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The research of the grow speed of $AgGa_{1-x}In_xSe_2$ monocrystalline synthesized by Vertical Bridgman method

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Abstract. $AgGa_{1-x}In_xSe_2$ is an infrared non-linear optical crystal which has been widely used in laser radar, infrared laser distant control and atmosphere environment monitoring area. The monocrystalline of $AgGa_{1-x}In_xSe_2$ usually synthesize by vertical Bridgman method. However, the melting and crystallization point of crystal can be changed by different x value of $AgGa_{1-x}In_xSe_2$. To synthesize high quality monocrystalline of $AgGa_{1-x}In_xSe_2$ with one sure x value, we should measure the melting point and crystallization point, calculate the degree of super-cooling, to design suitable temperature field distribution for this crystal.

1. Introduction

$AgGa_{1-x}In_xSe_2$, an infrared non-linear optical crystal with good performance, of which the crystallization and melting point are varied with the change of x value [1-3]. So far, several methods are normally used to synthesize $AgGa_{1-x}In_xSe_2$ monocrystalline, including Czochralski (CZ), Heat Exchange Method (HEM), Temperature Gradient Technique (TGT), kyropoulos (KY), Top Seeded Solution Growth (TSSG), Horizontal Bridgman (HB) and Vertical Bridgman (VB) method [4-6]. Due to the previous reason, we need to design suitable temperature field distribution for $AgGa_{1-x}In_xSe_2$ with one sure x value to match the following two requirements when using vertical Bridgman method to synthesize monocrystalline:

(1) $AgGa_{1-x}In_xSe_2$ have a big degree of super-cooling, thus a proper high temperature gradient is required to control the seed crystal into a short length to improve the quality of monocrystalline;

(2) Too high temperature gradient leads to the increasing of thermal stress, this may result in crystal defect or even cracking. To obtain good quality monocrystalline, we should avoid this situation [1,7].

In our work, we synthesized the $AgGa_{0.7}In_{0.3}Se_2$ ($AgGa_{1-x}In_xSe_2$, x=0.3) polycrystalline powder, which is the raw material of $AgGa_{0.7}In_{0.3}Se_2$ monocrystalline, then used Differential Thermal Analysis (DTA) to measure the melting point and crystallization point in different cooling speed, calculated degree of super-cooling of each speed, meanwhile we also measured the temperature distribution curve of growth furnace which was used to synthesizing $AgGa_{0.8}In_{0.2}Se_2$ ($AgGa_{1-x}In_xSe_2$, x=0.2). Finally, we combine DTA data with the temperature distribution curve to discuss how to change the temperature distribution to match the requirement of synthesizing $AgGa_{0.7}In_{0.3}Se_2$.

2. Experiment

2.1. Synthesize $AgGa_{0.7}In_{0.3}Se_2$ polycrystalline

We use high-purity In, Ga, Ag, Se elementary substance as raw material, mixture them as stoichiometric ratio with 0.3% surplus Se as a result of Se volatilize. Put Se, Ga, In, Ag into clean quartz ampoule in sequence and dry them in 100℃ then sealing quartz ampoule after vacuuming to 1×10^{-3}Pa. Use vertical synthesis furnace to heat them to 870℃ with the speed of 100℃/h, then stay in 870℃ for 6 hours, continue to heat with the speed of 50℃/h till 1070℃.finally cool quartz ampoule down to 20℃.Take the sample out of quartz ampoule and pulverize it.

2.2. DTA of $AgGa_{0.7}In_{0.3}Se_2$ polycrystalline

1. We put a little sample powder into crucible, gather it at the bottom of crucible.
2. Prepare another crucible without anything, then put both of two crucibles into SDT-Q600 differential thermal analyzer. The powder is protected by N_2 gas.
3. Select the heating speed of SDT-Q600 differential thermal analyzer as 10℃/min, the top temperature as 850℃，the cooling speed as 5℃/min, then waiting until SDT-Q600 operation finish, we obtain the heat flow-temperature data under 5℃/min cooling speed.
4. Then we select another two cooling-speed of 10℃/min and 15℃/min, repeat previous process.

2.3. The measure of growth furnace thermal field

The measure object is $AgGa_{0.8}In_{0.2}Se_2$ monocrystalline growth furnace made by lab, with Japannese shimada company's FP93 type precision digital temperature director. We use Pt-Pt&Rh alloy heat thermocouple to measure the thermal field.

