Czochralski Growth of 2 Inch Ce-Doped (La,Gd)₂Si₂O₇ for Scintillator Application

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ABSTRACT

Growth of 2-inch diameter Ce-doped (La,Gd)₂Si₂O₇ (La-GPS) scintillating crystals by Czochralski method using Ir crucible is reported. The composition of the host material was approximately equal to La_{0.5}Gd_{1.5}Si₂O₇ and the concentration of the Ce³⁺-activator was either 0.5 or 1.5 at.% with respect to the total content of the rare-earths forming the host crystal matrix. Effects of the hot zone construction including inductive coil position, presence/absence of the after-heater, rotation rate and other growth parameters on the crystal quality are discussed in some details. The crystals produced in optimized conditions were colorless, transparent, uniform in their shape, crack- and inclusions-free, and demonstrated smooth glass-like surface. The length of the crystals' cylindrically-shaped body parts exceed 100 mm. The growth results were well reproducible. The main disadvantage of the growth process is associated with short lifetime of the Ir crucible and its deformation caused by thermal expansion of the pre-solidified melt at each heating stage.

Keywords:

A2. Czochralski method, A2. Growth from melt, B2. Scintillator materials, A1. Solid solutions

1. Introduction.

Lanthanum-gadolinium pyrosilicate (or disilicate), $(\text{La,Gd})_2\text{Si}_2\text{O}_7$ (La-GPS) is a novel scintillating crystal that was originally considered as regular mixed crystal (or solid solution) formed by the two end members of $\text{La}_2\text{Si}_2\text{O}_7$ and $\text{Gd}_2\text{Si}_2\text{O}_7$ (GPS) [1,2]. Recent findings demonstrated that La-GPS in high degree behaves as an actual original compound because its structural and chemical properties do not correspond to simple linear superposition of the characteristics of $\text{La}_2\text{Si}_2\text{O}_7$ and GPS [1]. La-GPS have triclinic structure at least in the compositional range from $\text{La}_{0.2}\text{Gd}_{1.8}\text{Si}_2\text{O}_7$ to $\text{La}_{1.2}\text{Gd}_{0.8}\text{Si}_2\text{O}_7$ [3]. The end members $\text{La}_2\text{Si}_2\text{O}_7$ and GPS possess other crystallographic symmetries. Thus, the three compounds from $\text{La}_2\text{Si}_2\text{O}_7$ (1), through La-GPS (2), to GPS (3) have nothing in common regarding their structure except the number of atoms per formula unit (subscripts) in their chemical formulas. Furthermore, within the same range of compositions from $\text{La}_{0.2}\text{Gd}_{1.8}\text{Si}_2\text{O}_7$ to $\text{La}_{1.2}\text{Gd}_{0.8}\text{Si}_2\text{O}_7$ melting and solidification behavior of La-GPS corresponds well to congruently melting compounds, again opposite to the behavior of its end members $\text{La}_2\text{Si}_2\text{O}_7$ and GPS that melt incongruently and in different ways. Thus, La-GPS does not behave typically.

The Ce-doped La-GPS crystals of $\text{La}_{0.2}\text{Gd}_{1.8}\text{Si}_2\text{O}_7$ composition produced by floating zone method [4-6] demonstrated high light output of up to 41,000 photons/MeV and Full Width at Half Maximum (FWHM) energy resolution of 4.4% at 662keV at room temperature [5]. This excellent performance is in good agreement with recent observations that scintillation efficiency and light yield of the mixed crystals exceed those of the end members forming the mixed crystal [7]. On the other hand, the light output of Pr-doped La-GPS with monoclinic structure was reported to be low [8]. Also, Ce-doped La-GPS crystals have high temperature stability of light output and FWHM energy resolution in the range from 0°C to 100-150°C. Acceptable thermal stability of the luminescence was also demonstrated in the triclinic pyrosilicate crystals at temperatures up to 200°C in [9]. Similarly, high thermal stability of this material synthesized in poly-crystalline form was noticed in [10] for the same temperature range. This property is very important for natural resource survey instruments and other radiation detection devices operated at elevated temperatures [9].

