



Preparation of lithium niobate particles via reactive molten salt synthesis method

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Received 1 January 2013; received in revised form 29 June 2013; accepted 17 July 2013

Available online 3 August 2013

Abstract

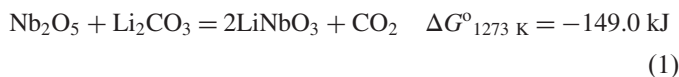
Lithium niobate (LiNbO_3 , LN) is one of the key materials for optical based technologies. In this paper, we report an effective, simple, cheap and very fast molten salt method for gram-scale synthesis of single-crystalline LN particles in which a mixture of Nb_2O_5 – LiCl is heat treated at a temperature above the melting point of LiCl for few minutes. The product consisted of LN and other Li – Nb – O phases when the mixture was heated in air. In contrast, single-phase LN was synthesised by heating the mixture in a humid argon flow. In this process, the molten salt acts as both the reaction medium and the Li -source. Synthesised LN was characterised by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, differential scanning calorimetry, and Raman spectroscopy. The mechanism of the process is also discussed. © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Lithium niobate; Lithium chloride; Molten salt; Crystal growth

1. Introduction

Considerable interest exists in lithium-metal-oxides due to their many industrial and academic applications. Particularly, LN is a key material for ferroelectric, pyroelectric, dielectric and piezoelectric devices and for holographic data storage, frequency doubling, waveguide structures and solid-state lasers [1–3] thanks to its excellent electro-optical, photo-refractive and nonlinear optical properties [4–7]. LN particles are used as an ideal feed material for crystal growth [8] or for preparation of LN thin films [9]. Moreover, the catalytic capability of LN particles has been recently addressed [10].

LN particles are conventionally fabricated through solid-state reaction between Nb_2O_5 and Li_2CO_3 , according to



The solid-state reaction process, however, requires high temperatures ($> 1000^\circ\text{C}$) to be carried out [11,12], and hence

causes the evaporation losses of Li_2O , which may yield not only LN but also Li_3NbO_4 and LiNb_3O_8 components in the whole system [13]. The loss of stoichiometry by Li_2O evaporation, together with the formation of Nb-rich grain boundaries deteriorates the piezoelectric properties of LN [14]. Therefore, development of a low-temperature processing method for the preparation of LN particles has attracted a great deal of attention. It was found that the synthesis temperature in the solid state mode can be reduced to below 600°C by using a combustion agent such as urea [15–17] or glycine [18,19] and also by applying a ball milling pre-treatment [20,21]. In the later case, the ball-milling caused enhancement of the kinetics of the reaction by favouring the formation of more reactive surfaces. No further progress of these methods, however, has been reported.

Wet chemistry, as an alternative method for the synthesis of LN, makes it possible to employ a lower calcination temperature, avoiding losses of lithium oxide. In this category, the Pechini method is one in which the starting materials of citric acid, ethylene glycol as well as Nb and Li compounds are employed to prepare a gel, and LN is subsequently obtained by calcination of the gel at a temperature more than 560°C [22]. Up to now, several works have been published based on this

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method for preparation of LN by using of Nb_2O_5 as the niobium source and Li_2CO_3 as the lithium source [23–26]. Apart from them, other materials such as NbF_5 [27], NbCl_5 [28], $\text{Li}_2\text{C}_2\text{O}_4$ [29], $\text{LiNb}(\text{OPr}^i)_6$ [30] and LiOH [31] have been employed as the source materials. In the wet chemistry methods, however, large amounts of expensive and mostly toxic organic compounds are required for synthesis of LN particles.

LN particles have also been synthesised via the hydrothermal method using different starting materials comprising of $\text{LiOH} \cdot \text{H}_2\text{O}$ (or LiNO_3) and Nb_2O_5 [32], LiOH and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ [33], Li_2CO_3 and Nb_2O_5 [34] as well as LiOH and Nb_2O_5 [35]. Hydrothermal synthesis was found to be an efficient method in decreasing the synthesis temperature of LN to about 250°C ; however, the reaction time was very long, usually more than 10 h.

