

# The crystal growth of ortho- and pyrosilicates from W and Mo crucibles

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# Crystal growth of ortho- and pyrosilicates from W and Mo crucibles

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# Abstract

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Ir-consuming expensive growth technology is the main obstacle at widening the area of ortho- and pyrosilicate crystals application. Possibilities to grow silicate single crystals from melt using Mo or W crucibles in crystallizers with graphite heaters are evaluated. Such feasibility is shown on the examples of Y<sub>2</sub>SiO<sub>5</sub>:Ce (YSO:Ce) and La<sub>2-x</sub>Gd<sub>x</sub>Si<sub>2</sub>O<sub>7</sub>:Ce (LaGPS:Ce) scintillation crystals. Application of Edge-defined film-fed growth (EFG) method for silicates growth is limited owing to non-stoichiometry because of the interaction of CO-containing atmosphere with the melt and crystals. The bulk YSO:Ce and LaGPS:Ce crystals are grown by the Bridgman and Czochralski methods for the first time using much cheaper (compared to Iridium) molybdenum (Mo) or tungsten (W) crucibles. The optical and scintillation parameters of the obtained crystals are determined and compared to the counterparts grown by the conventional Czochralski process in Ir crucibles. The ways of further optimization of technological processes are discussed.

#### 1. Introduction

Crystals of rare-earth silicate complex oxides are widely used in scintillator and laser applications. Ce-doped orthosilicates Lu<sub>2</sub>SiO<sub>5</sub> (LSO:Ce), Lu<sub>1-x</sub>Y<sub>x</sub>SiO<sub>5</sub> (LYSO:Ce), Y<sub>2</sub>SiO<sub>5</sub>

(YSO),  $Gd_2SiO_5$  (GSO)  $Lu_{1-x}Gd_xSiO_5$  (LGSO:Ce) are very popular scintillation materials with the density of up to 7.4 g/cm<sup>3</sup>, high light yield up to 38000 phot/MeV, a good energy resolution (7 - 9% at the 662 keV energy), and short luminescence decay time of 35 – 80 ns [1-3]. The main areas of orthosilicates application are medical PET tomographs [4] and high energy physics experiments [5]. Recently, Ce-doped disilicates (pyrosilicates) such as  $Gd_2Si_2O_7$  (GPS),  $La_2$ .  $_xGd_xSi_2O_7$  (LaGPS) have been developed. Despite the lower density and stopping power compared to the orthosilicates they provide even higher light yield of up to 40000 phot/MeV and better energy resolution up to 4.4 % [6]. Orthosilicates doped with Yb<sup>3+</sup> were proposed as laser media [7], and Dy<sup>3+</sup> and Sm<sup>3+</sup>-doped LSO, GSO and their solid solutions are promising white light emitters [8, 9].

The melting points of the Ln<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> compounds (Ln – lanthanide, or Y) are high –  $T_m$ =1900 – 2100 °C in orthosilicates Ln<sub>2</sub>SiO<sub>5</sub> and  $T_m$ = 1740 – 1860 °C in pyrosilicates Ln<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> [10]. Large LSO, LYSO, GSO, LGSO crystals with the diameters up to 100 mm are successfully grown by the Czochralski method under inert atmosphere of Ar or N using Ir crucibles [11 - 15], whereas the crystallizers are constructed from Al<sub>2</sub>O<sub>3</sub> or Y<sub>2</sub>O<sub>3</sub> thermal insulating ceramics. High Ir cost and limited crucible lifetime have a significant impact on crystal cost and limit scaling up of their production. Most the attempts of using cheap Mo and W crucibles were not successful. Few works are known on the melting and crystallization of yttrium silicates in W crucibles [16]. Interaction of orthosilicate and rare earth garnet melts with Mo was studied in [17]. It was shown that Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (YAG) and Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (LuAG) melts weakly interact with Mo that was supported by the growth of shaped plates with the length up to 320 mm by the EFG method. Orthosilicate and Ga-containing garnet crystals were not obtained owing to the melt interaction with Mo [17]. The mechanisms of orthosilicate and pyrosilicate melts interaction with Mo and W were not discussed.

