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Growth of lead-based functional crystals by the vertical bridgman method

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Abstract Some lead-based crystals show excellent ferroelectric, piezoelectric or scintillation properties and have attracted much attention in recent years. However, the erosion of the high temperature solution on platinum crucible and the evaporation of PbO component are the main problems often encountered during the crystal growth. In this paper, we reported recent progress on the Bridgman growth of lead-based functional crystals, such as novel relaxor ferroelectric crystals (PZNT and PMNT), scintillation crystals ($PbWO_4$, PbF_2 and PbClF) and piezoelectric crystals ($Pb_5Ge_3O_{11}$ and $Pb_2KNb_5O_{15}$), in Shanghai Institute of Ceramics, Chinese Academy of Sciences. The vertical Bridgman method has been modified to grow PZNT crystals from high temperature solution and as-grown crystals have been characterized. Large size lead-based scintillators, $PbWO_4$ and PbF_2 crystals, have been mass-produced by the vertical Bridgman method in the multi-crucible furnace. These crystals have been supplied to CERN and other laboratories for high-energy physics experiments. The Bridgman growth of piezoelectric crystals $Pb_5Ge_3O_{11}$ and $Pb_2KNb_5O_{15}$ are discussed also.

Key words Lead oxide, Piezoelectric, Relaxor ferroelectric, Scintillation, Bridgman method

1. Introduction

Although most of single crystals are grown by the Czochralski method, the vertical Bridgman method has become more and more important for industrial applications as well as scientific research in recent years. Compared with the Czochralski method, the vertical Bridgman method shows several advantages. For example:

The crystal shape depends on the shape of the crucible; which means high utility of as-grown crystals during processing these crystals for different applications.

The multi-crucible Bridgman furnace has been developed for mass-production of crystals with low cost.

A small temperature gradient in the solid-liquid interface and in-situ annealing process considerably reduce the thermal stress in as-grown crystals.

The vertical Bridgman method was initially employed to grow large size mica crystals in Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS) in the early of 1960s [1]. From then on, more than 30 crystals have been investigated by the modified vertical Bridgman method in SIC. Among them, several crystal products, such as $Bi_4Ge_3O_{12}$, TeO_2 and $Li_2B_4O_7$, have been grown for industrial applications of high energy physics, nuclear medical and SAW devices [2]. In the past decade, special attention was given to some lead-based functional crystals due to their excellent properties for ferroelectric, piezoelectric or scintillation applications. In this paper, we reported recent progress on the Bridgman growth of lead-based functional crystals, such as novel relaxor ferroelectric crystals (PZNT and PMNT), scintillation crystals ($PbWO_4$, PbF_2 and PbClF) and piezoelectric crystals ($Pb_5Ge_3O_{11}$ and $Pb_2KNb_5O_{15}$) in SIC.

2. Progress of Novel Relaxor Ferroelectric Crystals

It is well known that a solid solution can be formed between some complex perovskites, Pb(B'B")O_3 (B' = Mg, Zn, Ni, Fe, Sc, In and B" = Nb, Ta and W) and tetragonal $PbTiO_3$ (PT), which exhibit considerably large electromechanical coupling factors, piezoelectric coefficients and electric-field-induced strains at its composition near morphotropic phase boundary (MPB) [3]. These excellent properties render these novel ferroelectric crystals suitable as next-generation electromechanical transducer materials in a broad range of advanced applications, such as actuators, medical ultrasound imaging and underwater communication [4]. Among them, much attention has been paid to (1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$-x$PbTiO_3$ (PMN-PT) and (1-x)$Pb(Zn_{1/3}Nb_{2/3})O_3$-x$PbTiO_3$ (PZN-PT) crystals.

Due to their incongruent characteristics, PMN-PT and PZN-PT crystals were usually grown by the flux method [5]. It is difficult to obtain large size and high quality

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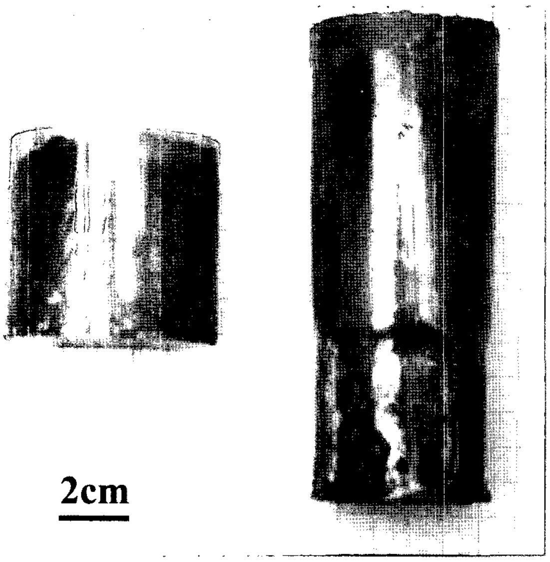

Fig. 1. As-grown PMN-PT crystal boules.

