Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 443 (2006) 122–124

thermochimica acta

www.elsevier.com/locate/tca

Short communication

Coupled TG–MS study on the intermediate for formation of PbO(t) from PbO(O) in synthesis of perovskite PMN–PT

Kyoung Ran Han[a,*], Chang-Sam Kim[a], Young-Soon Kwon[b]

[a] *Division of Materials Science and Engineering, Korea Institute of Science and Technology, Seoul 131-791, Republic of Korea*

[b] *Department of Chemistry, Catholic University of Korea, Puchon 420-743, Republic of Korea*

Received 13 September 2005; received in revised form 18 November 2005; accepted 22 November 2005

Abstract

$Pb(OH)_2$ was previously proposed as an intermediate in the synthesis of PMN $[Pb(Mg_{1/3}Nb_{2/3})O_3]$ and PMN–PT $[0.9Pb(Mg_{1/3}Nb_{2/3})O_3–0.1PbTiO_3]$ from a mixture of PbO, Nb_2O_5, $Mg(NO_3)_2\cdot 6H_2O$ (w/w$_0$) TiO_2 by the modified mixed oxide method based on TG/DSC and XRD data. Coupled TG–MS of the precursor reveals that the intermediate is $Pb_6O_5(NO_3)_2$, not $Pb(OH)_2$ because the evolved gas was nitric oxide and oxygen, not water.

Keywords: Oxide; Chemical synthesis; Differential scanning calorimetry; Thermogravimetric analysis; Ferroelectricity

1. Introduction

Pb-based ferroelectric, complex perovskite compounds are usually prepared by a mixed oxide method [1–3], which requires two calcination steps and sintering temperature of ∼1200 °C. Efforts have been made to lower calcination and sintering temperatures by chemical synthesis methods such as molten salt [4–6], sol–gel [7–9], spray pyrolysis [10], coprecipitation [11,12], and mechanochemical [13,14] processes. Recently Liou and Tseng [15] introduced a preparation method of PMN ceramics by reaction sintering of the stoichiometric mixture of PbO, Nb_2O_5, and $Mg(NO_3)_2\cdot 6H_2O$. A nearly pure perovskite phase was obtained by heat treatment at 1250 °C for 1 h, and further heating resulted in near fully densified single phase perovskite PMN ceramic with room temperature dielectric constant of 11,500. We have introduced a modified mixed oxide method for low-temperature-sinterable PMN using the same mixture plus a small amount of water [16,17]. This PMN precursor sintered at 900 °C for 2 h to 95.6% of the theoretical density and had a room temperature dielectric constant of 13,800. Water apparently induced a different pathway to pervovskite phase. Therefore, the previously proposed pathway [16] was re-examined by means of a coupled TG–MS analysis.

2. Experimental

The precursor of the PMN–PT $[0.9Pb(Mg_{1/3}Nb_{2/3})O_3–0.1PbTiO_3]$ was prepared by the modified mixed oxide method previously reported [16]. The precursor (∼20 mg) was heated in a Pt/Rh crucible to 800 °C at a heating rate of 10 °C/min under flowing air or argon in a TG/DSC (Model 409 STA, Netzsch Co., GmbH, Selb, Germany). To observe phase developments, the precursor was heated to the beginning of the endotherms or exotherms of the DSC curve at a heating rate of 10 °C/min under flowing air and then rapidly cooled to room temperature. The heated powders were subjected to the XRD analysis ($2\theta = 20–80$) with a scanning rate of 2° 2θ/min (Model PW 1800, Philips Research Laboratories, Eindhoven, Netherlands). The TG–MS measurements were done with a Netzsch TG 209 IRIS-MS capillary coupled system under flowing argon. The heating rate was 10 °C/min, the sample masses were ∼110 mg.

Consolidation and measurements of dielectric properties were carried out as described previously [16].

