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Lead-Free Ferroelectric Ceramics with Perovskite Structure

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1. Introduction

Ferroelectric ceramics were discovered in the 1940s in polycrystalline barium titanate (von Hippel et al., 1946; Wul & Goldman, 1945), since then, there has been a continuous succession of new materials and technology developments that have led to a significant number of industrial and commercial applications.

Structurally speaking there are four types of ferroelectric ceramics: (1) perovskites, (2) the tungsten-bronze group, (3) pyrochlores and (4) the bismuth layer-structure group. Of these, the perovskites (ABO_3) are by far the most important category. The families with composition $BaTiO_3$, $PbZr_{1-x}Ti_xO_3$ (PZT), PZT:La (PLZT), $PbTiO_3$ (PT), $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $(K_{0.5}Na_{0.5})NbO_3$ (KNN) represents most of the ferroelectric ceramics manufactured in the world (Haertling, 1999).

In this chapter the structure of calcium titanium oxide ($CaTiO_3$), the ferroelectrics ceramics $BaTiO_3$, $Na_{0.5}Bi_{0.5}TiO_3$ (NBT), $K_{0.5}Bi_{0.5}TiO_3$ (KBT) are described as well the concept of hysteresis loop, ferroelectric domains and why lead free materials are now in the top of the interest in ferroelectric and piezoelectric materials. The aim of this chapter is to present results of the synthesis, characterization and piezoelectric properties of two lead free piezoelectric compounds: $K_{0.5}Na_{0.5}NbO_3$ and $(K_{0.48}Na_{0.52})_{0.96}Li_{0.04}Nb_{0.85}Ta_{0.15}O_3$.

1.1 Perovskite structure

The mineral perovskite is calcium titanate, with chemical formula $CaTiO_3$, its ideal structure has space group $Pm-3m$. Most of the commercially important ferroelectric materials have perovskite related crystal structure. The family of the perovskite oxides has generic composition ABO_3 , where A is 12 fold coordinated with respect to oxygen (Fig. 1c) and B is octahedrally coordinated by oxygen (Fig. 1a and 1b). The A site is at the corner of the cube, the B site is at the center, and there is an oxygen at the middle of each face. Alternatively, the structure could be represented with the B site at the corner, the A site at the center and O ions at the midpoint of each edge, respectively.

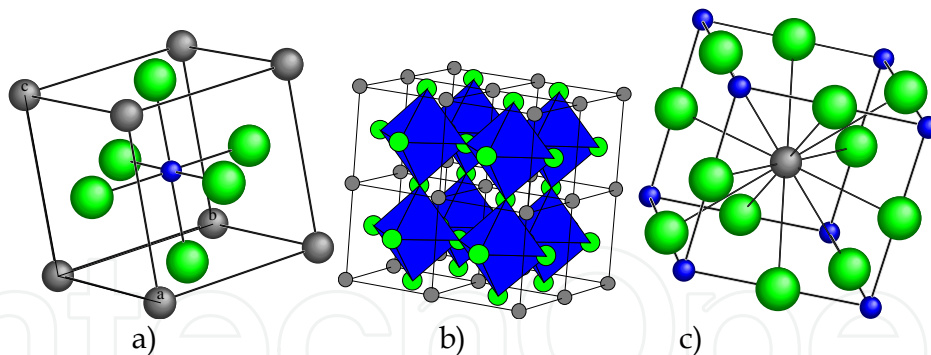


Fig. 1. The unit cell of the ABO_3 ideal cubic perovskite.

The perovskite type structure is enormously tolerant to variations in composition and distortions due to its ability to adapt a mismatch between the equilibrium A-O and B-O bond lengths, allowing the existence of a large number and variety of stoichiometric compounds. Those distortions, for instance tetragonal (Fig. 2), orthorhombic, rhombohedral and monoclinic, give rise to changes in the crystal symmetry, and one or more cations shift from high-symmetry positions in the lattice, producing ferroelectric or antiferroelectric behavior. In other words, the center of positive and negative charge within the unit cell is no longer coincident, which is the origin of the spontaneous polarization. However, in a ferroelectric material the spontaneous polarization is necessary but not sufficient, since it also requires the reorientation of the polarization by an electric field.

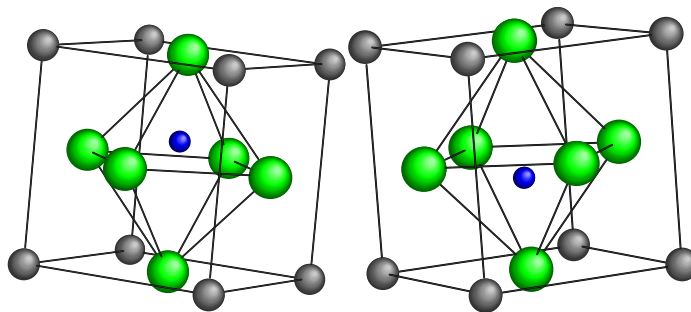


Fig. 2. Tetragonal ferroelectric distortion of the perovskite structure, illustrating two polarization states.

2. Some characteristics of ferroelectric materials

2.1 Hysteresis loop: the fingerprint of ferroelectricity

As mentioned-above, a distinctive feature of ferroelectricity is the reorientation of the polarization by an electric field. Thus, the observation of some evidence of switching is fundamental to establish the ferroelectricity. The experimental evidence is given by the electric hysteresis loop; actually, the term ferroelectric was coined in analogy with the similar magnetic loop $M-H$ (magnetization versus magnetic field) obtained from a ferromagnetic material, with the obvious exception that iron is not necessarily present in a ferroelectric. In its standard form, the $P-E$ (polarization versus electric field) hysteresis loop is symmetric and the remnant polarization and coercive field are straightforwardly determined. The remnant polarization is the saturation polarization at zero field, and the coercive field, if the complete loop is determined, is the field value at zero polarization. It is

crucial to be aware of the potential artifacts associated with the measurement of P - E loops (Scott, 2008). These loops must show saturation and have a concave region in P versus E for being considered satisfactory.

