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Effect of solvent and temperature on the preparation of potassium niobate by hydrothermal-assisted sol–gel processing

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Abstract

In this study the preparation of potassium niobate powder, a material with high electro-optic and nonlinear optical coefficients, by hydrothermal-assisted sol–gel processing from potassium-niobium ethoxide [$KNb(OC_2H_5)_6$] have been performed. The development of potassium niobate phases by hydrothermal hydrolysis of potassium niobium ethoxide at 100 and 200 °C in ethanol, toluene, and a mixture of benzene and ethanol was pursued by X-ray diffraction. Selected powders obtained from hydrothermal-assisted sol–gel processing were characterized by X-ray powder diffraction, thermal analysis (TGA/DSC), and scanning electron microscopy (SEM). X-ray diffraction results showed that the hydrothermal hydrolysis of potassium-niobium ethoxide in ethanol at 100 and 200 °C results in the formation of cubic phase $KNbO_3$. Hydrolysis in a mixture of benzene/ethanol and toluene at 200 °C produces an orthorhombic phase $KNbO_3$, which is a mixture of the potassium deficient phase, $K_4Nb_6O_{17}$, and cubic and orthorhombic $KNbO_3$ phases. The potassium niobate powder prepared by the hydrothermal method had the advantage of low weight loss during calcination. SEM micrographs showed that the shape of particles prepared by hydrothermal-assisted sol–gel processing is more uniform when compared with the sample prepared by conventional sol–gel processing.

Keywords: B. X-ray method; D. Niobate; D. Perovskite; Sol–gel; Hydrothermal

1. Introduction

Potassium niobate, $KNbO_3$, a ferroelectric material with high electro-optic and nonlinear optical coefficients and good photorefractive properties, is of interest for application of optical waveguide [1–3]. Along with the engineering of potassium niobate applications in acoustic devices, optical switching modulation, frequency conversion, and holographic storage systems, a number of preparation routes have been developed. Various approaches have been employed for the preparation of potassium niobate powders and single crystals. These approaches include prolonged calcination of a mixture of niobium oxide and potassium carbonate [4–6], sol–gel process [7–9], and hydrothermal and glycothermal methods [10,11]. The disadvantage of large aggregates and the formation of inhomogeneous composition as the result of loss of potassium oxide at elevated temperature, along with the formation of a potassium deficient phase is well recognized [6]. In contrast to the prolonged solid state reaction, sol–gel processing, hydrothermal, and glycothermal methods are effective routes for the preparation of potassium niobate with perovskite structure. The glycothermal method, which is a low temperature processing route, is particularly interesting. However, more than stoichiometric amounts of potassium hydroxide are required to achieve pure perovskite phase. In spite of the formation of a single-phase perovskite-type structure, a non-stoichiometric ratio of potassium to niobium was observed. A single-phase $KNbO_3$ has also been prepared with the sol–gel method from the hydrolysis of bimetallic alkoxide in appropriate solvent, but the control of particle size and morphology using this route is a difficult task [7].

In recent years, the hydrothermal method for preparation of electro-ceramic materials with tailored phases and morphology have been accelerated [12–14]. Hydrothermal technology not only produces fine powder, but also offers many advantages including high degree of chemical homogeneity, low processing temperature, ease of control of morphology, and possibility for the preparation of metal oxides in unusual oxidation states.

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Table 1
Effect of solvent and hydrothermal-processing temperature on hydrolysis product of potassium-niobium ethoxide.

(A) Experimental condition			(B) Results
Sample	Solvent	Hydrothermal temperature (°C)	Product[a]
KN1	Ethanol	100	Cubic $KNbO_3$
KN2	Ethanol	200	Cubic $KNbO_3$
KN3	Ethanol/benzene	100	Cubic $KNbO_3$
KN4	Ethanol/benzene	200	Orthorhombic $KNbO_3$
KN5	Toluene	100	Cubic $KNbO_3 + K_4Nb_6O_{17}$
KN6	Toluene	200	Cubic $KNbO_3 + K_4Nb_6O_{17}$
KN7	Ethanol	[b]	Cubic $KNbO_3$

[a] After calcinations.
[b] Conventional hydrolysis [7].

In addition, the elimination of the milling stage in the hydrothermal processing of materials makes this method suitable for the production of advanced ceramics. In spite of the higher purity of metal alkoxides, inorganic oxides or hydroxides are the precursors of choice in conventional hydrothermal reactions because of their ease of handling and the nature of the hydrothermal process, which needs to be carried out in water. On the contrary, metal alkoxides, due to their moisture sensitivity, cannot be used directly in hydrothermal reactions and alternative routes should be considered.

