Influence of synthesis process on the structural and microstructural behavior of neodymium doped sodium and potassium niobate powders

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Abstract. In this paper are presented the synthesis of sodium-potassium niobate doped with neodymium. The powders were obtained carried out by means of three synthesis methods (mixture of oxides, hydrothermal and pechini methods). It was possible to observe in function of the synthesis method, particles cohered to form agglomerates and variation in shape, and size particles. Changes in calcination temperatures were found as a function of synthesis methods (using thermogravimetric analysis). Secondary phases were not observed in neodymium-doped sodium-potassium niobate powders obtained by mixture of oxides; however, secondary phases formation was observed in the powders obtained by hydrothermal and pechini method. Into solid-state physics, this study is important because can be used as a reference for establish the synthesis parameters of sodium potassium niobate powders with other rare earth elements. Besides, the results are the input to obtain secondary phases free ceramics and be able to study multifunctional properties as future work.

1. Introduction
Piezoelectric materials from their discovery to the present have been the focus of research because there have a wide range of applications in the electro-electronic industry. For example, they are used in electronic and ultrasound devices, transducers, actuators, sensors, among others [1]. One of the piezoelectric ceramics with the greatest acceptance and activity in the industry is the lead zirconate titanate (PZT) due to their ferroelectric and piezoelectric properties. Additionally, this system has a great advantage, their structure can be altered by doping by various elements such as Lanthanum achieving other properties in the system without suppressing those that were already present [2]. On the other hand, in recent years, the increase in environmental awareness has led to measures being taken for the responsible and friendly use of materials. Organization such as the European Union have implemented regulations that limit the use of dangerous substances in electronic and electrical devices. Several industries have contributed to lead contamination for hundreds of years. Lead is one of the main elements by weight of piezoelectric materials such as PZT, hence, the desire to find materials that are environmentally friendly materials that and can replace lead-based systems. With this motivation, the focus of study of these in the last decades has been reoriented to produce lead-free materials that may have an acceptable and applicable response in the industry [3,4].

Lead-free piezoelectric ceramics have received increasing attention from a positive environmental perspective. It is carried out to protect human health as well as the environment by substituting hazardous substances used in electrical and electronic devices [5,6]. An alternative to the problem is sodium and potassium niobate (KNN), which has generated special attention because it is a material that
has piezoelectric, electrical, mechanical, and thermal properties and a can be chemically modified by doping, so that new properties such as electro-optical and photonic optics can be added [5,7]. However, a major problem concerning to KNN material reported is the difficulty of obtaining samples with a high density by conventional preparation and sintering methods [6,8]. Other problems include the formation of secondary phases [9,10]. Therefore, the processing and powder synthesis are critical steps in obtaining KNN-Systems through “soft chemistry” methods as sol gel, hydrothermal, and micro-emulsion [5,11,12]. These “soft chemistry” methods to prepare KNN nanoparticles can decrease the synthesis temperature, reducing the volatilization of alkali elements and densification problems compared to the traditional sintering process. Generally, achievements in the process of KNN have been obtained through the addition of dopants agents, such as a few types of aliovalent metals that are often used to tailor the KNN electrical properties by forming point defects [11].

Despite all these studies, the relation between synthesis process and structural, microstructural properties in neodymium doped sodium and potassium niobate (KNN: Nd) powders have not been studied, therefore, in this work, the synthesis of KNN: Nd powders was carried out by means of three synthesis methods (mixture of oxides, hydrothermal and pechini methods). The main aim was to study the relationship between the synthesis methods and their influence on the thermal, structural, and microstructural properties of KNN: Nd powders. The Nd influence in KNN structure and your potential use as multifunctional material in the electro-electronic industry was mentioned too. The powders obtained presented different structural and microstructural characteristics in function of the synthesis method. From them, and thermogravimetric analysis, changes in calcination temperatures were also found as a function of synthesis methods. Into solid-state physics, this study is important because are the input to obtain secondary phases free ceramics and be able to study your multifunctional properties as future works.

