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Solid-state reaction synthesis of sodium niobate ($NaNbO_3$) powder at low temperature

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Abstract A modified solid-state reaction was applied to produce lead-free piezoelectric sodium niobate ($NaNbO_3$) powders. The mixture of $Na_2C_2O_4$ and Nb_2O_5 was identified by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA). The powders were characterized using a scanning electron microscope (SEM) and the X-ray diffraction technique (XRD). The SEM image suggested that the particle size of the powders obtained ranged from 180 to 360 nm. The XRD pattern showed that the pure perovskite phase of $NaNbO_3$ could be synthesized at the low temperature of 475 °C for 1 h, with an average crystallite size of 31.45 ± 5.28 nm. This temperature was about 300 °C lower than that when using the conventional solid-state method with Na_2CO_3 as reactant, which resulted in a cost-, energy-, and time-saving method.

Introduction

Alkaline niobate materials are considered a lead-free candidate for the substitution of widely used commercial lead-based piezoelectric material, based on the aim to avoid highly harmful lead compounds [1–4]. Among several compounds, sodium niobate ($NaNbO_3$) has attracted considerable attention because of its unique properties [3] and high dielectric constant (2000–3000) at Curie temperature [5]. Unlike most oxidic perovskite, $NaNbO_3$ possesses six phase transitions from the ferroelectric phase at low temperature (rhombohedral) to the antiferroelectric room temperature phase (orthorhombic) and non-polar cubic structure at 640 °C [6]. It can form solid solution with other niobate compounds, such as $LiNbO_3$ and $KNbO_3$, to acquire good ferroelectric and piezoelectric properties [7–10]. Traditionally, alkali metal niobate powders have been synthesized via the solid-state reaction of alkali metal carbonates and Nb_2O_5 [3, 11]. This method requires a high calcination temperature (about 750 °C or more) for a long period of time, possibly causing volatilization of the alkali metal and leading to poor compositional homogeneity [3, 4, 11]. The powders can be agglomerated during heating, which affects their properties [3, 12]. Thereafter, powders with high sinterability and stoichiometric control are necessary for developing $NaNbO_3$-based piezoelectric ceramics. Numerous alternative methods are used to prepare $NaNbO_3$ such as hydrothermal [13], chemical [12], and polymeric precursor processes [14], and the mechanochemical process [3, 15, 16]. Although $NaNbO_3$ was performed by mechanochemical activation after thermal treatment of a stoichiometric Na_2CO_3/Nb_2O_5 mixture at 600 °C, this procedure required a long operational period of up to 30 days [3]. Moreover, $NaNbO_3$ was also obtained at a low temperature (450 °C) by the wet-chemical method

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using a water-soluble malic acid complex [17]. However, most chemical techniques require specialized experimental apparatus and high purity reactant, which are more expensive. Interestingly, sodium tantalate ($NaTaO_3$) powder, with high crystallinity has been successfully synthesized at 600 °C through a simple method called modified solid-state reaction or combustion synthesis, in which urea plays an important role. Unusual starting material ($Na_2C_2O_4$ instead of Na_2CO_3/Na_2O) has been described. This method was found to produce $NaTaO_3$ as a general route at the lower temperature of ~500–600 °C, when compared with conventional solid-state reaction [18]. On the other hand, urea, which was added as fuel in order to achieve the final product, could cause problems in this method, due to risks if performing on a large scale. Nonetheless, the aim of the present study was to produce $NaNbO_3$ using a simple, rapid, low cost, and environment friendly route, such as a solid-state reaction of $Na_2C_2O_4$ and Nb_2O_5 without the addition of any fuel.