2.2 Ferroelectric domains

The volume regions of the material with the same polarization orientation are referred to as ferroelectric domains. When the sample is under zero field and strain-free conditions, all the domain states have the same energy; but if an electric field is applied, the free energy of the system is lowered by aligning the polarization along the field. Thus, large applied electric fields can permanently reorient the polarization between the allowed domain states, which are restricted by crystallography. As a result, even ceramics, constituted by polycrystals randomly oriented can be electrically poled to produce net piezoelectric coefficients. Much of the importance of ferroelectric materials is due to their properties, leading to a wide range of applications. Among these applications are high dielectric constant capacitors, piezoelectric sonar, ultrasonic transducers, ultrasonic motors, actuators and pyroelectric detectors. Special mention is reserved for the ferroelectric memories, field effect and cooling devices.

2.3 A way to improve the electromechanical properties of ferroelectric ceramics: morphotropic phase boundary (MPB) and polymorphic phase transition (PPT)

In analogy to the characteristics of the PZT ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$) phase diagram, which presents a MPB between tetragonal and trigonal phases (Jaffe, 1971) (which means literally *the boundary between two forms*), where the electromechanical properties exhibit an outstanding behavior, a lot of work has been conducted in different ferroelectric ceramic systems in order to form MPBs. The renaissance of the issue was initiated with the finding of Noheda of a monoclinic phase which acts as a bridge between the trigonal and tetragonal phases in the PZT system (Noheda et al., 1999). Generally speaking, the enhancement of electromechanical properties is due to the larger number of possible polarizable directions in the monoclinic phase. Furthermore, enhancement of electromechanical properties has been observed in PPTs, they are temperature-dependent phase transitions, in contrast to the MPB which is composition-dependent and almost vertical. At the PPTs the electromechanical properties are improved. In general, PPTs are above room temperature; therefore, some research has the aim to modify the materials by the addition of dopants in order to shift PPT's to room temperature. At the PPT's, the increased polarizability associated with the transition leads to increased dielectric and piezoelectric properties (Guo et al., 2004).

2.4 The environmental issue: lead-free based materials

The most widely used ferroelectric ceramics are those based on the PbTiO_3 - PbZrO_3 solid solution, generically called PZT. The PZT is composed of about 60 wt.% of lead, which rises ecological concerns; thus, some countries have legislated to replace this material by lead-free ceramics (European commission, 2008) since lead is a toxic element that affects the human health and the environment. Consequently, in recent years diverse systems are being investigated, among them, barium titanate (Yoon et al., 2007), bismuth-alkaline metal titanates and niobates (Hao et al., 2005; Jing et al. 2003; Ma et al., 2006), especially the $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ solid solution abbreviated KNN (Du et al., 2006; Saito et al., 2004).

3. Important lead-free ferroelectric ceramics with perovskite structure

3.1 BaTiO₃

The first oxide with perovskite-type structure exhibiting ferroelectric behavior was BaTiO₃ (BTO) (von Hippel et al., 1946; Wul & Goldman, 1945). It played a major role in demonstrating that ferroelectric ceramics had piezoelectric response through the poling process. At these days, the prevailing opinion was that ceramics could not be piezoelectrically active, because the randomly oriented dipoles would, on the whole, cancel out each other. This was proved not to be true for ferroelectrics ceramics, in which the dipoles could be permanently aligned or reoriented with an electric field. One of the fundamental issues in the understanding of ferroelectricity and piezoelectricity in ceramics was the discovery of the unusually high dielectric constant of BTO (Jaffe, 1958). Although BTO does not exhibit high piezoelectric constants, it has high relative permittivity. For this reason, BTO is the most widely used material in capacitors. Billions of BTO condensers are still made annually, at a cost of less than one cent per capacitor (Scott, 2007). However, BTO has an important drawback, its relatively low Curie temperature (~120 °C) (Merz, 1949). While advances in order to improve the piezoelectric properties and to increase the Curie temperature are concurrently underway, they have had little success. The observation of large and colossal permittivity (10⁴-10⁶) (West, 2006, Yu et al., 2004) in the BTO, has consolidate it as a material for capacitors. For instance, (Ba_{0.92}Ca_{0.08})(Ti_{0.95}Zr_{0.05})O₃ has high piezoelectric coefficient $d_{33} = 365$ pC/N and high planar electromechanical factor $k_p = 48.5\%$; nevertheless, the Curie temperature diminishes to ~ 110°C. On the other hand, solid solutions of BTO with ferroelectrics of higher Curie temperature have been studied in order to increase the T_C of the system; unfortunately, although the T_C increases, the effects on the dielectric properties are undesirable. In the solid solution 0.80BTO-0.20(K_{0.5}Bi_{0.5})TiO₃ the T_C reaches a value around 240°C, but the relative permittivity at room temperature and at the T_C , has lower values than the pure BTO (Haertling, 1999; Takenaka, 2008). The colossal permittivity observed in BTO, is attributed to an interfacial polarization and is achieved in nanomaterials by the activation of a high number of carriers and their trapping at the interfaces (Guillemet-Fritsch et al., 2008).

3.2 Na_{0.5}Bi_{0.5}TiO₃ and K_{0.5}Bi_{0.5}TiO₃

Bismuth sodium titanate Na_{0.5}Bi_{0.5}TiO₃ (BNT), was discovered 50 years ago (Smolenskii et al., 1961), it shows strong ferroelectric properties with a significantly remnant polarization of 38 μC/cm², and a Curie temperature of 320°C. However, this ceramic has disadvantages such as high conductivity and large coercive field (~73 kV/cm), which cause problems in the poling process. Data on exact piezoelectric properties of the BNT ceramic are insufficient due to the as-mentioned difficulties at the poling process. On the other hand, the BNT ceramic needs a high sintering temperature (>1200°C) to obtain dense samples. It is thought that the vaporization of Bi³⁺ ions occurred during the sintering process at temperatures higher than 1200°C, resulting in the poor poling treatments because of the high conductivity. As in the case of BTO, there have been efforts to improve the piezoelectric response of NBT by the substitution of one or more of its ions. Different authors have studied solid solutions of NBT with BTO, K_{0.5}Bi_{0.5}TiO₃ (Takenaka et al., 2008) and KNN (Nagata et al., 2003; Yao et al., 2009; Zhang 2008). All these attempts try to exploit the morphotropic or polymorphic phase boundaries, where it is known that an improvement of dielectric and piezoelectric properties exist. In addition, some rare earths such as La, Y, Ce

and some transition metals such as Co, Nb and Mn (Li et al., 2004; Nagata & Takenaka, 2001; Takenaka et al., 1990; Zhou et al., 2009) have been used. Some results are promising, but still more work is needed to improve the dielectric and piezoelectric properties simultaneously. Just as the NBT, the KBT was discovered 50 years ago (Smolenskii et al., 1961). KBT has tetragonal symmetry at room temperature and a relatively high T_C of 380°C (Bührer, 1962). KBT has a better dielectric response and similar piezoelectric response than NBT (Lin et al., 2006). In view of the fact that low density materials are difficult to pole, one of the main challenges of KNT is to obtain enough dense ceramics.

