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Reaction of platinum crucible and melt during PMN-PT crystal growth

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Abstract

PMN-PT crystals have been of considerable interest in recent years due to their excellent ferroelectric, piezoelectric, photoelectric properties and promising applications in various electric and electric–optical devices. However, the crucible leakage is usually a fetal limitation during preparation of the crystal. In this work, the PMN-PT crystals were prepared by Bridgman-accelerated crucible rotation technique (ACRT) method. The morphologies of the bottom surface of the PMN-PT crystal and the inner surface of the platinum crucible, in which the crystal grew, were examined by scanning electronic microscope (JSM-840). The local composition was analyzed by EDAX spectrometer attached to the scanning unit. Investigated results indicated that there are evident reaction between the platinum crucible and $PbO–MgO–Nb_2O_5–TiO_2$ melt during PMN-PT crystal growth, which is the main cause of crucible leakage. Another cause of the crucible leakage is due to the unequally distorted platinum grain boundary.

Keywords: PMN-PT; Crystal growth

1. Introduction

Solid solution of $Pb(B_1,B_2)O_3$ (B_1 = Mg, Zn, Ni, Fe, Sc; B_2 = Nb, Ta, W) and $PbTiO_3$ were investigated extensively in the last decade as a promising crystal materials. The materials exhibit superior ferroelectric, piezoelectric, photoelectric properties and will be widely used in underwater sonar, modern medical ultrasound imaging and other high performance actuator and transducers. Frequently these binary or ternary system single crystals were prepared by flux method [1,2]and Bridgman or modified Bridgman technique [3,4]. Some problems are still left unresolved in the growth of these novel ferroelectric single crystals. For example, Pt crucible were apt to leak during the crystal growth by Bridgman or modified Bridgman method [3–5]. This was also reported in the investigations about crystal growth by flux method [1,2,6]. Xu et al. [3] reported that the adopted protective measure include (1) use high-purity starting materials since the mixed dissociative metal may react with Pt to form Pt-metal alloys with lower melting point; (2) use Pt crucibles with thick walls to enhance its resistance to chemical erosion; (3) set a support equipment to lessen the distortion degree of Pt crucibles under high temperature. The leak of Pt crucible could be suppressed to a great extent. Bertrama [6] suggested that because metallic lead came forth frequently in PbO solutions, the Pt crucibles can be destroyed if the experiments are not performed under an oxidizing atmosphere. During PMN-PT and PZN-PT crystal growth the highest temperature of melt was less than 1420 °C. But Pt crucible can be used in $LiTaO_3$ crystal growth under 1650 °C. These evidences indicate that some chemical reactions occur between the melt and Pt crucible in the Pb based relaxor crystal growing process. But the mechanism of Pt crucible leakage is not clear up till now.

2. Experimental procedure

The starting material of Pt was spongy platinum with purity 99.90%. The preparation process of Pt crucible was show in Fig. 1. The Pt crucible was 40 mm in diameter and 200 mm in length. The selected composition of relaxor crystal was PMN-32% PT. High purity chemicals (better than

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Spongy platinum → press → calcine → fusion → cast → rolling → weld

Fig. 1. Preparation process of Pt crucible.

99.95%), PbO, MgO, Nb_2O_5 and TiO_2 were used as starting materials. The powders of these chemicals were mixed together in a plastic mortar with addition of vaal water. After drying the powders were put into the Pt crucible with a Pt lid. Then the Pt crucible was put into a Al_2O_3 crucible. Al_2O_3 powder was put between the outer wall of Pt crucible and the inner wall of Al_2O_3 crucible to support the Pt crucible. The crucibles were placed at the selected height in the furnace of a ACRT-Bridgman crystal growth equipment. A thick lid of Al_2O_3 was placed upon the Pt lid to prevent the evaporation of PbO. During crystal growth the temperature of melt in the Pt crucible was hold at 1400 °C. After PMN-32% PT crystal growth, the Pt crucible was take out of the Al_2O_3 crucible and carefully cut. It can be seen there were yellow bur adhered to the outer wall near the bottom of Pt crucible. This was the mixture of released melt and Al_2O_3 powders supporting the Pt crucible and indicated the location of leakage. This place was carefully cut from the Pt crucible. The crystal abuted against this place was cut too. These samples were investigated by JSM-840 SEM and EDAX.

3. Results and discussion

3.1. Microstructure of leaked Pt crucible

Fig. 2 shows the SEM microstructure photograph around the leakage location of the inner wall on the Pt crucible. There were a lot of parallel lines on the surface of Pt crystal grains (Fig. 2a and b). The parallel lines were of different direction in different grains and crossed at Pt grain boundary. They were slipping bands and slipping lines which were resulted by the movement of dislocation in the crystal grain. This microstructural morphology indicated that before PMN-32% PT crystal growth the bottom of Pt crucible was suffer from the static pressure of melt and caused nonuniform distortion and high temperature creek. A lot of dislocations moved from the grain inside to the grain surface and boundary, which resulted in broadening of grain boundary and formed grooves (Fig. 2c) and stress concentration at grain boundaries.