---

[*] Corresponding author. Tel.: +822 958 5541; fax: +822 958 5489.
E-mail address: krlim@kist.re.kr (K.R. Han).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.11.040

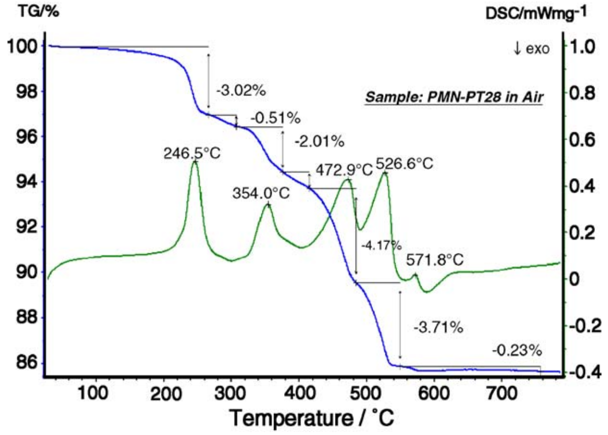

Fig. 1. TG–DSC curves of the precursor of PMN–PT heated at a heating rate of 10 °C/min under flowing air.

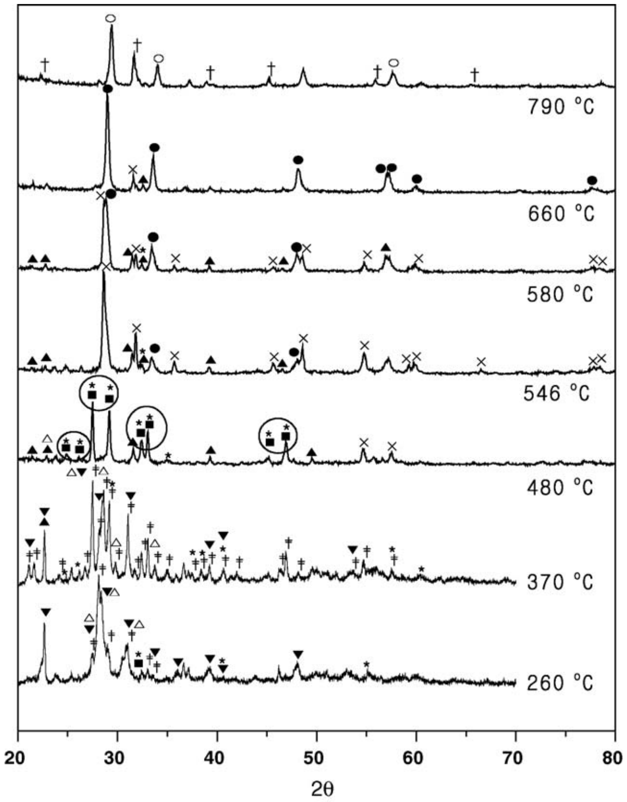

Fig. 2. XRD patterns of the PMN–PT precursor heated to various temperatures. Legend is as follows: $Pb_{10}O_7(NO_3)_6$ (‡), $Pb_6O_5(NO_3)_2$ (□), $Pb(OH)_2$ (■), perovskite (†), pyrochlore (○), P_3N (●), PbO (X), $3Pb(NO_3)_2 \cdot PbO \cdot H_2O$ (▼), $PbTiO_3$ (▲), and $Mg(NO_3)_2 \cdot H_2O$ (□).

3. Results and discussions

The oven-dried mixture was off-white, not yellow like Liou and Tseng's [15]. It implies that there is no free PbO (orange-yellow, massicot, orthorhombic), but a different Pb compound is formed. Fig. 1 shows the TG–DSC curves of the off-white PMN–PT precursor, which has four large endothermic peaks at 250, 361, 482, and 534 °C and a weight loss of 14.2%. The XRD patterns of the precursors heated to various temperatures are shown in Fig. 2. The precursor contains $Pb_{10}O_7(NO_3)_6 \cdot 5H_2O$ (JCPDS 30-0175) formed from reaction of PbO and $Pb(NO_3)_2$ where $NO_3{}^-$ is provided by dissociation of $Mg(NO_3)_2 \cdot 6H_2O$, and then decomposed to nano-sized PbO (litharge, tetragonal) at ∼540 °C. The PbO and MgO powder formed in situ during heat treatment are so fine and reactive that the solid solution reaction occurs at low temperature as seen in Fig. 2. The intermediate P_3N was formed at ∼580 °C and the perovskite phase started to form at 790 °C. This approach is similar to the mechanochemical reaction where pulverizing the mixture by high milling energy initiates the solid solution reaction. In this process the $Pb(OH)_2$ intermediate was previously suggested based on the XRD pattern [16]. The XRD pattern of the precursor heated to 480 °C was ambiguously assigned because the pattern of $Pb(OH)_2$ is similar to that of $Pb_6O_5(NO_3)_2$, circles in Fig. 2.

