the growth cycle show that P_{O_2} increases with P , and, correspondingly, with the melt temperature, and vice versa. The heater power increase (decrease) at GSO growth is an essential part of crystallization process. The presented data confirm the reversibility of the oxygen diffusion vector. This makes it possible to suppose that the oxygen stoichiometry in GSO during the growth cycle is subjected to changes and the lattice parameters along the crystal are inhomogeneous. This may result in elastic stresses (in our case, the most "dangerous" regions are situated near the upper and lower cones). In the case when these stress amplitudes are higher than the crystal tensile strength, those relax under crack formation. As a rule we observe this phenomenon at GSO growth.

Under these conditions the cerium incorporation coefficient also must be a variable value along the grown crystal. To check this hypothesis, the Ce^{3+} concentration was measured in a crystal of 47 mm dia. and

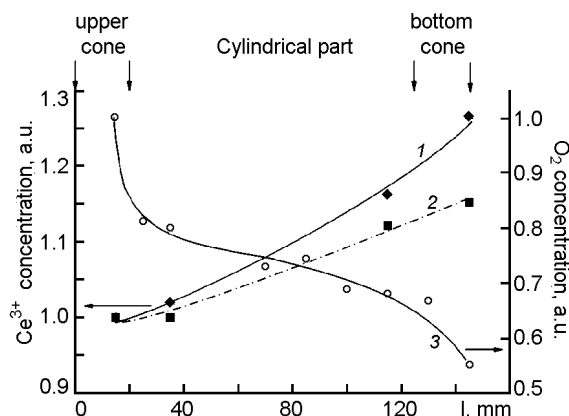


Fig. 2. Dynamics of the Ce^{3+} concentration changes in the melt and crystal and oxygen content in the growth atmosphere at GSO growth. 1 – calculated Ce^{3+} concentration in the crystal at $k_0 = \text{const} = 0.65$; 2 – measured Ce^{3+} concentration in the crystal; 3 – measured oxygen content in the growth atmosphere (Ar).

145 mm length, which was "frozen" into the melt at the final growing stage. The samples for chemical analysis were taken from the lower crystal cone (15 mm from the seed), upper and lower parts of the cylinder (35 and 115 mm from the seed, respectively), as well as from the lower cone (Fig. 1). The calculated Ce^{3+} concentrations in the melt and crystal at constant k_0 (curve 1), as well as the experimental Ce^{3+} concentrations in various crystal parts (curve 2) are presented in Fig. 2. Changes of oxygen partial pressure in the growth atmosphere are shown in the same Figure (curve 3). An insignificant k_0 decrease accompanied by the P_{O_2} monotonous decrease are observed at the cylinder growth. P_{O_2} decreases sharply at the lower cone growth together with the remarkable incorporation coefficient decrease. Basing on the experimental data and using the formula (1) taken from [9]

$$C_s = C_0 k_0 (1 - g)^{k_0 - 1} \quad (1)$$

we have calculated the Ce^{3+} incorporation coefficients along the crystal and compared those with oxygen partial pressure during the growth cycle (Table 1). Here, g is the crystallized melt fraction; C_s , the impurity concentration in the melt at some point; C_0 , the initial impurity concentration in the melt; and k_0 , the incorporation coefficient.

Table. Dynamics of oxygen concentration in the growth atmosphere and the Ce^{3+} incorporation coefficient along the crystal during the GSO growth cycle (g — crystalized melt fraction)

Length of growing ingot, mm	15	35	115	135
g	0.01	0.08	0.36	0.48
P_{O_2} , a.u.	1	0.8	0.68	0.55
k_0 (Ce^{3+})	0.67	0.66	0.65	0.61

Basing on the obtained results we can propose the following correlation mechanism between k_0 (Ce^{3+}) and P_{O_2} . At melt temperature decrease the oxygen diffusion from the gaseous atmosphere to the melt starts until the establishment of equilibrium between oxygen pressure in the atmosphere and its partial pressure above the melt. Increasing of oxygen concentration in the melt leads decrease of oxygen vacancies quantity in the crystal. It worsens the matching of cavities dimensions in the polyhedra with Ce^{3+} effective radius and leads to k_0 decrease. The inverse process leading to incorporation coefficient increase will be observed at melt temperature increase. Also, k_0 may decrease due to transfer of cerium ion to the fourth-valence state, as it was shown in [2], however, to confirm this hypothesis, parallel determination of Ce^{4+} and Ce^{3+} is necessary.

Thus, basing on the study results, we have established that the changes of the

oxygen diffusion vector direction in the "melt — gaseous medium" system take place during the GSO growth cycle. A correlation between oxygen content in the growth atmosphere and Ce^{3+} concentration in the growing crystal has been shown. The obtained results demonstrate that at obtaining of GSO single crystals with reproducible characteristics, the changes in oxygen partial pressure should be accounted for.

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Вплив атмосфери вирощування на входження Ce^{3+} в монокристали Gd_2SiO_5

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Обговорюються особливості вирощування оксидних кристалів методом Чохральського. Експериментально виявлено кореляцію між концентрацією кисню у газовому середовищі та коефіцієнтом входження іонів Ce^{3+} при вирощуванні кристалів GSO. Обговорюються можливі механізми впливу концентрації кисню на коефіцієнт входження іонів церію у кристал. Проведені дослідження показали важливу роль складу ростового середовища при отриманні оксидних кристалів із відтворюваними функціональними характеристиками.