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Synthesis of potassium niobates by the microwave-assisted solvothermal method.

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Abstract: Potassium niobates have been synthesized by different methods, but few papers use the microwave-assisted solvothermal method, with possibility of a deeper evaluation in this area. In this work, the synthesis of KNbO_3 , KNb_3O_8 and $\text{K}_4\text{Nb}_6\text{O}_{17}$ was performed by calcinations of precursors obtained by the microwave-assisted solvothermal method. This study evaluates the influence of various synthesis parameters such as reaction time, pH of the reaction medium, K^+ concentration in the precursor solution. The results show the formation of different niobates, KNbO_3 , KNb_3O_8 , $\text{K}_4\text{Nb}_6\text{O}_{17}$, depending on the short and long-range order of the precursor used in the post annealing process.

1. Introduction

Niobates have wide application in the chemical industry, for presenting versatile structures and thus make possible the development of a wide range of materials with different physicochemical properties [1–3]. For example, KNbO_3 exhibits properties and applications as optical devices, acoustic wave surface devices and others [4], while KNb_3O_8 and $\text{K}_4\text{Nb}_6\text{O}_{17}$ exhibit optical and electronic properties, high catalytic activity in hydrogen production by water splitting and are also used in composition of new nanostructured semiconductor materials [5–8].

Different synthesis routes, as solid-state reaction route, sol-gel, hydro/solvothermal, under different conditions are reported for obtaining KNbO_3 , KNb_3O_8 and $\text{K}_4\text{Nb}_6\text{O}_{17}$, as observed in table 1.

Since the mid 80s, the use of microwave-assisted hydro/solvothermal method has been studied in materials synthesis [9]. This technique has interesting advantages compared to other traditional synthesis processes, especially in relation to a lower energy consumption and time control of the morphology and reproducibility [9–11].



Table 1. Some methods of synthesis of niobates, reported in the literature.

Material	Methods and References
KNbO ₃	Solid State [12,13], Sol-Gel [14,15], Conventional Hydro/Solvothermal [4,16], Microwave Assisted Hydrothermal [3,17]
KNb ₃ O ₈	Solid State [18,19], Conventional Hydro/Solvothermal [16,20]
K ₄ Nb ₆ O ₁₇	Solid State [14,21], Sol-Gel [22], Conventional Hydro/Solvothermal [16,23]

2. Experimental

The precursor suspension was obtained using niobic acid and potassium hydroxide in an aqueous/ethanolic medium with a volumetric ratio of 1:1. 70 ml of the suspensions were solvothermalized at a constant reaction temperature of 150 °C. Three parameters were varied during synthesis: reaction time (1, 15, 45 min), K/Nb molar ratio 6.6:1 and 10.5:1 and pH (6, 8 and 14) of the solution, adjusted with acetic acid. Materials were centrifuged and dried at 100 °C for 8 h, and then heat treated at 650 °C for 120 min. The materials were characterized by X-ray diffraction (XRD 6000 – Shimadzu), Raman spectroscopy (micro-Raman LabRAM Horiba Jobin-Yvon, with argon laser) and field-emission scanning electronic microscopy (FEG-VP - Zeiss Supra 35)

3. Results and Discussion

XRD patterns of the material synthesized during 1 to 45 min, at pH = 14 and K:Nb molar ratio of 6.6:1 are shown in figure 1(a). The Lindquist salt (K₆H₂Nb₆O₁₉.13H₂O) was obtained in all of the conditions in agreement with the results of Santos et al. [24]. Raman spectrum showed in figure 1b, have good agreement with the results of Farrell et al. [25], as observed in Table 2.

