

Growth Method Research of LYSO: Ce Single Crystal

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Abstract. In this paper, growth problems of LYSO: Ce Single Crystal by Czochralski method are discussed such as crucible erosion, components volatilization, the production of episome, inclusion and not uniform components and light output. The suggestion of using flame fusion method to grow the crystal and how to avoid the above problems are put forward.

1. Introduction

With the rapid development of nuclear medicine, high-energy physics, nuclear technology and oil exploration, the application of inorganic scintillation crystals has been expanded continuously. The development of scintillation crystal material, the core element of the detection, is increasing, and its performance is also higher. The scintillation crystals with high density, high light output and fast delay time can increase the cut-off energy of the ray, improve the threshold of ray detection, and improve the detection energy resolution (~10%) and time resolution effectively. Cerium-doped lutetium yttrium oxyorthosilicate single crystal has been the most valuable material [1-4] in nuclear medical imaging and high energy physics experiments because of its advantages (density 7.10g/cm³, light output about ~30000ph/MeV, delay time ~40ns).

At present, LYSO:Ce single crystals can be obtained by Czochralski method and optical floating zone method[4-7]. Only the Czochralski technique can be used for commercial applications. The Czochralski technique is a basic method of crystal growth. Many but not all of the crystals used at present are grown by this method. Compared with the growth of crystals by flame fusion method, the typical characteristic of the Czochralski method is to use crucible with melt. Therefore, the basic requirement of crystal growth is that the crucible itself does not oxidize under the condition of growth, and there is no chemical reaction between the material melt and the crucible material, and the composition of the melt is kept uniform. The crucible materials often used are graphite, tungsten and its alloys, platinum and iridium etc. In order to ensure the chemical stability of the crucible under the conditions of growth, the growth process is generally in the vacuum and inert protection atmosphere. Obviously, not all materials can meet the above conditions. Such as rutile single crystal, the melt of its component breaks down under the condition of insufficient vacuum or oxygen partial pressure[8]. For another example, strontium titanate crystals have different melting points in the strontium oxide component and the titanium oxide component in the raw material powder, which will change the composition of the melt in the state of the melt.

2. Problems and reasons for growth of Ce:LYSO single crystal by Czochralski method

The first problem in the growth of Ce:LYSO crystals by Czochralski method is the melting of crucible. Ce:LYSO crystal is a high temperature oxide crystal. The crystal itself and its components have very high melting point, see Table 1, so they can not grow in vacuum or reducing atmosphere. A metal iridium crucible is used in the growth of the crystal. At such a high temperature, even if there is no oxygen in the growing environment, the oxygen molecules dissociation will be made from Lu_2O_3 due to the intensification of the molecular heat movement in production. In order to restrain oxygen molecules dissociating to the environment, the oxygen partial pressure in the atmosphere is often added, which is bound to add to the atmosphere. The iridium gold crucible is oxidized. In this case, the iridium crucible is particularly volatile or melted into the melt, which not only increases the growth cost, but also makes iridium gold particles easy to enter into the crystal and form the light scattering center, such as the growth process of cerium doped lutetium silicate single crystal(Ce: Lu_2SiO_5) by Czochralski method [9].

Table 1. The physical and chemical properties of Ce:LYSO raw materials and various components.

raw materials and their composition	Ce:LYSO	SiO_2	Y_2O_3	Lu_2O_3	CeO_2
density(g/cm^3)	7.3-7.4	2.2	5.01	9.42	7.65
melting point($^\circ\text{C}$)	2050-2070	1710	2410	2467-2510	2400-2600
boiling point($^\circ\text{C}$)	-	2230	4300	3980	3500

The second problem is that in the composition of Ce:LYSO, the melting points differ greatly among SiO_2 , Lu_2O_3 , Y_2O_3 and CeO_2 , as shown in Table 1. This leads to the following problems, first is that during the calcination process, Lu_2O_3 , CeO_2 and Y_2O_3 with high melting point are not easily diffused to form a single phase of Ce:LYSO structure, and the free Lu_2O_3 , CeO_2 and Y_2O_3 particles may exist in the formed Ce:LYSO matrix structure; next is that the components of Lu_2O_3 , CeO_2 and Ce:LYSO with high melting point may not melt yet in the formed melt, but remain in the melt in granular form. In these two cases, the solid phase inclusions are produced in the generated crystals; the last is that the SiO_2 components with low melting point are easy to volatilize, which results in the change of the composition of the melt and the difficulty in the growth of high quality crystals.