The precursor's TG–DSC curves in argon are similar to those in air but the peaks are shifted to higher temperatures as shown in Fig. 3. TG–MS analysis was carried out under flowing argon and the results are shown in Figs. 4 and 5. Mass peaks of H_2O (17, 18 amu) appeared strong at ∼250, 280, and 360 °C. They are attributed to the losses of hydrated water and decomposition of Mg compounds. Fig. 5 shows peaks of nitric oxide (30 amu) at ∼482, 534, and 340 °C. Mass peaks of oxygen (32, 16 amu) appear at the same temperatures as the nitric oxide, attributed to decomposition of $NO_3{}^-$ in argon atmosphere. The TG–MS analysis showed that the weight loss between 200 and 400 °C was mostly due to the loss of water and the loss occurred between 400 and 550 °C due to the decomposition of $NO_3{}^-$. If the intermediate $Pb(OH)_2$ was formed, one should expect the water peak in the TG–MS spectra above 400 °C, but it did not show any water peak above 400 °C. So the TG–MS analysis provided the crucial information that it did not go through $Pb(OH)_2$. The coupled TG–MS analysis revealed that the peaks were misinterpreted as $Pb(OH)_2$ and should be assigned as $Pb_6O_5(NO_3)_2$, which decomposes to PbO (tetragonal) with evolution of NO and O_2. The PbO formed in situ by thermal decomposition undergoes solid solution reaction with Nb_2O_5 to form $Pb_3Nb_2O_8$ (P_3N) and then react with MgO produced in situ from decomposition of Mg compounds and $PbTiO_3$ to give rise to the perovskite phase.

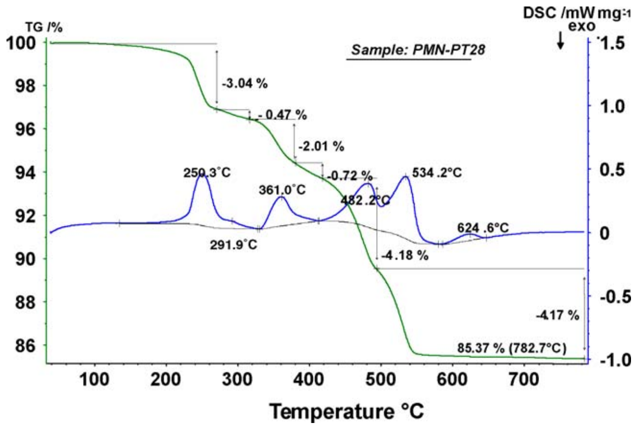

Fig. 3. TG–DSC curves of the precursor of PMN–PT heated at a heating rate of 10 °C/min under flowing argon.

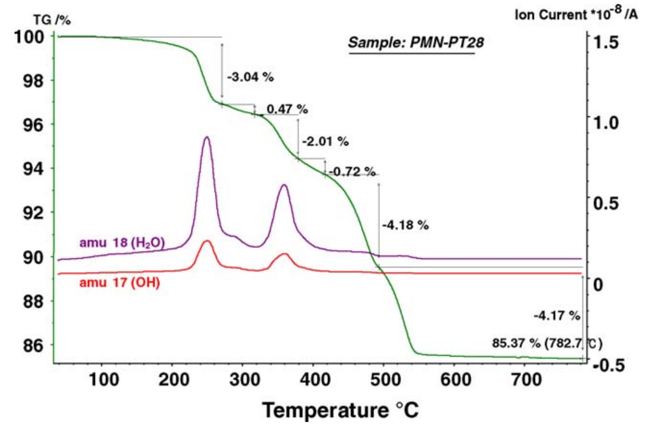

Fig. 4. TG–mass spectra of evolved water from the PMN–PT precursor in argon.