Growth of La-GPS crystals by Czochralski (CZ) method was inspected in the range of $\text{La}_{0.5}\text{Gd}_{1.5}\text{Si}_2\text{O}_7$ to $\text{La}_{1.0}\text{Gd}_{1.0}\text{Si}_2\text{O}_7$ compositions in the recent past [1], and the best growth results corresponded to the crystals grown from the melt of about $\text{La}_{0.5}\text{Gd}_{1.5}\text{Si}_2\text{O}_7$ composition. Growth of La-GPS crystals by the micro-pulling-down (μ -PD) method was also reported, and it was found that Ce:La-GPS single crystals of acceptable optical quality can be also produced from the melts ranging from $\text{La}_{0.5}\text{Gd}_{1.5}\text{Si}_2\text{O}_7$ to $\text{La}_{1.0}\text{Gd}_{1.0}\text{Si}_2\text{O}_7$ and containing about 1 at. %

Ce^{3+} with respect to the host rare earths of La^{3+} and Gd^{3+} . The CZ and μ -PD crystals were chemically uniform along the growth axis and radial direction and their compositions were approximately equal to those of the melts. Thus, this range of concentrations corresponded to vicinity of congruent melting composition. Spatial distribution of Ce^{3+} in La-GPS was also inspected, and no variation of Ce^{3+} content was detected as a result of its similarity to one of the host forming cation (La^{3+}) regarding the size.

This communication discusses recent results on Czochralski growth of 2 inch diameter crystals of approximately $\text{La}_{0.5}\text{Gd}_{1.5}\text{Si}_2\text{O}_7$ composition doped with Ce^{3+} . Such crystals demonstrated sufficient structural stability and adequate optical quality [1]. The details of the CZ process are discussed. It is demonstrated that partial substitution of Gd^{3+} with La^{3+} has no evident negative impact on the growth process and physical performance of the 2-inch diameter La-GPS crystals.

2. Melt and Crystal Compositions.

Regarding the crystal quality, the best growth results reported in [1] were observed for the CZ crystals produced from the melt of about $\text{La}_{0.5}\text{Gd}_{1.5}\text{Si}_2\text{O}_7$ composition. This composition represents only the host material without consideration of the Ce-dopant content. This composition is also in good agreement with the chemical formula of $[\text{RE}1][\text{RE}2][\text{RE}3][\text{RE}4]\text{Si}_4\text{O}_{14}$ introduced in [1] to reflect four types of rare-earth [RE] crystallographic sites detected in pyrosilicates with triclinic structure according to [11-13]. Following the above formula, the composition of $\text{La}_{0.5}\text{Gd}_{1.5}\text{Si}_2\text{O}_7$ can be easily transformed to $\text{LaGd}_3\text{Si}_4\text{O}_{14}$ assuming that La^{3+} cations occupy one type of [RE] crystallographic sites. This formula represents ideal distribution of RE-cations between crystallographic sites of the La-GPS structure. However, in real world, anti-site defects are often observed. Thus, some part of La^{3+} may be found in Gd-sites and vice-versa. These cross-substitutions were not well studied in the La-GPS structure and are not considered in this report. Thus, at the moment, the $\text{LaGd}_3\text{Si}_4\text{O}_{14}$ “stoichiometric” composition was confirmed to be the most favorable one regarding crystal growth results.

As for the Ce^{3+} cations accommodated in the La-GPS structure, they play roles of activator and stabilizer of the triclinic structure at the same time. From the point of view of scintillating performance, optimal Ce^{3+} content with respect to the overall amount of host rare-earth cations is approximately 1.0 at.% regarding all rare-earths forming the pyrosilicate structure [10]. Unfortunately, this amount of Ce^{3+} is not sufficient to improve stability of triclinic structure of the GPS compound [3] without partial substitution of Gd^{3+} with La^{3+} .