In this study, in a new approach, potassium niobate was prepared by combination of two powerful ceramic processing methods: sol–gel and hydrothermal. This work also reports the effects of solvent and temperature in phase development and morphology of the final material.

2. Experimental

2.1. Synthesis

All reagents were purchased from Merck and used as received. All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk line technique. Solvents were refluxed and dried over appropriate drying agents under an atmosphere of nitrogen and collected by distillation. Potassium-niobium ethoxide [$KNb(OC_2H_5)_6$] was prepared by method reported in the literature [7].

2.2. Hydrolysis

For the hydrothermal-assisted hydrolysis, a 0.25 M solution of potassium-niobium ethoxide in ethanol, toluene or a mixture of benzene/ethanol (10:1, v/v) was loaded into a glass container. The glass container was placed in a 300-ml stainless steel autoclave. The gap between the autoclave chamber and the glass container was filled with 50 ml of distilled water and then the autoclave was heated at either 100 or 200 °C. Transfer of potassium-niobium ethoxide into the autoclave was performed in a moisture-free atmosphere to prevent hydrolysis of alkoxide prior to being introduced into the hydrothermal chamber. After 5 h, the autoclave was cooled and the resulting powder was filtered off and dried at 100 °C overnight and then calcined at 550 or 700 °C. For a comparison of the morphology of hydrothermally prepared potassium niobate with the morphology of conventionally processed potassium niobate, a single-phase potassium niobate was prepared according to the earlier report by direct hydrolysis of potassium-niobium ethoxide in methanol and was calcined at 700 °C. Due to the insolubility of potassium-niobium ethoxide in benzene, a mixture of benzene and ethanol was used. Experimental conditions for hydrolysis of potassium-niobium ethoxide are given in Table 1(A).

2.3. Analytical methods and instrumentation

The X-ray diffraction (XRD) patterns of calcined powders were collected on a Philips PW-1730 diffractometer with Cu Kα radiation. Electron microscopy was performed on a Philips XL-30 scanning electron microscope (SEM). Thermal analysis was carried out on a Rheometric Scientific STA-1500 with a heating rate of 10 °C/min in air.

3. Results and discussion

The X-ray diffraction patterns of all powders that were obtained from hydrothermal hydrolysis of potassium-niobium ethoxide at various conditions showed amorphous phase. Effect of solvent and hydrothermal-processing temperature on hydrolysis products of potassium-niobium ethoxide (entry KN-1 through KN-6, after calcinations at 700 °C) are given in Table 1(B). The X-ray diffraction patterns of powders that were obtained from hydrothermal hydrolysis of potassium-niobium ethoxide at 100 and 200 °C in ethanol (Fig. 1, KN1 and KN2, respectively), and in mixture of benzene/ethanol at 100 °C (Fig. 1, KN3) after calcination at 700 °C showed single-phase cubic $KNbO_3$ [JCPDS, card No. 8-212]. Interestingly, the increase of processing temperature to 200 °C in ethanol did not change the potassium niobate phase (Fig. 1, KN2). In contrast, hydrothermal hydrolysis of potassium-niobium ethoxide in the benzene/ethanol mixture at 200 °C resulted in the development of the orthorhombic phase [JCPDS, card No. 32-0822] (Fig. 1, KN4), a thermodynamically stable phase at room temperature [15]. Furthermore, XRD showed that the powder prepared by hydrothermal hydrolysis of precursor in toluene at 100 and 200 °C (Fig. 2, KN5 and KN6, respectively) after calcination at 700 °C contains a potassium deficient phase, $K_4Nb_6O_{17}$ [JCPDS, card No. 31-1064], and cubic $KNbO_3$. The experimental results

