Thermal Decomposition and Kinetic Analysis of Relaxor Ferroelectric Lead Magnesium Niobate

Chung-Hsin Lu* and Cheng-Yen Wen

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan

(Received 24 November 1997; accepted 16 February 1998)

Abstract

The reaction mechanisms and kinetics of thermal decomposition of the relaxor ferroelectric Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$ powder at elevated-temperatures have been investigated. The decomposition of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$ is characterized by an initial formation of pyrochlore phase, associated with evaporation of PbO. Then pyrochlore phase subsequently gets dissociated, resulting in the formation of Mg$_2$Nb$_2$O$_7$ and MgNb$_2$O$_6$. The decomposition amounts of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$ as well as pyrochlore phase increase monotonously with increase in the reaction temperature and time. Based on the isothermal analysis of reaction kinetics, the rate-controlling step for decomposition of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$ is determined to be the chemical reaction of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$ itself with activation energy of 234 kJ mol$^{-1}$. On the other hand, during the decomposition of pyrochlore phase, a molten microstructure is formed, and reaction kinetics changes greatly. This decomposition of pyrochlore phase is confirmed to be a first-order reaction with higher activation energy of 407 kJ mol$^{-1}$. © 1998 Elsevier Science Limited. All rights reserved.

1 Introduction

Lead magnesium niobate (Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$), one of the representative materials in the family of relaxor ferroelectrics, has been known to possess high permittivity, high electric resistivity, and diffuse phase transition characteristics. Due to its excellent dielectric and piezoelectric characteristics, this material has been intensively investigated for its applications in multilayer capacitors and electrostrictive actuators.$^{1-11}$ The major problem encountered in the synthesis of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$ is that a pure perovskite compound is difficult to obtain. During the preparation of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$, the pyrochlore phases are often concomitantly formed along with Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$.$^{12,13}$ In order to eliminate these pyrochlore phases, many research groups have focused their studies towards developing new synthetic processes for preparing pure Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$. The columbite process,$^{14,15}$ which uses pre-reacted MgNb$_2$O$_6$ precursors, has been recognized to be an effective solid-state reaction process for synthesizing Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$. Other solution routes such as the precipitation,$^{16,17}$ sol gel,$^{18,19}$ molten salt,$^{20,21}$ and hydrothermal$^{22}$ processes have also been successfully developed.

Although monophasic Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$ can be successfully synthesized, the evaporation of PbO during sintering is another major problem that greatly affects the application of this material. Due to low sinterability of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$, it is essential to sinter Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$ at elevated temperatures.$^{23,24}$ It has been shown that the high-temperature heating causes the volatilization of PbO from Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$, and thereby brings about the thermal decomposition of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$. This decomposition of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$ in turn gives rise to the formation of pyrochlore phase and some other secondary compounds. The slight rotation of BO$_6$ octahedra in Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$ is responsible for the generation of pyrochlore phase.$^{26}$ Due to the low dielectric permittivity of pyrochlore phase, its presence is greatly detrimental to the dielectric properties of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$ itself.$^{27,28}$ Consequently, maintaining the perovskite structure of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$ during sintering is extremely crucial for improving its dielectric properties.

For adjusting the heating conditions of Pb(Mg$_{1/3}$-Nb$_{2/3}$)$_2$O$_3$, a fundamental understanding of the decomposition behavior of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$ is very important. The primary purpose of this study

*To whom correspondence should be addressed.
was therefore to elucidate the decomposition mechanisms and reaction kinetics of Pb(Mg₁/₃Nb₂/₃)O₃ powder. During the decomposition of Pb(Mg₁/₃Nb₂/₃)O₃, pyrochlore phase was noted to be formed first and subsequently decomposed. In order to analyze the reaction kinetics of the above two serial decomposition reactions, the conversion ratios of Pb(Mg₁/₃Nb₂/₃)O₃ and pyrochlore phase were calculated separately. Different types of reaction models were utilized to fit the decomposition behavior of each reaction, and the rate-controlling processes and the activation energies were also determined.