The intensity of silicate melt interaction with the crucible material depends on their stability under certain conditions. The stability of melted  $Y_2O_3$  and  $SiO_2$  under Ar, Ar+O<sub>2</sub>, and wet conditions in equilibrium with their vapours was studied in [18] at temperatures up to 1700 K based on thermodynamic calculations. Under Ar atmosphere, evaporation of  $Y_2O_3$  and  $SiO_2$ leads to the formation of gaseous YO, O,  $SiO_2$ , O,  $O_2$  and SiO compounds. Partial pressures of these substances in equilibrium above  $Y_2O_3$  is by 5 orders of magnitude lower than that above  $SiO_2$ . So,  $Y_2O_3$  is much stable than  $SiO_2$  in Ar atmosphere. In Ar+O<sub>2</sub> ( $n_{Ar} = 0.8$  mole,  $n_{O2} = 0.2$ mole, note the similar oxygen concentration in air) the volatility of  $Y_2O_3$  and  $SiO_2$  leads to the formation of gaseous YO<sub>2</sub>,  $SiO_2$  and SiO. YO<sub>2</sub> partial pressure in equilibrium with  $Y_2O_3$  is by several orders higher than those of SiO<sub>2</sub> and SiO. Therefore,  $Y_2O_3$  is less stable in air than SiO<sub>2</sub>.

Finally, in the wet conditions ( $n_{Ar} = 0,4$  mole,  $n_{O2} = 0,1$  mole,  $n_{H2O} = 0,5$  mole) the reactions of evaporating of Y<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> with water vapour lead to the formation of gaseous YOOFF, Y(OH)<sub>3</sub>, YO<sub>2</sub>, Si(OH)<sub>4</sub>, SiO(OH)<sub>2</sub>, SiO<sub>2</sub>, and SiO. At 1300–1700 °C temperatures in the wet conditions SiO<sub>2</sub> is more stable than Y<sub>2</sub>O<sub>3</sub>. Therefore, interactions of the lanthanide oxides and SiO<sub>2</sub> with W and Mo should be evaluated in the conditions of current experiment.

Silicate melts themselves can be the origin of W and Mo oxidation, namely excessive oxygen is formed at non-equilibrium dissociation of silica. The literature data collected in Table 1 show that the  $P_O$  and  $P_{O2}$  partial pressures at SiO<sub>2</sub> dissociation are higher than equilibrium pressure above the W – WO<sub>3</sub> system (Table 1), and YSO melt should react with tungsten leading to its oxidation.

Table 1. Calculated pressure and equilibrium dissociation constants of silicon oxides, and Mo and W-containing compounds.

System	Temperature (K)	$-\lg P_{0_2}(Pa)$	$-\lg P_0$ (Pa)	
SiO	2000	7.7	4.52	[19]
SiO <sub>2</sub>	2001	4.95	5.65	[20]
SiO <sub>2</sub>	1996	5.418	5.9	[21]
SiO <sub>2</sub>	2500	2.786	3.205	[21]
Mo-MoO <sub>2</sub>	2000	6.38	6.367	[21]
Mo-MoO <sub>2</sub>	2500	3.538	3.611	[21]
MoO <sub>2</sub> - MoO <sub>3</sub>	1873	3.871	5.9	[21]
$WO_2 - W$	1873	7.2778	7.266	[21]
$WO_2 - W$	1992	6 356	6.382	[21]
$WO_2 - W$	2000	6.286	6.321	[21]
$WO_2 - W$	2500	3.393	3.539	[21]
W – WO <sub>3</sub> (liquid)	2000	6.471	6.413	[21]
W – WO <sub>3</sub> (liquid)	2500	3.965	3.825	[21]

Metallic tungsten is inevitably formed in melt at the presence of  $WO_2$ , because the upper limit of  $WO_2$  thermal stability is 1530 °C [21, 22]. Additionally, metallic tungsten may form by the disproportionation (Eq. 1), or as the result of interaction between the oxides [22] (Eq. 2):