2. Methodology and materials

Powers of $K_0.5Na_0.5NbO_3$ were prepared by mixture of oxides, hydrothermal and pechini methods. In the mixture of oxides; niobium pentoxide, $Nb_2O_5$ (Aldrich, purity 99%); sodium carbonate, $Na_2CO_3$ (Aldrich, purity 99%); and potassium carbonate, $K_2CO_3$ (Alfa Aesar, purity 99%) were used as reagents. Initially, each reagent was macerated and heated two hours at 250 °C. Next, the stoichiometric amount of the reagents was mixed according to the Equation (1) [13] to carry out the grinding. The resulting powder mixture was washed and heated in an oven at 110 °C until dry, then, the sample was macerated and heat treatment at 850 °C.

$$\frac{1}{2}K_2CO_3(s) + \frac{1}{2}Na_2CO_3(s)Nb_2O_5(s) \rightarrow 2K_{0.5}Na_{0.5}NbO_3(s) + CO_2(g).$$ (1)

A solution of sodium hydroxide and potassium hydroxide was prepared for the Hydrothermal synthesis method. The mixture of which generated a total concentration of 14 M. Niobium (V) oxide was added to this system and stirring for 24 hours. The resulting suspension was transferred to an autoclave and taken to a preheated oven at 210 °C for 24 hours.

The solid product obtained was separated from the liquid by centrifugation, subsequently washed several times with distilled water and dried in an oven. In the case of pechini method, the niobium reactive precursor was synthesized from niobium oxide. A solid-state reaction was made between niobium (V) oxide and potassium hydroxide, at 350 °C, according to the Equation (2). $K_2NbO_3$ niobium precursor, soluble in water was titrated with nitric acid, the reaction of this process is shown in the Equation (3). With the synthesized niobium precursor, and sodium and potassium precursors as carbonates, the resin was formed. For this process, NaOH, KOH and $Nb_2O_5$ were used. First, a suspension of niobium hydroxide in citric acid was formed; the process was carried out at 90 °C for 5 minutes under stirring.

The sodium and potassium precursors were added slowly, until total dissolution was observed. Subsequently, ethylene glycol was slowly added and finally ammonium hydroxide additions were made until the system was basified. After allowing the system to homogenize for a few minutes, the
temperature was increased to 120 °C to allow polymerization and resin formation reactions. The system lost fluidity and turned yellow and then, formation of a black and very viscous resin was observed. After the formation of the resin, where a homogeneous mixture of the precursors was achieved, the system is subjected to heating for 24 hours at 250 °C, where the resin undergoes self-combustion. A spongy system is generated. After mashing a black powder was obtained. In all synthesis methods, Nd (III) was added 5% weight. The temperatures of calcined were selected after performing thermal analysis for each synthesis method.

\[
\text{Nb}_2\text{O}_5 + 6\text{KOH} \rightarrow 2\text{K}_3\text{NbO}_4 + 3\text{H}_2\text{O}, \tag{2}
\]

\[
\text{K}_3\text{NbO}_4 + 3\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{Nb(OH)}_5 + 3\text{KNO}_3. \tag{3}
\]

Thermogravimetry (TG) and differential scanning calorimetry (DSC) techniques using a Netzsch Simultaneous Thermal Analysis system (STA 409 ET), allowed us to determine the reaction sequence of the neodymium doped KNN powders. TG and DSC were realized at an incremental rate of 10 °C/min, starting at room temperature and up to 1200 °C, in an air atmosphere. The structural analysis of KNN:Nd calcined powders was realized via x-ray diffraction, with a scan from θ = 10º to θ = 60º, using a Rigaku diffractometer with CuKα radiation at room temperature. The particle size, the morphology of the particles, and the agglomerate formation of KNN:Nd calcined powders were observed via scanning electron microscopy using a Jeol JSM 5800 LV microscope.

3. Results and discussions

The TG and DSC curves of KNN:Nd powder obtained by a mixture of oxides and pechini methods with a heating rate of 10 °C/min are shown in Figures 1(a) and Figure 1(b), respectively. Weight loss in KNN:Nd powders obtained by mixture of oxides and hydrothermal method was 14%, while, weight loss in KNN:Nd powders obtained by pechini method was 40%. (TG and DSC hydrothermal curves of KNN:Nd are not shown here). The mass loss stages occurred over the approximate temperature ranges of room temperature-200 °C, (3.6 mass% loss), 200 °C to 620 °C, (3.0 mass% loss), and 620 °C to 800 °C (7.2 mass% loss) for the mixture of oxide, room temperature-200 °C (6.5 mass% loss) and 200 °C - 700 °C (39.7 mass% loss) for pechini method.

