JOURNAL OF MATERIALS SCIENCE **31** (1996) 1725–1728

Mechanochemical effects on the properties of starting mixtures for $PbTiO_3$ ceramics by using a novel grinding equipment

K. HAMADA
Nara Machinery Co., Ltd, Jonan-jima Ohta-ku Tokyo 143, Japan
M. SENNA
Faculty of Science and Technology, Keio University, Hiyoshi yokohama 223, Japan

The effects of milling were studied using a newly developed multi-ring media-type grinding machine on the synthesis processes of $PbTiO_3$ ceramics from $PbO–TiO_2$ mixed sols. The temperature of the endothermic and exothermic DTA peaks, corresponding to dehydration and crystallization, decreased with milling time. After milling the mixed sol for 5 min and heating to 823 K, the product was a single-phase $PbTiO_3$. This suggests rapid homogenization and formation of lead titanate precursors during milling. The effects of milling were revealed to be much less when mixtures of dry and wet powders were used.

1. Introduction

The versatility of lead titanate for various ferroelectric ceramics is well-known. One of the most important aspects for fabricating these ceramics is the homogeneity of the mixing and the accompanying chemical interaction between the ingredients [1, 2].

To obtain an intimate mixture as a starting material, it is usual to use a ball mill in which individual oxides such as PbO and TiO_2 are put together and ground for a prolonged period. This kind of conventional mixing does not always achieve the desired homogeneity. Even more serious is the substantial amount of contamination.

In order to avoid such drawbacks, a series of soft-mechanochemical processes has been developed in our laboratory [3–5]. In the latter alternative, precursor gels or hydroxides are mechanically activated for a period much shorter than in the conventional shake-and-bake technique. The advantage of these processes even over the co-precipitation techniques has also been discussed [6].

The purpose of the present study was to improve the process by using a newly developed multi-ring-type grinding machine [7] and to compare the properties of mixed sols with those from anhydrous oxide, powders and slurries.

2. Experimental procedure

2.1. Preparation of starting materials

TiO_2 or PbO sol was obtained by adding 500 ml 0.5 M NH_4OH to 500 ml 0.1 M $TiCl_4$ or $Pb(NO_3)_2$ aqueous solution, respectively. After impurity ions had been eliminated by repeated decantation, the two sols were mixed for 1 h using an agitator (EYELAMDC) to obtain a starting mixed sol, denoted SO. The Pb/Ti molar ratio was kept constant at 1/1, irrespective of the form of the starting material. The solid content in a mixed sol was also kept constant at 8.88 wt %.

The mixed powder was prepared by simply mixing the commercial oxide powders, i.e. PbO (Massicot; Wako, guaranteed grade) and TiO_2 (Anatase; Ishihara) in an agate motar. The mixed powder was denoted PO.

The mixed slurry, specimen SL, was prepared by adding water to the powder mixture PO, to give a water content the same as that of the mixture sol.

2.2. Mechanical treatment and characterization

All the mixtures were milled by the grinding machine shown in Fig. 1 (MICROS:MIC-0, Nara Machinery), equipped with a ZrO_2 liner and milling rings. The equipment can be categorized as a multi-ring media mill. The main body comprises a casing, rotating main shaft and six sub-shafts interlocked with the main shaft. A number of loosely stacked milling rings, serving as milling media, is centred around each sub-shaft, as shown in Fig. 2.