3.3 $K_{0.5}Nb_{0.5}O_3$ (KNN)

The pioneering work on $KNbO_3$ - $NaNbO_3$ solid solution was carried out in the mid-50s of last century (Shirane et al., 1954). KNN is a specific composition on a complete solid solution of antiferroelectric $NaNbO_3$ and ferroelectric $KNbO_3$, namely, 50:50. This composition is close to the MPB between two orthorhombic phases, resembling the PZT system. Undoubtedly, the KNN and the derived compounds are the most promising lead-free ferroelectric materials demonstrated by the results published some years ago (Saito et al., 2004). The major contribution of this work was to show the modification of the PPT, present in KNN (Shirane et al., 1954), by the addition of Li^{+1} and Ta^{+5} . Since then, this system has been caused a lot of interest and many studies have been done on this field. In fact, our research deals with this material which is presented in section 6. The main obstacles in the processing of KNN are the synthesis and sintering steps that will be treated in next two sections. These difficulties occur, since the alkaline elements undergo sublimation at the high temperature required to achieve the adequate densification, which changes the initial stoichiometry considerably. This problem has been addressed through different methods, one of these involves densification improvement by the addition of some oxides such as CuO , MnO_2 , CeO_2 (Gao et al., 2009; Yang et al., 2010; Yin et al., 2010). According to these researches, it is believed that these compounds form a liquid phase at low temperature, thus promoting densification. Another approach involves addition of A and B elements into the ABO_3 structure of the KNN solid solution. In the A site, several cations can be added, e. g. Li^{+} , Ba^{2+} , La^{3+} , Bi^{3+} , whereas for the B site it is possible to introduce Ti^{4+} , Sb^{5+} or Ta^{5+} (Ahn et al., 2009; Hagh et al., 2009; Jiang et al., 2009). The ion substitution can induce phase transformation and consequently a better performance of materials. A third way to improve densification is by reducing the particle size of the synthesized powders; however, since the conventional ceramic method does not achieve considerable reduction of particle size, then, the sol-gel, Pechini and hydrothermal methods have been used. Furthermore, the chemical homogeneity of the KNN compound with Li^{+1} and Ta^{+5} dopants synthesized by the conventional solid state reaction route has revealed an inhomogeneous distribution of Nb^{5+} , Ta^{5+} , K^{+} and Na^{+} cations, which leads to a considerable detriment of the piezoelectric properties, being one reason for the discrepancy among the data reported by several authors for the same or similar composition (Y. Wang et al., 2007). All these issues are addressed in the subsequent sections, which are the central part of our contribution.

4. Synthesis of KNN and co-doped KNN

This section will be dedicated to briefly review some methods used for the synthesis of KNN and related compositions. The ceramic method is discussed first, and then the chemical methods used in an effort to obtain chemical homogeneous powders. These

include the sol-gel, Pechini and hydrothermal methods. They have produced some interesting results, but there are still some issues that must have the attention of the researchers.

4.1 Conventional ceramic method

For the synthesis of KNN lead-free ferroelectrics, the initial point is the ceramic method (CM), this is the simplest method for the production of ceramic materials. The conventional method is well-known and extensively used, and was the first method reported for the synthesis of KNN (Egerton & Dillon, 1959; Jaeger & Egerton, 1962; Shirane et al., 1954), since it is simple and low cost. Basically, it consists of mixing carbonates and oxide powders of the desired elements. The process is carried out in a conventional ball mill, or in mills that supply more energy as the attrition or planetary ball mills (high energy mills), with the purpose to obtain a homogeneous mixture of the powders. The process is performed in liquid media for a better mixing; the most popular liquids are absolute ethanol and acetone, the former being cheaper and with low toxicity. During grinding, the powders undergo grain size reduction, and become amorphous if high energy milling is used. Once the mixture is ready, this is calcined at an adequate temperature, which depends on composition. In the case of the lead-free ceramics based in KNN, these temperatures are between 800 and 950° C. The heat treatment should be carried out for several hours. Finally, the crystalline powders are grinded again to reduce the particle size for their subsequent pressing and sintering. The advantages of this method are the inexpensive equipment and low cost of reagents. On the other hand, high temperature calcinations and long time of the heat treatments usually results in considerable loss of alkaline elements; furthermore, two steps of grinding are also needed.

4.2 The sol-gel method

Taking into account the characteristics of the powders obtained by means of the conventional method, the so-called chemical routes have been investigated for the synthesis of lead-free ferroelectric ceramic powders. Among them, the sol-gel method (Shiratori et al., 2005; Chowdhury et al., 2010) has been reported to produce KNN nanometric powders. The technique consists of mixing metal-organic compounds (mainly alkoxides) in an organic solvent, the subsequent addition of water generates two reactions, hydrolysis and polymerization, producing the gel which is dried and calcined for obtaining crystalline ceramics. The method has some advantages, such as the nanometric and chemical homogeneity of the powders and the low crystallization temperature (Shiratori et al., 2005). The disadvantages of this procedure are the utilization of metal-organic chemicals, which are expensive. Besides, they need of a strict control of the conditions for the reaction since they generally possess a different hydrolysis rate and must be handled under free moisture atmosphere for avoiding the rapid decomposition of alkoxides. The addition of organic compounds is necessary to improve the dispersion and to obtain fine powders.

4.3 Pechini method

One of the chemical methods that have attracted attention in the synthesis of ceramic materials is the Pechini method. The process implies the formation of a polymeric resin between an organic acid and an alcohol (generally ethylene-glycol). The precursor solution should be heated to evaporate the solvent and to promote the formation of the resin. Once

the resin is obtained, it is crushed and calcined at different temperatures to observe the crystallization evolution. As in the case of sol-gel, the Pechini route also uses niobium moisture sensitive reagents, so that the problems are similar in both methods. Despite these drawbacks, the very fine powders obtained are promising to produce dense ceramics, but there are not reports on the piezoelectric properties of ceramics synthesized by this method, only the synthesis of KNN powders is reported (Chowdhury et al., 2009). In this study the authors used an ammonium niobate oxalate hydrate instead the alkoxide. With this approach nanometric powders were synthesized.

