

Effect of Debinding Conditions on the Microstructure of Sintered $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$

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Abstract In order to fabricate complex-shaped polycrystalline ceramics by sintering, organic binders are usually pre-mixed with ceramic powders to enhance the formability during the shape forming process. These organic binders, however, must be eliminated before sintering so as to eliminate the possibilities of poor densification and unusual grain growth during sintering. The present work studies the effect of binder addition on grain growth behavior during sintering of 92(70Pb($\text{Mg}_{1/3}\text{Nb}_{2/3}$) O_3 -30PbTiO₃)-8PbO (mol%) piezoelectric ceramics. The microstructures of the sintered samples were examined for various heating profiles and debinding schedules of the binder removal process. Addition of Polyvinyl butyral(PVB) binder promoted abnormal grain growth especially in incompletely debinded regions. Residual carbon appears to change the grain shape from corner-rounded to faceted and enhance abnormal grain growth.

Keywords : PMN-PT, Abnormal grain growth, Binder, Debinding

1. Introduction

Complex-shaped polycrystalline ceramics have been widely used for structural, electronic, porous, and architectural components. Various shaping technologies, including uniaxial pressing, extrusion, slip casting, and injection molding, have been developed¹⁻³. For shaping, organic binders (e.g. PVB, PVA, PW, PP, PE, EVA, PEG etc.) are usually mixed with raw powders to enhance the shape formability. Selection of binder materials and control of debinding are considered critical for obtaining samples with a uniform sintered microstructure and preventing the formation of defects such as huge pores, cracks, and blistering.

$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) ceramic has been attracted by a number of investigations due to its excellent dielectric and piezoelectric properties. Material design and characterization of dielectric and piezoelectric properties have been intensively

studied⁴⁻⁶. However, few investigations have been made into the effects of organic binders on this ceramic's microstructure and properties. Understanding of the binder effect is required to produce complex-shaped PMN-PT. In the present work, the effect of binder on grain growth behavior during sintering of 92(70PMN-30PT)-8PbO piezoelectric ceramics has been studied.

2. Experimental Procedure

The general formula of the materials studied is 92(70PMN-30PT)-8PbO (mol%) + x wt% PVB (polyvinyl butyral), where $x = 0, 0.5, 1.0, 3.0$, respectively. The samples were prepared by the columbite method⁷. Proportioned powders of 4MgCO₃Mg(OH)₂4H₂O and Nb₂O₅ were ball-milled using zirconia balls and then calcined at 1100°C for 4 h in air to form MgNb₂O₆ (columbite). MgNb₂O₆ was mixed with PbO and TiO₂ by ball-milling and then calcined at

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800°C for 6 h in air to form 70PMN-30PT powder. The calcined 70PMN-30PT powder was examined by X-ray diffraction (D/MAX-3C, Rigaku Co., JPN) and was found to be pyrochlore-free. 92(70PMN-30PT)-8PbO powder mixture was ball-milled and then dried. The dried 92(70PMN-30PT)-8PbO powder was mixed with PVB, ball-milled and then dried again.

Powder compacts were prepared with 5 g powder for each by uniaxial pressing in a die of 14-mm diameter and subsequent cold isostatic pressing at 200 MPa. The double enclosed crucible method was used for sintering. The samples were placed on a piece of Pt foil on the lid of an alumina crucible. An inverted crucible was then placed over the samples. This crucible was placed in another inverted crucible with a lid. PbZrO_3 powder was packed between the crucibles to reduce the weight loss due to the evaporation of PbO.

In order to examine the effects of debinding, three different debinding schedules were selected: 1) sintering, where the sample was placed in a double enclosed crucible and then sintered without debinding; 2) debinding-sintering, where the sample was placed in a double enclosed crucible and then debinding-sintering was continuously carried out; and 3) debinding-cooling-sintering, where the sample was debinded on a piece of Pt foil on the lid of an alumina crucible, cooled down to room temperature, and then the debinded sample was sintered in a double enclosed crucible.

The debinding heating profile was determined based on a thermogravimetric analysis (TGA; SDT2960, TA Instruments, USA). Microstructures of the sintered samples were examined by optical microscopy (EPIPHOT 200, NIKON, JPN) and scanning electron microscopy (JSM-5800, JEOL, Japan). The content of the residual carbon of the debinded samples was analyzed using a Carbon Determinator (CS600C, LECO Co., USA).

3. Results and Discussion

3.1. Effect of heating profile on binder removal

Fig. 1 shows the thermograms of the 92 (70PMN-30PT)-8PbO compacts with various PVB contents. All the thermograms were obtained at a heating rate of 10 K/min in a static air environment. The thermograms show that the initial binder evolution temperature (T_s) and the maximum binder evolution rate temperature (T_m) (where the rate of change of the thermogram against temperature is the highest) decreases with increasing PVB content.

