Dendrite Growth Observed in $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ Single Crystals Prepared by the Bridgman Process

Jpn. J. Appl. Phys. Vol. 40 (2001) pp. L396–L397
Part 2, No. 4B, 15 April 2001

Dendrite Growth Observed in $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ Single Crystals Prepared by the Bridgman Process

Guisheng XU*, Haosu LUO, Haiqing XU, Zhenyi QI and Zhiwen YIN

Laboratory of Functional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201800, P. R. China

(Received February 5, 2001; accepted for publication March 2, 2001)

Several patterns of dendritic crystals of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ grown by the Bridgman process have been identified. This phenomenon arose from constitutional supercooling of the pseudo binary solid solution system. Therefore, macroscopic segregation and constitutional supercooling should be simultaneously restrained during crystal growth in order to obtain uniform crystals in composition and structure. A high growth temperature, larger temperature gradient and slower growth rate should be adopted to maintain stable a growth interface.

KEYWORDS: lead magnesium niobate-lead titanate, piezoelectric material, single crystal, Bridgman process, microstructure, dendritic growth, constitutional supercooling

Relaxor ferroelectric single crystals $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMNT) are attractive materials due to their excellent piezoelectric properties.[1–3] Recently, PMNT crystals with piezoelectric constant $d_{33} > 2500$ pC/N, dielectric constant $\varepsilon > 5000$ and electromechanical coupling factor $k_{33} > 94\%$, have been grown using the Bridgman process,[4–6] and the crystal size has reached up to $\phi 50\,\text{mm} \times 80\,\text{mm}$. The Bridgman process is promising for scaling up the crystal growth since rapid growth can be achieved. However, the compositional complexity in the PMN–PT pseudo binary solid solution system may result in some difficulties in the control of crystal perfection. Compositional inhomogeneity and structural defects in PMNT crystals have been recognized.[5] In addition, we found that dendritic growth occurred sometimes if the growth parameters were unsuitable.

In our experiment, PMNT (0.76PMN–0.24PT) single crystals were grown directly from PMNT melt formed by high-purity powders (99.99%) of PbO, MgO, Nb_2O_5 and TiO_2 using the Bridgman process. Platinum crucibles were used. Thin polished plates with the thickness of 0.5 mm and the orientation of {001} were processed from PMNT boules and then observed by the naked eye and under a polarizing microscope. Different patterns of dendritic crystals were observed.

Some PMNT dendritic crystals consist of coarser crystallites distributed in normal single crystals. They can be clearly visualized even by the naked eye. The assembled pattern of dendritic crystals can be regular, different branches crossing each other at an angle of 90° (Fig. 1), which is in agreement with the fourfold symmetry of crystal plates {001}. However an irregular pattern of dendrictic crystals also appears (Fig. 2). The latter morphology might originate from a too-rapid growth of crystallites.

Other dendritic PMNT crystals are composed of finer crystals surrounded by normal single crystals. They cannot be seen by the naked eye, but can result in a severe decrease of transparency in the degree. Under a polarizing microscope, they are shown as perfect crystal trees (Fig. 3) or long and thin intercrossed stripes (Fig. 4). The latter pattern can change into cellular structures gradually.

The dendritic growth implied the existence of instability of growth interfaces. In our growth method, a positive gradient was ensured from beginning to end. Therefore in our viewpoint, the instability of growth interfaces mainly originated from constitutional supercooling. The macroscopic segregation existed during the growth of PMN–PT pseudo binary solid solution crystals. X-ray fluorescence spectrometry indicated that the crystals contained a lower PT content than their melt and the PT content increased along the growth direction (the effective segregation coefficient k_e of 0.76PMN–0.24PT crystals was about 0.95 if the end-member PT was regarded as the solute in the PMN–PT system),[4,6] as was similar to the case of PSNT crystals unlike PZNT.[3,7] The freezing point of the melt dropped within the solution boundary layer where the concentration of PT with a lower melting point (about 1250°C) was higher than the average value of the melt, thus constitutional supercooling readily occurred.

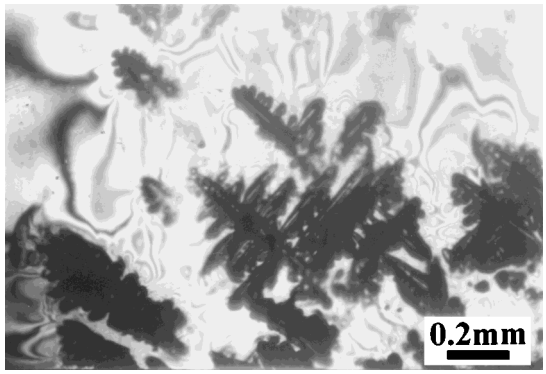

Fig. 1. Regular dendritic growth of 0.76PMN–0.24PT crystals on {001} plates, coarser branches outgrowing at an angle of 90° to trunks.