4.4 Hydrothermal method

With the aim to obtain KNN ceramic powders at low temperature and to avoid the loss of sodium and potassium, the hydrothermal method have been used recently (Sun et al., 2007; Maeda et al., 2010; N. Liu, et al., 2009). This method involves placing the reagents into a pressurized reactor or autoclave, the reaction is carried out at low temperature ($< 300^{\circ}\text{C}$) where the pressure generated depends on the temperature at which the reactor is heated. The studies reported until now suggest a processing time of 6-24 hours at the desired temperature. Nevertheless, these studies also indicate that the resultant products are composed of two phases, a sodium rich phase and another with greater quantity of potassium. The reagents that have been used in these experiments are potassium and sodium hydroxides, with a KOH/NaOH molar ratio between 3/1 and 4/1, and the total concentration around 6 M of hydroxides. Alternatively, the synthesis of KNN has also been reported by means of the microwave-hydrothermal method at 160°C for 7 hours with an alkalinity of 6 M (Zhou et al., 2010) the authors underline that improved piezoelectric constant d_{33} was obtained (126 pC/N), compared with other reports (80 and 90 pC/N), but important parameters like k_p and $\tan \delta$ were not reported.

As a final comment for this synthesis section, it is important to mention that the powder characteristics obtained by any synthesis method may aid the sintering stage, therefore the powders should be chemically pure i.e. without secondary phases, the calcination temperature (except in hydrothermal synthesis) must be as low as possible to avoid the considerable loss of alkaline compounds, and the nanometric powders are more suitable since these contribute to an additional driving force for sintering.

5. Sintering of KNN and related compositions

Just like the synthesis stage, the sintering process in the KNN lead-free ferroelectric ceramics is a crucial step to produce materials with high electromechanical properties. It has been found that a narrow sintering range exists (Y. Wang et al., 2007) where the materials experience considerable changes in the grain size, density, appearance of secondary phases, liquid phase, and then the piezoelectric and ferroelectric properties change as well. In the text below, are discussed some of the sintering methods used for the conformation of KNN ceramics. First, the conventional sintering (CS), then the hot pressing (HP) and finally the spark plasma sintering (SPS) are going to be described.

5.1 Conventional sintering

The method consists of pressing the powders in a uniaxial press or through cold isostatic pressing. Then, the green pellets are heat treated in a high temperature furnace. The

sintering temperature depends upon the composition for pure KNN samples the temperature is set between 1020 and 1120°C. The method is simple and economic comparing with HP or SPS which will be described in the next sections. Most studies about KNN and related compositions use conventional sintering (Chang et al., 2007; Egerton & Dillon, 1959; Hao et al., 2009; Park et al., 2007; Saito & Takao, 2006; Y. Wang et al., 2007; Zuo et al., 2007), and just some papers report lead-free piezoceramics sintered by HP or SPS. In conventional sintering two steps are commonly used during the treatment, first the binder burn out at 400-500°C, and then the sintering at high temperature proceeds. This high temperature stage is performed from 1 to ~ 12 hours. For instance sintering a Li doped KNN composition gave optimal results when the time was set at 8 h (Wang et al., 2010), but it is common to use 2 h. It has been observed the influence of the heating rate over the properties, these rates are close to 4-5°C/min (Du et al., 2006). The fundamental objective to investigate these issues is to determine the effects on the grain growth and hence on the ferroelectric and piezoelectric properties. Most of the investigations try to search for sintering conditions that avoid or reduce at least, the loss of alkaline elements. Combining the ceramic method for the synthesis and the conventional sintering results in low density materials. For this reason, the HP and the SPS methods are being explored, mainly the later, for the improvement of density and the correspondingly enhancement in the electromechanical performance of ceramics.

5.2 Hot pressing

This method has the advantage that pressure and temperature are simultaneously applied, being able to obtain a better densification. Nevertheless, the sintering temperatures are as high as in the conventional sintering. Furthermore, few data on electromechanical properties have been reported by means of this technique (Jaeger & Egerton, 1962). The piezoelectric properties have been improved considerably using this method, compared as those sintered conventionally.

5.3 Spark plasma sintering

The SPS technique is not new in the field of sintering, but its use was not exploited for sintering lead-free piezoelectric ceramics. Very recently it was applied for sintering KNN (K. Wang et al., 2008), and related compositions (Abe et al., 2007; Shen et al., 2010). The advantage of the SPS over CS or HP is that it requires lower temperatures and shorter times for producing ceramics with densities close to the theoretical values. Commonly, heating rates are around 100°C/min, so in few minutes the sintering temperature is achieved; as a result the sintering time is reduced by several hours. This is possible due to the heating mechanism. In this method, a very high electric current is passed through the sample and pressure is applied simultaneously, and liquid phase is generated rapidly which assist the densification, but for more details the reader is encouraged to revise some specialized publications on the subject (Hungria et al., 2009; Tokita, 1993). This sintering method allows reducing the loss of alkaline elements because of the low sintering temperature and short holding time; nevertheless, additional heat treatment is required to eliminate oxygen vacancies (Abe et al., 2007; Wang et al., 2007). In Fig. 3 the SEM images of KNLNT sintered samples by CS and SPS are shown (López-Juárez et al., 2011b), it is clearly observed the difference in densification (porosity). The difference in densification level affects directly the piezoelectric and dielectric properties.

