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Short communication

Preparation of potassium lithium niobate powders with low Li content via the Pechini method

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Abstract

Potassium lithium niobate (KLN) ceramic powders with low Li content have been synthesized by using the Pechini method. The composition of the powder can be written as $K_{2.95}Li_{1.38}Nb_{6.22}O_{17}$, which contains relatively fewer Li ions than $K_3Li_2Nb_5O_{15}$ powder. The thermal decomposition of the precursor gel has been studied by TG–DTA and the products calcined at different temperatures have been characterized by XRD and TEM. It is concluded that the $K_{2.95}Li_{1.38}Nb_{6.22}O_{17}$ powders, about 50 nm sized and uniformly shaped, are obtained through the calcination of the precursor gel at 900 °C for 2 h. The difference between the powder composition and starting composition is caused by the volatile loss of the lithium during high-temperature heat treatment. The control of pH value and the molar ratio of citric acid/metal cations of the precursor solution is important to obtain clear K–Li–Nb precursor solution and gel.

Keywords: A. Powders: chemical preparation; D. Niobates; Pechini method

1. Introduction

Potassium lithium niobate ($K_{3.0}Li_{2-x}Nb_{5+x}O_{15+2x}$, KLN, $x = 0.1$–0.5) with tungsten bronze structure is a useful material that produces strong pyroelectric, photorefractive, piezoelectric and second harmonic generation (SHG) effect [1–2]. However, the application of the KLN crystal is limited because many difficulties are encountered in the crystal growth, such as the cracking formation and the compositional change. In spite of the shortcomings, studies have focused on KLN crystal growing and its properties, and there have been few reports on the preparation of KLN powders or KLN polycrystalline ceramics. To our knowledge, only one paper has been published in which polycrystalline KLN were prepared by the solid-state reaction [3].

The Pechini method is a wet chemical technique which offers many advantages, such as homogeneous mixing at molecule level, good stoichiometric control, low-processing temperature, use of an aqueous-based processing system and the production of active powders. This method has been applied for a range of materials such as lead magnesium niobate (PMN), $SrTiO_3$, PZT, $SrBaNb_2O_6$ and $SrBiNb_2O_9$ [4–8], but has so far been not applied for the KLN powders. The aim of this work is the first of a serial work to determine the feasibility of utilizing the Pechini method to produce KLN ceramic powders. In addition, the effect of the ratios of the reactants and the pH value is also investigated.

2. Experimental procedure

2.1. Synthesis of KLN powders

The starting materials used were K_2CO_3, Li_2CO_3, Nb_2O_5, citric acid, ammonia solution, citric acid (CA) and ethylene glycol (EG). Citric acid and ethylene glycol were used as the chelating and polymerizing agents, respectively. The procedure used to prepare KLN powders by the Pechini method is shown in Fig. 1. Lithium citrate and potassium citrate were formed, respectively, by dissolution of lithium carbonate and potassium carbonate in an aqueous solution of

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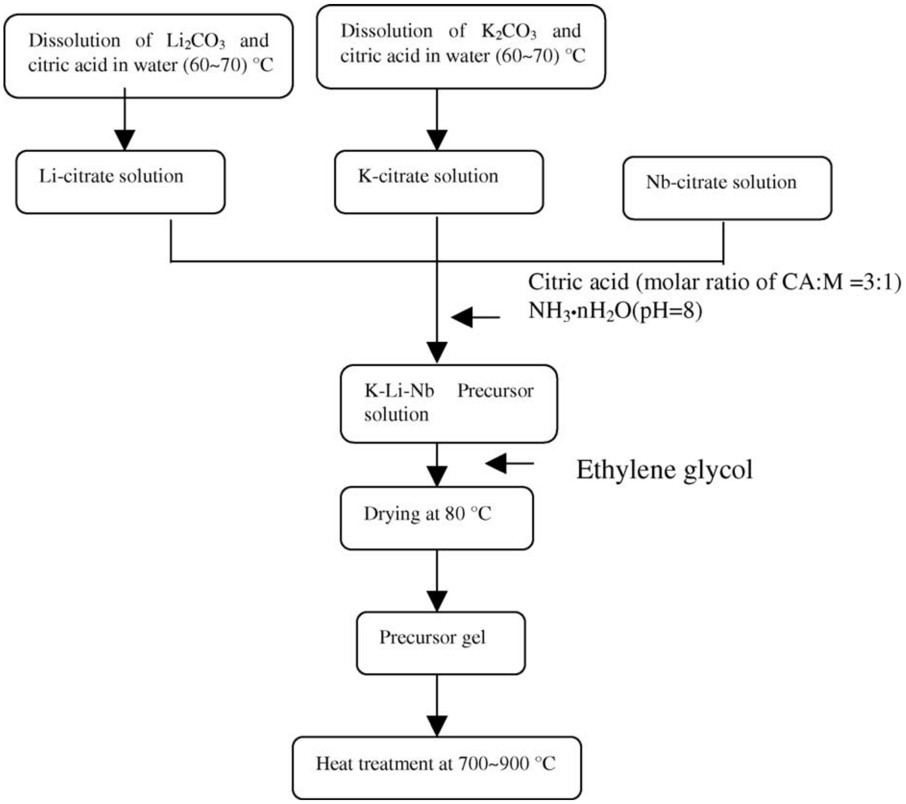