The third problem is the density difference among SiO_2 , Lu_2O_3 , CeO_2 and Y_2O_3 . See Table 1. The SiO_2 components with smaller density will float above the melt, which makes the composition of the melts different in the vertical direction. So the crystal composition is not uniform, even no crystal can grown.

The fourth problem is that due to the small segregation coefficient of Ce, about 0.20-0.25, the bottom concentration of Ce ions in the growing LYSO crystal is far higher than the top. This uneven distribution makes the bottom light output higher than the top light output, and the attenuation time will be increased accordingly, so only a part of the grown crystal is available. At the same time, the energy resolution becomes worse.

These factors have led to the technological complexity and crystal properties instability of Ce:LYSO single crystal grown by Czochralski method. Because of the use of the crucible, the corrosion of the crucible resulted in the contamination of the crystal and the increase of the growth cost. This problem can be avoided, if the crystal is grown by the flame fusion method which does

not use the crucible, In the compositions of Ce:LYSO, although the melting point among SiO_2 , Y_2O_3 , Lu_2O_3 and CeO_2 is very different, the damage will also be greatly reduced, if the low melting point components are not volatile in the growing environment and the time of the melt state is short. In the same way, although the density difference among SiO_2 , Lu_2O_3 and CeO_2 and Y_2O_3 is very large, the degree of component delamination will be greatly reduced if the crystal is grown directly after the raw material is melted rather than in the melt state for a long time. Although shortening the melt holding time can not eliminate the effect of too small segregation coefficient, increasing the growth speed can still reduce its effect.

3. Foundation analysis of the growth of Ce:LYSO single crystal by flame fusion method

In view of the problems above existing in the Czochralski growth method of Ce:LYSO single crystal, the author proposes to grow Ce:LYSO single crystal by flame fusion method. At present, this method has not been reported to grow the Ce:LYSO single crystal. Compared with Czochralski growth method, the flame fusion method is also a method of growing the single crystal from the melt. It is different that the flame fusion method does not need the melt crucible when the crystal is grown. At the same time, the melt droplet drops directly on the seed crystal or the growing crystal after melting through the high temperature hydrogen oxygen flame, and the melt keeps time very short. Therefore, the use of flame fusion method to grow Ce:LYSO crystals will avoid the problems encountered by the Czochralski method.

There is no need for crucible in the growth of crystals by flame fusion method, and the crystal growth process can be carried out in an oxidizing or reducing atmosphere according to the melt properties of the grown crystal. There is no problem of iridium crucible corrosion when Ce:LYSO single crystal is grown.

The growth of crystals by flame fusion method is often based on the hydrogen and oxygen flames, such as corundum, rutile and strontium titanate. The temperature of the hydrogen and oxygen flame center can reach 2800°C , and the temperature distribution of the flame is gradually reduced from the highest temperature center to around, the burner and the growth chamber are designed reasonably, the position of the growth interface is controlled well, and the raw materials and the components of the Ce:LYSO are normal at the same time. As the partial pressure of oxygen can be controlled in the growth environment, and the melt holding time is very short, as shown in Figure 1, the possibility of the loss of the SiO_2 component with low melting point is greatly reduced, eliminating the problems of the solid phase inclusions in the crystals of high melting point components, Y_2O_3 , Lu_2O_3 and CeO_2 .