1. Select three heat resistance wire valus of fusant temperature field as 950℃, 905℃, 800℃, then preheat 12 hours.
2. Put thermocouple into furnace, measure the temperature of furnace from 10cm under the opening to 45cm. at the area of 10-32cm, descend 2cm then stay 1min; at the area of 32-45cm, descend 1cm then stay 1min. Record the data after the thermodetector have a stable display each time.
3. Select three heat resistance wire valus of fusion temperature field as 930℃, 910℃, 660℃, then preheat 12 hours.
4. Measure the temperature of furnace from 39cm under the opening to 59cm. at the area of 39-59cm, descend 1cm then stay 1min. Record the data after the thermodetector have a stable display each time.
5. Select three heat resistance wire valus of fusion temperature field as750℃, 715℃, 690℃, then preheat 12 hours.
6. Measure the temperature of furnace from 59cm to 39cm by rise thermocouple at the area of 59-39cm, descend 1cm then stay 1min. Record the data after the thermodetector have a stable display each time.

3. Result and Discussion

3.1. Representation of $AgGa_{0.7}In_{0.3}Se_2$ polycrystalline

Use XRD to analysis the powder sample, we obtain XRD pattern as Figure 1 and it agrees with standard PDF card (No35-1096). So we can guarantee the sample is $AgGa_{0.7}In_{0.3}Se_2$.

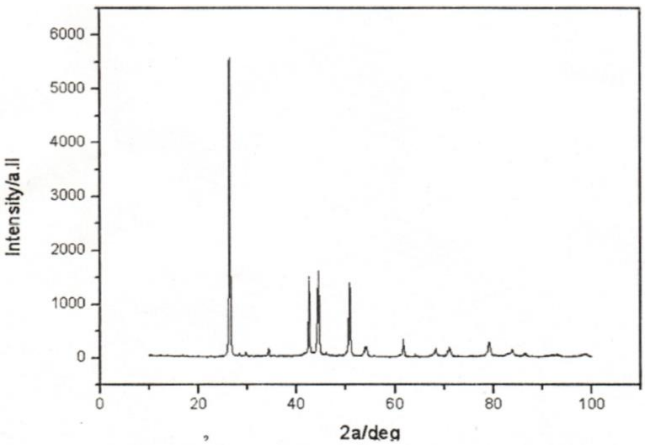

Figure 1. The image of XRD of $AgGa_{0.7}In_{0.3}Se_2$.

3.2. The heat flow-temperature influenced by cooling speed

Actually, the temperature of molten mass (T) is lower than melting point(T_m) in melt system,the difference between two value is the degree of super-cooling (ΔT):

$$\Delta T = T_m - T$$

The degree of super-cooling provide a driving force of phase change, enable crystal to grow. We obtain data and heat flow-temperature curve as table 1 and Figure 2.

Table 1. The relationship of cooling-speed and melting point

Cooling-speed	Melting point	Crystallization point	Degree of super cooling
5℃/min	811℃	793℃	18℃
10℃/min	810℃	790℃	20℃
15℃/min	811℃	788℃	23℃

Heat speed: 10℃/min

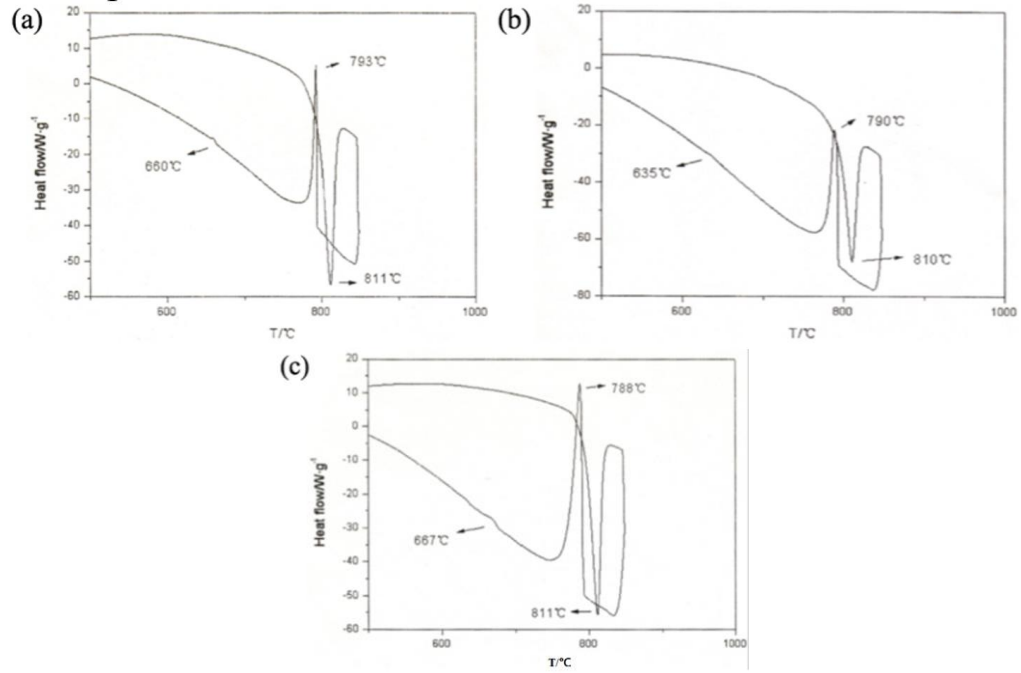

Figure 2. The relationship of heat flow and temperature in different cooling speed. (a) 5℃/min cooling speed. (b) 10℃/min cooling speed. (c) 15℃/min cooling speed (b)

It is obvious that the crystallization point and the degree of super-cooling decrease with the improving of cooling speed.