Fig. 2 shows the thermograms of 3 wt% PVB added samples with various heating rate. The thermograms show that T_s and T_m increase with increasing heating rate. In order to optimize the

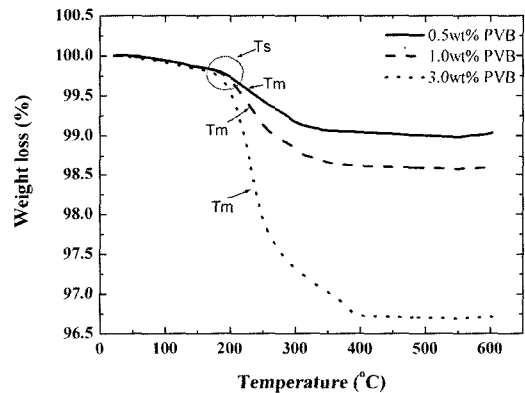


Fig. 1. Thermograms for various binder contents.

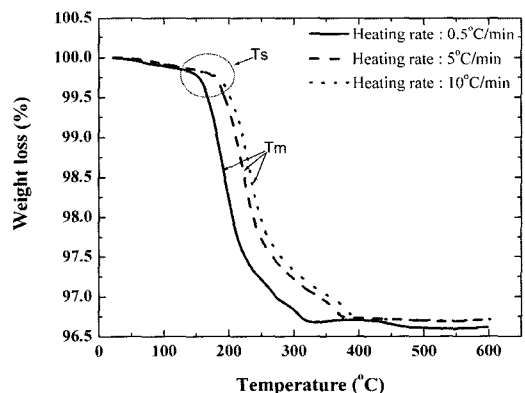


Fig. 2. Thermograms for various heating rates.

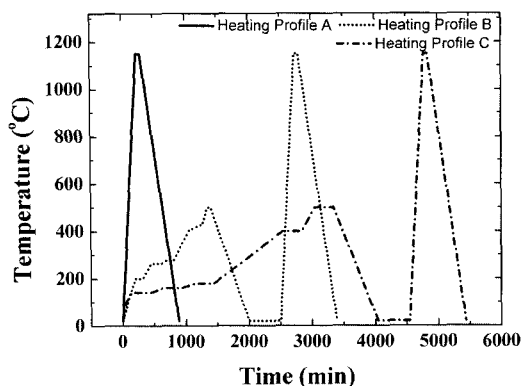


Fig. 3. Heating profiles for debinding and sintering of ceramic preforms.

heating profile for binder removal, binder content and heating rate should be considered simultaneously, as shown in Figs 1 and 2. If the heating profile is designed using the thermogram results at a fast heating rate, T_s and T_m should be higher than those at a low heating rate. Consequently, the sample would contain unexpected defects due to abrupt binder evolution.

To investigate the effects of heating profile on binder removal, three different heating profiles were adopted, as schematically shown in Fig. 3. Heating profile A consists of a monotonous increase in temperature from 20 to 1150°C at a heating rate of 5 K/min. Heating profile B was established considering a TGA analysis at a heating rate of 20 K/min and had five holding steps, at 200, 265, 275, 410, and 425°C. The holding time for each step was 1-3 hours and the heating rate between steps was 0.2-1.0 K/min. For heating profile C, the starting temperature, ending temperature, and step number were the same as those in profile B but the step temperature, holding time, and heating rate were different. The step temperatures were 140, 160, 180, 400, and 500°C, and the holding time for each step was 5 hours. The heating rate before and after binder evolution was 0.5-1.0 K/min and the heating rate during binder evolution was 0.1 K/min. Heating profile C was established considering a TGA analysis at a heating rate of 0.5 K/min.

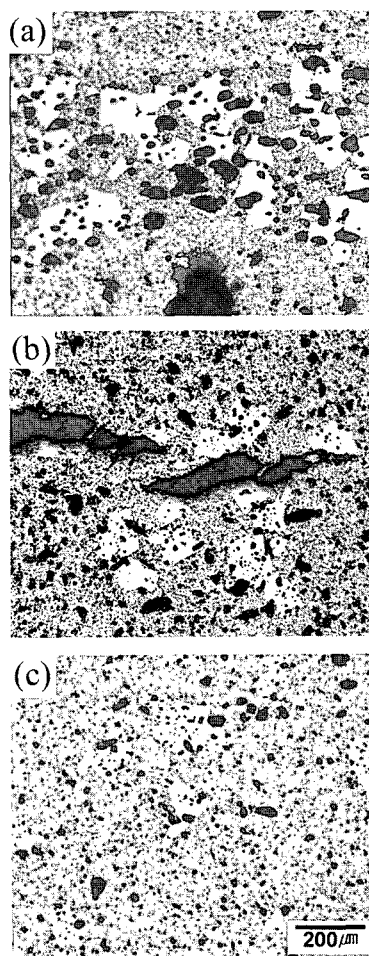


Fig. 4. Micrographs of the samples using different heating profiles in Fig. 3. (a) Heating profile A, (b) Heating profile B, and (c) Heating profile C.

The residual carbon was measured after debinding treatment with heating profiles B and C. Upon addition of 1.0 and 3.0 wt% PVB, the residual carbon was 0.07 and 0.11 wt%, respectively, for profile B and 0.016 and 0.019 wt% for profile C. The amount of residual carbon is closely related to the debinding heating profile and decreases, in general, as the intermediate holding steps are extended.