![Figure 1. Thermogravimetric analysis (TGA and DSC) of Nd-KNN obtained by (a) mixture of oxides; (b) pechini method.](image)

Hydrothermal method presents similar behavior in mass loss to the oxide mixture, but with variation in the temperature ranges. Similar behavior in TG curves was observed by Quintero and Chaudhury in KNN powder obtained by a mixture of oxides and pechini method respectively [13,14]. In all curves
can be noted weight loss prior to 200 °C. These results are attributed to simultaneous losses of H₂O and CO₂. In the case of the mixing of oxides, the presence of water in the carbonate-oxide powder mixture is due to the hygroscopic nature of both carbonates particularly K₂CO₃ as affirmed by Quintero [13]. The second region is at around 700 °C and is related to the formation of the perovskite phase [15]. This result is interesting for physics of materials since it can give hints the calcination temperature for future work in earth rares doped KNN powders.

Based on DSC curves it was possible to determine as a first indication the calcination temperatures to KNN:Nd powders in the function of the synthesis method, being the temperatures of 430 °C, 450 °C, and 700 °C, the adequate temperatures for the formation of the desired phase. It is evident that the incorporation of Nd in KNN decreases the calcination temperature in powders obtained by a mixture of oxides [13]. In state-solid physics, the decrease of calcination temperature is important because reduces the possibility of stoichiometric alterations in synthesis and densification of KNN-based systems.

Figure 2 shows the XRD pattern of KNN:Nd powders obtained by the mixture of oxide, hydrothermal, and pechini methods. Orthorhombic and perovskite phases were detected majority in all the synthesis methods used in this work. Characteristics peaks of the KNN phase can clearly be seen at 2θ = 45 – 47, and 2θ = 51 – 53, which indicate a coexistence of tetragonal and orthorhombic phases of the perovskite structure [16,17]. Peaks corresponding to neodymium oxide were not detected, indicating that it was assimilated into the KNN structure. Nevertheless, it was found a high percentage of secondary phases of K₂CO₃ and Nb₂O₃ in powder obtained by pechini and hydrothermal methods. The XDR pattern also reports many minor peaks which are attributed to the heterogeneous nature due to presence of the starting materials.

We attribute this to the low calcination temperature using in this work for pechini, and hydrothermal synthesis methods. Additionally, the powders obtained by the mixture of oxides exhibit a lower percentage of secondary phases (Nb₂O₃). It is also clear that calcined powder obtained by the mixture of oxide is the most suitable option to be doped because it presents a lower quantity of secondary phases.

![X-ray diffraction pattern of Nd-KNN obtained by mixture of oxides, pechini and hydrothermal methods.](image)

Figure 3 shows the micrographs of Nd-KNN powders obtained by pechini, hydrothermal, and mixture of oxides methods, respectively. The morphology of the particles is different among the three method types as shown in Figure 3. The micrographs of the powders obtained by the mixture of oxides are parallelepipeds and other cubic morphologies, with the formation of the agglomerate. This morphology also was observed by Quintero et al. in powders KNN system [13]. Regarding the micrographs obtained by means of chemical methods (hydrothermal and pechini), it has been observed the formation of many agglomerates being possible to see nanometric particle sizes. At present, this particle size would be very important for the fabrication of multifunctional materials [18].

![Micrographs of Nd-KNN powders obtained by pechini, hydrothermal, and mixture of oxides methods.](image)
Figure 3. Micrographs of Nd-KNN powder calcined to (a) 450 °C; (b) 430 °C; (c) 700 °C obtained by pechini, hydrothermal, and mixture of oxides methods, respectively.

4. Conclusions

KNN:Nd powders were prepared by a mixture of oxide, Hydrothermal, and pechini methods. The parameters studied and analyzed allowed us to define the mixture of oxides as the better option for the calcined powders.

The oxide mixing method allowed obtaining a majorly perovskite phase in powders of KNN:Nd, furthermore powders obtained by pechini and hydrothermal methods showed a lot of secondary phases, and from the micrographs, the three synthesis methods showed the formation of agglomerates with a size range from nanometers to micrometers.

The results obtained in this work allow in solid-state physics to begin the densification process of KNN:Nd for analysis of optical, luminescence and piezoelectric properties in order to find applications as multifunctional materials.

It was found that the incorporation of Nd in KNN decreases the calcination temperature in powders obtained by a mixture of oxides. In state-solid physics, those behavior is important because reduces stoichiometric alterations in synthesis and densification of KNN-based systems due to that potassium and sodium are moderately volatile elements.

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