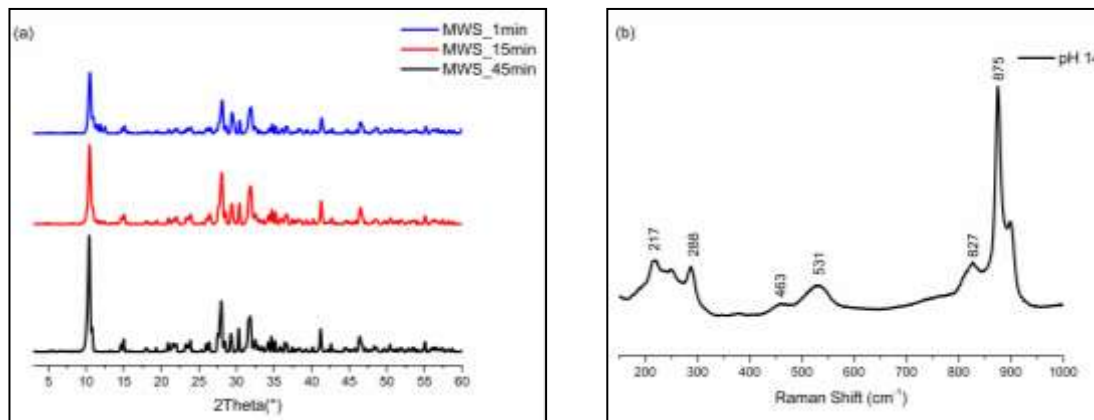


Figure 1. Characterization of the precursor obtained after solvothermalization at pH = 14 and K:Nb molar ratio of 6.6:1. (a) XRD patterns (starred peaks are assigned to the Lindquist salt); (b) Raman spectra.

Table 2. Calculated and observed frequencies (cm⁻¹) for Nb₆O₁₉⁸⁻.

Modes	Calcd. ^a	Obsd. ^a	Obsd. ^b	Modes	Calcd. ^a	Obsd. ^a	Obsd. ^b
A _{1g}	879	875	875	A _{1g}	500	495	*
E _g	834	823	827	T _{2g}	469	460	463
E _g	726	730	*	A _{1g}	292	290	288
E _g	521	532	531	T _{2g}	224	220	217

* Not cleared observed, ^a From [25], ^b This study.

The post-annealing of the precursor ensures the formation of KNbO_3 , with orthorhombic structure, in agreement to JCPDS Card 00-032-0822, figure 2(a). The Raman spectra (figure 2.b) is also in excellent agreement with those previously reported in the literature [26,27]. For this authors, the band located at 192 cm^{-1} can be attributed to internal vibrational modes of the NbO_6 octahedron and/or translational modes of K^+ cation, the two bands at 595 and 531 cm^{-1} are two stretching modes (ν_1 and ν_2 respectively), the broad band at 280 cm^{-1} is a bending mode (ν_5) and the weak band at 834 cm^{-1} is a combinational band ($\nu_1 + \nu_5$) [26,27]. FE-SEM micrograph showed a high degree of sintering among particles, as presented in Figure 2c.