Because the inner diameter of the ring is larger by 4 mm than the diameter of the sub-shaft, rings can rotate freely around the sub-shaft. The rings move radially outwards by the centrifugal force and keep turning around, while being pressed towards the inner wall of the grinding vessel. Particles captured between the rotating rings and the wall surface are compressed by a centrifugal force on the rings and subjected to milling. The machine was operated batchwise in air at a constant rate of revolution of the main shaft,

0022–2461 © *1996 Chapman & Hall*

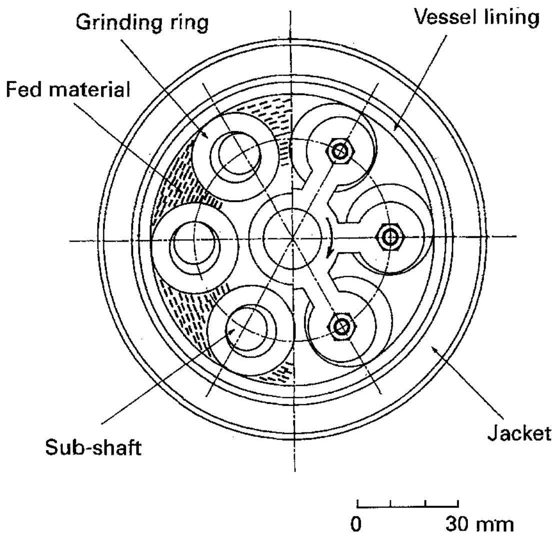

Figure 1 Inter-relation of the inside movement of the MIC-O.

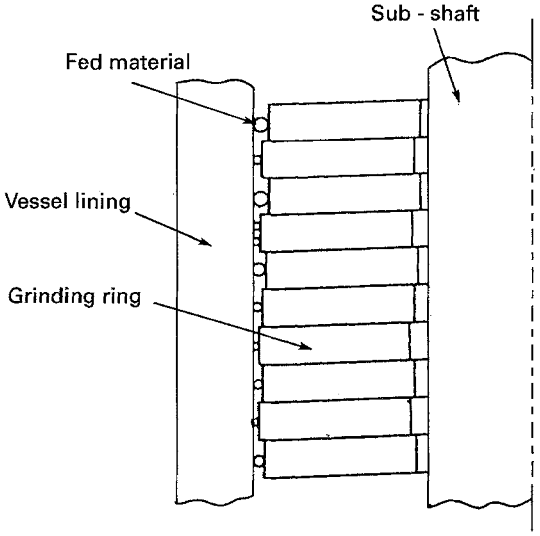

Figure 2 Independent movement of the grinding rings in MIC-O.

2000 rpm. The milled specimens were dried at 325 K in air for 15 h.

Thermal behaviour of the specimen was examined by differential thermal analysis (DTA) and thermogravimetry (TG, Mac Science 2000) up to 1023 K at a constant rate of heating, 10 K min^{-1}, under nitrogen gas flow (200 $\mathrm{cm}^3\,\mathrm{min}^{-1}$). After heating to the predetermined temperatures, the specimen was quenched to room temperature, and subjected immediately to X-ray powder diffractometry (Mac Science MXP3V).

3. Results and discussion

3.1. Change in TG–DTA profiles by milling

As shown in Fig. 3, the weight loss of the SO specimen took place in two stages. The TG curves of the SO specimens showed a gentle slope between the first stage and the second stage.

The DTA profile comprised two endothermic and one exothermic peaks, as shown in Fig. 4. According to Komatsubara *et al.* [1], the first endothermic peak is attributed to the desorption of free water molecules, and the second one to the simultaneous dehydroxilation and decomposition of NO_3^-.

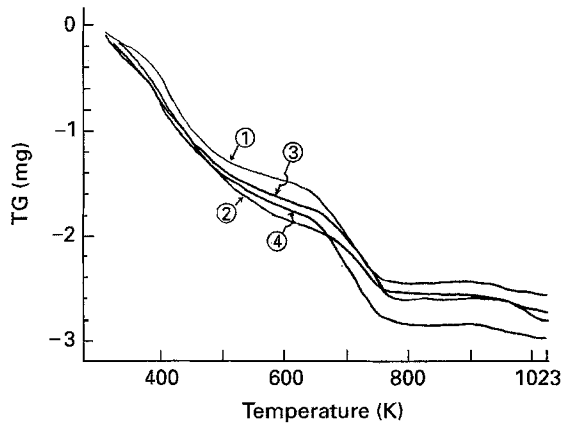

Figure 3 Change in the TG profile of SO after milling. (1) 0 min (2) 5 min, (3) 20 min, (4) 60 min.