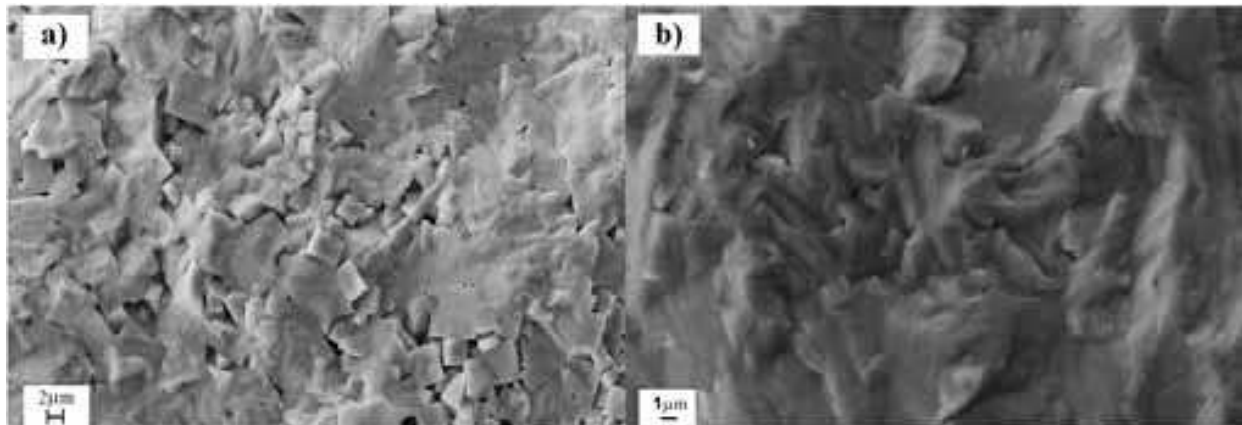


Fig. 3. SEM images of fractured samples sintered by: a) CS at 1200 °C and b) SPS at 900 °C.

6. Synthesis of $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ and $(\text{K}_{0.48}\text{Na}_{0.52})_{0.96}\text{Li}_{0.04}\text{Nb}_{0.85}\text{Ta}_{0.15}\text{O}_3$ by spray drying

As already mentioned, the key problem with the synthesis of KNN is there are no stable niobium chemical reagents to use in sol-gel, Pechini or whatever the method employed. The only stable niobium compound is the oxide (Nb_2O_5). Then, the synthesis of KNN based ceramics has been reviewed in previous sections, emphasizing the chemical methods used until now. In this work a new approach is described as is reported elsewhere (López et al., 2010, 2011b). The spray drying method was employed to synthesize chemically homogeneous powders. For this purpose the chelation of niobium and/or tantalum is necessary. In our preparation method it was possible to synthesize lead-free ferroelectric ceramics stabilizing niobium with an organic acid, by previously dissolving Nb_2O_5 and precipitating the corresponding hydrated oxide (López et al., 2010), this is also applicable to Ta_2O_5 because it behaves in a similar manner. Actually, tantalum is introduced into the KNN solid solution structure. The $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ and $(\text{K}_{0.48}\text{Na}_{0.52})_{0.96}\text{Li}_{0.04}\text{Nb}_{0.85}\text{Ta}_{0.15}\text{O}_3$ compositions were synthesized. It was probed that the crystallization can be set at 800°C with a heating time of 1 hour. Finally, the microwave-hydrothermal method was tested for KNN synthesis, and interesting results are going to be released.

6.1 Characterization of the synthesized powders

In Fig. 4 the X-Ray diffraction patterns of the two compositions are shown. The most interesting feature is that the powders are chemically pure when calcined at 800°C for 1 h, irrespective of the composition. It is observed that the as sprayed powders are amorphous in both compositions. For the KNN powders, the subsequent heat treatment at 600°C generates the formation of two phases; the $\text{K}_6\text{Nb}_{10}\text{O}_{30}$ phase (JCPDS 70-5051) with tetragonal structure and the KNN perovskite phase with orthorhombic lattice.

When powders were calcined at 700°C the amount of tetragonal phase diminishes considerably, this fact is noticed by the reduction in the Bragg reflections corresponding to the tetragonal phase, and at 750°C only perovskite phase is observed. The calcination temperature and time are lowered compared with those required in the synthesis by the ceramic method. For the KNLNT composition (Fig. 4b), once the powders were thermally treated at 600°C several Bragg reflections appeared, corresponding to the tetragonal

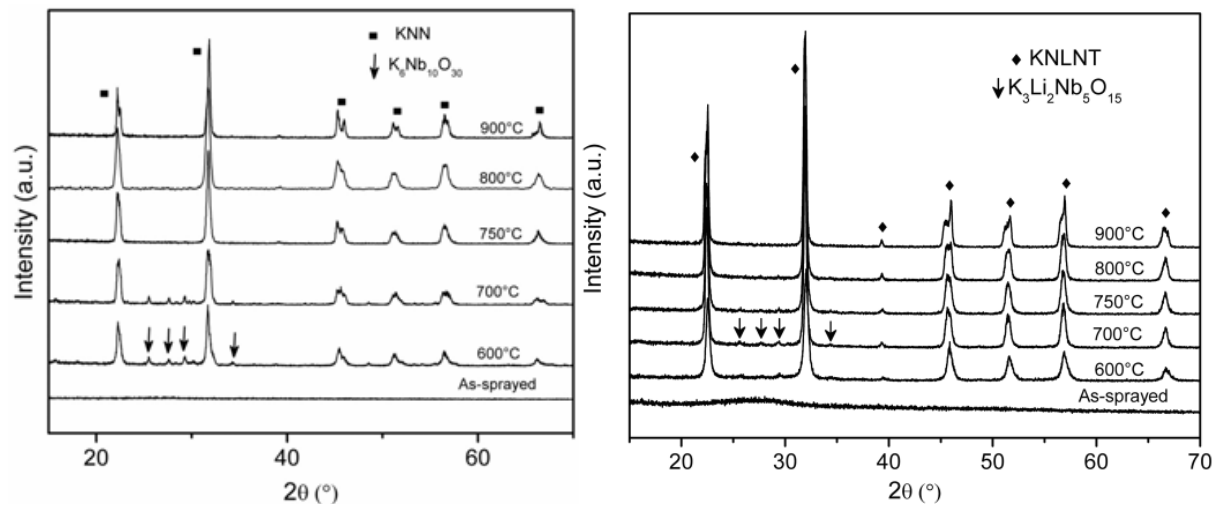


Fig. 4. a) KNN powders calcined at different temperatures (Left), b) KNLNT powders calcined at different temperatures (Right) (López et al., 2010).