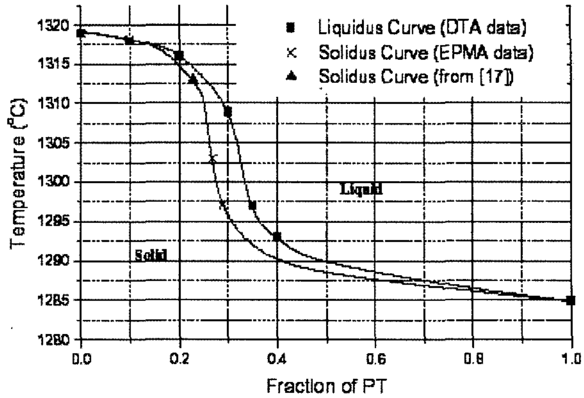

Fig. 2. The phase diagram of the (1-x)PMN-xPT binary systems.

crystals because of the coexistence of perovskite and pyrochlore phases, multi components of the solution and evaporation of PbO component. Considering the successful experiences and advantages of the vertical Bridgman method, our institute investigated the Bridgman growth of PMN-PT and PZNT crystals from 1996. Initially, PMN-PT crystal was grown by spontaneous nucleation from its MPB compositions of 67 mol% PMN and 33 mol% PT. After some seed crystals were obtained, seeded growth has been carried out in the modified Bridgman furnace [6]. Figure 1 shows as-grown PMN-PT crystal boules.

The growth defects of as-grown PMN-PT crystals have been investigated [7]. These defects included compositional nonuniformity, scattering particles, pores, negative crystal structures, cellular structures, fissure structures, and so on. The compositional nonuniformity and the fissure were main problems to influence crystal quality. Figure 2 shows the phase diagram of the (1-x)PMN-xPT binary systems [8]. It indicated that the segregation coefficient $k = C_S/C_L$ is less than 1 and as a result, the $PbTiO_3$ content in the initial part of the boule will be less than that in the melt when grown directly from its melt, which means obvious chemical and physical inhomogeneity in as-grown crystal. Furthermore, it is difficult to grow PMN-PT crystal along <001> direction and <001>-oriented wafers should be cut sloping to the growth direction. This means that even single wafer is inhomogeneous. For example, the Curie temperature T_C varies from 144.4°C at the initial part of the boule to 172.8°C at the ending part and the rhombohedral/tetragonal phase transition temperature (T_{RT}) changes from 46.2°C to 88.6°C [8]. Many approaches have been employed to improve crystal quality. For example, excess PbO was added to the starting materials to restrain the deviation of PbO component. Another effective way is to presynthesize PMNT powders. So far, PMN-PT boules up to 60 mm in diameter and 80 mm in length have been grown and the crystal quality has been improved to meet the applications.

Although large size PMNT crystal has been obtained, there are still some problems for its applications. For example, its T_{RT} is only about 50°C, as discussed above. For PZN-PT, this situation should be improved considerably. Generally, it is impossible to grow perovskite PZN-PT crystal directly from its melt because of the competition of perovskite and pyrochlore phases. Thus, it is necessary to use some flux to inhibit crystallization of pyrochlore phases. We have investigated the crystallization behaviors of PZN-PT from different fluxes, such as B_2O_3, PbF_2, $BaTiO_3$ and PbO [9]. The results show that B_2O_3 and PbF_2 fluxes restrain the crystallization of perovskite phases while $BaTiO_3$-PbO fluxes are helpful to the crystallization of the perovskite PZN-PT but the crystal yield is lower. PbO was confirmed to be a good flux although the erosion of the Pt crucible is a tiresome problem. The ratio of PbO flux is optimized as about 50 mol%. Due to the existence of PbO flux, as-grown PZN-PT crystals were buried into the solidified flux. PZN-PT crystals were usually obtained after removing the flux and leaching the ingot in hot HNO_3 for one day. Figure 3 shows a typical PZN-PT crystal.