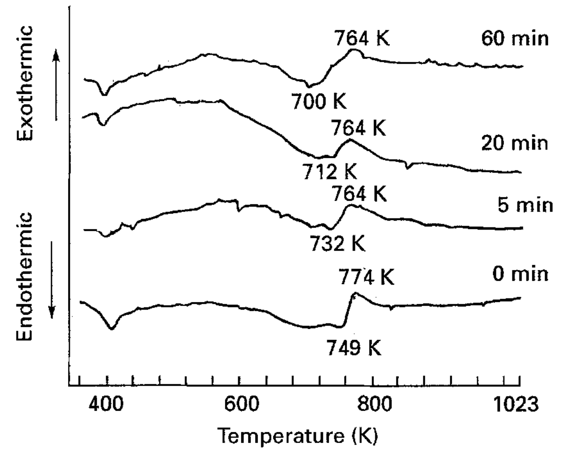

Figure 4 Change in the DTA profile of SO after milling.

It should be noted that the temperature of the second endothermic peak decreased from 749 K to 700 K after milling for 60 min. The temperature of the exothermic peak, appeared immediately after the endothermic peak, also decreased, but to a smaller extent, i.e. from 774 K to 764 K by milling for 60 min.

Simultaneously, the temperature interval between the endothermic and exothermic peaks increased with milling time. The temperature of the exothermic peak, being attributed to the crystallization of $PbTiO_3$, decreased with increasing milling time, indicating the increase in the reactivity of the starting mixture, i.e. a mixed sol.

3.2. Change in the X-ray diffraction pattern by milling

After heating at the predetermined temperature, the SO specimens with and without milling for 60 min were analysed by XRD. As shown in Fig. 5, the crystallization of $PbTiO_3$ was observed at 823 K for both samples. The PbO peak was observed only for the intact specimen. The disappearance of the PbO peak after milling the starting mixture was not due to the amorphization caused by milling. Instead, PbO was consumed during heating of the milled specimens. The only way to achieve PbO consumption is by conversion

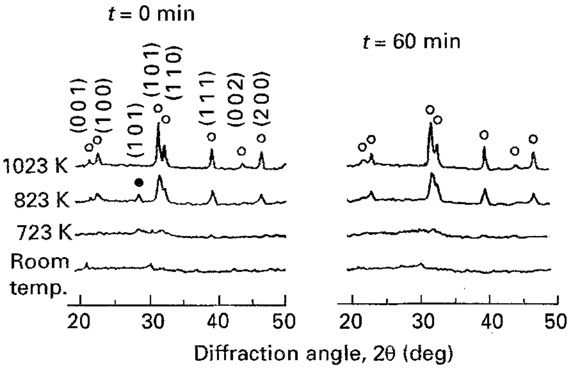

Figure 5 Change in the XRD pattern of SO before milling and after milling for 60 min. (○) $PbTiO_3$, (●) PbO-L.

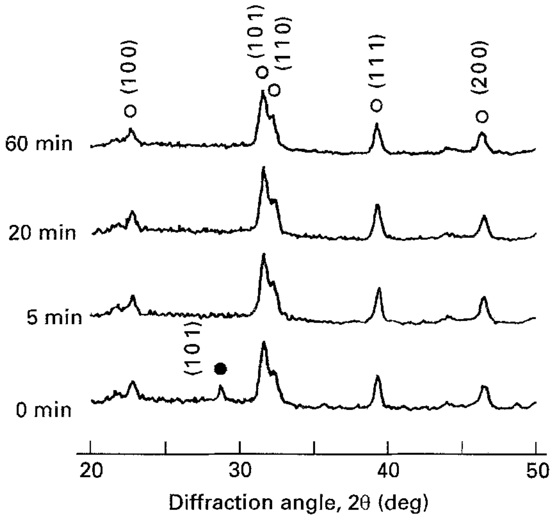

Figure 6 Change in the XRD pattern of SO after heating at 823 K. (○) $PbTiO_3$, (●) PbO-L.

to $PbTiO_3$, because of the enhanced chemical interaction between PbO and TiO_2 during milling.

