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Growth of BaBrI Crystals by the Czochralski Method

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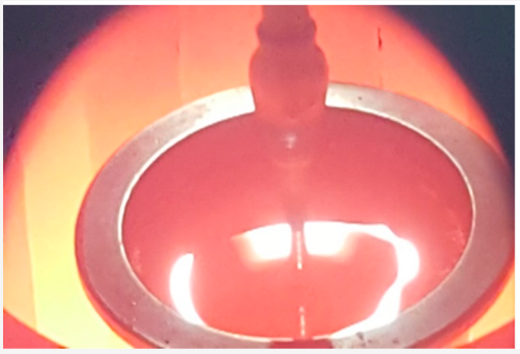

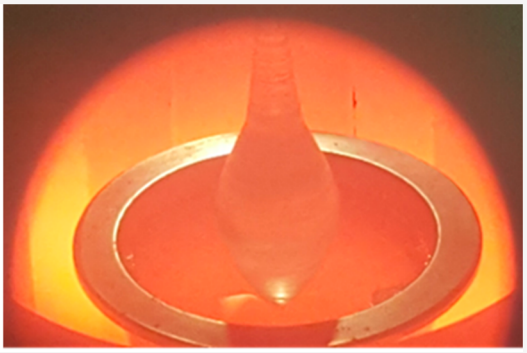

ABSTRACT: BaBrI crystals activated by rare-earth-metal ions are promising scintillation materials. In this work, were research the aspects of growing such crystals by the Czochralski method. This method makes it possible to grow single crystals and to avoid crystallization processes from the crucible walls. The Czochralski method may be the best way to obtain an affordable and controlled growth of large crystals. This method allows crystals to grow at different rates, depending on the conditions.

1. INTRODUCTION

BaBrI crystals belong to the group of alkaline-earth halides. Of most interest is the use of BaBrI crystals as scintillators[1−7] activated by rare-earth elements, at various concentrations. The main advantages of such scintillators are their luminosity and high resolving power on energy. A parameter such as the luminosity[8] for BaBrI:Eu^{2+} of 97000 photons/MeV may be achievable. The parameters of scintillation crystals can vary significantly due to growth conditions and the presence of hydroxyl groups. Thus, BaBrI crystals (when there are OH^- groups) lose their advantage and become comparable with scintillators such as NaI:Tl (40000 photons/MeV) and CsI:Tl (54000 photons/MeV). This leads to a difference in the parameters of the obtained crystals, depending on the growth conditions and quality of the feedstock.

The crystals can grow under various conditions. Two main methods should be identified: (1) a method in which the melt with the crucible moves along the temperature gradient (can be performed using elements that give shape and size to the crystal) and (2) a method in which a crystal is pulled upward from a melt (growth on an inverse gradient). Crystal growth occurs depending on morphogenesis and nucleation conditions.[9]

The main method used for the growth of BaBrI crystals is the Bridgman−Stockbarger method.[10,11] The distinctive features of crystal growth by this method include the use of crucibles or ampules. Therefore, in the process of growth, the crucible (ampule) moves in a thermal field, through a temperature gradient. This method, due to the reduction of thermal fluctuations (effective shielding), allows creation of a low-temperature gradient. The typical growth rate of BaBrI crystals for the Bridgman−Stockbarger method is 1 mm/h. In the process of performing experiments using this method, problems arose with obtaining single crystals. The resulting crystals are blocks with different isotropy. This disadvantage is associated with the fact that the crystallization process can occur from the walls of the crucible (ampule). The absence of visual observation does not allow determination of the optimal parameters of crystal growth in a short time. Crystal growth by the Czochralski method allows visual observation of the process and the possibility to make adjustments, unlike the Bridgman−-Stockbarger method. The crystal growth conditions in the Bridgman−Stockbarg method are determined from the obtained crystal. For crystal growth the Czochralski method was used, which in turn suggests the use of seed crystals or seeds; growth, in contrast to the Bridgman−Stockbarger method, occurs on the inverse gradient.[12] In the Czochralski method, growth occurs above

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the surface of the melt; by pulling the crystal at a given speed, rotation is used to impart axial symmetry. This method of directed crystallization makes it possible to obtain large crystals; thus, this method is more convenient for the mass production of crystals.