The conventional flux Bridgman method has limitations for achieving large single crystals with high quality due to spontaneous nucleation. Harada et al reported large size PZN-PT crystals grown by the vertical Bridgman method with bottom cooling [10]. We have also

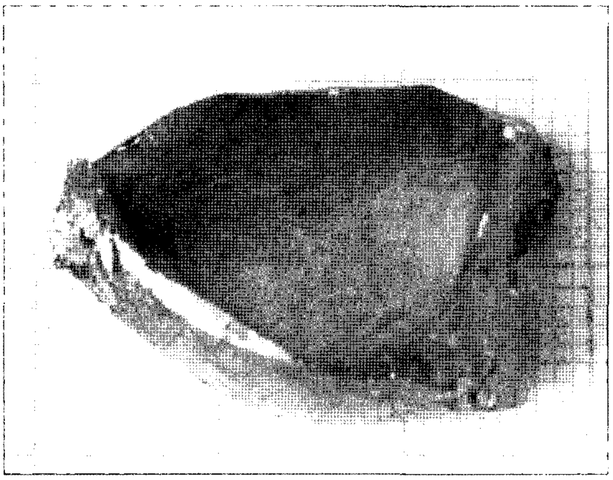

Fig. 3. A typical PZN-PT crystal grown by the flux Bridgman method.

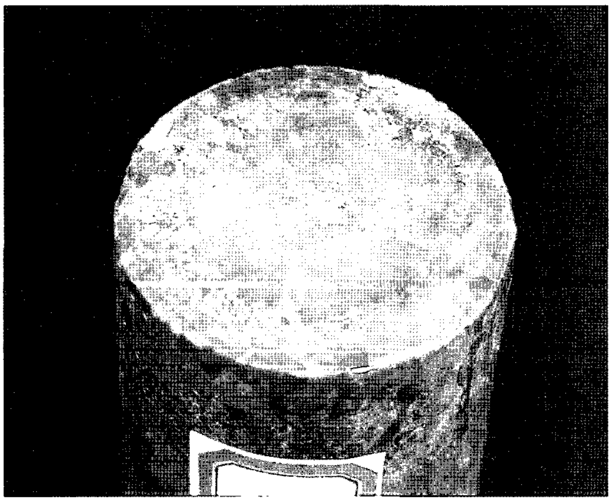

Fig. 4. A successful nucleation formed by fast cooling.

designed a gas-cooling system to induce a single nucleus during the Bridgman growth. The diameter of the gas pipe and the rate of the gas flow are key parameters for a successful growth process. Figure 4 shows a successful nucleation formed by gas cooling. PZN-PT crystal about 40 mm in diameter has been grown with a flow rate of 1.6 l/min [11, 12]. However, serious inclusions were observed after the crystal was oriented and cut along (001) face. The inclusion was attributed to the fluctuation of the gas flow.

In order to improve crystal quality, a two-step process was developed to grow PZN-PT crystals [13]. In the first step, the growth process was the same as the gas-cooling growth. However, the gas flow was closed and the lowering mechanism stopped working for several hours when the crystal had been grown in a certain length. Subsequently, self-seeded growth of PZNT crystal was carried out when the previous grown crystal was partially melted and a stable solid-liquid interface was re-established. By optimizing the growth parameters, PZN-PT crystal up to 30 mm in diameter and 15 mm in thickness were obtained, as shown in Fig. 5. Compared with the samples grown by the flux-Bridgman method, the inclusions were reduced considerably. Figure 6 shows the comparative photos of PZN-PT wafers. The piezoelectric constants d_{33} of several wafers were measured and the fluctuation of the values were limited in ±10%. This result showed a good homogeneity for PZN-PT wafers.

Fig. 5. PZN-PT crystal grown by the two-step process.

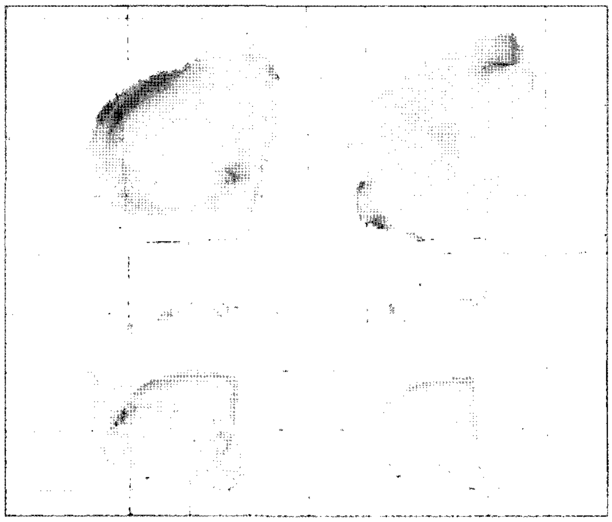

Fig. 6. PZN-PT wafers obtained by the two-step process (upper) and the gas cooling nucleation (lower).