As a different approach, molten salt synthesis (MSS) has been used for the preparation of a large number of multi-component oxides from their precursors [36]. In order to prepare LN particles by this method, first, the Nb-source (Nb_2O_5 [37–39]) and the Li-source (Li_2CO_3 [38,39] or $\text{LiOH} \cdot \text{H}_2\text{O}$ [37]) were well mixed together with an appropriate salt mixture (KCl – NaCl [37–39] or Li_2SO_4 – Na_2SO_4 [38]) by means of wet techniques. The mixed powders were then heated above the liquidus temperature of the salt mixture (over 600°C). The main advantage of the MSS lies in the fact that the reaction between the reactants is facilitated due to the enhanced mobility of the species in the molten salt, which is 10^{10} – 10^{13} times greater than

that in the solid state [36]. As a consequence, the reaction can take place at a significantly reduced temperature and time. However, several hours are still required for the entire process to be completed, as the precursors should be mixed thoroughly before the heat-treatment.

In conclusion, the above mentioned processes are time consuming, expensive and/or complicated for mass-production of LN particles, and therefore more effective synthesis methods are required.

It should be noted that in the MSS approach the molten salt is used as the reaction medium and remains inert during the process. We have recently employed a molten salt synthesis approach [40,41], in which the salt can react with the other components during the process. This approach can be called the “reactive molten salt synthesis” (RMSS) in contrast with the common MSS approach. In the current study, for the first time, RMSS has been investigated as a method of preparing single-crystalline LN particles. The process consists of heating Nb_2O_5 powder in LiCl molten salt for a short period of time. The molten salt, therefore, is one of the precursors and is reactive.

2. Experimental procedure

2.1. Materials and methods

2.0 g Nb_2O_5 powder (208515, Sigma Aldrich) and 50.0 g LiCl (213233, Sigma-Aldrich) were mixed and the mixture was placed in an alumina crucible. Two sets of experiments

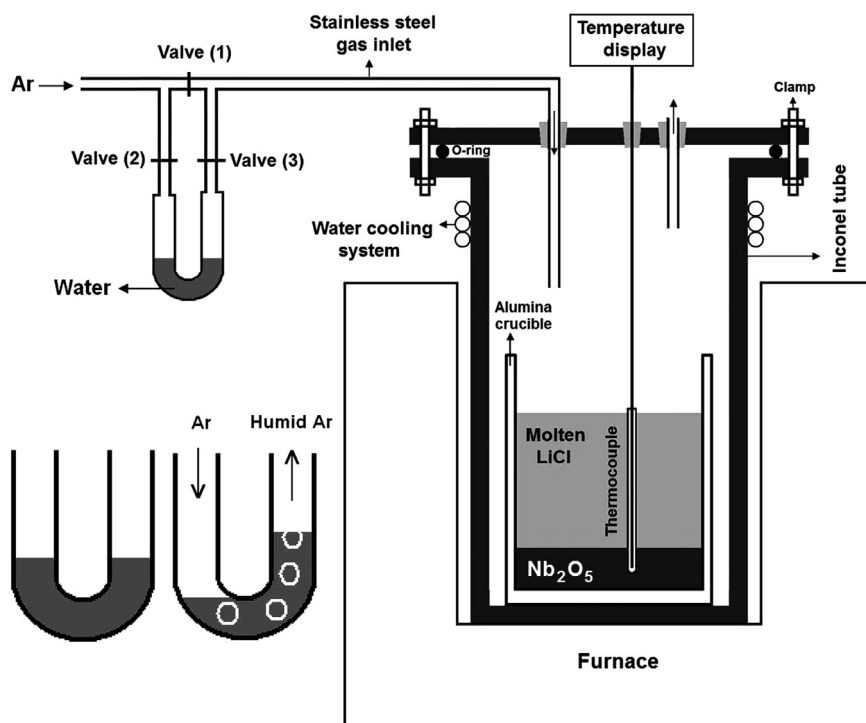


Fig. 1. A schematic representation of the experimental set-up used for the synthesis of LN. A mixture of Nb_2O_5 and LiCl was heated up to 700°C under a flow of argon gas, while the valve (1) was open and the valves (2) and (3) were closed. At the target temperature, when the salt is in the molten state, a water containing atmosphere above the molten salt was provided by reversing state of the valves. In this situation, the Ar forms bubbles in the water bath to produce a humid gas stream (left bottom corner of the figure). Thereafter, the valves were switched into the initial state and the temperature was allowed to be reduced to the room temperature.

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