In this work, was consider the Czochralski method as an alternative to the Bridgman−Stockbarger method. The aim of this work was to obtain BaBrI single crystals by the Czochralski method. In particular, the work pays attention to the problems of the hygroscopicity of BaBrI crystals.

2. EXPERIMENTAL SECTION

2.1. Temperature Changes in Raw Materials during Heating. The growth temperature of BaBrI crystals in the Chohralski method depends on the thermal field. At the top part of the open type of the crystallization apparatus (for visual observation), there is a significant temperature change with height. From analysis data, we can conclude that the melting point (peak 3) is 781 °C (Figure 1).

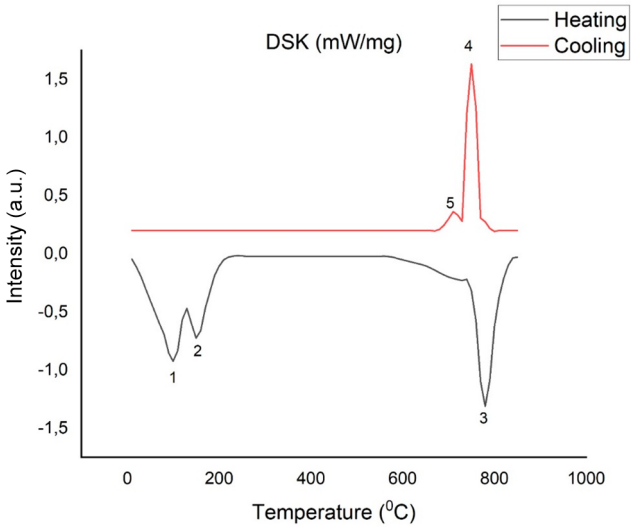

Figure 1. Differential scanning calorimetry method for the BaBrI system: peaks 1 and 2, associated with a phase transition of water leaving the raw material; peak 3, melting temperature of BaBrI, 781 °C; peak 4, crystallization process at 754.5 °C; peak 5, phase transition associated with a change in the type of lattice at 730 °C.

For crystal growth, preliminary drying under vacuum (10^{-4} mm hg and higher) on temperature shelves is required. Since the BaBrI feedstock is hygroscopic when it is heated to 180 °C, it loses about 10% of the total mass. There are two temperature regimens for 120 °C, 5.1% (peak 1) weight loss, and 180 °C, 5.4% (peak 2) weight loss, according to the data of thermogravimetric analysis. When BaBrI is heated from 180 °C to the melting temperature, the mass charge does not change.

Before the moment of melting, argon is pumped into the chamber in order to avoid a violation of the stoichiometry associated with the volatility of raw materials. There is a substitution reaction in BaI_2 in which BaO is formed and iodine escapes as a gas. Violation of the dehydration conditions leads to the formation of compounds of hydroxyl groups, which lead to irreversible changes. As a result, the optical transparency of the crystals obtained decreases significantly. Contaminants are pushed onto the melt surface. During growth, they can become secondary crystallization centers and lead to dislocation. In this work, growth was carried out under an especially pure argon atmosphere.

It should be noted that peak 5 (Figure 1) is characteristic of this group of crystals. In work on the growth of BaBrCl crystals by the Czochralski method,[13] this peak is associated with a change in the type of crystalline lattice. In the case of BaBrI crystals, this transition can be associated with a change in the type of lattice from orthorhombic to cubic. These processes are complicated by a high temperature close to the crystallization temperature. This means that at a gradient on the order of 20 °C/cm an uncontrolled transition will occur, causing crystal destruction due to thermal stresses. The phase transition depends on stoichiometry and temperature in the region where the crystal is cooled. Therefore, to remove thermal stresses from the crystal, it may be effective to create an additional thermal zone.