Fig. 1. Flow chart for preparation of KLN powders by the Pechini method.

citric acid under constant agitation to homogenize the Li-citrate and K-citrate solutions. The procedure for preparation Nb-citrate was reported previously [7]. For the preparation of K–Li–Nb precursor solution, Li-citrate, K-citrate and Nb-citrate solutions were mixed together with molar ratio of K^+:Li^+:Nb^{5+} = 3:2:5, followed by the addition of citric acid, and the molar ratio of citric acid:metal cations was varied from 1 to 3. The pH was adjusted with ammonia solution and varied from 2 to 10. Ethylene glycol was added to promote mixed citrate polymerization by polyesterification reaction. The citric acid/ethylene glycol molar ratio was varied at 0.9, 1.8 and 3.6. The obtained K–Li–Nb precursor solution was heated at 80 °C for 24 h to produce a gelatinous precursor, which was then calcined between 700 and 900 °C for 2 h in air to form the KLN powders.

2.2. Characterization methods

The powder composition was determined by using a inductively coupled plasma emission spectrophotometer (Shimadzu ICP-1000). We performed the ICP analysis at least five times for the samples. Thermal analysis and thermogravimetric analysis were used to analyze the thermal decomposition behavior of the gelatinous precursor with a heating rate of 10 °C min^{-1} in air up to 900 °C. The phase composition of the heat-treated powders were analyzed by using X-ray diffraction with Cu Kα radiation. The microstructure and the particle distribution studies were performed on a transmission electron microscope (TEM, Philips CM12/STEM, Holland).

3. Results and discussion

Fig. 2 shows the DTA and TG curves of the K–Li–Nb precursor gel. The TG–DTA curve involves three primary stages. The slight weight loss in the temperature range 100–250 °C, which is accompanied by an endothermic event,

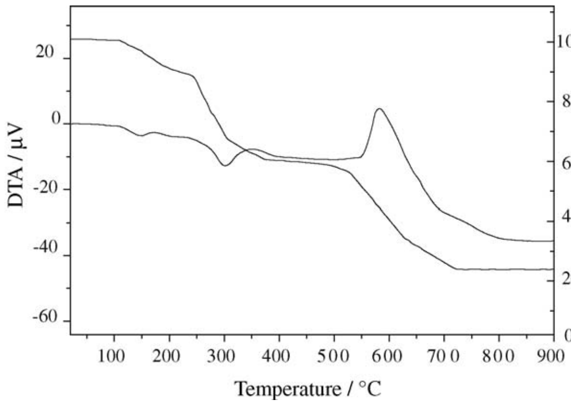

Fig. 2. TG–DTA curves of the K–Li–Nb precursor gel.

corresponds to the loss of free and bound water from the gels. The weight loss in the temperature of 250–350 °C, which is accompanied by another endothermic event, is supposed to be related with the removal of excessive ethylene glycol. The third weight loss between 500 and 700 °C corresponding to an exothermic peak is due to polymeric chain decomposition, leading to CO_2 elimination, besides the decomposition of carboxyls linked to metals, with oxide formation from about 650 °C.

