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Stability and Single Crystal Growth of Dielectric Materials Containing Lead Under Hydrothermal Conditions

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Abstract

Stability of lead magnesium niobate (PMN; $Pb(Mg_{1/3}Nb_{2/3})O_3$), lead scandium niobate (PSN; $Pb(Sc_{0\cdot5}Nb_{0\cdot5})O_3$), a solid solution in the PSN–lead titanate system (PSNT), and lead zirconate titanate (PZT; $Pb(Zr_{0\cdot53}Ti_{0\cdot47})O_3$) were all examined in a platinum capsule under hydrothermal conditions. The perovskite PMN was formed from the low crystalline pyrochlore PMN at 600°C by the hydrothermal treatment in pure water. However, the perovskite was decomposed to the pyrochlore by further hydrothermal treatment in pure water for a longer time or at higher temperature. In KF solutions, single crystals of PMN, PSN and PSNT with a pyrochlore structure were grown at the top of the capsule by hydrothermal treatments at 600°C with a temperature gradient of 40°C. In the case of PZT, single crystals of the tetragonal PZT were grown, but the content of Zr in the grown crystals decreased in comparison with that of the starting material. © 1999 Elsevier Science Limited. All rights reserved

Keywords: hydrothermal conditions, chemical properties, perovskite, PZT.

1 Introduction

Dielectric ceramic materials containing lead such as solid solutions of lead titanate (PT; $PbTiO_3$) with lead magnesium niobate (PMN; $Pb(Mg_{1/3}Nb_{2/3})O_3$), lead scandium niobate (PSN; $Pb(Sc_{0\cdot5}Nb_{0\cdot5})O_3$), and lead zirconate (PZ; $PbZrO_3$) have many desirable electric properties and are attractive materials for use in electronic devices. Their practical use is, however, limited to sintered ceramics consisting of randomly oriented fine crystals. If the respective single crystals were artificially grown for electronic devices, it is expected that the properties of the devices may be improved.

The melt growth method cannot be employed to grow single crystals of these compounds, because they melt incongruently. For example, PZ melts incongruently at 1570°C and the solid solutions in the lead zirconate titanate (PZT) system with a $PbZrO_3$ content of more than 14 mol% melt incongruently.[1] PSN also melts incongruently at 1425°C.[2] These crystals should be grown by a solution growth technique. The flux method has been widely used to grow the single crystals of PZT,[3–8] PSN, and their solid solutions in the PSN–PT system (PSNT).[9–12] The high vapor pressure of PbO at high temperatures, however, causes the loss of flux, or compositional gradients in the grown crystals.

The hydrothermal method is another candidate for crystal growth of compounds that melt incongruently. This route has the advantage of yielding high-quality crystals with less thermal strain at lower temperatures in comparison with those produced using the flux method. However, few studies on hydrothermal crystal growth of dielectric ceramic materials containing lead have been reported, except growth of crystals in the PZT system.[13–15]

For the hydrothermal crystal growth in the PZT system, KF solutions were used as a mineralizer (solution as a solvent for hydrothermal crystal growth). In this study, hydrothermal crystal growth of PMN, PSN, PSNT, PT, PZ, and PZT, was performed mainly in KF solutions, and stability of these compounds under hydrothermal conditions is discussed.

2 Experimental

The starting materials of PZT ($Pb(Zr_{0\cdot53}Ti_{0\cdot47})O_3$), PSN, and PSNT (58%PSN–42%PT) were prepared

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from oxides of each component by the conventional solid state reaction and then ground into powder. Those of PZ were prepared from aqueous solutions in the presence of urea as described by Oren *et al.*[16] The commercially available chemical (Wako Pure Chem. Ind., Japan) was used for PT. In the case of PMN, a powder hydrothermally prepared at 160°C,[17] was used as a starting material.

All experiments were conducted in a platinum capsule with an outside diameter of 3·0 mm, thickness of 0·2 mm and length of 50 mm. A mineralizer was injected into the capsule with the starting materials (50 mg) and the capsule was welded shut with an electric arc. The volume of the solution added to the capsule was determined in order to balance the pressure between the outside and the inside of the capsule at the temperature required for hydrothermal treatment. The capsule was placed in a test-tube-type pressure vessel made of Stellite-25, and water was subsequently pumped into the vessel as a pressure medium. The vessel was heated by an electric furnace. Temperature measurements were conducted by a pair of thermocouples, each situated on the wall of the vessel at positions corresponding to the top and bottom of the capsule. In most experiments, by adjusting the position of the vessel in the vertical furnace with a temperature gradient, the temperature at the top (the growth temperature), was maintained at 600°C, and the temperature at the bottom was maintained at 640°C. The pressure inside the vessel was adjusted to 100 MPa by releasing water from the vessel during heating. The temperature and pressure were maintained for a controlled time. At the conclusion of a run, the vessel was cooled down to room temperature in the furnace. The capsule was cut open, and the contents were washed with water. X-ray powder diffractometry was used to identify the solids, and grown crystals were observed using an optical microscope and a scanning electron microscope equipped with an energy dispersive X-ray analyzer.