Experiment

$NaNbO_3$ was synthesized by a solid-state reaction method. Reagent grade sodium oxalate ($Na_2C_2O_4$, 99.9%) and niobium oxide (Nb_2O_5, 99.9%) were employed as raw material. Firstly, starting materials were weighed according to the required stoichiometric ratio that related to the reaction below.

$$Na_2C_2O_{4(s)} + Nb_2O_{5(s)} \rightarrow 2NaNbO_{3(s)} + 2CO_{2(g)} \qquad (1)$$

Then, raw materials were mixed together by ball-milling in ethyl alcohol using partially stabilized zirconia balls for 18 h. After drying on a hot plate by regularly stirring at about 80 °C for an approximate period, the thermal behavior during heat treatment was determined by thermo gravimetric analysis (TGA, Perkin Elmer) and differential thermal analysis (DTA, Perkin Elmer). According to TG-DTA results, the mixture was subsequently placed in a closed alumina crucible and calcined for different periods of time in air at various temperatures, ranging from 300 to 600 °C, in order to investigate the formation of $NaNbO_3$.

Afterward, calcined powders were subsequently inspected by room temperature X-ray diffraction (XRD, Advance D8), using Ni-filtered Cu K_α radiation, to examine the effect of thermal treatment on phase development and the optimal calcination condition for the formation of crystalline $NaNbO_3$ powders. Powder morphologies and particle size were figured directly using a scanning electron microscope (SEM, LEO1455 VP).

Results and discussion

The TGA and DTA of a powder mixed in the stoichiometric proportions of $NaNbO_3$ are illustrated in Fig. 1. The TG curve accordingly revealed a weight loss of 16.8%, occurring during the temperature rise from 400 to 500 °C. This observation corresponded to the endothermic peak of the DTA curve, which cantered at 484.8 °C. This endotherm may be related to the decomposition of $Na_2C_2O_4$ to Na_2CO_3, which lies on the temperature of 450–550 °C, and abruptly to the decomposition of Na_2CO_3 to Na_2O (decomposition temperature in the range of 400 °C) before releasing CO and CO_2 molecules, as revealed below [19].

$$Na_2C_2O_4 \rightarrow Na_2CO_3 + CO \qquad (2)$$

$$Na_2CO_3 \rightarrow Na_2O + CO_2 \qquad (3)$$

It is interesting to note that there was no weight loss or thermal effect at a temperature of about 100 °C, at which no decomposition occurrence was indicated. The endothermic peak correlates at the range of 100 °C with the release of water molecules. This confirmed that non-absorptive $Na_2C_2O_4$ raw material contrasts with Na_2CO_3, because Na_2CO_3 is the hygroscopic compound which can lead to the erroneous stoichiometric ratio. Therefore, powders with good compositional homogeneity, when comparing with the conventional solid-state method with Na_2CO_3 as reactant, may possibly be produced via this solid-state reaction.

Thus, based on TG-DTA data, the powders were calcined at temperatures ranging from 300 to 600 °C for 4 h in order to investigate the calcination temperature outcome in the development phase. The mixture of starting material was calcined in air using the steady heating/cooling rate of 20 °C at various temperatures, and followed by phase analysis using the XRD technique. Figure 2 shows the XRD pattern of the $NaNbO_3$ powders calcined at different

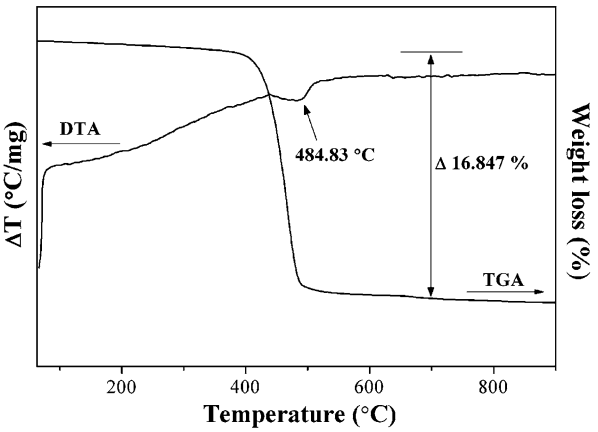

Fig. 1 TG-DTA result of an uncalcined powder mixed in the stoichiometric proportion of $NaNbO_3$