In fact, seeded growth of PZN-PT is the basic way to improve crystal quality. However, the whole seed tended

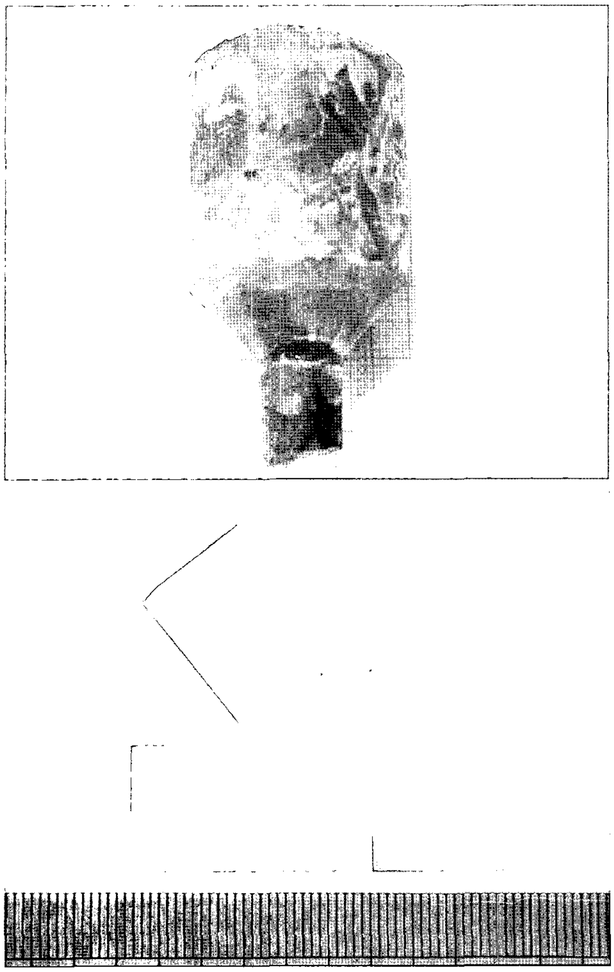

Fig. 7. PZN-PT crystal grown by the BSSG technique and its wafers.

to be dissolved by the PbO flux because the seed was located in the bottom of the crucible. A long seed was used and a larger temperature gradient of 80~120°C/cm was employed in the Bridgman furnace to prevent the seed from dissolved thoroughly [14, 15]. Like TSSG technique to Czochralski method, sometimes we called this modified Bridgman technique as the bottom seeded solution growth or BSSG [16]. Figure 7 shows PZN-PT crystal grown by BSSG technique and its wafers. The wafers looked homogeneous.

3. Industrial Growth of Scintillation Crystals

3.1. Growth of PWO crystals

Lead tungstate (PWO) crystal is a promising scintillation material for electromagnetic spectrometers due to their unique physicochemical properties, such as high density (8.3 g/cm^3), low radiation length (0.89 cm^{-1}), high efficiency of detection of ionizing radiations, fast response and sufficient radiation resistance [17]. So, PWO crystals were chosen to construct a precision electromagnetic calorimeter (ECAL) at the Large Hadronic Collider (LHC) and the Compact Muon Solenoid (CMS) experiment at European Organization for Nuclear Research (CERN), Switzerland [18, 19]. The CMS-ECAL will contain about 80,000 PWO crystals of 23 cm in length and 5 cm^2 in section. To reach good crystal quality required, our institute (SICCAS) was invited to undertake this R & D program from 1994 [20].

$PbWO_4$ crystal has a scheelite structure, which is characterized by the WO_4 tetrahedron and the PbO_8 cube along the c-axis. The regular stacking parallel to the c-axis of Pb and W atoms forms the crystal skeleton, while O atoms distribute around Pb and W atoms according to corresponding coordinate sites [21]. $PbWO_4$ is a congruent compound melted congruently at 1123°C and can be grown by the Czochralski method and the modified Bridgman method, without a phase transition during cooling. The Bridgman method shows obvious advantages in mass production and uniformity control. Multi-crucible Bridgman furnace for the growth of PWO crystals has been developed and near 30 crystals can be grown in the furnace at the same time [22]. Figure 8 shows polished PWO crystals for the CMS-ECAL experiment. The radiation hardness of PWO crystals is crucial because of the severe application environment with unprecedented high levels of radiation. The mechanism of radiation damage in $PbWO_4$ was investigated related to crystal defects, such as oxygen and lead vacancies [23, 24]. Ion doping and post-annealing are the main approaches to improve radiation properties [25-27].