 $1.5 \text{ WO}_{2(g)} \leftrightarrow \text{WO}_{3(g)} + 0.5 \text{W}_{(s)} \quad (1)$ 

$$WO_{2(g)} + WO_{(g)} \leftrightarrow WO_{3(g)} + W_{(s)}$$
 (2)

Under the reducing conditions of CO-containing atmosphere, CO participates in exchange view Article Online interactions with the melt. At 800 °C, CO reduces WO<sub>3</sub> to WO<sub>2</sub>, and then to metallice transstered at higher temperatures [23]. These processes (W dissociation, disproportionation, or interaction with CO) are responsible for the creation of metallic film. Their contribution depends on many factors including partial pressure of C and CO. A saturated vapour above graphite at 2000 K contains 50.57 vol.% of C and 45.38 vol.% of C<sub>3</sub>, and the resulting pressure lg  $P_C$  reaches -9.94 Pa [21].

Overall, this work aims at detailed study of interactions between melts of ortho- and pyrosilicates with metallic Mo and W and determination of factors affecting their crystal growth. The growth conditions of orthosilicates and pyrosilicates in these crucibles are proposed and illustrated by the examples of Ce-doped LaGPS and YSO crystals.

# 2. Experimental

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#### 2.1. Crystal growth

Inert or reducing atmosphere containing H<sub>2</sub> or CO is necessary when using Mo or W crucibles. Graphite heaters and heat insulation used to achieve temperatures around 2000°C automatically create a reducing atmosphere. W is preferable under the presence of CO and high temperatures, because the W-W<sub>2</sub>C eutectic temperature is 2710 °C versus 2205 °C in Mo-Mo<sub>2</sub>C [24]. Keeping in mind the melting points of orthosilicates around 2000 °C [10], they were crystallized in W crucibles, while pyrosilicates with the melting points around 1800 °C [10] were melted and crystallized mainly in Mo crucibles. Ground crystals grown from Ir crucibles or powders synthesized by solid state reaction from Y<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> oxides powders with the purity not less than 99.99% were used as starting raw materials. Crystals were grown by the conventional Czochralski and Vertical Bridgman methods under 99,999% purity Ar atmosphere in RF heating setups at 8 kHz, with graphite heaters and glassy carbon heat insulation. W and Mo crucibles of 50 mm in diameter were filled with 50-330 g of raw materials. The reducing atmosphere was formed due to the interaction between graphite and residual oxygen in the growth camera, as well as oxygen formed at dissociation of oxides in raw material. In the Czochralski process the pulling rates were 0.5-1.5 mm/hour and the crystal rotation rates were 6-12 rpm, whereas in the Bridgman the crucible translation rate was 1-2 mm/hour, and in the Edge-Defined Film-Fed Growth (EFG) the pulling rates were 5-15 mm/hour. The seeding in Czochralski method was made on W wire, a crystalline seed with random orientations were used in EFG method, while no seed was used in the Bridgman process.

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# 2.2. Determination of crystalline structure and composition

Crystalline structures were determined by the X-ray diffraction in the thod.<sup>CE01</sup>The FullProf&WinPLOTR program [25] was used for the Rietveld refinement of powder pattern. The Al<sub>2</sub>O<sub>3</sub> plate (NIST SRM1976) was used as external standard to determine the instrumental profile function.

Morphology and element composition of sample surfaces were controlled by a JSM-6390LV scanning electron microscope (SEM) with AZtechEnergy X-max<sup>n</sup> 50 microanalysis system (EDS). Structure and phase composition were determined with a Siemens D500 diffractometer. Admixture content was controlled by an ElvaX Light X-Ray Fluorescence Spectrometer.