2.2. Apparatus for Crystal Growth by the Czochralski Method. The apparatus is a closed vacuum chamber made of stainless steel (Figure 2), which allows the creation of a vacuum of

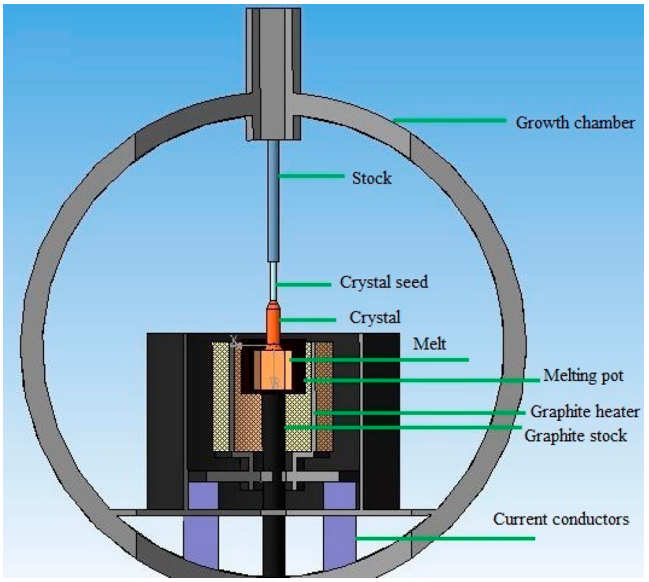

Figure 2. Scheme of the apparatus for crystal growth.

about 10^{-5} mmHg or filling of the chamber with an inert gas. In the system a graphite heater was used as a heat source (this is a spiral cut from a graphite billet). Graphite shields to reduce temperature fluctuations in the crucible zone protect the crystal.[14,15] Cooling of the apparatus is performed using water; this is necessary in order to reduce thermal fluctuations during the crystal growth process. This allows isolation of the internal region from the external system. The main task of the cooling system is to remove heat from the growing crystal. With a change in the pressure of water, the growing conditions can be varied. Improving the heat sink from the crystal can increase the growth rate.

The heater is connected to a single-phase step-down transformer. Electricity is supplied to the heater using a current lead system. The control is carried out through a thyristor unit, which in turn is controlled by a PID regulator (PROTERM 100). Vacuum is achieved by means of two pumps: a plate-rotor pump is used to create a preliminary vacuum and then pumping out is performed by means of a steam−oil pump.

The heater and the heat shield system are made of graphite, as graphite allows the production of heaters with a given heat field. Graphite has resistance to high temperature in the absence of contact with air.

2.3. Seed and Seed Crystals. A distinctive feature of crystal growth by the Czochralski method is the use of seeds. In these experiments, three types of seeds (Figure 3) were used: (1) a quartz tube with a fixed crystal (the crystal was previously obtained by the Stockbarger method), (2) a steel tube with a fixed crystal, and (3) a quartz capillary.

The use of a previously obtained crystal is not optimal, as it requires the use of auxiliary methods of growth. It is necessary to

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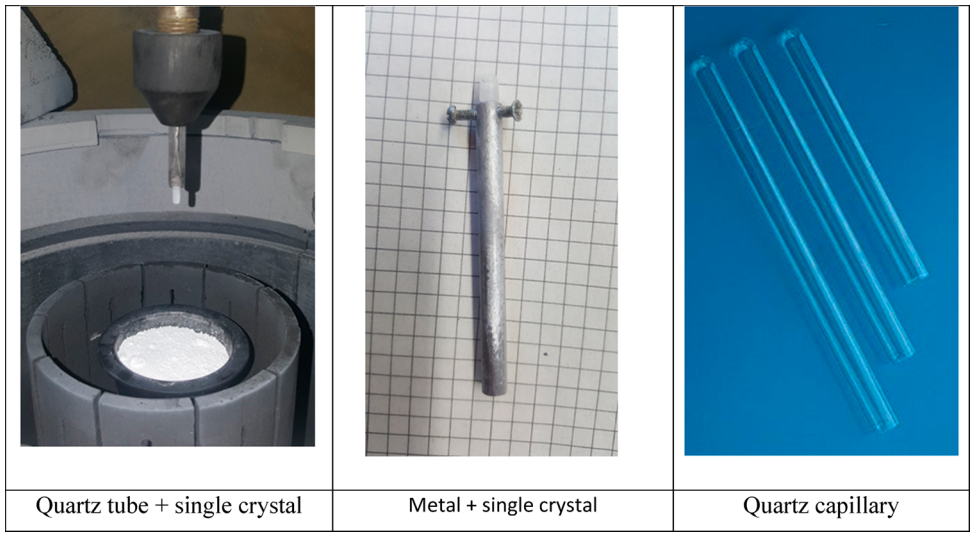

Figure 3. Different types of seeds.

select the optimal crystal from which the seed is subsequently made. When the wrong cooling rate is chosen, the seed crystal is destroyed, which makes it impossible to reuse it. Experiments were carried out using a metal tube as a seed crystal holder in order to improve heat removal from the grown crystal. The use of a metal tube did not give significant improvements, as probably there was not enough contact with the stock. The crystal parameters do not depend on the type of holder, only on the quality of the seed crystal and growth conditions.