2 Experimental Procedure

The Pb(Mg₁/₃Nb₂/₃)O₃ powder was prepared according to a modified columbite precursor method. Reagent-grade raw materials viz. PbO, MgO, and Nb₂O₅ were used. For accurately weighting MgO, the MgO powder was heated to 800°C for half an hour to eliminate the CO₂ and H₂O absorbed on the particle surfaces. After weighing according to the desired stoichiometry, Nb₂O₅ and MgO were mixed in ethyl alcohol by ball-milling for 48 h. The mixtures were dried and pressed to form pellets. After heating the pellets at 800°C for 2 h, the columbite compound-MgNb₂O₆ was formed. This MgNb₂O₆ was then mixed with a stoichiometric amount of PbO in the same way as described above. The mixtures were dried and calcined at 900°C for 2 h. After calcination, monophase Pb(Mg₁/₃Nb₂/₃)O₃ powder, without any contents of pyrochlore phase, was obtained. This powder was then used for the following decomposition experiments.

The Pb(Mg₁/₃Nb₂/₃)O₃ powder was heated in a temperature-controlled furnace at temperatures ranging from 1150°C to 1300°C for different reaction time. After the reaction time was reached, the samples were quenched in air, and the weight loss during the heating process was measured. The compounds formed in the heated samples were analyzed by X-ray diffraction (XRD) using copper radiation. The relative contents of the compounds present in the samples were semi-quantitatively determined from the intensity of XRD peaks by using the following equation:

\[
\text{Content of compound } i(\%) = \frac{\text{Intensity of the major peak of compound } i}{\sum_i \text{Intensity of the major peak of compound } i} 
\]

The (110) plane of Pb(Mg₁/₃Nb₂/₃)O₃, (222) plane of pyrochlore phase, (104) plane of Mg₄Nb₂O₉, and (131) plane of MgNb₂O₆ were used for calculation. Variations in the microstructures of the heated samples during decomposition processes were examined by scanning electron microscopy (SEM). As for the analysis of reaction kinetics, the details concerning the calculation of decomposition ratios of Pb(Mg₁/₃Nb₂/₃)O₃ and pyrochlore phase after heat-treatment are described in Section 3.1 and 3.2, respectively.

3 Results and Discussion

3.1 Decomposition reactions of Pb(Mg₁/₃Nb₂/₃)O₃

The X-ray diffraction spectra of Pb(Mg₁/₃Nb₂/₃)O₃ powder heated at various temperatures for 30 min are presented in Fig. 1. The corresponding spectrum of pure Pb(Mg₁/₃Nb₂/₃)O₃ is also shown in this figure for comparison [see Fig. 1(a)]. It is observed that, after heating at 1200°C for 30 min, a new compound exhibiting a pyrochlore phase is formed. At 1250°C-heating, the amount of Pb(Mg₁/₃Nb₂/₃)O₃ significantly decreases, associated with the corresponding increase in the amount of pyrochlore phase. Another new product—Mg₄Nb₂O₉ is also produced along with pyrochlore phase at this stage. At 1300°C, Pb(Mg₁/₃Nb₂/₃)O₃ disappears entirely, and the products remaining in the sample are pyrochlore phase, Mg₄Nb₂O₉, and MgNb₂O₆. The above results reveal that heating at elevated temperatures results in the decomposition of Pb(Mg₁/₃Nb₂/₃)O₃, accompanied with the formation of several types of secondary phases.

![Fig. 1. X-ray diffraction spectra of (a) pure Pb(Mg₁/₃Nb₂/₃)O₃, and Pb(Mg₁/₃Nb₂/₃)O₃ heated at (b) 1200°C, (c) 1250°C, and (d) 1300°C for 30 min.](image-url)
The thermal decomposition and kinetic analysis of relaxor ferroelectric lead magnesium niobate

For further investigation on the decomposition behavior of Pb(Mg\textsubscript{1.3}Nb\textsubscript{2.3})O\textsubscript{3}, isothermal heating at 1150°C, 1200°C, 1250°C, and 1300°C for different time was performed. The weight loss and the resultant compounds formed in the heated samples were analyzed. Figure 2 summarizes the weight loss percentage of Pb(Mg\textsubscript{1.3}Nb\textsubscript{2.3})O\textsubscript{3} powder, under each reaction condition. A substantial weight loss was detected in all heated samples. While heating at 1150°C, the percentage of weight loss increases with increase in reaction time. At 1200°C, the weight loss percentage increases rapidly until the reaction time reaches 60 min, while after 60 min, the rate of increase in weight loss decreases. This change in the rate of weight loss during reaction implies that the decomposition behavior of the powder is different at the latter stage of reaction, and more than one kind of mechanisms controls the overall decomposition process. As for the variations in weight loss at 1250°C, a discontinuity can be observed in this curve. While heating at 1300°C, the percentage of weight loss saturates after 120 min of heating. By considering the melting points of the constituent materials in Pb(Mg\textsubscript{1.3}Nb\textsubscript{2.3})O\textsubscript{3}, and the reports in the literature regarding the heating processes of Pb(Mg\textsubscript{1.3}Nb\textsubscript{2.3})O\textsubscript{3}, evaporation of PbO is responsible for the weight loss of the specimens.