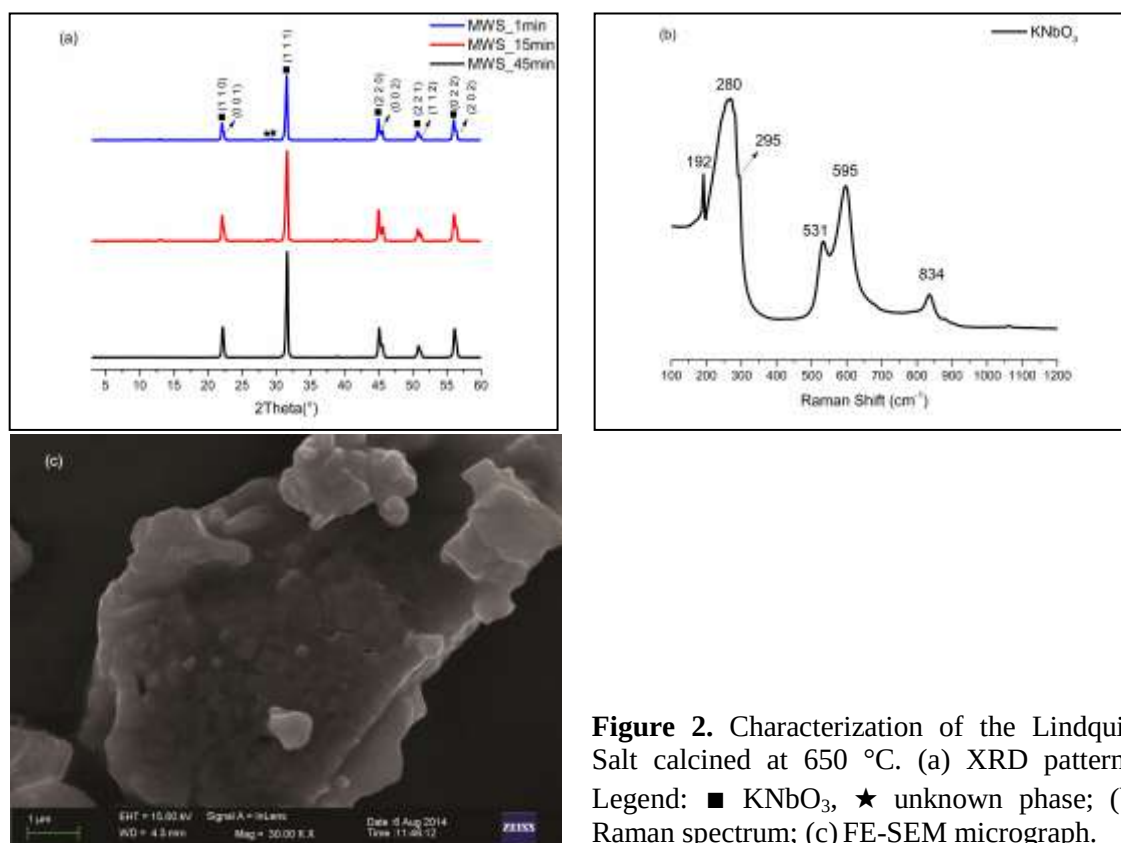


Figure 2. Characterization of the Lindquist Salt calcined at $650\text{ }^{\circ}\text{C}$. (a) XRD patterns. Legend: ■ KNbO_3 , ★ unknown phase; (b) Raman spectrum; (c) FE-SEM micrograph.

After modification of the potassium concentration, a K/Nb ratio of 10.5:1 was used with pH values of 6 and 8. The highest amount of potassium in solution associated with the lowest pH led to the formation of an amorphous precursor, ensuring the crystallization of lamellar niobates, KNb_3O_8 and $\text{K}_4\text{Nb}_6\text{O}_{17}$, after post annealing.

Figures 3(a) and 3(b) show the XRD patterns of the niobates, before and after calcination and its indexing according to JCPDS 00-032-0822 (KNbO_3), 01-075-2182 (KNb_3O_8), 00-021-1295 ($\text{K}_4\text{Nb}_6\text{O}_{17}$) and 00-021-1295 ($\text{K}_4\text{Nb}_6\text{O}_{17} \cdot 3\text{H}_2\text{O}$) cards. The appearance of the peaks related to the lamellar planes (0×0), at angles below 15° is a clear distinction between these XRD patterns and those shown in Figure 2.a. This is the main characteristic of lamellar compounds.

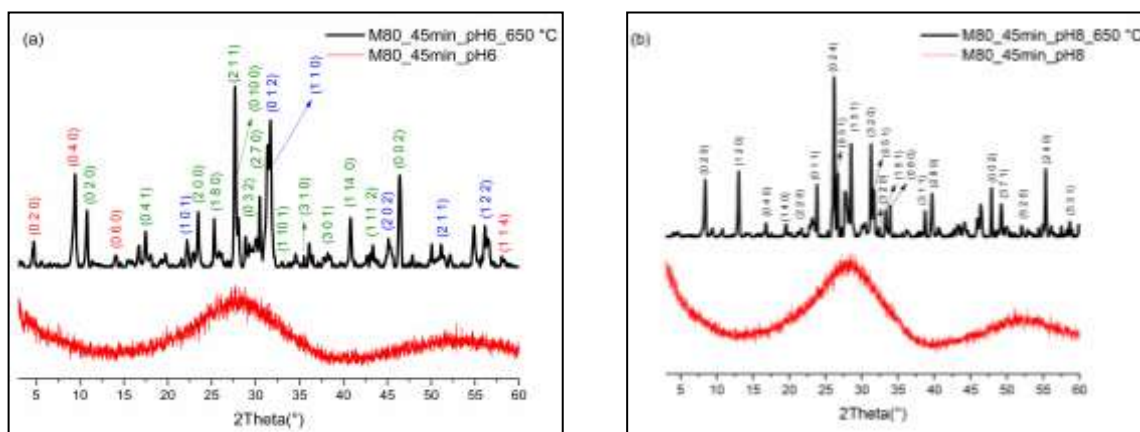


Figure 3. XRD patterns of the precursors obtained from solutions with different values of pH, before and after post annealing at 650 °C. (a) pH = 6; (b) pH = 8. Legend: red - $\text{K}_4\text{Nb}_6\text{O}_{17} \cdot 3\text{H}_2\text{O}$; green - $\text{K}_4\text{Nb}_6\text{O}_{17}$; blue - KNbO_3 ; black - KNb_3O_8 .

It was possible to observe a high dependence on the product direction with the pH since, even when working with higher K/Nb ratio, fact that should favor the formation of KNbO_3 , by adjusting the solutions pH to less basic values benefited the formation of lamellar species.