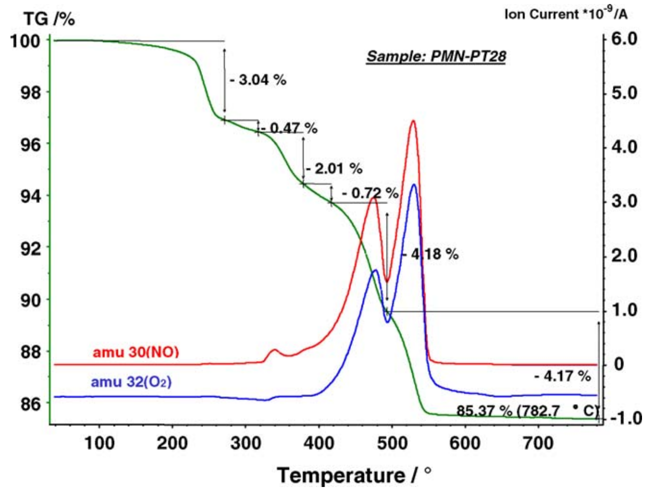

Fig. 5. TG–mass spectra of evolved NO and O_2 from the PMN–PT precursor in argon.

The presence of a little water promotes the chemical reaction between PbO and $Mg(NO_3)_2$, which results in low-temperature-sinterable PMN–PT powder with a single perovskite phase by a single calcination step at as low as 750 °C and can be sintered >95% T.D. at as low as 900 °C. Without water the mixture stays just as a mixture and heat treatment at 1250 °C for 1 h was not enough to develop a single perovskite phase.

Acknowledgement

This work was supported by the KOSEF and the authors are indebted.

References

[1] S.L. Swartz, T.R. Shrout, W.A. Schulze, L.E. Cross, J. Am. Ceram. Soc. 67 (1984) 311–315.

[2] T.R. Shrout, A. Halliyal, Am. Ceram. Soc. Bull. 66 (1987) 704–711.

[3] S.L. Swartz, T.R. Shrout, Mater. Res. Bull. 17 (1982) 1245–1250.

[4] Y. Zupei, Q. Shaobo, T. Changsheng, J. Mater. Sci. Lett. 19 (2000) 1743–1746.

[5] D.M. Wan, J. Wang, S.C. Ng, L.M. Gan, J. Alloys Compd. 274 (1998) 110–117.

[6] C.-H. Wang, J. Eur. Ceram. Soc. 22 (2002) 2033–2038.

[7] H.C. Wang, W.A. Schulze, J. Am. Ceram. Soc. 73 (1990) 825–832.

[8] P. Ravindranathan, S. Komarneni, A.S. Balla, R. Roy, L.E. Cross, Advances in ceramics, in: G.L. Messing, S. Hirano, H. Hausner (Eds.), Ceramic Powder Science. I, 21, American Ceramic Society, Westerville, OH, 1987, pp. 182–189.

[9] J. Zhai, B. Shen, L. Zhang, X. Yao, Mater. Chem. Phys. 64 (2000) 1–4.

[10] A.L. Costa, C. Galassi, E. Roncari, J. Eur. Ceram. Soc. 22 (2002) 2093–2100.

[11] Y. Narendar, G.L. Messing, J. Am. Ceram. Soc. 80 (1997) 915–924.

[12] W.B. Ng, J. Wang, S.C. Ng, L.M. Gan, J. Mater. Chem. 8 (1998) 2239–2244.

[13] M. Alguero, C. Alemany, B. Jimenez, J. Holc, M. Kosec, L. Pardo, J. Eur. Ceram. Soc. 24 (2004) 937–940.

[14] J. Xue, J. Wang, T.M. Rao, J. Am. Ceram. Soc. 83 (2001) 660–662.

[15] Y.-C. Liou, K.-H. Tseng, Mater. Res. Bull. 38 (2003) 1351–1357.

[16] K.R. Han, H.J. Koo, C.S. Lim, J. Am. Ceram. Soc. 83 (2000) 2214–2218.

[17] K.R. Han, S. Kim, J. Mater. Sci. 35 (2000) 2055–2059.