3 Results and Discussion

3.1 PMN

The starting powder of PMN was a low crystalline pyrochlore phase. In order to investigate the stability of the PMN perovskite phase, the pyrochlore powder was hydrothermally treated in pure water at various temperatures for 3 h without the temperature gradient. The perovskite phase was obtained at above 580°C and its relative amount was 99% at 620°C. The hydrothermal treatment enhanced the formation of the perovskite at much lower temperatures than the calcination of the same pyrochlore powder in air (over 750°C). The perovskite, however, changed to the pyrochlore by the further hydrothermal treatment at high temperatures over 700°C for a long time (over 24 h), due to release of lead from the PMN composition by formation of a lead alloy with platinum. It was concluded that the perovskite PMN was not stable under extreme hydrothermal conditions.

When the pyrochlore PMN was hydrothermally treated at 600°C with the temperature gradient of 40°C in various salt solutions with a concentration of 5 N, lead compounds including anions such as F, Cl, and I were formed. The formation of these lead compounds resulted in the formation of the pyrochlore PMN due to the release of lead. In alkaline solutions such as 5 N KOH solution, the perovskite was not obtained due to the preferential formation of PbO and $Mg(OH)_2$ from the PMN.

The exception was found by the hydrothermal treatment in KF solutions. When the pyrochlore PMN was treated in KF solutions at 600°C, or 650°C with a temperature gradient of 40°C, single crystals were formed at the top of the capsule [Fig. 1(a)] and fine crystals remained at the bottom of the capsule. The fine crystals treated at 600°C, were the pyrochlore phase. However, the fine crystals obtained at 650°C were mainly the perovskite phase, though the X-ray diffraction lines of the perovskite obtained by the hydrothermal treatment in KF solutions shifted to higher angle in comparison with those of the pure perovskite obtained by conventional processing, mainly due to the contamination by K resulting in a slight compositional change. The single crystals were black in color and were assigned to the pyrochlore phase. Energy dispersive X-ray analysis showed that the content of Mg in these crystals was reduced and that of Nb was increased in comparison with that of the starting material. Furthermore, a relatively large amount of K was also detected in the grown crystals.

3.2 PSNT and PSN

Both of the PSNT and PSN starting materials had the perovskite structure. When the PSNT was hydrothermally treated in KF solutions, bulky crystals [Fig. 1(b)] were grown at the top of the capsule and a powder remained at the bottom of the capsule.

X-ray diffraction patterns of the powder resembled those of the perovskite PSN, but included diffractions due to small amounts of $K_4Ti_3O_8$ and PbO. The needle-like crystals observed in Fig. 1(b) were considered to be $K_4Ti_3O_8$. X-ray diffraction patterns of the grown crystals resembled those of $Pb_2Ti_2O_6$ with the pyrochlore structure. The energy dispersive X-ray analysis showed that the content of Ti was increased in the grown crystals and a small amount of K was also detected. It also showed that