The relation between the relative amounts of products formed and reaction time at 1150°C, 1200°C, 1250°C, and 1300°C are illustrated in Figs 3–6, respectively. Figure 3 indicates that during the initial stage of reaction at 1150°C, Pb(Mg\textsubscript{1.3}Nb\textsubscript{2.3})O\textsubscript{3} is gradually decomposed, and pyrochlore phase is formed as the product. As the reaction time increases, the amount of pyrochlore phase increases, with a corresponding decrease in the amount of Pb(Mg\textsubscript{1.3}Nb\textsubscript{2.3})O\textsubscript{3}. When the reaction lasts for 180 min, Pb(Mg\textsubscript{1.3}Nb\textsubscript{2.3})O\textsubscript{3} is entirely decomposed, and only pyrochlore phase now exists in the specimen. At the latter stage of reaction at 1150°C, the amount of pyrochlore phase starts decreasing slightly and a small amount of Mg\textsubscript{4}Nb\textsubscript{2}O\textsubscript{9} is formed, which implies that pyrochlore phase is also decomposed. Pyrochlore phase is found to be the product of the decomposition of Pb(Mg\textsubscript{1.3}Nb\textsubscript{2.3})O\textsubscript{3} only. As for Mg\textsubscript{4}Nb\textsubscript{2}O\textsubscript{9}, it appears only after the decomposition of Pb(Mg\textsubscript{1.3}Nb\textsubscript{2.3})O\textsubscript{3} is completed; therefore, Mg\textsubscript{4}Nb\textsubscript{2}O\textsubscript{9} is
believed to be the product of the decomposition of pyrochlore phase rather than that of Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})\textsubscript{O\textsubscript{3}}.

For heating at 1200°C, the rate of decomposition of Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})\textsubscript{O\textsubscript{3}} becomes greater than that at 1150°C (see Fig. 4). Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})\textsubscript{O\textsubscript{3}} decomposes completely after reacting for 120 min. Pyrochlore phase is formed at the initial stage of reaction. Besides pyrochlore phase, Mg\textsubscript{4}Nb\textsubscript{2}O\textsubscript{9} also appears at this stage. According to the results in Fig. 3, Mg\textsubscript{4}Nb\textsubscript{2}O\textsubscript{9} is the product generated from decomposition of pyrochlore phase. Therefore, the appearance of Mg\textsubscript{4}Nb\textsubscript{2}O\textsubscript{9} at the initial stage of reaction reveals that the formation and decomposition processes of pyrochlore phase occur simultaneously. The amount of pyrochlore phase reaches maximum at 60 min, and then decreases slightly. At the later stage of reaction, a small amount of MgNb\textsubscript{2}O\textsubscript{6} is also observed.

The reaction diagram at 1250°C is shown in Fig. 5. This graph is obviously different from that in Fig. 4. After 90 min, Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})\textsubscript{O\textsubscript{3}} is completely decomposed. The amount of pyrochlore phase reaches its maximum value at 60 min, and then rapidly decreases. The amount of Mg\textsubscript{4}Nb\textsubscript{2}O\textsubscript{9} reaches a maximum value at 75 min, while the amount of MgNb\textsubscript{2}O\textsubscript{6} correspondingly increases with decrease in the amount of pyrochlore phase. It
Thermal decomposition and kinetic analysis of relaxor ferroelectric lead magnesium niobate

3.2 Kinetic analysis of the decomposition reaction of Pb(Mg1/3Nb2/3)O3

From the results in Section 3.1, one can notice that at elevated temperatures Pb(Mg1/3Nb2/3)O3 thermally decomposes to form pyrochlore phase, which subsequently decomposes to produce Mg4Nb2O9. Therefore, two stages of decomposition processes are involved in the thermal treatment of Pb(Mg1/3Nb2/3)O3. In the following sections, the kinetic analysis of these decomposition processes of Pb(Mg1/3Nb2/3)O3 and pyrochlore phase is presented.