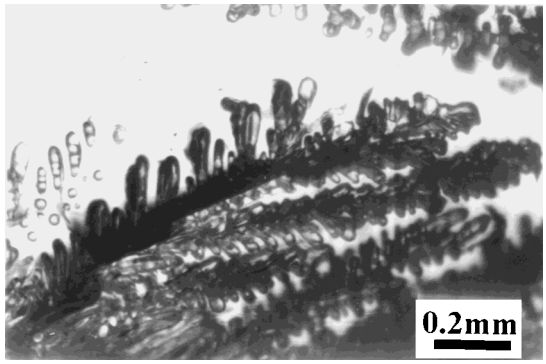

Fig. 2. Irregular dendritic growth of 0.76PMN–0.24PT crystals on {001} plates, the crossed angle of branches deviates from 90°.

*E-mail address: gshxu@sina.com

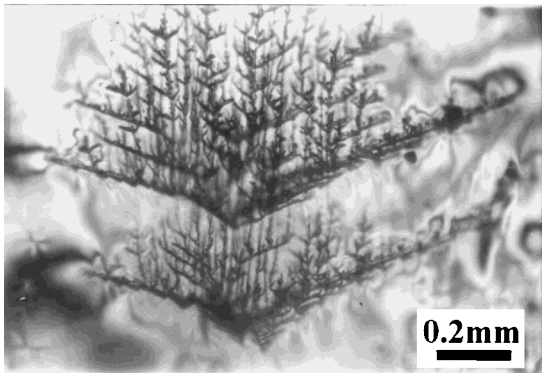

Fig. 3. Typical and perfect crystal trees made up of fine grained PMNT crystallites.

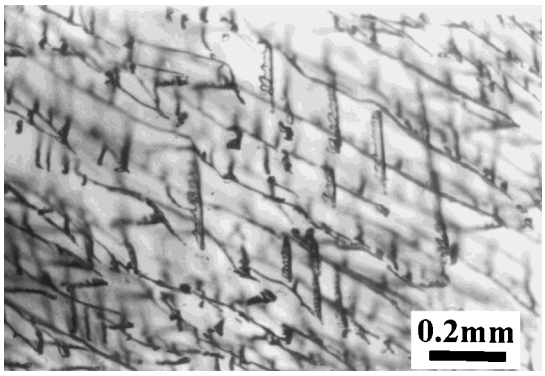

Fig. 4. Slim intercrossing crystal branches.

The constitutional supercooling can be restrained. The condition in which the constitutional supercooling takes place can be represented by the following formula:

$$\frac{G}{v} < \frac{mC_1(k_o - 1)}{Dk_o}$$

where G is the temperature gradient of the melt on the growth interface, v is the growth rate, C_1 is the concentration of the solute in melt, m is the slope of the liquid phase curve, k_o is the equilibrium segregation coefficient of the solute, and D is the diffusion coefficient of the solute in melt. Therefore, a larger temperature gradient and slower growth rate are needed to suppress constitutional supercooling.

On the other hand, it was found that the area in which dentritic crystals developed only occupied about 1/5 of the entire growth interface. Obviously, the constitutional supercooling took place locally on the interfaces. Owing to the fact that the temperature gradient and growth rate on the growth interface were almost the same, the local constitutional supercooling should be related to the inhomogeneity of the solute content in the melt, which was also illustrated by the difference of Curie temperature (T_c), from 108°C to 112°C, in the same crystal sample. PT content was variable along the growth interface, thus constitutional supercooling took place more readily in the region where PT content (C_1) was higher.

Therefore, not only the segregation, but also the constitutional supercooling should be taken into account in the growth of PMNT solid solution crystals. In order to maintain stable a growth interface and suppress constitutional supercooling, the following measures should be taken: (1) modify the homogeneity of the melt by raising the growth temperature or by other means; (2) adopt a larger temperature gradient; (3) decrease the growth rate.

This work was supported by the National Natural Science Foundation of China (Grant No. 59995520, 50072038 and 59872048), and the Natural Science Foundation of Shanghai (00ZE14070).

1) R. E. Service: Science **275** (1997) 1878.
2) S. E. Park and T. R. Shrout: J. Appl. Phys. **82** (1997) 1804.
3) S. Shimanuki, S. Saitoh and Y. Yamashita: Jpn. J. Appl. Phys. **37** (1998) 3382.
4) G. S. Xu, H. S. Luo, P. C. Wang, H. Q. Xu and Z. W. Yin: Chin. Sci. Bull. **45** (2000) 491.
5) G. S. Xu, H. S. Luo, H. Q. Xu, Z. Y. Qi, P. C. Wang, W. Z. Zhong and Z. W. Yin: J. Cryst. Growth **222** (2001) 202.
6) H. S. Luo, G. S. Xu, H. Q. Xu, P. C. Wang and Z. W. Yin: Jpn. J. Appl. Phys. **39** (2000) 5581.
7) Y. Yamashita and S. Shimanuki: Mater. Res. Bull. **31** (1996) 887.