When a quartz capillary is used, the growth process begins with supercooling of the melt surface. It is necessary that a polycrystalline structure form on the lower part of the quartz capillary. From this structure, by a change in the crystallization front to concave, a single crystal can be obtained. Changing the crystallization front reduces the diameter of the crystal, making it possible to reduce the number of dislocations and move from a polycrystalline material to a single crystal.

2.4. Growth Parameters of BaBrI Crystals. The Czochralski method is not characterized by a certain temperature. Since the upper part of the crystallization apparatus is open for visual observation, the temperature values depend on the position of the thermocouple. In this case, a tungsten−rhenium thermocouple was used, the error of which is insignificant. During the experiment, due to the design features of the apparatus, the thermocouple was fixed outside the heater; because of this, the crystal growth temperature varied from 640 to 670 °C. The Czochralski method is very demanding on the position of the thermocouple, so that when the thermocouple is displaced or its attachment point is changed, the crystal growth regimes change.

One should distinguish between the low-gradient method and the standard Czochralski method. In the case of a low-gradient method (2−3 °C/cm), the system is completely shielded, while the possibility of visual observation disappears. At the same time, during growth, when the crystal moves in the gradient, it does not collapse due to thermal stresses. This occurs when a large gradient. In this case, the gradient[16] was 15−25 °C/cm depending on the heater used, which made it possible to increase the growth rate of such crystals[17] to 8 mm/h (with the standard being 0.5−1 mm/h). The disadvantage of a large gradient is cracking of crystals due to thermal stresses.[18] In order to perform crystal growth at high speed, it is necessary to create an additional thermal zone with a constant temperature. During growth, the crystal will move to the area where slow cooling will take place. Such refinement will help to avoid cracking of the crystal during its growth. A decrease in the gradient will result in a low crystal growth rate.

BaBrI crystals cannot be quickly removed from the surface of the melt or transferred to a colder zone. This leads to cracking of the crystal. In order to separate the crystal from the melt surface, it is necessary to change the crystallization front (gradually reducing the crystal diameter).

After completion of the growth process cooling is carried out by two methods: (1) a gradual decrease in temperature of 10−15 °C/h; (2) excerpt on temperature shelves in combination with a slow decrease in temperature. It is believed, as reported above, that these crystals have a phase transition at a temperature on the order of 730 °C, which, in combination with thermal stresses, can lead to cracking of the crystal. There are several opinions regarding the stabilization of the phase transition: (1) it is necessary to perform cooling to determine the temperature of the phase transition, to allow the crystal to withstand a given temperature for a long time of about 10 h, or to gradually reduce the temperature to about 1.5 °C /h;[20] (2) to stabilize this transition,[13,21] it is necessary to vary the ratio of Br in the compound, changing its concentration and stabilizing the phase transition. In the first case, it is impossible to perform annealing, because, due to the large gradient, the crystal passes through the thermal zone of the phase transition during growth. Experiments were performed with a change in the $BaBr_2$/BaI_2 ratio, during which the concentration of $BaBr_2$ increased. These experiments did not give noticeable results because the problem with hygroscopicity was not resolved, when the raw material is heated and melted, the water reacts with it, which leads to the formation of oxide and hydroxide compounds. This in turn does not allow drawing conclusions about the effectiveness of this method.

3. RESULTS AND DISCUSSION

The main attention during the growth of BaBrI crystals was given to the crystallization front,[19,23] since crystal growth is carried out by changing the crystallization front. The crystallization front in the Czochralski method should be understood as the ratio of the rate of crystal drawing from the melt to the surface temperature of the melt (Figure 4). In most of the experiments, the change in the crystallization front was carried out by changing the temperature of the melt surface. This method is not optimal, since temperature fluctuations lead to instability of the thermal equilibrium of the system.