The holes about 10 μm in size are non-continuously distributed along the grain boundaries of the Pt crucible (Fig. 2c

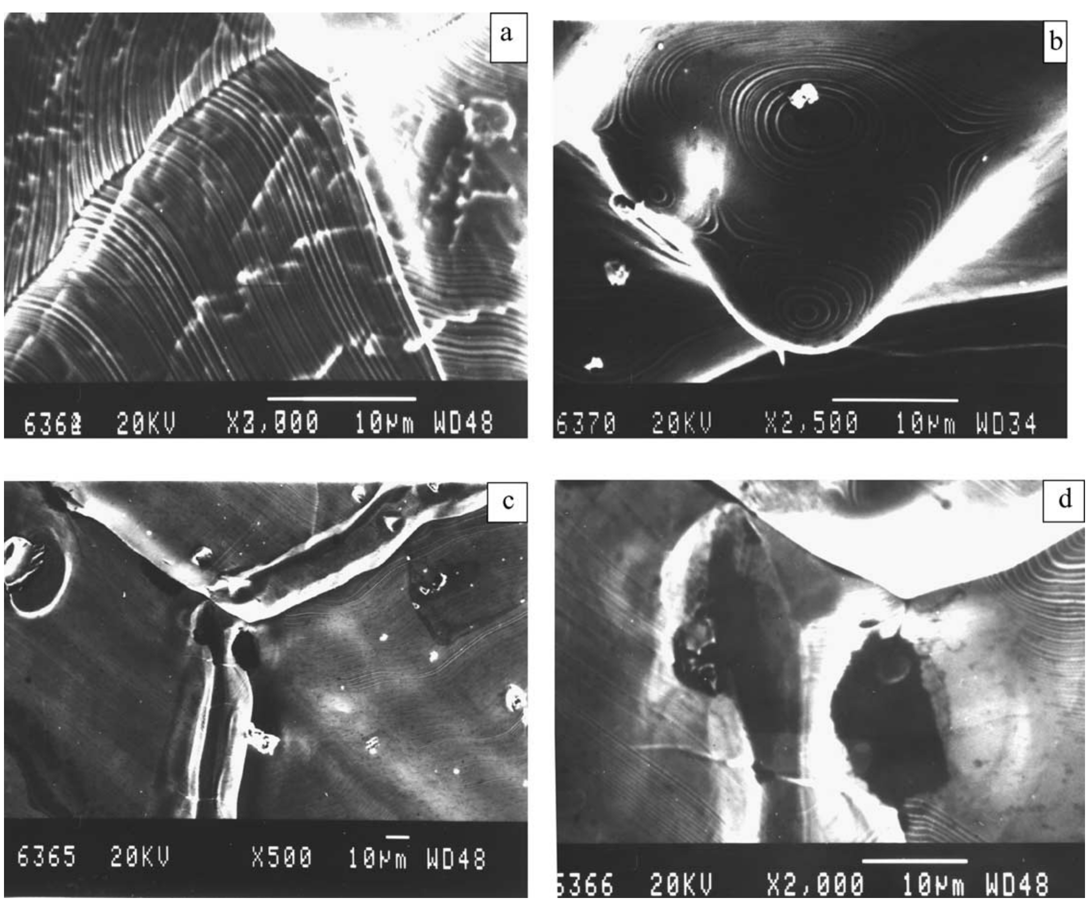

Fig. 2. SEM microstructure around the leakage location of the inner wall on the Pt crucible (a) slipping bands and lines around the grain boundary, (b) slipping bands and lines at grain surface, (c) holes along the wider grain boundary, (d) magnification of (c).

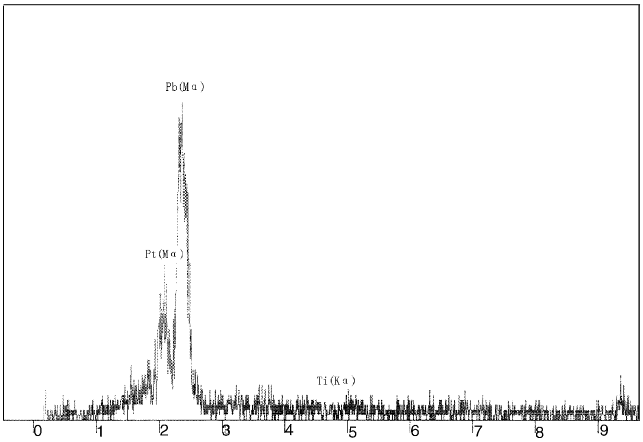

Fig. 3. EDAX result of phases inside the holes at Pt grain boundary.

and d). In addition, EDAX analysis shown in Fig. 3 demonstrated the existence of the Pb-enriched phases inside the above-mentioned holes. Those Pb-enriched phases having the different chemical composition from PMN-32% PT were formed by the chemical reaction between melt and the grain boundary of the Pt crucible at high temperatures. It was suggested that the stress concentration at the grain boundary of the Pt crucible resulted in the stress corrosion. In such a case, the wider and thinner grain boundaries are perforated as that shown in Fig. 2c and d.