Considering substitution of original $\text{Gd}_2\text{Si}_2\text{O}_7$ (GPS) with both La^{3+} and Ce^{3+} , the recent study [10] has shown that the composition of the $\text{La}_{0.2}\text{Ce}_{0.02}\text{Gd}_{1.78}\text{Si}_2\text{O}_7$ demonstrated the most intensive X-ray luminescence, fast decay time of 26.7 ns, and good thermal stability. This conclusion was made based on systematic inspection of a matrix of 64 polycrystalline specimens of different compositions. Probably, the $\text{La}_{0.2}\text{Ce}_{0.02}\text{Gd}_{1.78}\text{Si}_2\text{O}_7$ composition is the best one regarding its scintillating performance. However, it is not regarding its chemical properties and especially congruent melting as found in [1] where the best quality crystals were produced from the melt of $\text{La}_{0.5}\text{Gd}_{1.5}\text{Si}_2\text{O}_7$. Therefore, the compromise compositions of $\text{La}_{0.49}\text{Ce}_{0.01}\text{Gd}_{1.50}\text{Si}_2\text{O}_7$ and $\text{La}_{0.49}\text{Ce}_{0.03}\text{Gd}_{1.48}\text{Si}_2\text{O}_7$ were chosen to perform growth experiments in the current project. Thus, content of Ce-dopant in the first composition was 0.5 at.% and it was 1.5 at.% in the second one.

3. Crystal Growth

The crystal growth was performed using conventional Czochralski (CZ) process with inductive heating source powered from radio-frequency (RF) generator as schematically illustrated in Fig.1. An iridium crucible with original dimensions of $\varnothing 100 \times 100$ mm was used for these growths. The hot zone was constructed with two thermal insulation screens. The interior screen was made from zirconia ceramic having greater melting point. However, the outer one was manufactured from porous alumina with lower melting point as its position was relatively distant from the crucible and the melt. The rate of pulling the seed in the upward direction in the processes discussed here was approximately 0.5 mm/h. The crystal and the crucible diameters were about 50 and 100 mm, respectively. Thus, actual growth (solidification) rate was around 0.7 mm/h. The CZ system used was equipped with a growth chamber that was well isolated from environmental atmosphere. The predominantly inert and slightly oxidizing growth atmosphere of $\text{N}_2 + 2 \text{ vol.\%O}_2$ was established in the chamber to protect the iridium crucible from oxidation and chemical destruction. The total fraction of the melt used for the crystal growth was approximately 50% for the all growths discussed here.

The seed rotation rate ranged from 3 to 10 rpm, relatively low when compared to 20-40 rpm applied in the La-GPS growth by the TSSG process reported in [14]. Two types of seed rotation management were examined. For some growths, the seed rotation rate was fixed (Table 1). However, in most of the processes, the rotation rate was modified just after starting the body (cylindrical) part of the crystal to correct forced convection, melt flow pattern, temperature distribution, and shape of the solid-liquid interface. In such cases, the rotation was continuously reduced during the body's growth and fixed again when decrease of the

crystal diameter was started to establish the “tail” part of the crystals as it is illustrated in Fig.2.

The position of the RF coil was not always fixed. In most of the processes (Table 1), its position was continuously lowered, also starting from the moment when growth of the body part began (Fig.2). It is evident from the diagram shown in Fig.1 that the melt level drops when crystal growth progresses. As a result of this drop, the temperature distribution and thermal gradients at the vicinity of the growth interface change [18]. To compensate this change the position of the RF coil was also corrected according to Fig.2.

The hot zone was in most cases equipped with iridium after-heater that was required to improve thermal gradient conditions. The modification of the gradient was performed through revision of the positions of the components of the hot zone (Fig.1) as discussed in the following section.

4. Growth Results and Discussions

The results of the crystal growths are summarized in Table 1. In the first set of the experiments (Crystals 1-3, Fig.3), preliminary adjustment of the elements of the hot zone was performed. The crystal No.1 was produced using normal conditions as described in the previous section. The crystal was milky under visual observation and contained many bubbles. The No.2 growth was carried out without the after-heater and in an atmosphere that contained CO₂ instead of O₂. No positive effect of CO₂ was detected. Therefore, all the next growths were performed using N₂ + 2 vol.%O₂ atmosphere.