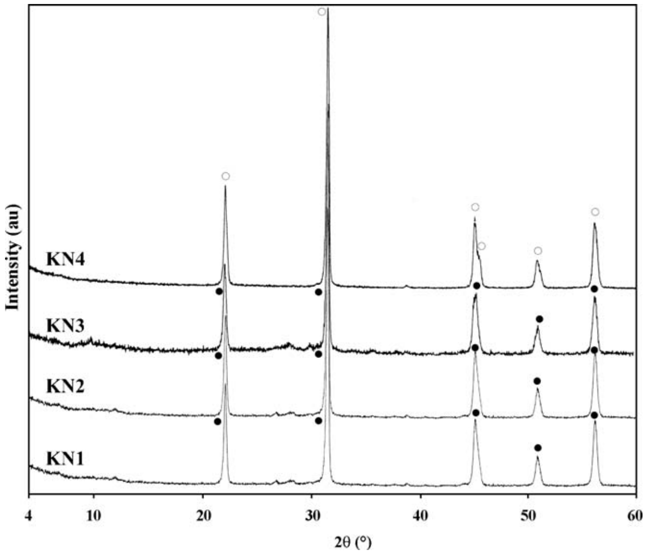

Fig. 1. XRD patterns of the samples prepared from hydrothermal hydrolysis of potassium-niobium ethoxide and calcined at 700 °C, (KN1) in ethanol at 100 °C, (KN2) in ethanol at 200 °C, (KN3) in mixture of ethanol/benzene at 100 °C, and (KN4) in mixture of ethanol/benzene at 200 °C. Peaks with a closed circle (●) are associated with the cubic phase, and peaks with an open circle (○) with orthorhombic phase.

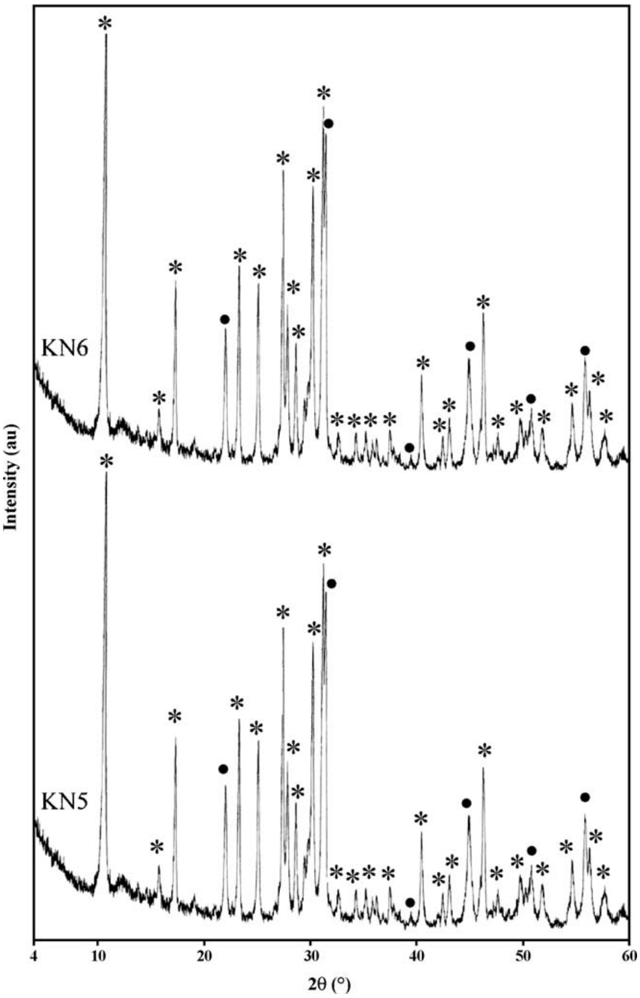

Fig. 2. XRD patterns of the samples prepared from hydrothermal hydrolysis of potassium-niobium ethoxide and calcined at 700 °C, (KN5) in toluene at 100 °C, and (KN6) in toluene at 200 °C. Peaks with a closed circle (●) are associated with the $KNbO_3$ cubic phase, and peaks with an asterisk (*) are with $K_4Nb_6O_{17}$ phase.