For analyzing the kinetics of decomposition of Pb(Mg1/3Nb2/3)O3, accurate conversion ratio of Pb(Mg1/3Nb2/3)O3 during the decomposition process is required to be calculated. The decomposition ratio of Pb(Mg1/3Nb2/3)O3 is denoted as C (0≤C≤1). When C is equal to zero, it means that Pb(Mg1/3Nb2/3)O3 is not decomposed at all, and Pb(Mg1/3Nb2/3)O3 is completely decomposed when C is equal to unity. In order to calibrate the effect of weight of samples on the XRD intensity, all samples were mixed with an internal standard, viz. silicon powder. First, equal weights of pure Pb(Mg1/3Nb2/3)O3 powder and silicon powder were mixed, and the mixture was analyzed by XRD. From the XRD spectra, the ratio of the intensity of (110) diffraction peak of Pb(Mg1/3Nb2/3)O3 to that of the (111) peak of silicon was calculated, and this ratio is defined as (IPMN/ISi)0. In the above reference sample, the weights of Pb(Mg1/3Nb2/3)O3 and silicon were equal. If this reference sample is heated at elevated temperatures, the weight of the decomposed Pb(Mg1/3Nb2/3)O3 sample will be less than that of silicon, since the decomposition of Pb(Mg1/3Nb2/3)O3 results in weight loss. Therefore, in the heated samples, the weight loss due to decomposition of Pb(Mg1/3Nb2/3)O3 has to be calibrated. Therefore, the heated samples were mixed with silicon powder in a weight ratio of 1:(1−ΔW), where ΔW is the percentage of weight loss percentage of pure Pb(Mg1/3Nb2/3)O3 after each heating process. The ratio of the intensity of (110) diffraction peak of Pb(Mg1/3Nb2/3)O3 to that of the (111) peak of silicon, defined as (IPMN/ISi)0, was then calculated from the XRD spectra of these samples. Using the values of (IPMN/ISi)0 and (IPMN/ISi)L, the decomposition ratio C of Pb(Mg1/3Nb2/3)O3 was calculated by the following equation:

\[ C = 1 - \frac{(IPMN/ISi)_L}{(IPMN/ISi)_0} \]

Considering that at certain reaction conditions the decomposition of Pb(Mg1/3Nb2/3)O3 occurs simultaneously with that of pyrochlore phase, these two reactions have to be analyzed separately for...
simplifying the kinetic analysis. For the analysis of Pb(Mg$_{113}$Nb$_{2/3}$)O$_3$ decomposition, only the low-temperature region, wherein most of pyrochlore phase has not decomposed, was considered. Figure 7 illustrates the relationship between the decomposition ratio (C) of Pb(Mg$_{113}$Nb$_{2/3}$)O$_3$ and the reaction time. As can be seen in this figure, the decomposition ratio of Pb(Mg$_{113}$Nb$_{2/3}$)O$_3$ rises monotonously with the reaction time at all the temperatures. Furthermore, the higher the reaction temperature, the faster is the rate of the increase in the decomposition ratios. After heating at 1150°C for 60 min, around 70% of Pb(Mg$_{113}$Nb$_{2/3}$)O$_3$ is decomposed, whereas when the temperature is increased to 1250°C heating for only 15 min results in nearly the same decomposition ratio of Pb(Mg$_{113}$Nb$_{2/3}$)O$_3$.

At the beginning of the decomposition of Pb(Mg$_{113}$Nb$_{2/3}$)O$_3$, PbO vaporizes directly from the surface of Pb(Mg$_{113}$Nb$_{2/3}$)O$_3$, and pyrochlore phase is formed around unreacted Pb(Mg$_{113}$Nb$_{2/3}$)O$_3$. Once pyrochlore phase is formed, this phase becomes a barrier for PbO vaporization. Based on the above mechanism and considering general solid-gas reactions, three major controlling steps can be envisaged, viz. (1) decomposition reaction at unreacted Pb(Mg$_{113}$Nb$_{2/3}$)O$_3$ surface, (2) diffusion of vaporized PbO through pyrochlore phase, and (3) diffusion of vaporized PbO through the gaseous film surrounding the particles. Based on these three controlling processes, the relations between decomposition ratio and reaction time can be obtained. The functions of decomposition ratio and reaction time are expressed as below:

\[
1 - (1 - C)^{1/3} = k t \quad (3)
\]