Regarding the growth atmosphere, earlier growths were performed in pure N₂ environment. However, in these conditions, formation of black particles on the fragments of surrounding ceramic thermal insulation was observed. According to XRD analysis, these particles were mainly composed of SiO₂. Therefore, their deposition was associated with high evaporation of SiO₂ from the melt during the growths. This could result in undesired change of the melt composition making it different from the initial congruently melting one. Therefore, growth in N₂ + 2 vol.%O₂ atmosphere was also attempted. In such circumstances, formation of the SiO₂ particles was not detected. This way, evaporation of SiO₂ was suppressed. It is also noted that the presence of a small amount of O₂ is often considered a suitable way to avoid or reduce formation of oxygen vacancies and other structural defects associated with oxygen deficiency in the crystals. Such defects often result in crystal coloration. Nevertheless, in the experiments discussed here no difference in the crystal

coloration was detected, and the crystals grown in both atmospheres were colorless (Figs. 3-6).

Moreover, in the process No.2, the crystal No.1 was used as a raw material, and it was re-melted to charge the crucible for the growth No.2. This growth was performed with continuous reduction of the rotation rate during the stage of growth of the body part of the crystal (Fig.2) from 7 to 3 rpm (7-3 rpm, Table 1). The shape of the as-obtained crystal No.2 was slightly degraded compared to the crystal No.1. The crystal No 2 contained fewer amounts of bubbles, and these bubbles being accumulated mostly at the end portion of the crystal. The growth of crystal No.3 was again performed with the after-heater and at reduced (and varied) rotation rate of 5-3 rpm. The crystal No.3 had improved appearance regarding both the shape of the crystal and its surface within this set of growths. Nevertheless, all three crystals Nos.1-3 had some cracks.

Results of the second set of growths (Crystals 4-6) are illustrated in Fig.4. At this stage, the effect of the seed rotation was examined for another starting position of the coil (Fig.1) that was shifted 10 mm in upward (+) direction. These crystals were produced with different seed rotation routines including fixed and varied rotation rates. The appearance of the crystals was not improved. Therefore, it was concluded that the position of the coil in the first set of the experiments (0) was more favorable regarding the final quality of the crystals. Therefore, the following growths were performed with the standard starting position of the coil similar to the first set of the experiments (Crystals 1-3).

The crystals of the third set of growths (Crystals 7-8) were produced from the melt of $\text{La}_{0.49}\text{Ce}_{0.01}\text{Gd}_{1.50}\text{Si}_2\text{O}_7$ composition that contained reduced amount of Ce-dopant. The crystals were bubble-free. However, in the case of the crystal No.7, a crack was formed after removal of the crucible from the hot zone of CZ system (Fig.5, top). Therefore, the crystal No.8 produced in the next growth was treated at 1200°C for 36 hours to perform annealing and to reduce the probability of its fracture following remaining stress. This treatment resulted in relaxation of the stresses and the as-grown crystal remained crack-free as illustrated in Fig 5, bottom. As a general tendency, the crystals Nos. 1-7 produced without post-growth treatment (annealing) had some probability of the crack formation including small cracks non-visible in the photographs of the crystals. Alternatively, the crystals Nos. 8-10 produced with such treatment were crack-free.

The last set of experiments (Fig.6) was performed to confirm the best established growth conditions for the melt composition of $\text{La}_{0.49}\text{Ce}_{0.03}\text{Gd}_{1.48}\text{Si}_2\text{O}_7$ and to inspect the reproducibility of the growth results. Both crystals demonstrated very similar appearance,

were crack-free and had comparatively smooth surface. It is noted that deposition of some black particles was observed on the surfaces of the crystals grown at the initial experiments (Figs.3-4). These particles originated from iridium crucible material and were composed of iridium oxide because the growth atmosphere contained 2 vol.% of oxygen. However, number of such particles was detectably reduced when the growth conditions were optimized (Figs.5-6). Thus, the growth process was established due to optimization of the hot zone configuration, including position of the coil. Similarity of most of the applied growth conditions in these two processes resulted in similarity of the crystals produced in two different growths. Actually, the growth conditions were not exactly the same. In particular, the crucible shape was not kept constant from process to process as a result of its deformation. This observable fact is discussed in some details in the following section.