appear to indicate that the processing temperature and type of solvent has a crucial role in the phase development of potassium niobate by hydrothermal hydrolysis. Formation of the potassium deficient phase, $K_4Nb_6O_{17}$, in toluene can be attributed to the disruption of potassium-niobium ethoxide molecules at some point during hydrothermal hydrolysis of potassium-niobium ethoxide. Formation of the potassium deficient phase is very common in fast hydrolysis of potassium-niobium ethoxide. The reason for the formation of the orthorhombic phase when the solvent is changed from ethanol to a benzene/ethanol mixture is not understood at this time. It seems the formation of the orthorhombic phase at higher processing temperatures in a mixture of benzene and ethanol is somehow related to the higher vapor pressure of water and nature of solvent simultaneously. For the elucidation, all powder that was obtained from the hydrothermal hydrolysis was calcined at 550 °C and analyzed by XRD. The XRD pattern of samples that were hydrolyzed in ethanol and calcined at 550 °C, similar to the ones calcined at 700 °C (KN1 and KN2), showed a cubic phase but with a lower degree of crystalinity. In contrast the XRD pattern of a sample that was hydrolyzed in a mixture of benzene and ethanol and calcined at 550 °C (Fig. 3) showed only a meta-stable $KNbO_3$ phase [JCPDS, card No. 31-1058]. The meta-stable $KNbO_3$ phase was changed to an orthorhombic phase by calcination at 700 °C (Fig. 1, KN4). Interestingly, the formation of a meta-stable $KNbO_3$ phase also was observed in the synthesis of potassium niobate using the hydrothermal method from Nb_2O_5 and KOH [16] in contrast to conventional hydrolysis or Pechini-type reaction route [17]. Also, the extensive peaks splitting of the cubic phase and the development of an orthorhombic phase, which was reported in the conventional sol–gel processing of potassium niobate, was not observed in the samples prepared by hydrothermal hydrolysis [7]. The formation of a meta-stable phase shows the significant role of processing strategy in the preparation of binary metal oxide in general and potassium niobate in particular.

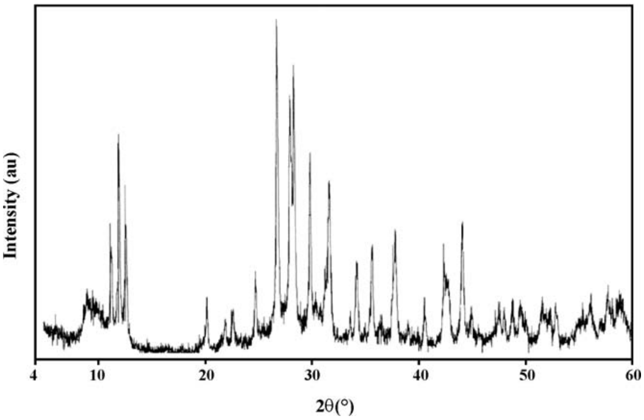

Fig. 3. XRD pattern of sample prepared from hydrothermal hydrolysis of potassium-niobium ethoxide in a mixture of ethanol and benzene at 200 °C and calcined at 550 °C.

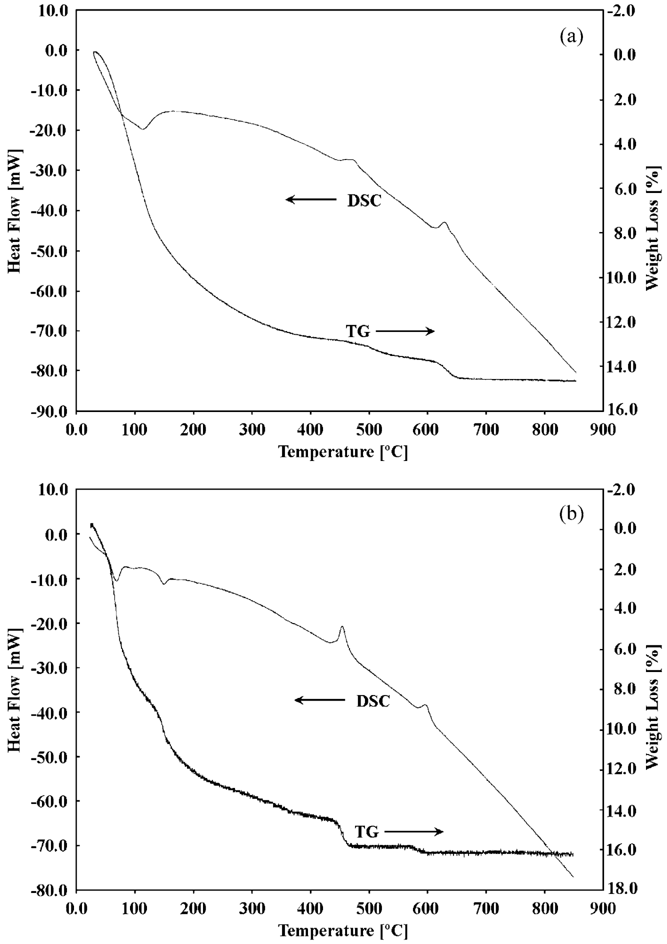

Fig. 4. TGA/DSC curves of samples (a) KN2: hydrothermal hydrolysis in ethanol at 200 °C, and (b) KN4: hydrothermal hydrolysis in mixture of benzene and ethanol at 200 °C.