## 2.3. Optical and scintillation characterization

Absorption spectra in UV-VIS regions were recorded by a SPECORD 40 (Analytic Jena) spectrophotometer. X-ray luminescence spectra were measured in reflection mode with X-ray tube and photodetector Hamamatsu R1926A located at the same side from the samples under a steady-state X-ray excitation (Ag anode, 40 kV, 40  $\mu$ A). Emitted light was dispersed with a monochromator (grating 1200 grooves/mm). Obtained spectra were not corrected for the spectral sensitivity of the detection system.

Light yield (LY) and energy resolution (R) were measured under irradiation with a 662 keV  $^{137}$ Cs gamma source. A R1307 Hamamatsu PMT ran at 800 V and HV with linear dynode voltage divider were used for registration of YAG:Ce,C parameters. The shaping time was 2 µs. PMT output was connected to the charge-sensitive preamplifier BUS 2-94 and BUI-3K shaping amplifier. Signal from preamplifier was shaped by a shaping amplifier with 2 µs shaping times. In order to collect the whole scintillation light the samples together with open part of PMT photocathode were covered with Teflon reflector. No optical contact between samples and PMT window was provided. For absolute light yield determination the yields were compared to Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> (BGO) produced by a standard technology by the Czochralski method. Energy resolution was determined as FWHM of the <sup>137</sup>Cs 662 keV photopeak at pulse-height spectra by its approximation with the Gaussian function.

## 3. Results and Discussion

3.1. Growth of orthosilicates

To evaluate the interaction of YSO melt with tungsten, chunks of crystals obtained from 4 crucibles were melted in W crucible under the Ar+CO atmosphere ( $P_{Ar+CO}$ = 1.02 atm). An opaque grayish-metallic film was formed at melt surface in 40 min after melting as shown in Fig. 1. XRD showed that this film is tungsten (JCPDS#04-0806) with few unidentified admixtures (Fig. 2a). Therefore, tungsten was oxidized, melted, reduced at melt surface, and stuck to the grown crystal. The W film thickness reached 2 µm, and W overall concentration in crystallized melt was 0.1 wt.%. In some experiments W crystallized at the melt-gas boundary in the form of hexagonal stepped cavities (Fig. 1b). In the crystallized melt the gas bubbles were partially covered with metallic tungsten. Additinally, tungsten dendrite branches and inclusions were observed at crystal surfaces (Figure 1c,d).



Figure 1. W film on the side surface of the crystal grown on a YSO crystalline seed (a), crystallized tungsten (b), tungsten dendrite branches on a crystallized melt surface (c), (d).

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This means that in open crucibles used in the Czochralski method the SiO<sub>2</sub> evaporation intensity heavily increases due to the reaction (3) [26]:

$$\operatorname{SiO}_{2(l)} + \operatorname{CO}_{(g)} \rightarrow \operatorname{SiO}_{(g)} + \operatorname{CO}_{2(g)}(3).$$

Transport of SiO and  $CO_2$  to the graphite heater results in formation of SiC films at graphite surfaces and increase of CO concentration.

$$\operatorname{SiO}_{(g)} + \operatorname{C}_{(s)} \to \operatorname{SiC}_{(g)} + \operatorname{CO}_{(g)} (4)$$
$$\operatorname{CO}_{2(g)} + \operatorname{C}_{(s)} \to 2\operatorname{CO}(g) (5)$$

CO also interacts with the seed and growing crystal resulting in depletion of their surface layer with  $SiO_2$ . This creates non-stoichiometry in the layer and decreases its melting temperature. The surface layer melts earlier than the bulk and drains off. This is not important in Czochralski method, but critical for EFG growth, because even inessential non-stoichiometry in melt meniscus changes its properties and hinders crystal growth. In our experiments the composition of the depleted surface layer was  $Y_{2,46}Si_{0,66}O_5$ . Therefore, stoichiometric YSO growth under CO atmosphere is practically impossible.

During Czochralski growth, the crystal is exposed to high temperatures for a long time (up to several days) due to the low pulling rate. This results in a heavy depletion of silica from the surface near the dendrites (see Figure 1c,d) to the  $Y_{3,2}Si_{0,1}O_5$  (i. e. almost  $Y_2O_3$ ) composition during 6 hours. There are no available conditions preventing or limiting CO concentration in the YSO–W–C system that strongly complicates the crystal growth. In addition, SiO<sub>2</sub> dissociation is another obstacle at YSO growth from W crucibles.