5. Crucible Lifetime

Regarding possible industrial application of the La-GPS crystals, the lifetimes of all parts of the hot zone play an essential role. A crucible is a most expensive and probably most important component of the growth setup. Its shape determines melt flow pattern, meniscus configuration, spatial temperature distribution, shape of the growth front, and other parameters affecting quality of the grown crystal. In addition, regarding the growths discussed above, the short lifetime of the crucibles was found to be one of the shortcomings to overcome. It was assumed that this disadvantage is associated with multiple heating and cooling cycles when the growths are performed for many times using the same crucible. Results of this phenomenon are illustrated in Fig. 7. Deformation of the crucible resulted in change of the electric (or eddy) currents generated in the crucible material. As a result, coupling between the RF coil and the crucible changed due to aging of the crucible. The new shape of the crucible required adjustment of the RF power that was necessary to establish the temperature of the melt suitable for the controlled growth. Specifically, the RF power supplied at the stage of the growth initiation when the seed touches the melt at the beginning of the growth was reduced by about 10% with respect to its original value after four growth cycles. This observation is illustrated in Fig.8.

In the above experiments, every growth run required four heating-cooling cycles. The first three cycles were associated with step-by-step charging of the crucible with starting materials, and the last one was the actual crystal growth course. Each cycle included a stage of solidification of the melt inside the crucible. The observed deformation of the crucible

after seven growths runs (total number of heating-cooling episodes equal to 28) is demonstrated in Fig.7.

Regarding the crucible deformation, the main reason for this negative outcome was associated with the coefficients of thermal expansion (CTE) of triclinic La-GPS (also referred as B- or α -phase [1]) that were studied in details in [15]. According to these findings, the evolution of CTE with temperature in isomorphic pyrosilicates having the same crystallographic structure is very similar, and it does not depend considerably on the type of the RE cations forming the structure. Also, considerable anisotropy of triclinic pyrosilicates was noticed with biggest expansion corresponding to the c-axis, and lowest one for the a-direction. However, the melt solidified in the crucible (Fig.6) is formed by randomly oriented crystallites that make this substance integrally isomorphic regarding its thermal expansion. Therefore, normalized cell volume change, $V/V(30^\circ\text{C})$ should be considered as most appropriate parameter describing thermal volume expansion of the melt resulting in deformation of the crucible.

The $V/V(30^\circ\text{C})$ parameters measured in [15] and those obtained by linear extrapolation for the approximate melting point of La-GPS of 1700°C based on the results reported in [1,16] are presented in Fig.9. It is noted that according to [17] the melting point of La-less $\text{Gd}_2\text{Si}_2\text{O}_7$ is equal to 1750°C , that is comparable to the 1700°C value accepted here and does not affect estimation of CTE very much (Fig.9). Both [16] and [17] do not discuss the La-GPS with triclinic structure discussed in this report. However, it was assumed that the composition of the solid to be melted is not much relevant to its melting point. Moreover, the effect of incorporation of La^{3+} into $\text{Gd}_2\text{Si}_2\text{O}_7$ structure on melting point is generally unknown, but most probably it results in some reduction of the melting point [1]. According to these assumptions, the maximum volume expansion of the solidified La-GPS melt heated from room to melting temperature is $V(1700^\circ\text{C})/V(30^\circ\text{C}) \approx 1.042$ (Fig.9). Again assuming statistically isomorphic expansion of the melt, the linear expansion of the solidified melt during the heating stage can be determined as the cube root of the above value, resulting in average (and isomorphic) $\text{CTE} \approx 1.014$. This number corresponds to an Apparent Bulk Coefficient of Thermal Expansion (ABCTE) [15] equal to $[V(1700^\circ\text{C}) - V(30^\circ\text{C})] / V(30^\circ\text{C}) \approx 0.014$.

Considering the growths reported here, only three of four heating/cooling cycles can be considered as damaging the crucible because the first heating is performed with the crucible not containing any dense melt in it. Thus, only 21 threatening heating cycles out of 28 total ones are taken into account when discussing deformation of the crucible during 7

growth cycles. Assuming irreversible plastic deformation of the crucible containing some melt at every heating stage, the accumulated deformation can be estimated to be $[ABCTE] \times [\text{NUMBER OF HEATING CYCLES}] = 0.014 \times 21 = 0.294$. Thus, the accumulated expansion of the crucible after performing seven growths can be estimated to be 29.4%. This value is unexpectedly close to the 30% observed experimentally (Fig.7, top).