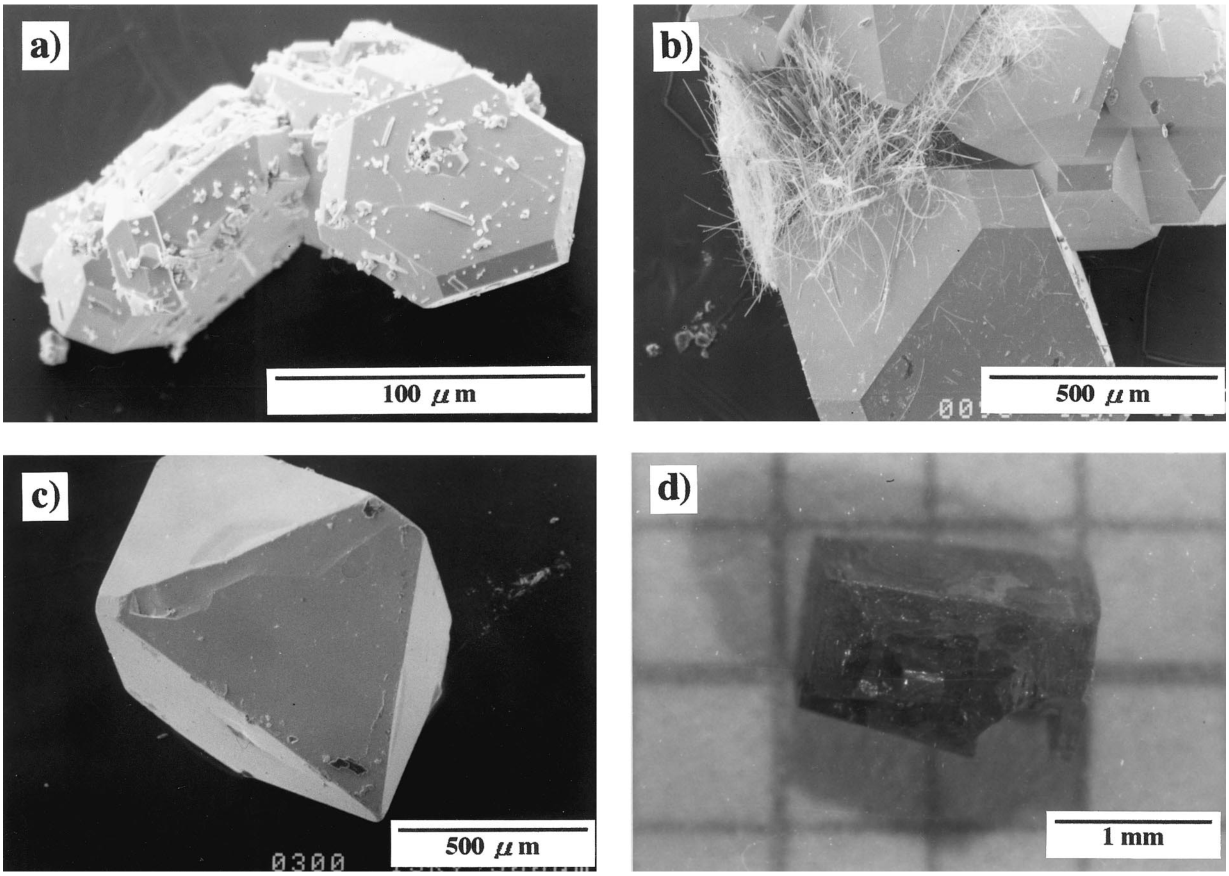

Fig. 1. Crystals grown at the top of the capsule under hydrothermal conditions at 600°C with a temperature gradient of 40°C: (a) crystals of the pyrochlore PMN grown in 5 N KF solution for 3 days; (b) crystals of the pyrochlore PSNT grown in 25 wt% KF solution for 5 days; (c) crystals of the pyrochlore PSN grown in 6·2 N KF solution for 5 days; (d) crystals of the tetragonal PZT grown in 45 wt% KF solution for 5 days.

the amount of Sc was reduced in the grown crystals, which may result in the formation of the pyrochlore phase. The same results were also obtained in CsF solutions.

When the PSN was hydrothermally treated in KF solutions, bulky crystals were again grown at the top of the capsule [Fig. 1(c)]. However, the content of Nb in the bulky crystals increased in comparison with that of the starting material, and the crystals were assigned to the pyrochlore phase.

3.3 PZT

When the PZT powder was hydrothermally treated in KF solutions, bulky crystals were grown at the top of the capsule in all growth runs [Fig. 1(d)]. Large plate-like PbO (massicot) crystals up to 2·0 mm were floating in the solution. In the powders remaining at the bottom of the capsule, fine crystals of ZrO_2 (baddeleyite) were formed. The formation of PbO and ZrO_2 suggested that a part of the PZT ceramic powder decomposed in the KF solutions under hydrothermal conditions.

The crystals grown at the top of the capsule were yellow in color, and cubic or regular prisms were commonly the basic shape of the crystals. Large crystals up to 1·8 mm in length were grown in a 45 wt% KF solution, but a decrease in the concentration of the KF solutions resulted in a reduction of the amount and size of the grown crystals.

Both the starting material and the grown crystals were assigned to a tetragonal crystal system, though the peaks of the crystals were shifted to higher angle in comparison with those of the starting ceramic powder. According to the chemical analysis, the mole ratio of Zr/(Zr + Ti) of the crystals grown in a 45 wt% KF solution, was remarkably reduced to 17·1 from 54·8 of the starting material. The shift of the X-ray diffraction peaks is attributed to the compositional difference between the grown crystals and starting material. The chemical analysis of the crystals revealed that they were contaminated by K_2O (0·28 wt%).

When the PT powder was hydrothermally treated in 45 wt% KF solution, single crystals of the PT tetragonal phase were grown at the top of the capsule. In the case of the hydrothermal treatment of the PZ powder under the same conditions, the PZ was decomposed to PbO and ZrO_2 and no single crystals were grown at the top of the capsule. It is considered that the limited solubility of ZrO_2 under the hydrothermal conditions resulted in the change of the composition of the PZT grown crystals from that of the PZT starting powder.