(b) Controlled by the diffusion of vaporized PbO through products
\[
1 - 3(1 - C)^{2/3} + 2(1 - C) = k t \quad (4)
\]

(c) Controlled by the diffusion of vaporized PbO through gaseous film
\[
C = k t \quad (5)
\]

where C is the decomposition ratio of Pb(Mg$_{113}$Nb$_{2/3}$)O$_3$ and t is the reaction time.

For identifying the rate-controlling step for decomposition of Pb(Mg$_{113}$Nb$_{2/3}$)O$_3$, the decomposition ratios at 1200°C were substituted into the above three equations and plotted as a function of reaction time. As illustrated in Fig. 8, only the function \(1 - (1 - C)^{1/3}\) displays good linearity with respect to reaction time (t), implying that eqn (3) holds well during the decomposition process. Consequently, this suggests that the rate of decomposition of Pb(Mg$_{113}$Nb$_{2/3}$)O$_3$ is controlled by the rate of chemical reaction rather than the rate of diffusion of vaporized PbO through pyrochlore phase or gaseous film. Figure 9 shows the curves corresponding to the function of \(1 - (1 - C)^{1/3}\) at 1150°C, 1200°C, and 1250°C as a function of reaction time. As can be seen from this figure, all three are linear curves. This result verifies that the rate-controlling step for the decomposition of Pb(Mg$_{113}$Nb$_{2/3}$)O$_3$ is the chemical reaction of Pb(Mg$_{113}$Nb$_{2/3}$)-O$_3$ itself at the examined temperature range.

According to eqn (3), the reaction rate constant \(k\) can be calculated from the slope of each line in Fig. 9. The values of \(k\) at 1150, 1200, and 1250°C were thus determined to be 6.06×10^{-3}, 1.30×10^{-2}, and 2.21×10^{-2} min^{-1}, respectively. The activation energy (E) of the reaction was also calculated using Arrhenius’s equation:

\[
k = k_o \exp(-E/RT) \quad (6)
\]

where \(E\) is the activation energy and \(T\) is the reaction temperature. From eqn (6), the activation energy of the decomposition of Pb(Mg$_{113}$Nb$_{2/3}$)O$_3$ was calculated to be 234 kJ mol$^{-1}$, and the value of \(k_o\) as 1.11×10^{8} min$^{-1}$.

3.3 Kinetic analysis of the decomposition reaction of pyrochlore phase

As described in Section 3.1 pyrochlore phase is formed during the decomposition of Pb(Mg$_{113}$Nb$_{2/3}$)O$_3$. At temperatures ≥1200°C, once pyrochlore phase is formed, the formation and decomposition
Thermal decomposition and kinetic analysis of relaxor ferroelectric lead magnesium niobate

processes for this phase occur simultaneously. When Pb(Mg_{1/3}Nb_{2/3})O_3 is completely consumed, no more pyrochlore phase can be produced, and consequently it continuously decomposes. One can notice that the kinetic analysis in the region after Pb(Mg_{1/3}Nb_{2/3})O_3 is entirely consumed can neglect the formation of pyrochlore phase and can simplify the analysis. Based on this concept, the time at which all the Pb(Mg_{1/3}Nb_{2/3})O_3 is decomposed is taken as the reference point, and the relative decomposition ratio (F) of pyrochlore phase is defined as a ratio of the content of pyrochlore phase decomposed from the reference point to the content of pyrochlore phase at the reference point.