The change in the XRD pattern of SO specimens after heating at 823 K is shown in Fig. 6. The PbO peak disappeared after milling for only 5 min, indicating that the mechanochemical interaction had taken place in such a short time due to milling.

The change in the XRD pattern of the PO specimen after milling, and subsequently heating at 823 K, are shown in Fig. 7. After milling for 5 min, the specimen still contained PbO, both massicot (M) and litharge (L) phases, together with $PbTiO_3$. Only after milling for 60 min, was the product almost single-phase $PbTiO_3$, but it still contained a small amount of PbO-M and L.

This is very similar to the case of the SO specimen after milling for 5 min. Therefore, it is suggested that the PO specimen needed to be milled for longer periods than the SO specimen to reach the state of intimate mixing necessary for the formation of $PbTiO_3$ precursor.

In contrast, much larger amounts of TiO_2, PbO-M and L were observed for the SL specimen even after milling for 60 min and subsequently heating at 823 K, as shown in Fig. 8. The difference in the XRD patterns of the specimens milled for 5 min and subsequently heated at 823 K are compared in Fig. 9. The relative amount of $PbTiO_3$ phase of the SO specimen was 2.7 times larger than that of the SL specimen, as determined from total XRD peak area of $PbTiO_3$ (1 0 0), (1 0 1), (1 1 0), (1 1 1), (2 0 0), in spite of the same water content. The water in the SL specimen showed no significant influence on complex formation.

The relative amount of $PbTiO_3$ phase in the PO specimen was 2.3 times that of the SL specimen, compared with the samples milled for 5 min. It is known that amorphization takes place more easily for dry milling than for wet milling [8]. Accordingly, the experimental results indicate that free water added externally is not effective for the mechanochemical complex formation, in line with the report by Longo and Voight [9]. The obtained results suggest that the process starting from a mixed sol makes it possible to synthesize $PbTiO_3$ by using only slight mechanical energy.

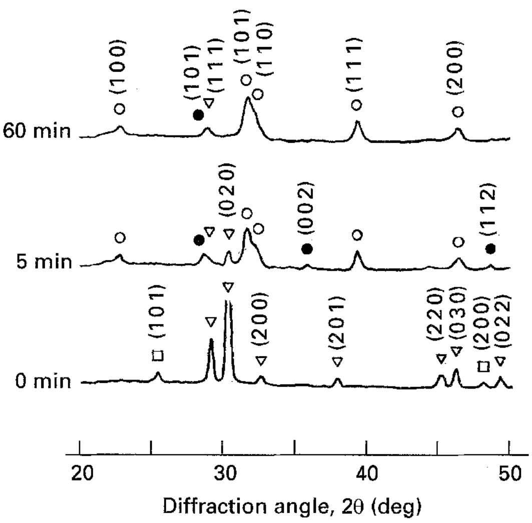

Figure 7 Change in the XRD pattern of PO after heating at 823 K. (○) $PbTiO_3$, (●) PbO-L, (▽) PbO-M, (□) TiO_2.

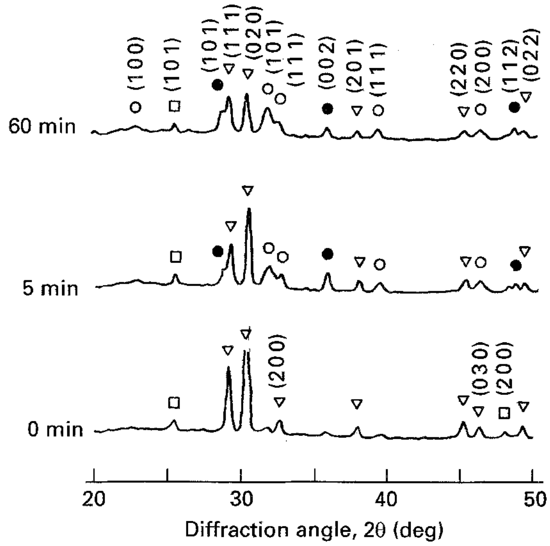

Figure 8 Change in the XRD pattern of SL after heating at 823 K. (○) $PbTiO_3$, (●) PbO-L, (▽) PbO-M, (□) TiO_2.