3.2. *Microstructure of the surface of PMN-32% PT crystal nearby the leakage location*

Fig. 4 shows the SEM photograph of the PMN-32% PT crystal grown near the leakage location of the Pt crucible. A large number of inclusions are appeared on the crystal surface nearby the crucible. In addition, the holes with clear inner walls were observed at some of those inclusions. Furthermore, as shown in Fig. 5a and b, EDAX analysis demonstrated that the Pt contents in the inclusions are higher than

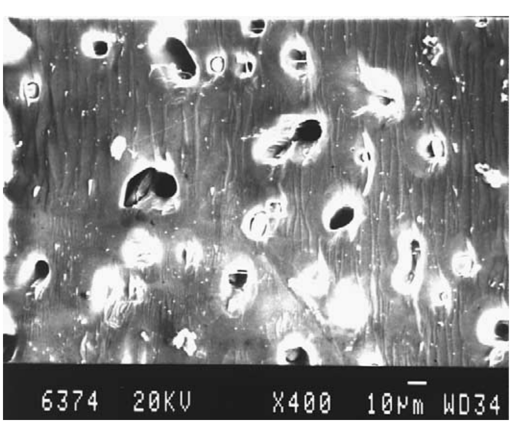

Fig. 4. SEM microstructure of the PMN-32% PT crystal surface nearby the leakage location of Pt crucible.

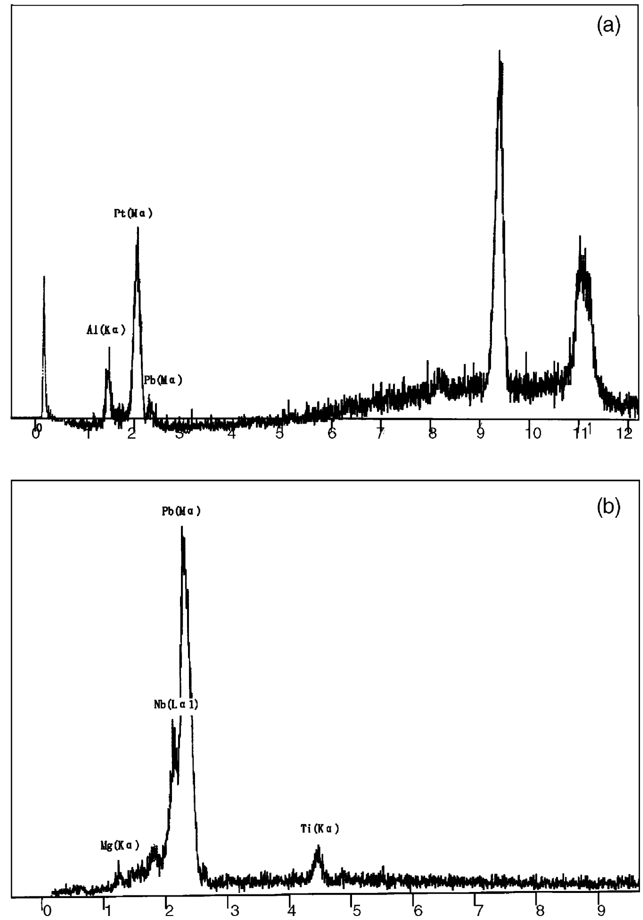

Fig. 5. EDAX results of the inclusions and the around area on crystal, (a) on inclusions (b) on the area around the inclusions.

their surroundings. It could be suggested that, the stress corrosion occurred between the melts and crucible before the start of the solidification of starting melt, and then, the productions formed between PMN-32% PT and crucible were wrapped nearby the surface of crystal during the solidification process.

From the above experimental results, we supposed that some impurity elements Me in the crucible reacted with PbO in the melts with the following equation:

$$m\text{PbO} + n\text{Me} \rightarrow \text{Me}_n\text{O}_m + m\text{Pb}$$

Pb was deoxidised and dissolved in the Pt crucible, forming a Pt–Pb alloy which has the lower melting point. Under the static pressure of melt, the grain boundary was apt to be pierced.

4. Conclusion

The manchanism of the leakage of Pt crucible during PMN-PT crystal growth was proposed. Under the static pressure of the melt, the bottom of Pt crucible undergoes nonuniform distortion and high temperature creek. A lot of dislocations moved from the grain inside to the grain boundary, which resulted in broadening of grain boundary and formed grooves and stress concentration at grain boundaries. The stress concentration resulted in the stress corrosion at the grain boundary of the Pt crucible. The active impurity elements in the Pt crucible could react with PbO in melt, which caused Pb to be deoxdised. The Pb element dissolved in the Pt, forming a Pt–Pb alloy which has the lower melting point. Under the static pressure of melt, the grain boundary was apt to be pierced.

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