For the CMS-ECAL experiment, the PWO crystals must meet the requirements: (1) longitudinal optical transmission (LT) more than 25 %, 55 % and 65 % for wave-

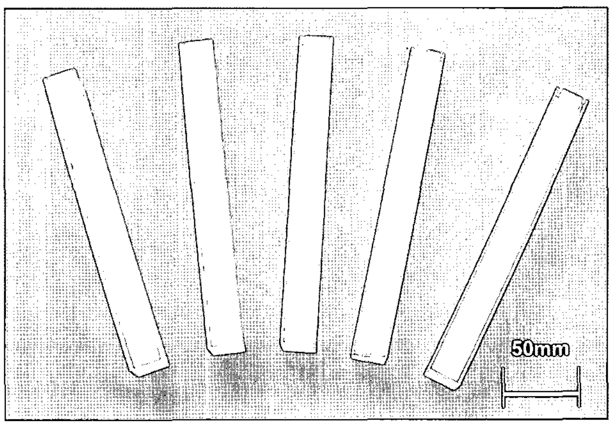

Fig. 8. Polished PWO crystals for the CMS-ECAL experiment.

lengths of 360, 420 and 620 nm, respectively; (2) a light yield (LY) more than 8 p.e/MeV; (3) Radiation hardness (μ) must be $0 \le \mu \le 1.5\ m^{-1}$ at 420 nm after lateral ^{60}Co irradiation with a dose rate of 150 Gy/h. SICCAS has supplied 400 (300 ECAL End Caps, 100 ECAL Barrel) PWO pre-produced crystals to CERN in the past year. Now about 200 blocks of PWO crystals are required per month.

3.2. Growth of PbF_2 and PbClF crystals

Cherenkov radiation is electromagnetic radiation emitted when charged particles pass through an optically transparent medium at speeds greater than the speed of light in that medium. The requirements for a Cherenkov radiator for total-absorption electromagnetic shower are as follows: (1) short radiation length; (2) no fluorescence; (3) high refractive index; and (4) transparent, especially in UV region [28]. The ideal Cherenkov radiator would be a "transparent lead brick" and a near approximation of this is cubic lead fluoride (PbF_2) crystal [29].

PbF_2 crystal has high density (7.7 g/cm^3), short radiation length (0.93 cm), large average atomic number and good transmission extending to UV and its light output is sufficient to have a good electromagnetic energy resolution [28]. PbF_2 crystal is usually grown with a vacuum atmosphere because it is easy to be contaminated by oxygen at high temperatures. However, the cost of the vacuum method is higher and residual oxygen may induced needle-like defects, which result in absorption of UV light in PbF_2 crystals [28]. In order to reduce the growth cost and deoxidize effectively, a non-vacuum growth technique has been invented in SIC [30]. In this method, a small amount of the chemical scavenger was mixed with raw materials and the platinum crucible was sealed during the growth. The scavenger can remove oxygen impurities, such as O^{2-} and OH^-, but does not cause any harmful effects on the crystal properties and growth equipment. Up to now, more than 870 blocks of PbF_2 crystals have been supplied to Mainz University, Germany.

PbFCl crystal is another halide crystal. As an X-ray storage phosphor, it is expected to be used in medical imaging in the last two decades. However, there are many difficulties in the growth of PbFCl crystals. First, PbFCl has a tetragonal layered structure, which consists of two adjacent planes of chloride ions perpendicular to the C-axis. So it will cleave easily along (0 0 1) plane and only some slices can be obtained. Second, even traces of oxygen contamination in the lattice of PbFCl will affect its properties. The Bridgman growth of PbFCl crystals has been investigated and the influence of impurities and F/Cl ratio on crystal growth and properties has been discussed in SICCAS [31].

4. Bridgman Growth of other Piezoelectric Crystals

Single crystal of lead germanate ($Pb_5Ge_3O_{11}$: PGO) has some applications in pyroelectric detectors, information storage and light signal processing, acousto-electronic devices, opto-electronic devices due to its sensitive optical activity, small dielectric constant and a relatively high pyroelectric coefficient in a wide range of temperature [32]. PGO single crystal was previously grown by the Czochralski method [33]. To our knowledge, the Bridgman method is applied to grow PGO crystal for the first time.