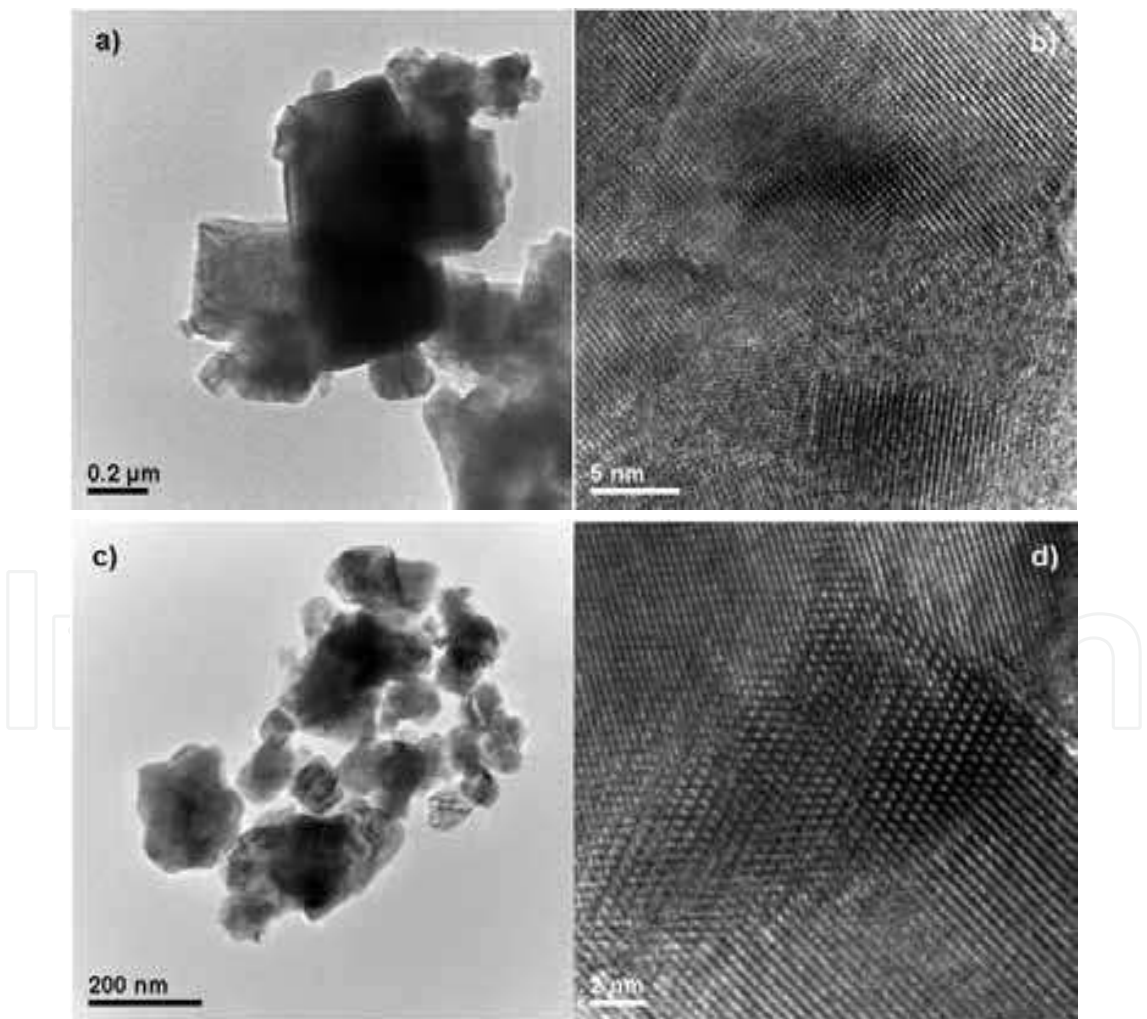


Fig. 5. a) BF and b) HR images of KNN, c) BF and d) HR pictures of KNLNT powders calcined at 800°C for 1 h.

secondary phase $K_3Li_2Nb_5O_{15}$ (JCPDS-ICDD 52-0157) and those expected for KNLNT phase were observed. The secondary phase diminish for the samples calcined at 750°C and at 800°C only reflections of the KNLNT phase remains. The TEM images of the calcined powders reveal the fine particle size with average grains $< 0.3 \mu m$ (Fig. 5). In Fig. 5a the bright field and 5b the high resolution images of KNN powders are shown. The typical cubic shape of KNN is clearly seen (Jenko et al., 2005). The KNLNT crystalline powders are shown in Figs. 5c and 5d, a bright field (BF) image and the corresponding high resolution (HR) picture are observed, where it is shown that the addition of tantalum has inhibited the grain growth, as reported before (Saito & Takao, 2006) compared with KNN. In the high resolution image the coalescence between two nanocrystals is depicted with the crystalline planes well developed. The average grain size for KNN powders was 281 nm and 100 nm for KNLNT, the measurements were done over several bright field TEM images using the ImageJ software. The particle size achieved by the spray drying route is comparable with those results of sol-gel and Pechini method. The small grains contain high surface energy that is one of the driving forces for sintering. It is known that in addition to the surface energy, the pressure and chemical reactions would aid the sintering (Rahaman, 2006), the later being uncommon for this purpose.

The combination of pressure and heating at the same time in hot-pressing or spark plasma sintering, does not require necessarily very small particles in order to obtain high density materials, but for conventional sintering it is desirable to synthesize finer particles to get high densities in bulk ceramics.

6.2 Sintering, piezoelectric and ferroelectric properties of lead-free ceramics

The synthesis is only the first step in the processing of ferroelectric ceramics. Pressing and sintering are another two important issues for completing the whole process. Then, in the following paragraphs the sintering and the properties of the prepared ceramics are presented.

6.2.1 Sintering of KNN powders

The consolidation and sintering of ferroelectrics ceramics with KNN composition is described in our previous publication (López et al., 2011a). For a sort of clarity, here we are giving some more details. The calcined powders at 800°C for 1 h were pressed in a uniaxial press at 443 MPa. Then the pressed samples were placed into a high temperature furnace and sintered for 2 hours. The heating rate was set at 7°C/min, the sintering temperature was established at 1060-1120°C, that is the ideal sintering treatment for which the highest piezoelectric properties were measured. The density was measured by the Archimedes method in distilled water.

In Fig. 6 the images of KNN sintered samples are shown. Evidently, with increasing of the sintering temperature the grain size increases. But, first the density increases when passing from 1060°C to 1080°C, and then decreases at 1100 and 1120°C, this coincides with the SEM images, where considerable pores are seen in the sample sintered at 1060°C and diminished at 1080°C (Fig. 7b). The higher density was that of the sample sintered at 1080°C, 4.33 g/cm³ (96% of theoretical value, 4.51g/cm³ being the reference value). The low density of the samples sintered at 1100 and 1120°C are due to the formation of liquid phase and the considerable volatilization of alkaline elements (Jenko et al., 2005; López et al., 2011a; K. Wang et al., 2010).