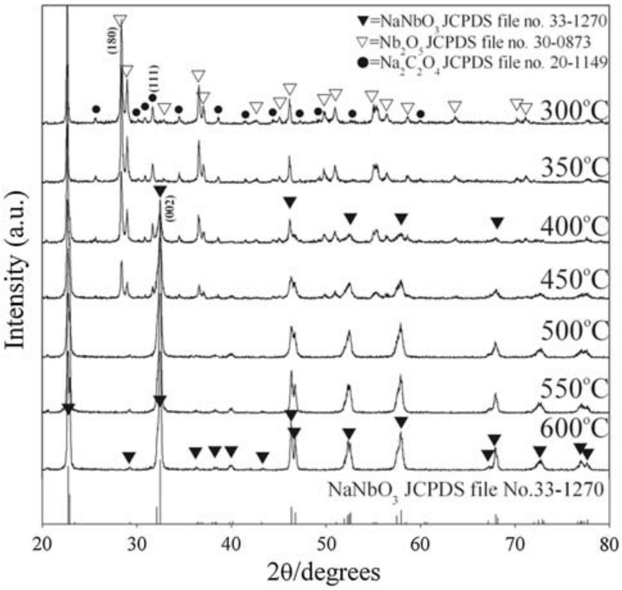

Fig. 2 XRD patterns of $NaNbO_3$ powder calcined at various temperatures for 4 h with a heating/cooling rate of 20 °C/min

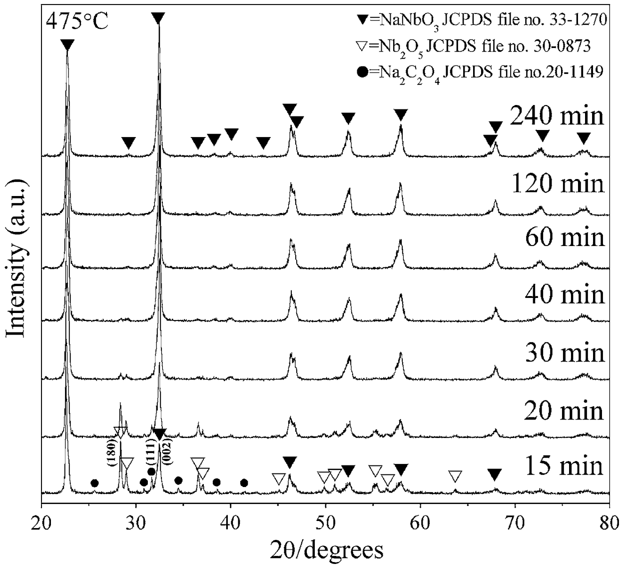

Fig. 3 XRD patterns of $NaNbO_3$ powder calcined at the calcination temperature of 475 °C for various dwell times with a heating/cooling rate of 20 °C/min

temperatures for 4 h. It can be seen that fine $NaNbO_3$ crystallites were developed at a calcination temperature as low as 400 °C, accompanied by the phase of unreacted Nb_2O_5 (JCPDS file no. 30-0873) and $Na_2C_2O_4$ (JCPDS file no. 20-1149). This observation suggests that nucleation of the perovskite $NaNbO_3$ phase did occur. In addition, the minor phase of Nb_2O_5 and $Na_2C_2O_4$ was also decreased with escalating calcination temperature, and disappeared completely after the powders were calcined at the calcination temperature of 500 °C for 4 h. Whereas, the intensity of the perovskite $NaNbO_3$ peak was enhanced further and an essentially monophasic $NaNbO_3$ perovskite phase (yield of 100% within the limitations of the XRD technique) was observed. This $NaNbO_3$ phase could be indexed according to an orthorhombic structure with the space group *Pbma* (no. 57), which was consistent with JCPDS file No. 33-1270. Although the calcination temperature rose at 550 and 600 °C, the monophasic $NaNbO_3$ perovskite phase was also obtained. There was no evidence of the pyrochlore diffraction peak. This result also correlates with the TG-DTA analysis shown above. As the calcination temperature increased, so too did the amount of the $NaNbO_3$ crystallite phase, and this can be seen as intensity of the amplified peak. Since the diffusion coefficient is a temperature dependence parameter, the higher temperature has the most intense effect on the rate of diffusion [20], and can enhance higher atomic mobility [11].