The deficiency of the Li^+ is dominating in the as-prepared powders by means of ICP analysis. The results are 11.5 wt.% K, 0.96 wt.% Li and 57.8 wt.% Nb, and the molecular formula can be written as $K_{2.95}Li_{1.38}Nb_{6.22}O_{17}$, although the starting composition is $K_3Li_2Nb_5O_{15}$. The result is also confirmed by XRD experiment.

Fig. 3 shows the XRD patterns of the sample powders after calcinations at 700, 800 and 900 °C for 2 h. The results indicate that the main phase is similar to that of the $K_3LiNb_6O_{17}$ rather than $K_3Li_2Nb_5O_{15}$. The samples obtained at 700 and 800 °C both contain $LiNbO_3$ as a secondary phase. It can be seen that as the temperature increases, the peak intensity assigned to $LiNbO_3$ decreases and disappears at 900 °C. This result suggests that there is a lithium loss at high temperature, which leads to $LiNbO_3$ formation. The difference between the powder composition and starting composition is caused by the evaporation of the lithium during high-temperature heat treatment [9].

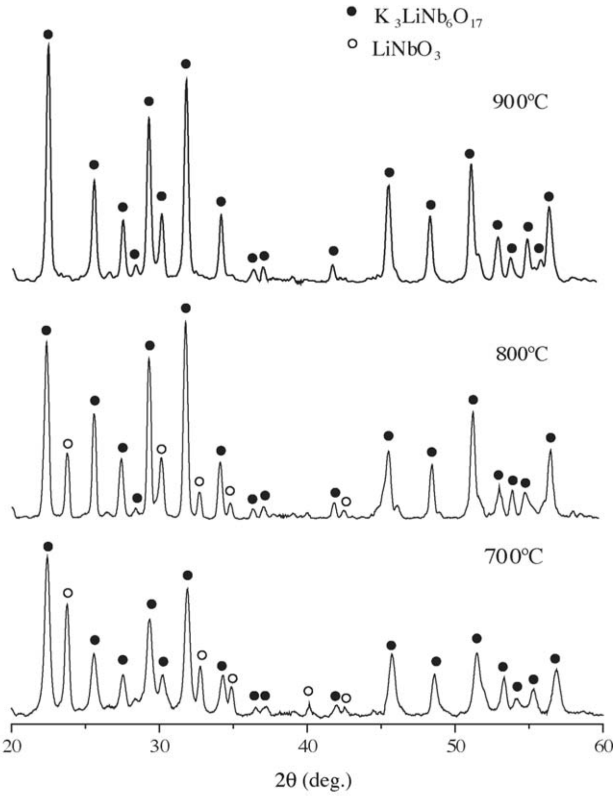

Fig. 3. The XRD patterns of the sample powders calcined at 700, 800 and 900 °C (pH 8; CA/M = 3; CA/EG = 2).

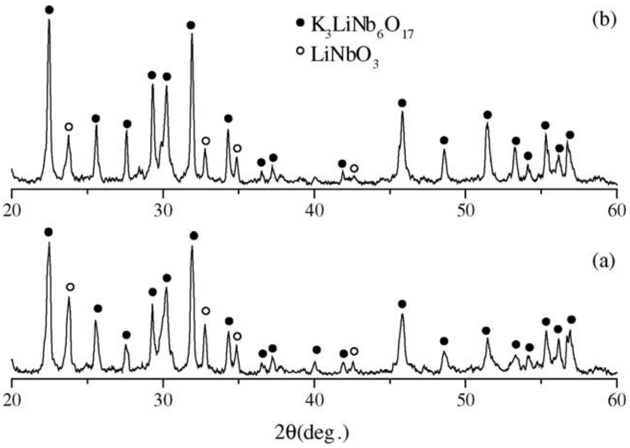

Fig. 4. The XRD patterns of the KLN powders prepared with different citric acid/ ethylene glycol molar ratios and calcined at 900 °C (pH 8; CA/M = 3). (a) CA/EG = 1; (b) CA/EG = 0.5.

In order to compare the effect of the content of ethylene glycol on the formation of KLN phase, the K–Li–Nb precursor gels with different citric acid/ethylene glycol molar ratio were calcined at 900 °C for 2 h. Fig. 4 shows the XRD patterns of the KLN powders prepared with different CA/EG molar ratios. It clearly shows that the peak intensity assigned to the KLN phase increases with a decrease of CA/EG molar ratio. The reason may be explained as follows: small additions of ethylene glycol are considered to provide less organic material into the precursor gel, and therefore, the calcinations temperature to form KLN phase decreases.