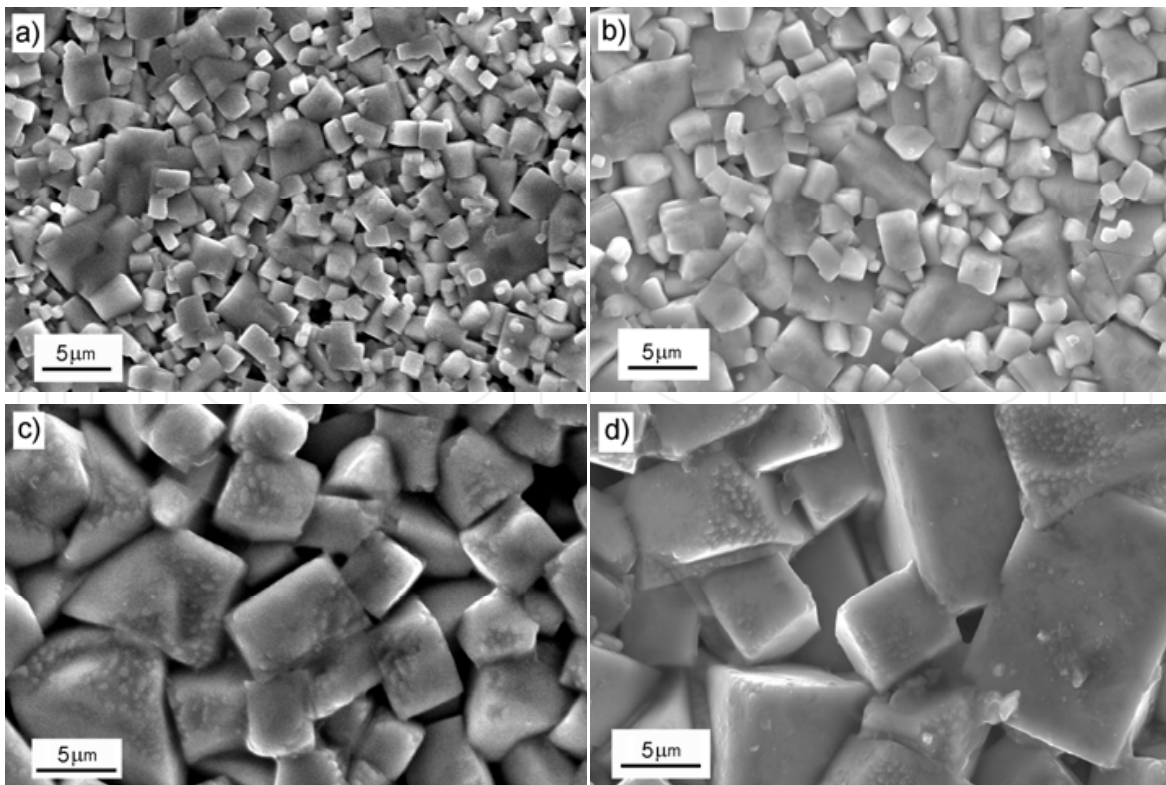


Fig. 6. SEM images of KNN sintered samples at: a) 1060, b) 1080, c) 1100 and d) 1120°C for 2 h (López et al., 2011a).

6.2.2 Piezoelectric, dielectric and ferroelectric properties of KNN

For the piezoelectric properties evaluation, the measurements were done on the poled samples, also the dielectric constant and losses were acquired, the d_{31} and k_p parameters were calculated with modeling the impedance profile as reported elsewhere (Alemany et al., 1995; Pardo et al., 2010). The d_{33} piezoelectric constant was measured with a d_{33} -meter, this parameter was measured for the sample with better k_p and d_{31} . The ferroelectric loops were obtained in a Radiant workstation at room temperature. The dielectric constant and dielectric losses are shown in Fig. 7, the T_{O-T} and T_C are clearly observed, the T_{O-T} is close to 200°C as reported in several works (Du et al., 2006; Egerton & Dillon, 1959). The Curie temperature also agrees well with that reported previously which is near to 420°C (Ringgaard & Wurlitzer, 2005; Singh et al., 2001). The dielectric constant and dielectric losses are improved when the sintering temperature is 1060 and 1080°C, but at 1100 and 1120°C the dielectric constant diminishes and $\tan \delta$ increases, this is directly related with density that depends on the liquid phase formation and vacancies generated when potassium and sodium are lost.

The piezoelectric properties are also related with the remnant polarization (P_r) and coercive field (E_C). These are extracted from the hysteresis loops shown in Fig. 8. The P_r and E_C are improved for the sample sintered at 1080°C and are degraded for the sample sintered at 1120°C where the ferroelectric loop is rounded; this behavior is typical of a conduction process related to high concentration of vacancies (Chen et al., 2007; Kizaki et al., 2007). If the phase diagram is invoked, 1120°C is close to the melting point of the KNN composition (~1140°C) then it is obvious that high volatilization of alkaline elements takes place,

generating also oxygen vacancies for electro-neutrality within the crystals. The ferroelectric properties are also summarized in table 1. The existence of vacancies is common in KNN lead-free ferroelectric ceramics after being sintered at high temperature. The measurement of leaking current has been used for the indirect determination of vacancies. The higher the electrical conduction the higher the concentration of vacancies (Kizaki et al., 2007). According to the authors knowledge, it has never been reported the observation of vacancies by HR-TEM in KNN lead-free ferroelectrics. In Fig. 9 the bright field and high resolution images of the KNN sintered sample at 1080°C are shown, this sample was mechanically polished with SiC paper following with alumina powder with 50 nm grain size and finally ion-milled.