Similarly, for the analysis of Pb(Mg_{1/3}Nb_{2/3})O_3, the decomposed-pyrochlore samples were mixed with standard silicon powder, and the effect of sampled weight on the XRD intensity and loss of weight during decomposition were calibrated. From the XRD spectra, the ratios of the intensity of (222) diffraction peak of pyrochlore phase to that of the (111) peak of silicon at the reference point as well as at certain reaction time were calculated, which are defined as \((I_{PY}/I_{SI})_0\) and \((I_{PY}/I_{SI})_t\), respectively. Consequently, then the relative decomposition ratio (F) of pyrochlore phase was calculated from the equation written as

\[
F = 1 - \frac{(I_{PY}/I_{SI})_t}{(I_{PY}/I_{SI})_0}
\]  

The relations between the decomposition ratio of pyrochlore phase and the reaction time are presented in Fig. 10. Since pyrochlore phase does not decompose at 1150°C, no data at 1150°C are shown in this figure. As the decomposition behavior of Pb(Mg_{1/3}Nb_{2/3})O_3, the decomposition ratio of pyrochlore phase increases monotonously at all three temperatures (1200°C, 1250°C, and 1300°C) with reaction time as well as reaction temperature. However, during the decomposition of pyrochlore phase, the microstructures of samples vary rapidly. A representative SEM micrograph of the decomposed pyrochlore phase (1200°C for 90 min) is compared with that of pure Pb(Mg_{1/3}Nb_{2/3})O_3 in Fig. 11. As can be seen from this figure, the decomposed pyrochlore phase exhibits a molten texture. Notably, this kind of texture was not found during decomposition of Pb(Mg_{1/3}Nb_{2/3})O_3.

Observing the SEM micrographs, one can realize that decomposition of pyrochlore phase occurs in a molten-state rather in a powder state. Therefore, the decomposition reaction for pyrochlore phase is believed to belong to the nth order reaction. If the decomposition of pyrochlore phase is assumed to be a first-order reaction \((n = 1)\), then the relation between the relative decomposition ratio (F) and reaction time \((t)\) can be expressed as

\[
-ln(1 - F) = k_p t
\]  

where \(t\) is the reaction time and \(k_p\) is the reaction rate constant. The values of \(-ln(1 - F)\) at 1200, 1250, and 1300°C are plotted as a function of reaction time in Fig. 12, which yields three straight lines. This result confirms that the decomposition of pyrochlore phase is a first-order reaction. From the slopes of the lines in Fig. 11, the rate constants \(k_p\) at 1200, 1250, and 1300°C were determined to
be $4.88 \times 10^{-3}$, $1.32 \times 10^{-2}$, and $4.03 \times 10^{-2}$ min$^{-1}$, respectively. According to the Arrhenius equation, the natural log of $k_p$ was plotted versus the reciprocal of reaction temperature, and from the value of the corresponding slope, the activation energy for decomposition of pyrochlore phase was determined to be $407 \text{kJ mol}^{-1}$, and the value of $k_0$ as $1.23 \times 10^{12}$ min$^{-1}$.

The above results confirm that decomposition of Pb(Mg$_{1.3}$Nb$_{2.3}$)O$_3$ and that of pyrochlore phase are controlled by different mechanisms. It can be also noted that the activation energy for decomposition of pyrochlore phase is significantly higher than that of Pb(Mg$_{1.3}$Nb$_{2.3}$)O$_3$. During general serial reactions, change in the reaction rate would be more sensitive to the increase in temperature for a reaction with higher activation energy. Therefore, the above description is consistent with the fact that increase in reaction temperature has a more pronounced effect on the decomposition process of pyrochlore phase than that of Pb(Mg$_{1.3}$Nb$_{2.3}$)O$_3$.

**4 Conclusions**

The decomposition processes of ferroelectric Pb(Mg$_{1.3}$Nb$_{2.3}$)O$_3$ powder at elevated temperatures have been examined. During the decomposition of Pb(Mg$_{1.3}$Nb$_{2.3}$)O$_3$, pyrochlore phase is formed and a large amount of PbO is evaporated, which results in a substantial weight loss. The pyrochlore phase is subsequently dissociated, during which Mg$_4$Nb$_2$O$_9$ and MgNb$_2$O$_6$ are produced. The decomposition processes of Pb(Mg$_{1.3}$Nb$_{2.3}$)O$_3$ and pyrochlore phase are accelerated with increase
in reaction temperature as well as reaction time. From the isothermal analysis of reaction kinetics, the decomposition of Pb(Mg1/3Nb2/3)O3 is shown to be controlled by the chemical reaction of Pb(Mg1/3Nb2/3)O3 itself, with activation energy of 234 kJ mol⁻¹. When pyrochlore phase is decomposed, a molten microstructure is formed. Furthermore, the reaction kinetics for pyrochlore phase decomposition is a first-order reaction with higher activation energy of 407 kJ mol⁻¹.

References