Due to lack of seed crystal, PGO crystal is initially grown by spontaneous nucleation in the Bridgman furnace. After a seed crystal up to Φ10 mm × 40 mm has been obtained, seeded growth of PGO crystal is carried out with <100>-oriented seed. Small quantities of black slag are observed on a certain side surface of as-grown boule, as shown in Fig. 9. XRD analysis shows that two phases, $Pb_5Ge_3O_{11}$ and Pb_3GeO_5, are co-existed in the black slag. The chemical composition analysis demonstrates that the compositions of black slag deviate seriously from the stoichiometric compositions of $Pb_5Ge_3O_{11}$ crystal and the GeO_2 content was less than that of the nominal composition [32]. The formation of Pb_3GeO_5 phase is attributed to the incomplete solid-state reaction of GeO_2 and PbO during soaking the raw materials.

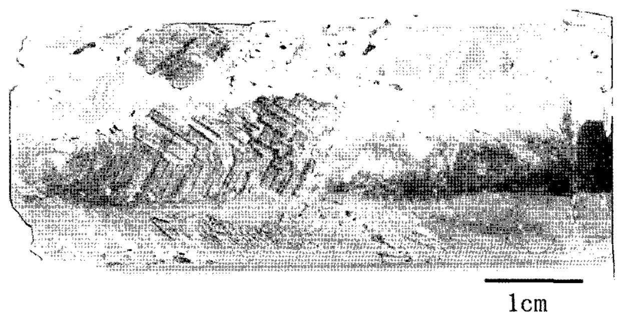

Fig. 9. The black slag region on PGO boule.

Fig. 10. Negative crystal in PGO crystal.

Higher furnace temperature and longer soaking time can eliminate the black slag.

The growth defects, such as inclusion, negative crystal and bubble in Bridgman grown PGO crystals have been observed [34]. The inclusions demonstrate cone-like, pillar-like or snake-like morphologies. EPMA results show that the main composition of the particles is PbO. To eliminate these particles, the mixture of GeO_2 and PbO raw materials should react completely at a higher temperature and polycrystalline PGO should be used to grow PGO crystals. The inclusions may induce negative growth in the BR-grown PGO crystals and result in "negative crystal". Figure 10 shows a typical morphology of the hexagonal negative crystal. The sudden temperature fluctuation sometimes occurs because of the instability of heating elements or ambient temperature. In this case, rapid constitutional super-cooling may take place and some melts are wrapped in the crystal. The droplet of the melt then is frozen gradually and forms the negative crystal in the subsequent cooling stage.

$Pb_2KNb_5O_{15}$ (PKN) has a large electromechanical coupling factor of bulk waves ($k_{24} = 0.73 \pm 0.3$) and surface acoustic waves ($k^2 > 10\,\%$ for stiffened Releigh mode, $k^2 > 23\,\%$ for Bleustein-Gulyaev mode) and a small temperature dependence of fundamental resonant frequency [35]. The lack of large size PKN crystal limited its practical application. The main problems for the growth are serious volatilization of PbO during the growth and twinning and cracking in the as-grown crystals during cooling. For the Bridgman growth, the raw materials were sealed in the platinum crucible to restrain the evaporation and a small temperature gradient was used to reduce crystal cracking due to the anisotropy of its thermal expansion. PKN crystal up to 1 inch in diameter and 2 inches in length has been obtained and the primary results have been reported [36].

5. Summary

The vertical Bridgman method has been employed to grow several lead-based functional crystals, such as novel relaxor ferroelectric crystals (PZNT and PMNT), scintillation crystals ($PbWO_4$, PbF_2 and PbClF) and piezoelectric crystals ($Pb_5Ge_3O_{11}$ and $Pb_2KNb_5O_{15}$) in Shanghai Institute of Ceramics, Chinese Academy of Sciences. We have modified the growth technique considering the characteristics of different crystals. The growth results show that the vertical Bridgman method is suitable to grow lead-based crystals and its advantages include: (1) The crystal shape depends on the shape of the crucible, which means high utility of as-grown crystals during processing for different applications; (2) The multi-crucible Bridgman furnace makes a high yield of crystals and very helpful for mass-production of crystals with lower cost; (3) The raw materials is sealed in the crucible to restrain the evaporation of PbO and a small temperature gradient in the furnace can reduce the thermal stress in as-grown crystals.

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