One of the ways to increase lifetime of the crucible is to perform the charging process in one cycle only. If so, about three times increase of lifetime of the crucible can be expected. In the best case scenario, combining the charging and growth cycles in one heating/cooling and melting/solidification routine may also be proposed as efficient way for improvement of the process performance and reproducibility of the growth results.

6. Crystal Characterization

XRD data (not shown) for the crystals grown from the melts of practically same composition were very similar and they confirmed that all the crystals were single phase materials. Formation of secondary phases was not detected in any of the crystals.

Spatial distribution of the crystal constituents was inspected by an electron probe microanalyzer (EPMA) JXA-8621MX produced by JEOL. The measurements were performed at accelerating voltage of 20 kV and current of 1.2×10^{-8} A. Figure 10 shows the results of the chemical composition analysis for the crystal specimen cut parallel to its growth axis (crystal No.8, Fig.5). The results demonstrated that Si and Ce were distributed homogeneously. Content of La slightly decreased when the solidification fraction increased. On the contrary, Gd content slightly increased when the solidification fraction increased. Other samples had identical trends because the starting melt compositions were similar (Table 1). Spatial distribution of all the constituents of the Ce-doped La-GPS crystals along the growth axis is also illustrated by the EPMA data shown in Fig. 11 for the crystal No.7 (Table 1), and these results were almost identical to those of Fig.10.

Large dispersion of Ce content in the Fig.10 was associated with the relatively low concentration of Ce in the melt and in the crystal. As stated in Table 1, the concentration of the Ce^{3+} -activator was only 0.5-1.5 at.% with respect to the total content of the rare-earths, and it was even lower with respect to all atoms forming the crystal. On the other hand, it is well known that the accuracy of EPMA for the major elements is about 1%, and relative analytical error may exceed $\pm 50\%$ for the elements present in negligible amounts (less than 1 wt%) [19]. According to Fig.10, dispersion of the Ce content was within $\pm 40\%$ that is not in conflict with the above value of 50%. Thus, it was concluded that large dispersion of the Ce content in the

crystals reported here follows from large uncertainty of the measurements, not from non-uniform distribution of Ce.

The radio-luminescence (RL) spectra were recorded at room temperature. The measurements were performed using X-ray source RINT-2000, which was equipped with Cu target. The X-ray tube (Seifert GmbH) operated under voltage of 40 kV and current flow of 40 mA. The emission spectra were measured using Andor DU-420-OE CCD camera. The temperature of the camera was set to be 213K that was controlled by a Peltier module. The CCD was coupled with a monochromator made by ORIEL INSTRUMENTS designed for 285 grooves/mm and 280 nm blaze wavelength. The scintillation light output was sent to the CCD through a 2m optical fiber to avoid direct X-ray hit to the CCD. The as-obtained radio-luminescence spectra of crystals Nos.3, 6, and 10 are illustrated in Fig. 12. The emission peak at around 370 – 390 nm wavelength originating from Ce^{3+} 5d-4f transition was detected for this material. The results obtained for other crystals discussed here were identical.

7. Summary

2-inch diameter Ce-doped La-GPS single crystals were successfully produced from the $\text{La}_{0.49}\text{Ce}_{0.01}\text{Gd}_{1.50}\text{Si}_2\text{O}_7$ and $\text{La}_{0.49}\text{Ce}_{0.03}\text{Gd}_{1.48}\text{Si}_2\text{O}_7$ melts. The crystals grown in optimized conditions did not contain any cracks and/or inclusions, had well developed body part shapes, and smooth surfaces. The growth process was well reproducible demonstrating that CZ technology is suitable for the mass production of the La-GPS crystals for scintillator applications. A considerable disadvantage of the process is associated with relatively short lifetime of the Ir crucible used as a melt container that negatively affects possible commercialization of the process. Expansion of the crucible in the horizontal direction for up to 30% is most probably caused by the thermal expansion of the solidified melt sited in the crucible: the diameter of the crucible containing some melt increased by about 1.5% in average for every heating run including those performed for charging the crucible and actual growths.

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Table 1. Conditions and results of crystal growth of Ce-doped La-GPS by CZ method.