Heating control was carried out using a PID controller. When the crystallization front is controlled by changing the temperature of the melt surface, a significant error arises due to the large inertia of the system. This at low growth rates does not allow stable support of the crystallization front. The

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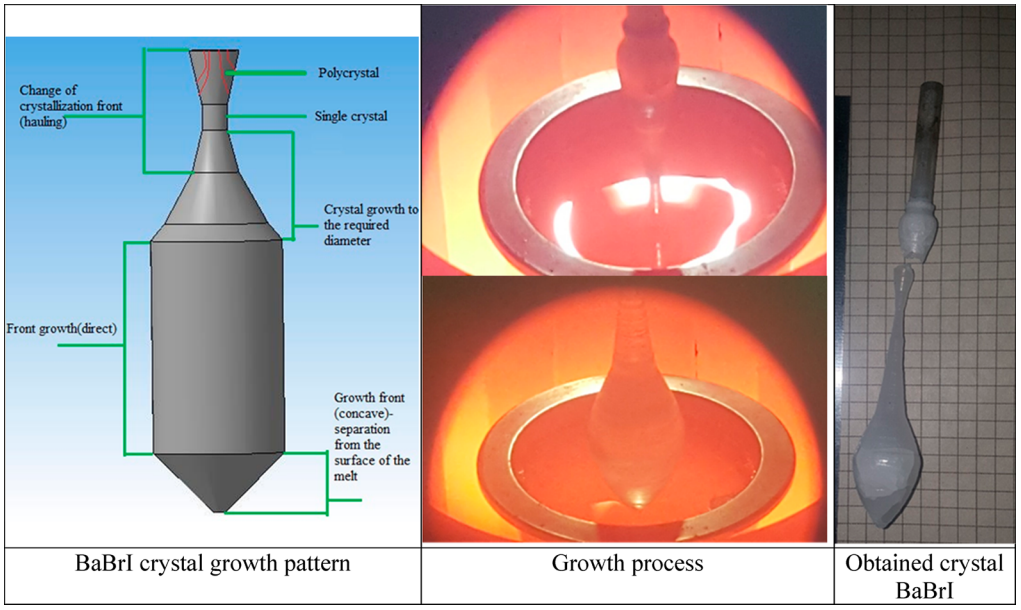

Figure 4. Structure of BaBrI crystals: polycrystal, formed from a supercooled melt; single crystal, formed by changing the surface temperature of the melt; growth of a single crystal (permanent form), the ratio of the growth rate and the surface temperature of the melt is maintained; separation from the surface, temperature increase (crystal decrease) and movement to the cooling area.

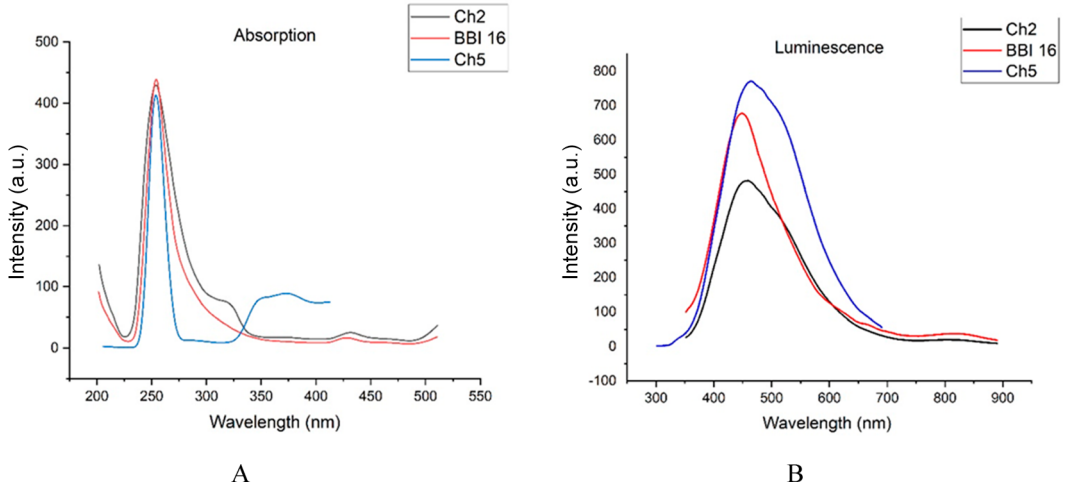

Figure 5. Excitation (A) and luminescence (B) spectra of BaBrI crystals.