Component layering due to the different density of each component in the melt in the Ce:LYSO single crystal grown by flame fusion method can be well inhibited, as shown in Figure 1. The degree of component layering is directly proportional to the height of melt and the duration of melt state. The height of the melt is h , the density of the low density component of the SiO_2 melt is ρ , the floating velocity is v and the component is uniform when time is t_0 . Then the distribution of the low density component SiO_2 along the Y direction of the melt is:

$$\frac{\partial C_{\text{SiO}_2}}{\partial y} = \rho v (t_1 - t_0) \quad 0 \leq y \leq h \quad (1)$$

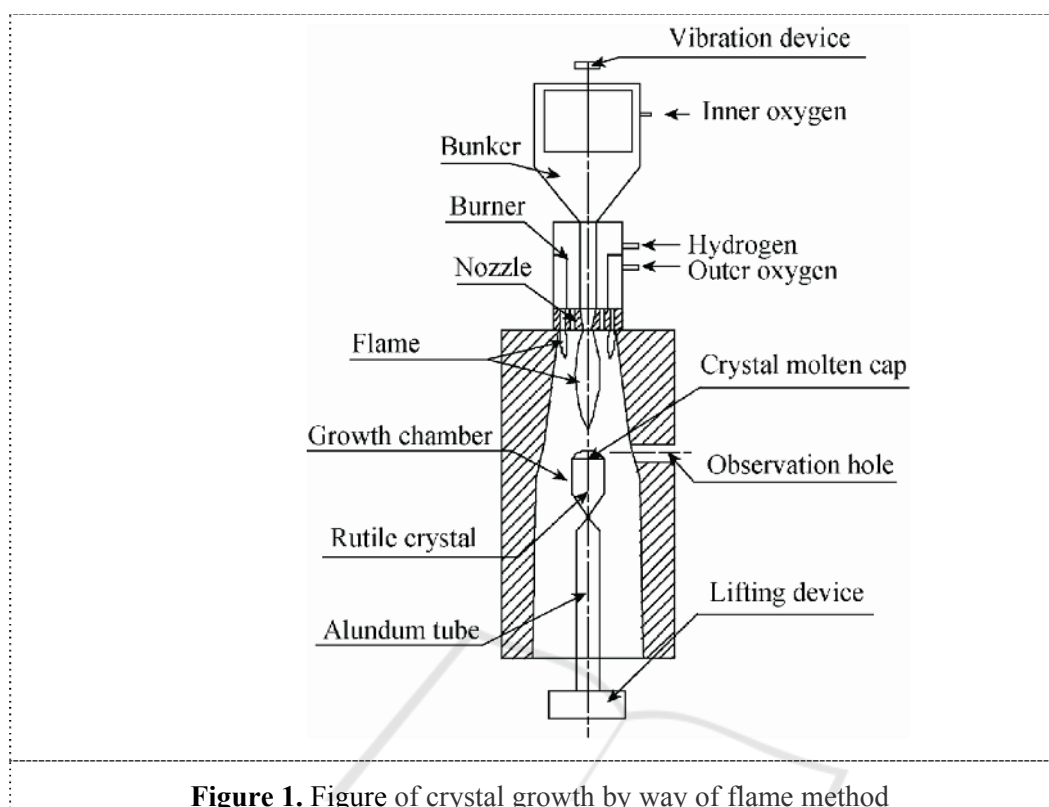


Figure 1. Figure of crystal growth by way of flame method

The growth rate of the flame fusion method is generally about 10mm/h, but the speed of the growth of the crystal is generally at 0.5-1.0mm/h by Czochralski growth method. We can see from the formula (1) that the degree of the melt delamination is more than 10 times of the flame fusion method. Therefore, the growth of Ce:LYSO single crystal by the flame fusion method can effectively restrain stratification of the different density components in the melt.

The growth rate of Ce:LYSO single crystal from melt by Czochralski growth method is about 10 times slower than that by flame fusion method. It can be seen as about 10 times the speed of the growth interface (solid liquid interface) advancing to the melt. Because the segregation coefficient of Ce is between 0.22-0.25, that is, the effective segregation coefficient is less than 1. When other factors (boundary layer thickness and so on) remain unchanged, the effective segregation coefficient increases with the acceleration of the solid liquid interface[10], which reduces the uneven distribution of Ce in the Ce:LYSO single crystal, and effectively solves the instability of the crystal properties caused by the Ce segregation of the Ce:LYSO single crystal grown by Czochralski growth method.

4. Conclusions

This paper give the suggestion of using flame fusion method to grow Ce:LYSO single crystal which can avoid the problems such as crucible erosion, components volatilization, the production of episome ,inclusion and not uniform components and light output.

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