To reduce the interaction of C and CO with the YSO melt, the crucible with raw material was tightly covered with W lid. Despite no visible inclusions were observed after YSO melting and keeping during 40 minutes the crystallized melt contained 0.01 wt% of W. According to XRD, the melt crystallized into the  $Y_2SiO_5$  single phase with the I2/a space group (Fig. 2b) and corresponded to the ICSD#28021. Therefore, one may avoid W film formation at the surface and decrease W concentration in bulk by preventing the melt interaction with C and CO.



Figure 2. XRD of W film at the surface of crystallized YSO melt (a), and crystallized YSO melt after its heating in W crucible covered with W lid (b).



Figure 3. YSO:Ce crystallized melt after its heating in W crucible with W lid: under daylight (a) and UV light (b).

A W crucible with the 18 mm diameter and 30 mm height and with a mechanically fit lid still allowing some reduced gas exchange was fabricated for YSO:Ce growth by the Bridgman method. The chunks of YSO:Ce crystal grown from Ir crucible were used as the raw material. The crucible translation rate was 2 mm/h. The crystal stuck to the crucible and cracked (Figure 3a). A characteristic Ce<sup>3+</sup> blue phosphorescence in YSO:Ce was observed under UV light (Figure 3b). No W film was observed on the crystal surface. This example illustrates the significant effect of C and CO gas in the tungsten film formation. The role of dissociation decreased under these conditions, because the equilibrium of vapours was reached faster in the closed volume. The concentration of W in the crystal was 0.002 % wt.

## 3.2. Growth of pyrosilicates

Using W crucibles in growth of pyrosilicates is more promising, because the latter possess approximately 200 °C lower melting points compared to those in orthosilicates, as well as lower vapour pressure and dissociation rates [19]. Gadolinium-lanthanum pyrosilicate Gd<sub>1.2</sub>La<sub>0.8</sub>Si<sub>2</sub>O<sub>7</sub> was grown by the Czochralski method in W crucible. Mo wire was used as a seed, and the raw material weight was 60 g. The obtained crystal (Figure 4a) contained a lot of bubbles, and its surface became milky after the interaction with CO. No signs of metal at the melt surface were observed after 24 hours of crystal growth (Figure 4b). However, the concentration of W dissolved in the crystallized melt and in crystal reached 0.05 and 0.01 wt%, respectively. Lowering of melting temperature reduced the W dissolving that excluded the formation of a

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uniform metal film, but metal particles were observed between the grains in the crystallized melt (Figure 4c).



Figure 4. LaGPS:Ce crystal grown from W crucible (a), W crucible with remnants of LaGPS:Ce melt after crystallization (b), fragment of its surface with Mo inclusions (c).

The lower melting temperature of pyrosilicates (~1800°C) enables usage of Mo crucibles. Mo crucibles are preferable, because the vapour pressure of Mo oxides is by several orders higher than that of W [27], and the Mo vapour pressure is by four orders higher than that of W [28]. The intensive evaporation of Mo and its oxidation decrease the probability of metal film formation at the melt surface. The quantity of dissolved and reduced metal directly depends on the dissociation and the quantity of the loaded raw material into the crucible, and process duration. Then the crucible was loaded with 330 g of raw material and Ce activator was added. The resulting chemical formula was Ce<sub>0.02</sub>Gd<sub>1.48</sub>La<sub>0.5</sub>Si<sub>2</sub>O<sub>7</sub>. The growth rate was in the range of 0.5 - 1 mm/hour. After 100 hours the Mo island remained at the melt surface and most of Mo stuck to crystal surface in the form of wires and spots (Figure 5a). The SiO<sub>2</sub> dissociation continued during the crystal growth, but its intensity was not critically high. Continuous Mo film at the melt surface was not formed; however, the crystal contained a lot of visible macroscopic