4 Conclusion

The low crystalline pyrochlore PMN could be converted to the perovskite at 600°C by hydrothermal treatment in pure water, but the stability of the perovskite phase was limited. The perovskite structure of PMN, PSN and PSNT was not stable in KF solutions under hydrothermal conditions, and changed to a pyrochlore structure by the decrease of the amount in the B′ site cation of the ideal perovskite structure, $A(B'B'')O_3$. Thus single crystals of the pyrochlore PMN, PSN and PSNT were grown by spontaneous nucleation in KF solutions under hydrothermal conditions at 600°C. Single crystals of the tetragonal PT were grown in KF solutions from the starting tetragonal PT powder, but PZ decomposed to PbO and ZrO_2. The limited solubility of ZrO_2 in KF solutions resulted in the growth of single crystals of the tetragonal PZT with a small ratio of $Zr/(Zr+Ti)$ compared to the starting PZT powder with a composition near to the morphotropic phase boundary.

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References

1. Fushimi, S. and Ikeda, T., Phase equilibrium in the system $PbO–TiO_2–ZrO_2$. *J. Am. Ceram. Soc.*, 1967, **50**, 129–132.
2. Yanagisawa, K., Rendon-Angeles, J. C., Kanai, H. and Yamashita, Y., Determination of melting point of lead scandium niobate. *J. Mater. Sci. Lett.*, in press.
3. Clarke, R., Whatmore, R. W. and Glazer, A. M., Growth and characterization of $PbZr_xTi_{1-x}O_3$ single crystals. *Ferroelectrics*, 1976, **13**, 497–500.
4. Clarke, R. and Whatmore, R. W., The growth and characterization of $PbZr_xTi_{1-x}O_3$ single crystals. *J. Cryst. Growth*, 1976, **33**, 29–38.
5. Fushimi, S. and Ikeda, T., Single crystals of lead zirconate titanate solid solutions. *Jpn. J. Appl. Phys.*, 1964, **3**, 171–172.
6. Eremkin, V. V., Smotrakov, V. G., Tsikhotskii, E. S., Aleshin, V. A. and Fesenko, E. G., Preparation of crystals of PbZrxTi1-xO3 and investigation of their perfection. *Izv. Akad. Nauk. SSSR Neorg. Mater.*, 1987, **23**, 284–287.
7. Yamaguchi, O., Koshiyama, S. and Shimizu, K., Crystal growth of $Pb(Zr_xTi_{1-x})O_3$ by flux method. *J. Jpn. Soc. Powder & Powder Met.*, 1973, **20**, 121–125.
8. Tsuzuki, K., Sakata, K., Ohara , G. and Wada, M., The growth of ferroelectrics $Pb(Zr_xTi_{1-x})O_3$ single crystal. *Jpn. J. Appl. Phys.*, 1973, **12**, 1500–1503.
9. Galasso, F. and Darby, W., Preparation of single crystals of complex ferroelectrics and semiconductions compound. *Inorg. Chem.*, 1965, **4**, 71–73.
10. Smotrakov, V. G., Raevskii, I. P., Maltitskaya, M. A., Zaitsev, S. M., Popov, Yu. M. and Strekneva, N. A., Preparation and properties of single crystals of Pb_2ScNbO_6. *Inorg. Mater.*, 1983, **19**, 105–109.
11. Yamashita, Y. and Shimanuki, S., Synthesis of lead scandium niobate–lead titanate pseudo binary system single crystals. *Mater. Res. Bull.*, 1996, **31**, 887–895.
12. Yamashita, Y. and Harada, K., Crystal growth and electrical properties of lead scandiumniobate–lead titanate binary single crystals. *Jpn. J. Appl. Phys.*, 1997, **36**, 6039–6042.
13. Barsukova, M. L., Kuznetsov, V. A., Lobachev, A. N. and Lider, V. V., Hydrothermal crystallization of solid solutions. *Sov. Phys. Crystallogr.*, 1971, **16**, 178–180.
14. Kuznetzov, V. A., Crystallisation of titanium, zirconium and hafnium oxides and some titanate and zirconate compounds under hydrothermal conditions. *J. Cryst. Growth*, 1968, **3**(4), 405–410.
15. Yanagisawa, K., Kanai, H. and Yamashita, Y., Crystal Growth of Lead Zirconate Titanate with Additives under Hydrothermal Conditions. *Jpn. J. Appl. Phys.*, 1997, **36**, 6031–6034.
16. Oren, E. E., Taspinar, E. and Tas, A. C., Preparation of lead zirconate by homogeneous precipitation and calcination. *J. Am. Ceram. Soc.*, 1997, **80**, 2714–2716.
17. Watanabe, M. and Shimizu, Y., Effect on specific surface area on sintering of PMN–PT powder by hydrothermal production. In *Proceedings of the Annual Meeting of the Ceramics Society of Japan*. The Ceramics Society of Japan, Tokyo, 1990, p. 138.