As the finest calcination temperature was established at 500 °C, a dwell time ranging from 15 min to 4 h was applied at 475 °C (instead of 500 °C). This temperature was preferred because of the rapid diffraction peak change of the powder calcined at 450 and 500 °C. The XRD pattern of the $NaNbO_3$ powders, which were calcined at 475 °C with different dwell times, is shown in Fig. 3. It was found that the single-phase of $NaNbO_3$ powder was also successfully synthesized at the calcination temperature of 475 °C, with a dwell time of 60 min or more applied. The increase in crystallinity of the $NaNbO_3$ phase was seen to relate with the escalation of dwell time. Although the calcination temperature of 475 °C was higher than the nucleation temperature of the powder obtained by a polymeric precursor [14], this was a single-step and low-cost starting material method that could save time, energy, and cost. Likewise, this temperature was much lower than the conventional solid-state reaction process with Na_2CO_3 as reactant, which was in the range of 750 °C [3]. This observation indicated that calcination temperature and dwell time might play an important role in evolution of the pure phase product and also be consistent with other systems [21].

The volume fraction of the perovskite phase formation was considered at various calcination temperatures and dwell times. These relative amounts of perovskite, $Na_2C_2O_4$ and Nb_2O_5 phases, were approximated by calculating the ratio of the main X-ray peak intensities of perovskite $NaNbO_3$, $Na_2C_2O_4$, and Nb_2O_5 phase using the following equation [22]:

$$\text{Wt\% perovskite} = \frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{Na}_2\text{C}_2\text{O}_4} + I_{\text{Nb}_2\text{O}_5}} \times 100 \qquad (4)$$

where I_{perov}, $I_{\text{Na}_2\text{C}_2\text{O}_4}$, and $I_{\text{Nb}_2\text{O}_5}$ stand for the intensities belonging to the strongest reflection peak of (002)

Table 1 Fraction of perovskite phase formed as a function of calcination temperature and dwell time

NaNbO$_3$	Calcination temperature (°C)						
	300	350	400	450	500	550	600
%Perovskite	0	0	35.42	62.86	100.00	100.00	100.00
NaNbO$_3$	Dwell time (min) at 475 °C						
	15	20	30	40	60	120	240
%Perovskite	41.89	60.56	89.13	97.00	100.00	100.00	100.00

perovskite, (111) $Na_2C_2O_4$, and (180) Nb_2O_5, respectively. A volume fraction increase of the perovskite $NaNbO_3$ phase formation of the calcined powders, resulting from the calcinations process at various temperatures and dwell times, is shown in Table 1. As the calcination temperature rose, the yield of the perovskite phase increased significantly until the temperature reached 500 °C, and a pure phase of $NaNbO_3$ was established. Likewise, in observing powders calcined at 475 °C for different dwell times, the $NaNbO_3$ phase was enlarged as the dwell time increased up to 60 min, and the monophasic phase of $NaNbO_3$ was seen to form.

Accordingly, the Johnson–Mehl–Avrami, or JMA equation was used in the present study. This equation was found appropriate for describing a wide variety of isothermal solid-state transformations [23, 24]. It was used to study the kinetic of the reaction and mechanism involving nucleation and growth, and has the general form of:

$$x(t) = 1 - \exp[-(kt)^n]. \tag{5}$$

where x is the volume fraction of the perovskite phase formed, k the reaction rate constant, t the calcination time, and n the Avrami exponent. For analyzing the results, the relation of ln [ln $1/(1 - x)$] versus ln t was plotted. Figure 4 shows a good linear fit of the Avrami plot for $NaNbO_3$ powders calcined at 475 °C. This shows that the isothermal formation of the perovskite phase can be described accurately by the theory of phase transformations. The constant n, which can be calculated from the slope of this Avrami plot, was found to be 1.79. This indicated that the reaction of solid solution formation is diffusion controlled (n is less than 2.5) [25]. The beginning stage of transformation is a fixed number of perovskite nuclei [26].