It is obviously that each of three heat flow-temperature curve has two sharp phase change peaks. The peak of 810℃ is endothermic peak. This moment the sample melt, the solid-liquid phase change takes place and endotherm. In the following cooling process, there are three exothermic peaks of 793℃, 790℃, 788℃ at each heat flow-temperature curve, this moment the sample crystalize, the liquid-solid phase change take place and exotherm. Meanwhile, we should note there is a weak exothermic peak near 660℃ in each curve. Consider the melt point of InSe is 660℃, this exothermic peak may be related to the InSe phase change resulted from the crystalline inner component segregation [1].

In differential thermal analysis, we can regard the speed of cooling as the degree of sample's temperature difference. The change trend of super-cooling degree under different cooling speed can reflect the change trend of temperature difference between crystal and fusant in the solid liquid interphase under different vertical temperature gradient distribution. They are positive correlation.

The growth process of monocrystalline is complex in the crucible. We use simple model to discuss. Assume the grow speed of crystal as the conduction of heat in one- dimensional space. Base on the heat conduction equation:

$$v=\Delta T\,(KS-KF)/\,(\rho_m L)$$

In the equation, ΔT is the temperature difference of solid liquid interphase. K_S and K_F is the heat conductivity of crystal and fusant. ρ_m is the fusant desity near the melting point. L is the crystallization of latent heat released from grow unit mass of crystal.

It is obviously that ΔT have positive correlation with crystal grow speed. So we are able to consider that the sample's change trend of super-cooling degree in DTA are consistent with the grow speed of $AgGa_{1-x}In_xSe_2$ crystal in grow furnace.

3.3. The temperature distribution situation of temperature field

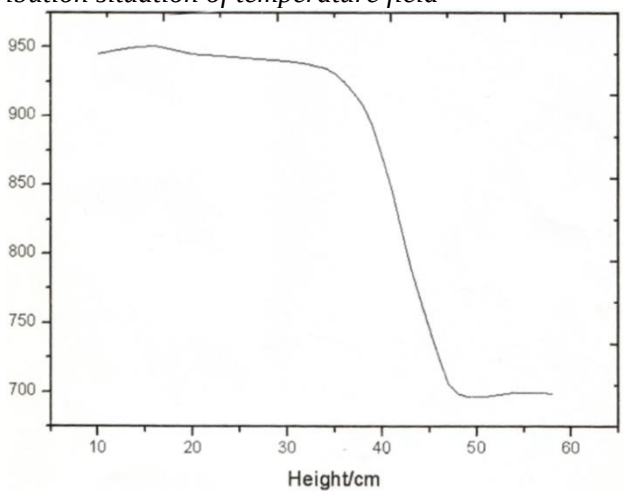

Figure 3. The curve of furnace temperature field

From the curve of furnace temperature field, we can see, the area from 10cm to 36cm belongs to fusant temperature field. There is a little difference in temperature distribution, ensure raw material fully melt. The curve fluctuates slightly because of outside environment temperature interfering. Area from 36 cm to 47 cm is crystal growth temperature field. This area has a large temperature degree, provide grow driving force to the crystallize of fusant. The temperature of 42-43 cm is close to the melting and crystallization point. The crystallization of $AgGa_{1-x}In_xSe_2$ monocrystalline mainly take place in this area. From 47 cm to 59 cm is the area of post processing temperature field. The temperature distribution is equally, and lower than the crystallization point but higher than 660℃, which may segregate InSe independent phase. Enable crystal mold further and avoid the component segregation phenomenon, which have effect on the quality of monocrystalline.

3.4. Discussing of grow furnace temperature curve

3.4.1. Discussing of fusant temperature field curve. The fusant area from 10cm to 32cm is theoretically a constant temperature field. The temperature of this area is higher than raw material. But there exist following interfere factors:

1. The outer insulating layer of grow furnace can't completely prevent the thermal exchange between grow furnace and out environment.
2. A lot of heat run away from the opening area of furnace.
3. Temperature director feedback control mechanism.