Fig. 4 shows the optical micrographs of the 3 wt% PVB-added samples after binder removal following different heating profiles. A number of large pores are observed when binder removal was conducted

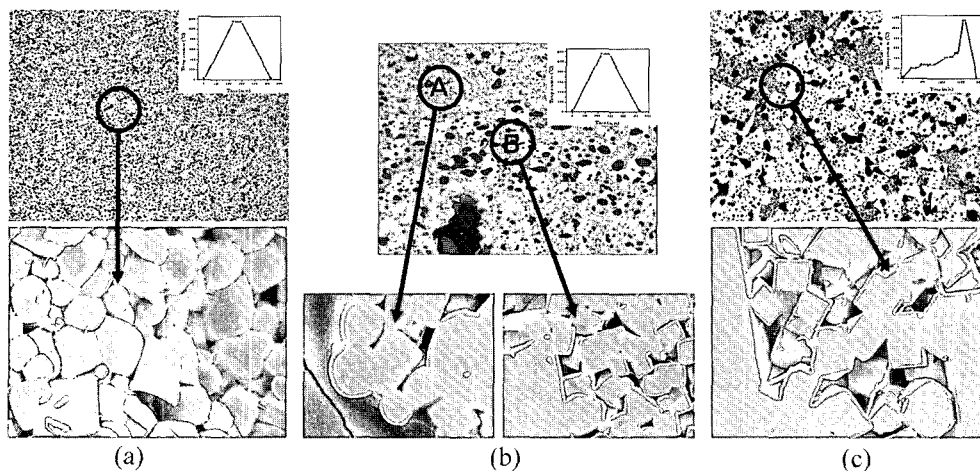


Fig. 5. Shapes of grains after sintering of samples without (a) and with (b and c) binder. (a) 0% binder-added sample with direct sintering, (b) 3% binder-added sample with direct sintering, and (c) 3% binder-added sample with debinding + sintering.

using heating profiles A and B. However, for heating profile C, the number of large pores is considerably reduced. The formation of large pores was obviously induced by abrupt binder removal from the samples because of the fast heating rate and an inappropriate heating profile.

Consequently, an inappropriate debinding heating profile causes insufficient reduction of the residual carbon and the formation of large pores in the sample. These factors will affect the microstructure and properties of the sample after sintering. An appropriate heating profile design is required to minimize residual carbon and large pore formation in the sample.

3.2. Effect of debinding schedule on sintered microstructures

When the sample was sintered without debinding (Fig. 4(a)), many abnormal grains as well as a large number of large pores were observed in the center region of the sample. In the case of debinding-sintering, abnormal grains were present throughout the sample whereas large pores were not observed, as shown in Fig. 5(c). In the case of debinding-cooling-sintering (Fig. 4(c)), the number of abnormal

grains as well as that of large pores was reduced compared with those in the sample with debinding-sintering.

For the sample sintered without debinding, incomplete debinding should occur near the sample center because of the fast heating rate. For debinding-sintering, although large pores were not observed in the sample, debinded binder would remain in the double enclosed crucible, potentially leading to incomplete debinding throughout the sample. For debinding-cooling-sintering, debinding would occur effectively because the debinding was not performed in a double enclosed crucible but on a Pt foil in air. Incomplete debinding appears to enhance unexpected abnormal grain growth and an improper debinding schedule seems to induce large pore formation in the sample.

Recent investigations have shown that abnormal grain growth can take place in systems with faceted solid/liquid interfaces or grain boundaries. Examples include BaTiO_3 , SiC , Si_3N_4 , and PbO excess PMN-PT^{8-11} . On the other hand, systems that display normal grain-growth behavior have spherical grains, e.g., W grains in Ni and NbC grains in B -added Co^{12-13} . Fig. 5 shows the shapes of grains in

different samples. Without binder (Fig. 5(a)), the grain shape is corner-rounded. A similar grain shape is observed in a binder-added sample but with proper debinding (region A in Fig 5(b)). However, if the debinding is incomplete (e.g. Region B in Fig. 5(b) and Fig. 5(c)), the grains are well faceted. It appears therefore that residual carbon yield faceted the grains and enhances abnormal grain growth.

IV. Conclusions

Microstructures of binder-added 92(70PMN-30PT)-8PbO (mol%) ceramics during debinding have been investigated in order to establish proper debinding schedules. Incomplete debinding due to an improper heating profile resulted in a high content of residual carbon and the formation of numerous large pores in the sintered sample. The debinding schedule critically affected the microstructures of 92(70PMN-30PT)-8PbO (mol%) ceramics. In the case of debinding in a double enclosed crucible, debinding was not complete because of the saturated binder environment in the crucible. Abnormal grains with faceted shapes were observed in incompletely debinded regions. Residual carbon appears to be responsible for the change in grain shape from corner-rounded to well faceted and for subsequent abnormal grain growth.

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