The average crystallite size of the powders obtained can be determined from the XRD pattern according to Scherrer's equation [27]:

$$D = \frac{k\lambda}{\beta \cos \theta_B} \tag{6}$$

where D is the average crystallite size, k a constant equal to 0.89, λ the wavelength of X-ray radiation, β the full width at half maximum (FWHM), and θ_B the diffraction angle. The average crystallite size of powders calcined at 475 °C for 15 min to 4 h was found to be from 21.52 to 35.56 nm, and that of powders calcined at the optimum condition (475 °C for 60 min) was about 31.45 nm. The increase in crystallinity of the $NaNbO_3$ phase was affected by increasing dwell time. This may confirm that the dwell time also plays an important role in development of the pure phase creation.

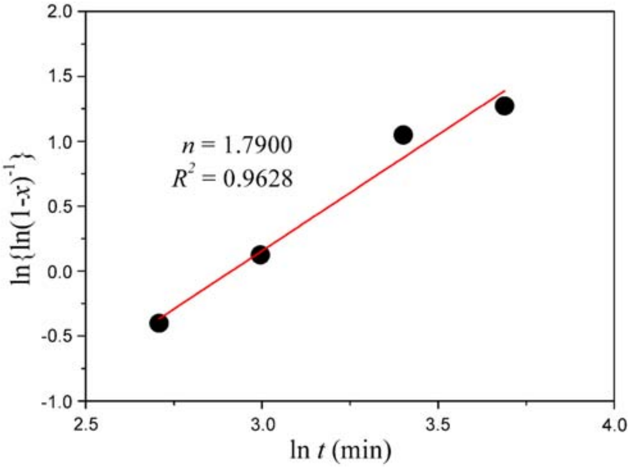

Fig. 4 Johnson–Mehl–Avrami for the formation of perovskite phase in $NaNbO_3$ powders isothermally heat treated at 475 °C

SEM micrographs of the powder calcined at 475 °C for 60 min are given in Fig. 5. The particle size, which can be estimated from these micrographs, was found to be in the range of 180 to 360 nm. This value is greater than the average crystallite size calculated from XRD patterns. The inconsistency value could point out the agglomeration

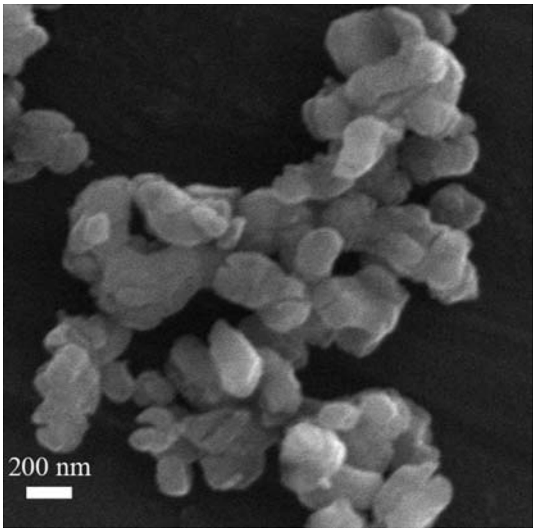

Fig. 5 SEM micrographs showing $NaNbO_3$ powders synthesized at 475 °C for 60 min, with a heating/cooling rate of 20 °C/min

of the calcined powders. No evidence of difference phase or pyrochlore phase was found. This outcome relates to the XRD result, in which the monophasic perovskite phase of $NaNbO_3$ can be established after calcination at 475 °C for 60 min.

Conclusion

Crystalline powders of sodium niobate $NaNbO_3$ were synthesized from a modified solid-state reaction of $Na_2C_2O_4$ and Nb_2O_5. This method is an excellent, simple and cost effective way to prepare stoichiometric, homogeneous, and fine powders. The perovskite phase of $NaNbO_3$ was successfully synthesized at the low temperature of 475 °C for 1 h, with an average crystallite size of 31.45 ± 5.28 nm. This temperature is about 275 °C lower than that used in the conventional method, which lies in the 750 °C range. As dwell time increased, XRD peaks became narrower, and a pattern similar to that expected for orthorhombic $NaNbO_3$ was achieved, as indicated by the separate peaks. The resulting $NaNbO_3$ powders comprised agglomerated particles of 180 to 360 nm in size.

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