Fig. 4(a) and (b) shows TGA/DSC curves of powders obtained from hydrothermal hydrolysis of potassium-niobium ethoxide in ethanol and a mixture of benzene and ethanol at 200 °C. The total weight loss for both samples that were hydrothermally hydrolyzed is about 16%. The weight loss from 50 to 150 °C (12%) for the former with an endothermic peak in its DSC curve in the same temperature range indicates that the weight loss is primarily associated with the elimination of ethanol and possibly physically adsorbed water and chemically bound water. This weight loss, for the sample that was processed in the mixture of benzene and ethanol (Fig. 4(b)) in the above temperature range, is about 11% and is accompanied by two small endothermic peaks. The endothermic peak below 100 °C is attributed to the elimination of physically adsorbed water and the peak above 100 °C is to chemically bound water. As expected, the water content of the sample hydrolyzed in a mixture of benzene and ethanol is lower. The samples processed in ethanol and the mixture of benzene and ethanol also show about 1 and 2% weight loss around 475 °C along with exothermic peaks in their DSC curves. These peaks, which are associated with the combustion of carbonaceous materials, are significantly smaller than that of a conventionally processed sample [7]. The small amount of organic residue in the hydrothermally processed samples, in comparison with conventionally prepared samples shows that a more efficient hydrolysis is achievable by the hydrothermal hydrolysis of potassium-niobium ethoxide. The small exothermic peak at 650 °C in the DSC curve of the sample hydrolyzed in ethanol is probably due to crystallization of orthorhombic phase, $KNbO_3$. Similarly, the exothermic peak at 600 °C in the DSC curve of the sample processed in the mixture of benzene and ethanol is associated with the crystallization of the orthorhombic phase. These results agree with the XRD data of samples (KN2 and KN4) calcined at 700 °C, and also with the thermal analysis results reported for the conventionally processed potassium niobate [7]. The total weight loss of samples prepared in this work is comparable to the weight loss of material prepared by hydrothermal treatment of niobium oxide and potassium hydroxide solution at 200 °C [18]. This weight loss is significantly lower than the weight loss of the potassium niobate precursor prepared by the citrate gel method [17]. The lower weight loss of powders prepared by hydrothermal hydrolysis of metal alkoxide can be an advantage in the preparation of monolithic parts by casting and sintering.

Fig. 5 shows scanning electron micrographs of calcined (700 °C) potassium niobate samples that were prepared by hydrothermal-assisted sol–gel processing at 200 °C in: (a) ethanol, (b) a mixture of benzene and ethanol, and (c) toluene. The micrograph of the potassium niobate sample synthesized by conventional hydrolysis of potassium-niobium ethoxide in ethanol according to the earlier report is depicted in Fig. 5(d) for comparison [7]. It shows that the particle size and morphology of samples are different to some extent. The average grain size of potassium niobate prepared from hydrothermal hydrolysis in ethanol, a mixture of benzene/ethanol or toluene was estimated to be about 300–500 nm. The cubic phase of potassium niobate that was prepared in ethanol is more uniform and somewhat are smaller than the orthorhombic phase prepared in the mixture of benzene/ethanol. Interestingly, two different shapes of particles are evident in the micrograph of the sample prepared in toluene. Results are consistent with the XRD data, which indicated a mixture of phases exists, and also with the earlier report that the existence of a second phase has an effect on the morphology of the powder [19]. The potassium niobate that was synthesized by a conventional sol–gel process, in contrast to the hydrothermally synthesized potassium niobate, contains agglomerated particles. Generally, the morphologies of potassium niobate prepared by the hydrothermal hydrolysis of potassium-niobium ethoxide is more uniform and well defined when compared with the coarse particles obtained by the solid state reaction [18], supercritical method [18], and hydrothermal reaction using Nb_2O_5 in a KOH solution [20,21]. Particle size and morphology of potassium niobate powder prepared in this study is somewhat similar to that prepared by the sol–gel process from potassium-niobium ethoxide in 2-methoxyethanol [19].