TEM was used to estimate the particle size and morphology for the KLN powders heated for 2 h at 900 °C (Fig. 5). It clearly shows uniform-sized and weakly agglomerated KLN particles, which have an average size of about 30–50 nm.

The stability of the K–Li–Nb precursor solution and gel at various citric acid (CA)/metal cations (M) ratio and pH values was evaluated, and the experimental parameters and

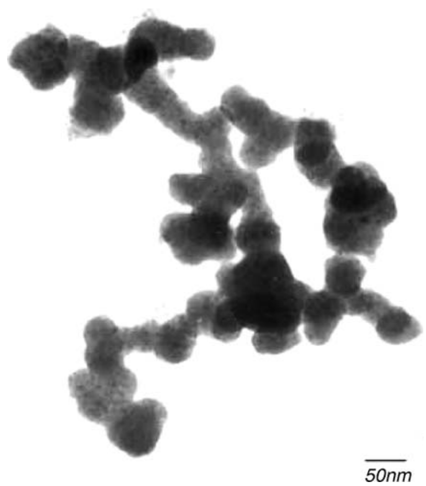

Fig. 5. TEM micrograph of KLN powder obtained at 900 °C (pH 8).

Table 1
Experimental parameters and stability of the K–Li–Nb precursor solutions and gels

pH	Molar ratio of citric acid/metal cations	State of precursor solution	State of gel
2	3:1	White precipitate	Muddy gel
4	3:1	White precipitate	Muddy gel
6	3:1	Yellowish clear solution	Muddy gel
8	3:1	Yellowish clear solution	Transparent gel
10	3:1	Yellowish clear solution	Transparent gel
8	1:1	White precipitate	Muddy gel
8	1.5:1	White precipitate	Muddy gel
8	2:1	White precipitate	Muddy gel
8	2.5:1	Yellowish clear solution	Muddy gel
8	3:1	Yellowish clear solution	Transparent gel

results are illustrated in Table 1. As shown in Table 1, obtaining clear gels without precipitation depends on the molar ratio of citric acid to metal cations and pH of the solution. The pH value affects the chelation between the cation and the associated citric acid ion greatly. At higher pH conditions, more citric acid is ionized and more carboxylic groups ($COOH^-$) can be available to chelate the metallic ions in the solution. In the experiments, the optimum pH value for the formation of clear homogeneous K–Li–Nb gel is 8. The concentration of citric acid also has an influence on the chelation of metal cations. It can be seen that the citric acid plays an important role in forming stable K–Li–Nb precursor solution and gel, which are generally stabilized in excess of citric acid. This can be explained by the fact that the more citric acid is used, the more carboxylic groups are available to chelate the metal cations, and led to the higher uniformity of metallic elements in the ester. Table 1 shows that the precipitates can be circumvented in the precursor solution as the molar ratio of CA:M increases to 2.5:1. However, precipitation and an unclear gel were observed during the thickening of the solution upon drying. Consequently, the optimum molar ratio of CA:M for obtaining homogeneous K–Li–Nb precursor gel is 3:1.

4. Conclusions

Nanosized potassium lithium niobate powders with low Li content were synthesized, for the first time, using the Pechini method. The KLN powders obtained are in the size of about 50 nm through the calcination at 900 °C for 2 h. The molecular formula of the KLN powder can be written as $K_{2.95}Li_{1.38}Nb_{6.22}O_{17}$. The change of the composition is caused by the evaporation of the lithium during high-temperature heat treatment. The required calcinations temperature to form KLN phase decreases with the increase of the CA/EG molar ratio in the precursor gel. The pH of the precursor solution and molar ratio of citric acid and metal cations play an important role in the formation of stable K–Li–Nb gels. Increasing the concentration of citric acid and pH values can circumvent the precipitate in the precursor gel and ensure complete chelation of all the cations. A homogeneous K–Li–Nb precursor gel with no precipitate was formed at pH 8 and the optimum molar ratio of CA/M is 3:1.

Acknowledgements

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