Lamellar niobates are characterized by having two different types of octahedra. The first one has shorter Nb-O bonds causing a sharp deformation of such NbO_6 units. These are the octahedra that stuck out into interlayers. The other have longer Nb-O bonds and are slightly distorted [28,29]. These differences are evidenced in the Raman spectra, showed in figure 4. The sharp and intense bands observed at 953 and 881 cm^{-1} (figures 4.a and 4.b respectively) are assigned to the stretching mode of the short Nb-O bonds. The region between 700-500 cm^{-1} is assigned to Nb-O stretching mode of the slightly distorted octahedra. Bands related to the bending modes of Nb-O-Nb linkages are presented in lower Raman shift [28,29].

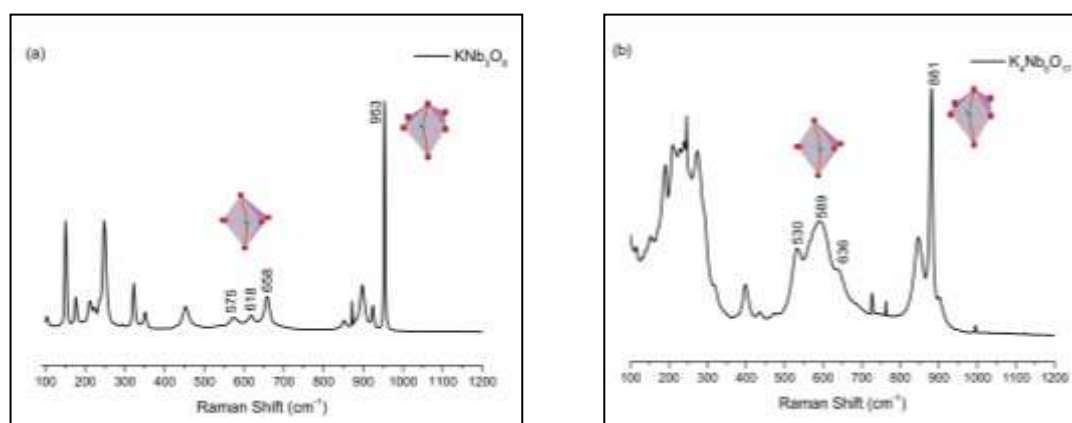


Figure 4. Raman spectra of the lamellar niobates. (a) KNb_3O_8 ; (b) $\text{K}_4\text{Nb}_6\text{O}_{17}$.

Morphologies of lamellar potassium niobates are presented in the figures 5a and 5b. The formation of superimposed thin small plates is observed as well as some degree of sintering.

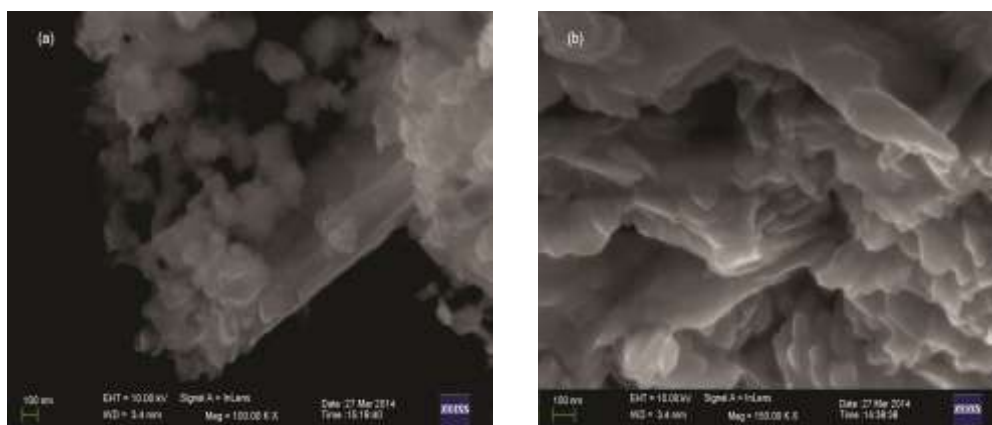


Figure 5. FE-SEM micrographs of the lamellar niobates. (a) KNb_3O_8 ; (b) $\text{K}_4\text{Nb}_6\text{O}_{17}$.

4. Conclusions

The microwave-assisted solvothermal method was used to obtain precursors for different potassium niobates. Each structure was obtained in a different reaction condition, and the pH of the suspension and potassium concentration determined the niobate structure obtained after post annealing. For instance, post annealing of the highly ordered Lindquist salt formed KNbO_3 , a material with more ordered octahedra. When a disordered precursor was obtained, post annealing led to lamellar phases which show highly distorted octahedra.

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