control of the crystallization front is necessary to select the optimal angle (diameter) of crystal growth.[12,13] The second point of the crystallization front is crystal growth at a constant diameter. In the course of the experiments performed, it was not possible to perform growth with a constant diameter. This is due to a change in the heat sink of the crystal and a decrease in the level of the melt in the crucible. To perform growth at a constant diameter, an automatic system is needed that allows measurement of the mass of the grown crystal and adjustment of the crystal growth parameters.[22]

In experiments, a set of crystals was grown according to the method of Czochralski. To process the data, three samples were selected. (1) Ch2 represents a single-crystal slice, with a thickness of 3.24 mm and growth rate of 0.5 mm/h. (2) BBI-16 is a crystal obtained by the Stockbarger method on a multizone vertical furnace, with a thickness of 0.8 mm; (3) Ch5 is a slice crystal, with a thickness of 3.09 mm; as the cut is taken from the region of the constriction of the crystal, this part has a greater optical transparency than other samples. To characterize these samples, photoluminescence spectra (Figure 5) were measured using an LS55 PerkinElmer spectrometer.

As can be seen from the excitation spectrum (Figure 5A), BaBrI crystals have an excitation band in the region of 253 nm. Fourer Transform Infrared (FTIR) absorbtion spectra measured with a Simex FT-801 spectrometer are shown in Figure 6. If we compare the luminescence spectra (Figure 5B) of the BaBrI crystals with the FTIR absorption spectra (Figure 6), we can observe a direct dependence of the luminescence drop on the growth of hydroxyl groups. A main problem for these crystals is hygroscopicity. In this case, we observe a dependence on the number of OH^- groups in the crystals, which lead to a decrease in optical transparency and a decrease in luminescence.

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Peaks of 1602 and 3452 cm^{-1} (peaks associated with the fluctuations of H_2O and OH^-) characterize these impurities. For the luminescence spectra (Figure 5B) of the samples Ch2, BBI-16, and Ch5 there is a difference in the luminescence intensity depending on the optical transparency of the materials. Thus, depending on the conditions of growth and preparation of materials, the number of hydroxyl groups that are introduced into the crystalline structure changes, worsening the optical parameters of the crystals.

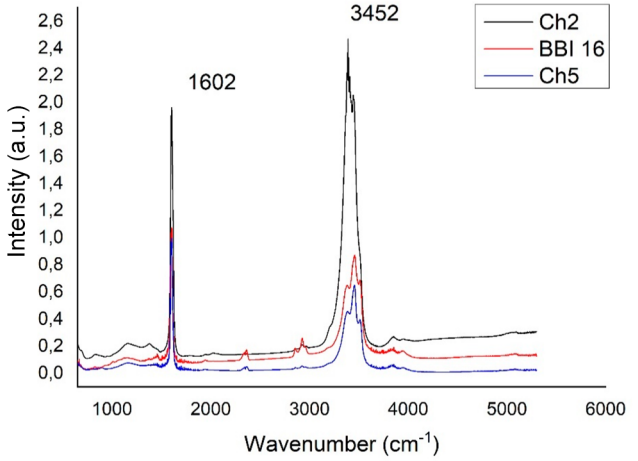

Figure 6. Fourer Transform Infrared (FTIR) absorption spectra of BaBrI crystals.

4. CONCLUSIONS

During the experiments, a set of BaBrI crystals was obtained. For crystal growth by the Czochralski method, optimal growth conditions were selected. Due to the disadvantages associated with the hygroscopicity of the materials, the crystals have differences in parameters. The reason for the differences is the inclusion of hydroxyl groups. Therefore, the inclusion of hydroxyl groups significantly impairs the optical properties of crystals, which may make them unsuitable for use as scintillators. In this case, additional cleaning of the raw materials is required, including the exclusion of contact of the raw materials used with the atmosphere.

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Notes

The authors declare no competing financial interest.

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