No.	Melt Composition	[Ce], at. %	Rotation, rpm	Coil position, mm	After- Heater	Coil Move	Cracks	Bubbles	Fig.
1	$\text{La}_{0.49}\text{Ce}_{0.03}\text{Gd}_{1.48}\text{Si}_2\text{O}_7$	1.5	7	0	Yes	No	Yes	Yes	3
2	$\text{La}_{0.49}\text{Ce}_{0.03}\text{Gd}_{1.48}\text{Si}_2\text{O}_7$	1.5	7-3	0	No	No	Yes	No/Yes	3
3	$\text{La}_{0.49}\text{Ce}_{0.03}\text{Gd}_{1.48}\text{Si}_2\text{O}_7$	1.5	5-3	0	Yes	Yes	Yes	No/Yes	3
4	$\text{La}_{0.49}\text{Ce}_{0.03}\text{Gd}_{1.48}\text{Si}_2\text{O}_7$	1.5	5-3	+10	Yes	Yes	Yes	No/Yes	4
5	$\text{La}_{0.49}\text{Ce}_{0.03}\text{Gd}_{1.48}\text{Si}_2\text{O}_7$	1.5	5	+10	Yes	Yes	Yes	No/Yes	4
6	$\text{La}_{0.49}\text{Ce}_{0.03}\text{Gd}_{1.48}\text{Si}_2\text{O}_7$	1.5	10	+10	Yes	Yes	Yes	No/Yes	4
7	$\text{La}_{0.49}\text{Ce}_{0.01}\text{Gd}_{1.50}\text{Si}_2\text{O}_7$	0.5	5-3	0	Yes	Yes	Yes	No	5
8	$\text{La}_{0.49}\text{Ce}_{0.01}\text{Gd}_{1.50}\text{Si}_2\text{O}_7$	0.5	5-3	0	Yes	Yes	No	No	5
9	$\text{La}_{0.49}\text{Ce}_{0.03}\text{Gd}_{1.48}\text{Si}_2\text{O}_7$	1.5	5-3	0	Yes	Yes	No	No	6
10	$\text{La}_{0.49}\text{Ce}_{0.03}\text{Gd}_{1.48}\text{Si}_2\text{O}_7$	1.5	7-5	0	Yes	Yes	No	No	6

Notes: In the case of “+10” coil position, the top edge of the coil was above the top edge of the crucible by 10 mm (See Fig. 1 for reference). Double numbers for rotation represent rotation rates at the beginning and the end of the body part growth (Fig.2), respectively.

Fig.1. Schematic diagram of the Czochralski process performed for the growth of La-GPS crystals from the crucible of $\varnothing 100 \times 100$ mm in dimensions with “+10” coil position.

Fig.2. Rotation rate and RF coil position adjustment schedule. Note that the position of the top of the coil was adjusted to be the same as the melt level.

Fig.3. View of the 2-inch diameter La-GPS crystals Nos. 1-3 according to Table 1

Fig.4. View of the 2-inch diameter La-GPS crystals Nos. 4-6 according to Table 1

Fig.5. View of the 2-inch diameter La-GPS crystals Nos. 7-8 according to Table 1

Fig.6. View of the 2-inch diameter La-GPS crystals Nos. 9-10 according to Table 1

Fig.7. Deformation of the crucible observed after seven growth cycles. Original dimensions of the crucible were $\varnothing 100 \times 100$ mm.

Fig.8. RF power necessary for the growth initiation at the stage of seeding versus serial number of the growth process performed with the same crucible.

Fig.9. Normalized cell volume change, $V/V(30^\circ\text{C})$ measured for the $\text{Gd}_2\text{Si}_2\text{O}_7$ and $\text{Dy}_2\text{Si}_2\text{O}_7$ in [15], and those extrapolated for the melting point of La-GPS (approximately 1700°C)

Figure 10. Distribution of the elements along growth axis of the crystal No.8 according to the results of EPMA. C is concentration in the crystal, and C_0 is concentration in the melt. Estimated error bar for the measurements of Ce content is shown on the right side.

Figure 11. Distribution of the elements along growth axis of the crystal No.7 according to the results of EPMA.

Figure 12. X-ray induced luminescence spectra of the samples cut from the crystals Nos.3, 6, and 10.