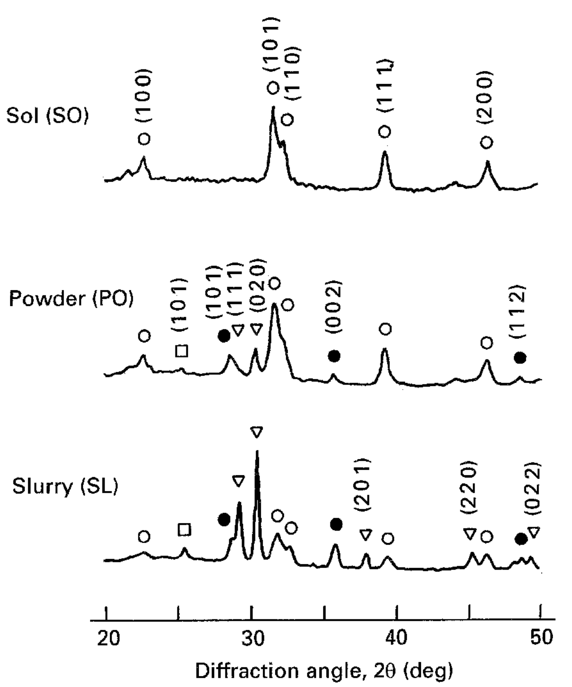

Figure 9 Change in the XRD pattern of SO, PO, SL after milling for 5 min and subsequently heating at 823 K. (○) $PbTiO_3$, (●) PbO-L, (▽) PbO-M, (□) TiO_2.

4. Conclusion

A newly developed multi-ring grinding machine is proved to be appropriate for mechanochemical synthesis of precursors of complex oxides for ceramic products. A 5 min milling of the sol mixture resulted in an effective interaction between the two oxide components, leading to easier synthesis of crystalline lead titanate on subsequent heating at a temperature as low as 823 K. Chemical interaction during mixed milling is the severest in the sol mixture, followed by the powder mixture and then slurries. This shows the inability of the water subsequently added to the dry powdery mixture, to aid the reaction in contrast to the water molecules *a priori* hydrated in the sol mixture.

References

1. S. KOMATSUBARA, T. ISOBE and M. SENNA, *J. Am. Ceram. Soc.* **77** (1994) 278.
2. K. TAKEUCHI, T. ISOBE and M. SENNA, *J. Solid State Chem.* **109** (1994) 401.
3. M. SENNA, *Solid State Ionics* **63–65** (1993) 3.
4. Y. KOJIMA, T. ISOBE, M. SENNA, S. EI-ESCANDARANY K. SUMIYAMA and K. SUZUKI, *Int. J. Mechanochem. Mech. Alloying*, **1** (1994) 32.
5. J. LIAO and M. SENNA, *Solid State Ionics* **66** (1993) 313.
6. Y. OKAMOTO, T. ISOBE and M. SENNA, *J. Non-Cryst. Solids* **180** (1995) 171.
7. K. HAMADA and M. SENNA, *Kagaku Kogaku Ronbunshu* **21** (1995) 334.
8. K. KUBO, *J. Soc. Powder. Technol. Jpn* **15** (1978) 17.
9. J. M. LONGO and K. C. VOIGHT, *Solid State Ionics* **32/33** (1989) 409.

Received 1 December 1994
and accepted 9 November 1995