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inclusions (Figure 5b). The characteristic  $Ce^{3+}$  violet phosphorescence was observed under UV light (Figure 5c). The measured crystal density was 5.274 g/cm<sup>3</sup>. It is comparable/with the density of 5.5 g/cm<sup>3</sup> in La<sub>0.2</sub>-Ce<sub>0.05</sub>Gd<sub>1.75</sub>Si<sub>2</sub>O<sub>7</sub> [29] (but note the lower La concentration leading to the density increase in our case). The silicon-depleted milky surface layer reached the thickness of 0.3 mm as the result of interaction with CO. Mo concentrations in the crystallized melt and crystal were 0.04 and 0.013 wt%, respectively. As one can see, the crucible metal concentrations in the melts and crystals are significantly higher in the Czochralski grown La-GPS:Ce compared to the Bridgman grown YSO:Ce due to covering the crucible with the lead in the latter.



a



c

Figure 5. As-grown LaGPS:Ce crystal grown from Mo crucible (a), its parts under illumination with daylight (b) and UV-light (c).

## 3.3. Optical and Scintillation parameters

Absorption spectra of LaGPS contain a series of  $Ce^{3+}$  absorption bands in the UV range. Some of them are not resolved due to the high  $Ce^{3+}$  concentration. The sharp peaks around 275 nm are attributed to the  ${}^{8}S_{7/2} \rightarrow {}^{6}I_{J}$  transitions in  $Gd^{3+}$ , the same as observed in GSO:Ce [30]. No other distinct bands were observed in the visible and near–IR ranges up to 1100 nm. Absorption

spectra were not measured, because YSO:Ce samples contained a lot of inclusions and view Article Online DOI: 10.1039/DOCE01128B

YSO:Ce grown from W crucible possesses a typical luminescence band peaked at 425 nm related to 5d-4f radiative transitions in Ce<sup>3+</sup>. The strong long-wavelength shoulder of this peak around 500 nm can be ascribed to oxygen vacancies in the vicinity of Ce<sup>3+</sup> in LYSO:Ce crystal grown under oxygen-poor atmosphere [31], or, as proposed recently [32] to Ce<sup>3+</sup> - Ce<sup>3+</sup> dimers. X-ray luminescence spectrum of LaGPS:Ce is typical for rare-earth pyrosilicates with the triclinic structure [28, 33] and consists of the two bands peaked around 370 and 390 nm ascribed to the same 5d-4f (5d to  ${}^{2}F_{5/2}$  and  ${}^{2}F_{7/2}$  states, respectively) radiative transitions in Ce<sup>3+</sup> [33].



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Figure 6. (a) Absorption spectra of LaGPS:Ce (in the inset – enlarged view of the UV band), (b) Normalized XRL spectra of the obtained YSO:Ce and LaGPS:Ce crystals. Pulse height spectra of the obtained crystals in comparison with BGO standard 9x9x1.5 mm: (c) 10x3x2 mm size YSO sample and (d) 8x8x1.75 mm La-GPS sample. The difference in BGO spectra in (c) and (d) is related to various amplification coefficients and dynode voltages.

The channel number of the YSO:Ce 662 keV photopeak was up to 75 % of that in  $Bi_4Ge_3O_{12}$  (BGO). Therefore, the light yield of crystal grown from Mo crucible is well below 10000

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phot/MeV. Meanwhile, light output of the LaGPS:Ce was 360-370% in respect to a BGO standard that corresponds to 22150 phot/MeV following the light quantum efficiencies<sup>12</sup>at registration with a R1307 PMT. The energy resolution at 662 keV energy was 13.9 % for YSO:Ce and 17.3 % for La-GPS. The demonstrated scintillation parameters are worse than the best values obtained with crystals grown in Ir crucibles: up to 26700 phot/MeV and 6.8% in YSO:Ce [3] and 39000 phot/MeV and 5.4 % in La-GPS [6]. Obviously such results are called by the presence of scattering centres and point defects, which nature should be determined in further work.