So, the temperature is not equality everywhere in this area. Meanwhile, the fusant temperature field should meet following requires:

1. This area dynamic temperature should not lower than 811℃ to make sure $AgGa_{0.7}In_{0.3}Se_2$ raw material completely melt.
2. Consider that the volatilizing temperature of Se is 684℃, enable to reduce the loss of Se volatilize, the dynamic temperature should not too high.
3. Because of the upside and downside curve of growth temperature field connect with the fusant temperature field and the post-processing temperature field smoothly. The fusant temperature should not too low, enable the growth temperature has a suitable temperature gradient.

Consider these situation, we should let the temperature properly high.

3.4.2. Discussing of growth temperature field. The area of 32cm to 36cm is a transition between fusant and growth temperature field. This area near the fusant area, The temperature gradient in this area is small, the growth of crystal is not in this area, so we don't discuss any more. From the 32cm to 47cm area, this part is the main growth area of crystal. From heat flow-temperature curve we can see that the crystallization point is located in the 41cm-43cm area, $AgGa_{0.8}In_{0.2}Se_2$ monocrystalline grow in this area. For a suitable fast grow speed and control the size of other direction seed crystal, the temperature gradient of this area should be the largest.

3.4.3. Discussing post-processing temperature field. From the area 47cm to 59 cm is the post-processing temperature field, this area the distribution of temperature is equality. The temperature is lower than crystallization point, but higher than 660℃. The main function of Post- processing temperature field is enable crystallize further more, and avoid possibly InSe phase component segregation.

3.4.4. Possibly change ways of growth temperature field curve. In order to reform the furnace temperature distribution of $AgGa_{0.8}In_{0.2}Se_2$ to suit the the synthesize of $AgGa_{0.7}In_{0.3}Se_2$ monocrystalline, first we should consider measures of change temperature gradient, then combine the different melt and crystallization point of two crystalline with measures to discuss witch measure is better.

The influence of increase the growth temperature gradient:

1. Remain the post processing temperature, increase the fusant area temperature to rise the temperature gradient. That can increase the growth driving force, and decrease the risk of break after crystallization. But the shortage are that may case to the decomposing and volatilization of raw material. Meanwhile, improve the fusant temperature will lead to the temperature increase in same position. The crystallization will happen under original situation; this will short the post-processing temperature field distance.
2. Remain the fusant temperature, Decrease the post processing temperature to improve the temperature gradient. This measure can ensure the monocrystalline has enough length to get post processing. But that will product large thermal stress, which may break the crystal structure. Meanwhile, crystallization will take place above the original situation, the raw material may not fully melt.

The influence of decrease the temperature gradient:

1. Remain the post processing temperature, decrease the fusant temperature to reduce the temperature gradient. This measure can reduce decomposing and volatilization. But reducing the temperature gradient equals to slowing down the grow speed of monocrystalline, the size of other direction seed crystal will bigger than that of not reduce the fusant temperature. Moreover, the raw material will crystallize above original situation.

2. Remain the fusant temperature, increase the post processing to reduce the temperature gradient. That can decrease thermal stress, but short the length of post processing.

3.4.5. Comprehensive discussion. According to those situation, the temperature curve of $AgGa_{0.7}In_{0.3}Se_2$ growth furnace should match the following requires:

1. In order to avoid drastically volatilize of Se, the value of $AgGa_{0.7}In_{0.3}Se_2$ fusant temperature field should not higher than that of $AgGa_{0.8}In_{0.2}Se_2$.

2. Consider that the $AgGa_{0.8}In_{0.2}Se_2$ has a crystallization point of 814℃ and a melting point of 843℃, with a super-cooling degree of 29℃ [2], each of them are higher than that of $AgGa_{0.7}In_{0.3}Se_2$. Enable to provide equally growth driving force, we can properly improve the temperature gradient of growth temperature field.

3. The temperature gradient leads to thermal stress. The max temperature gradient crystal allowed can be calculate through the following formula [3]:

$$G_{max}=\frac{2\varepsilon}{\alpha R^{3/2}}\left(\frac{2}{h}\right)^{1/2}$$

$\boldsymbol{\varepsilon}$ is critical fracture strain value, $\boldsymbol{\alpha}$ is crystal coefficient of thermal expansion, $\boldsymbol{R}$ is crystal radius, $\boldsymbol{h}$ is crystal heat exchange coefficient. Considering that different of each valus between $AgGa_{0.8}In_{0.2}Se_2$ and $AgGa_{0.7}In_{0.3}Se_2$ is much less than reality experiment error, so we can regard both G_{max} as equality.

4. The post processing temperature should higher than 660℃.

4. Conclusion

In conclusion, we can change the temperature field curve of $AgGa_{0.8}In_{0.2}Se_2$ to that of $AgGa_{0.7}In_{0.3}Se_2$ in the way that we remain the fusant and post processing temperature, improve the temperature gradient. But to solve the problem of making accurate curve, we should do more research about fusant volatilize speed, the exothermic peak at 660℃ and calculate G_{max}.

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