The variation in the properties of potassium niobate powder prepared by hydrothermal hydrolysis assisted sol–gel processing of potassium-niobium ethoxide in various solvents can probably be attributed to the different hydrolysis-condensation

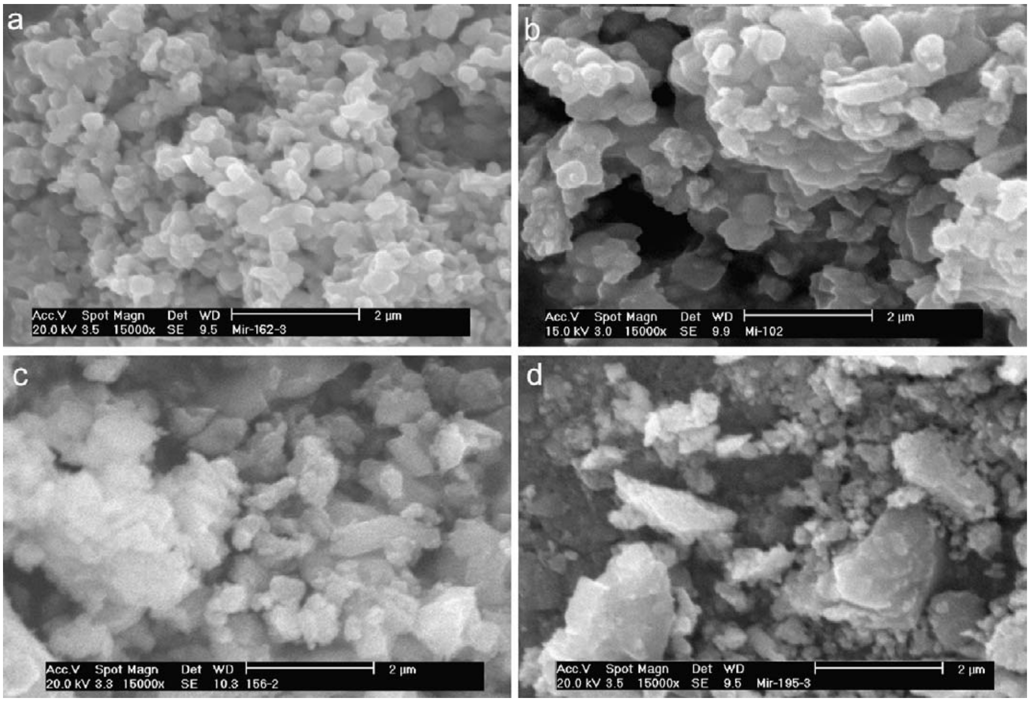

Fig. 5. SEM micrographs of samples (a) KN2: hydrothermal hydrolysis in ethanol at 200 °C, (b) KN4: hydrothermal hydrolysis in a mixture of benzene and ethanol at 200 °C, (c) KN6: hydrothermal hydrolysis in toluene at 200 °C, and (d) KN7: conventional hydrolysis in ethanol. All samples are after calcination at 700 °C.

mechanism of the precursor and solvent's hydrophobicity. In a hydrophilic solvent, such as pure ethanol or a mixture of benzene/ethanol, because of the interaction between water and ethanol, the rate of the hydrolysis process differs from hydrolysis in a pure hydrophobic solvent such as toluene. The interaction of water vapor with a hydrophilic solvent during the diffusion of water under autogenous pressure in the hydrothermal process is stronger than its interaction with the alkoxide precursor. Consequently, the rate of hydrolysis decreases to some extent. In contrast, the interaction of water vapor with hydrophobic solvents is weak during the hydrothermal process but strong with an alkoxide precursor, which results in a higher hydrolysis rate. Formation of a potassium deficient phase, $K_4Nb_6O_{17}$, along with cubic and orthorhombic $KNbO_3$ phases can possibly be attributed to the higher rate of hydrolysis and dissociation of bimetallic alkoxide to single alkoxides in toluene. Furthermore, during heat treatment, due to the volatility of K_2O at elevated temperatures, some of K_2O sublimes from hydrolysis products and potassium deficient phase along with other phases forms.

The effect of temperature was also investigated in the hydrothermal-assisted sol–gel processing of potassium niobate. Interestingly, the increase of processing temperature from 100 to 200 °C in the mixture of ethanol and benzene resulted in the formation of an orthorhombic phase. Formation of the orthorhombic phase can most probably be attributed to the higher vapor temperature of water and, consequently, the higher rate of hydrolysis and different hydrolysis mechanism. However, additional work is required for a deeper understanding of this. These results show that the modification of processing conditions can be an alternative route in the preparation of material instead of modification of precursors and design of complex molecules.

4. Conclusion

This work showed that the processing temperature and solvent in the hydrothermal-assisted sol–gel processing of potassium niobate from potassium-niobium ethoxide, plays a crucial role on the phase development and texture of potassium niobate. In addition, a specific phase of potassium niobate can be easily tailored by choosing proper hydrolysis conditions. By hydrothermal-assisted sol–gel processing it is possible to prepare a specific phase of metal oxides, which are not accessible by other routes.

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