Summarizing, in this work the crystals were obtained by the Czochralski and Bridgman – the essential methods of industrial crystal growth from melt. Basically, the Czochralski method would be preferable as it provides no contact of crystal with the crucible, good melt convection, growth on a seed, and simple scaling up. We have succeeded in growing LaGPS:Ce crystals by the Czochralski, whereas this process process was hardly possible with YSO:Ce possessing the higher melting temperature. The intense interaction of silicon oxide in YSO:Ce melt with the CO-containing reducing atmosphere results in crucible oxidation and formation of metal film at the melt surface. In the Bridgman method, the melt was protected from the environment by crucible covering with W lid that minimized silicon oxide interactions in the Bridgman-grown crystals (0.002 vs. 0.01-0.013 wt%). However, YSO:Ce ingots grown by the Bridgman without a seed were mainly polycrystalline, and stuck to the crucible after crystallization.

This study is a starting point for further assessment of growth conditions and materials for which the issues could be mitigated. Meanwhile it shows the feasibility to obtain bulk ortho- and pyrosilicate crystals from melt without using expensive Ir crucibles and heat shields. There is a room for improvement of scintillation parameters by minimizing scattering centres and point defect concentrations. For example, La-GPS crystals contain a lot of gas bubbles that definitely deteriorate the luminescence yield. Additionally, the peculiarities of carbon incorporation into these crystals at growth under CO-containing atmosphere should be elucidated. Further work will be devoted to the tuning gaseous atmosphere composition and/or crucible sealing procedure to minimize the light scattering in crystals. The crystal quality eventually may be also improved by using crystalline chunks as raw materials instead of powders.

# Conclusions

A feasibility of growing rare earth silicate oxides using W and Mo crucibles with graphite heaters and thermal heat insulation was shown. The process is complicated by the low thermodynamic stability of  $SiO_2$  at temperatures around 2000°C and its interaction with CO gas.

The SiO<sub>2</sub> dissociation results in liberation of excessive oxygen and crucible surface oxidation that leads to dissolving of crucible material in the melt and its reduction at the melt surface. The metal film formed at the melt surface constitutes a main barrier for a steady crystal growth under such conditions.

EFG growth technique is practically not implementable using Mo or W crucibles and shapers because of the precise requirements to melt stoichiometry, which are difficult to sustain under critical conditions of melt dissociation and its interaction with CO. We have not succeeded in growing any shaped ortho- or pyrosilicate crystal.

The Czochralski method is less sensitive to the deviations of melt stoichiometry. However, it also suffers from the interaction between  $SiO_2$  and CO, crucible oxidation, as well open melt surface that promotes its interaction with atmosphere. Our experiments showed that bulk pyrosilicate crystals can be grown by the Czochralski from Mo crucibles. Formation of metal film on the melt surface can be avoided by reducing CO content in the growth atmosphere.

The Bridgman growth in closed crucibles is advantageous as it reduces melt dissociation and its interaction with CO. However, this method not provides a visual control over crystallization process, and the problem of crystal sticking to crucible walls is not resolved. The similar approach can be applied as well in other methods of crystal growth in closed or sealed crucibles, such as Temperature Gradient, or Vertical Gradient Freeze Techniques. Meanwhile, all these methods do not exclude the introduction of crucible material and gaseous inclusions into crystals.

YSO:Ce and LaGPS:Ce crystals obtained by the Czochralski and Bridgman methods under the specified conditions show low-to-moderate scintillation parameters owing to the presence of gas bubbles and oxygen vacancies formed in the oxygen-poor atmosphere conditions. There is a good opportunity for the improvement of crystal quality by optimizing technological parameters of the process. For example, La-GPS crystals contain a lot of gaseous bubbles that definitely serve as light scattering centres deteriorate the luminescence yield. Tuning the gaseous atmosphere composition and/or crucible sealing procedure should be helpful in this context.

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A feasibility to grow bulk La-GPS:Ce scintillation crystals by the Czochralski method using Mo crucibles has been reported

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