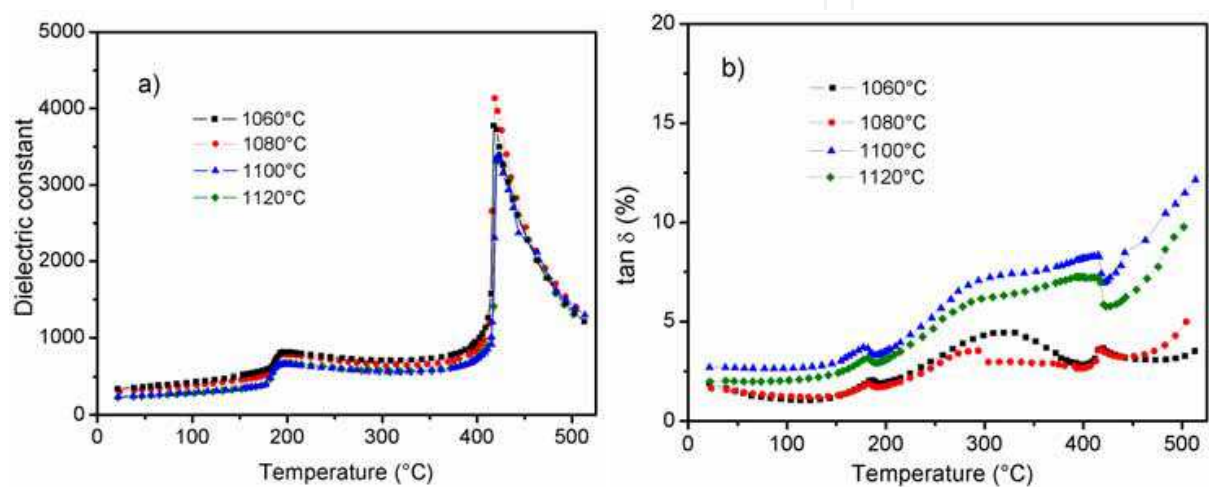


Fig. 7. a) Dielectric constant and b) $\tan \delta$ for KNN sintered pellets at 100 kHz (López et al., 2011a).

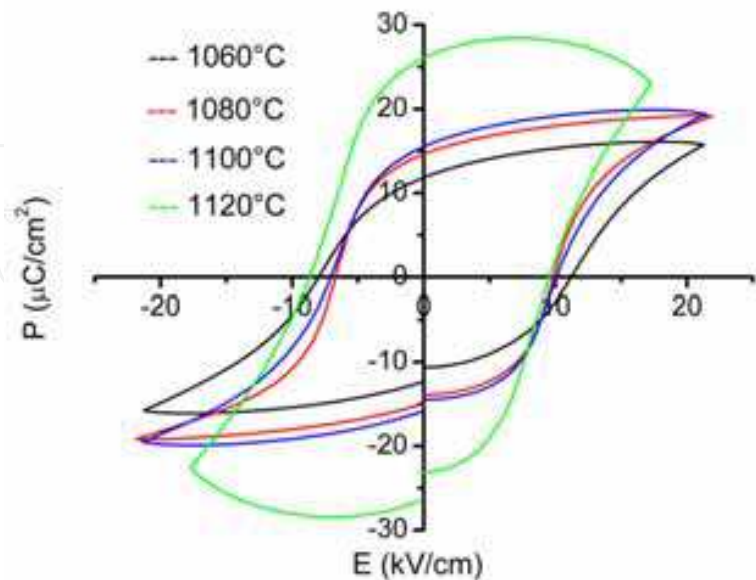


Fig. 8. Ferroelectric loops of KNN ceramics.

In the high resolution image the atomic columns are observed, and some vacancies are highlighted with arrows that are seen as unfilled gaps. The image was taken in the [111] direction of the orthorhombic lattice, the typical hexagonal geometry of atomic columns is clearly distinguished.

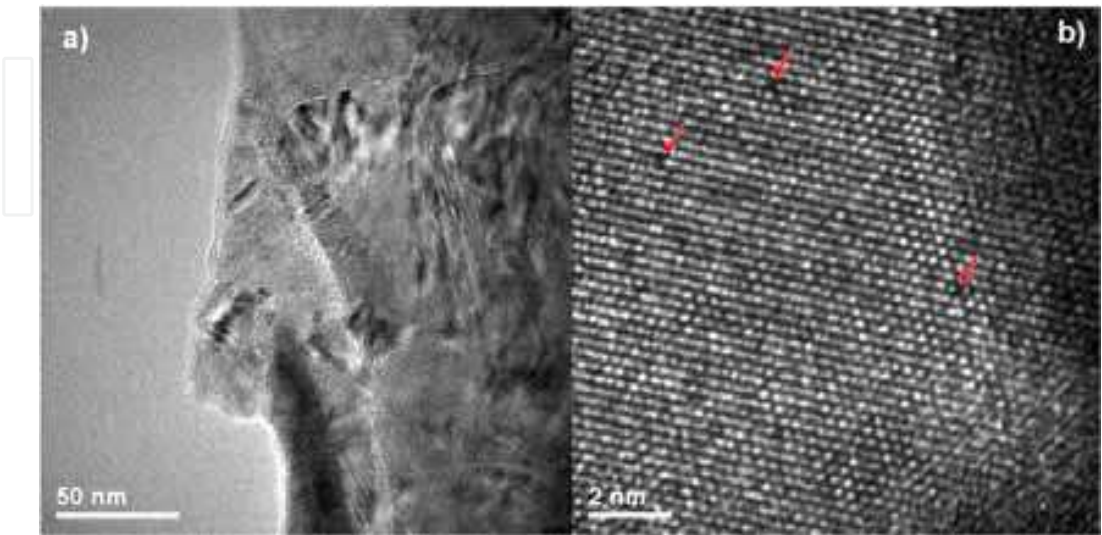


Fig. 9. TEM images of KNN sintered at 1080°C, a) BF and b) HR.

The piezoelectric properties obtained for the sintered samples are summarized in table 1. As was stated above, the best properties are those for the sintered pellet at 1080°C. In table 2, the properties of KNN reported for several authors are shown. It can be seen that the properties of the ceramics processed by spray drying and conventionally sintered are comparable with those previously reported.

Parameter	Sintering temperature (°C)			
	1060	1080	1100	1120
k_p	0.33	0.36	0.23	0.20
$-d_{31}$ (pC/N)	29.6	30	20.9	19.1
$\tan \delta$ (%) (100 kHz)	1.9	1.6	2.7	2
T_c (°C)	418	419	423	423
$2P_r$ (μC/cm ²)	23.2	29	30.57	51
$2E_c$ (kV/cm)	19.1	16.5	17.23	18.1
S_{11}^E (10 ⁻¹² m ² N ⁻¹)	11.082	9.131	9.949	12.04
S_{12}^E (10 ⁻¹² m ² N ⁻¹)	- 2.807	-2.171	-3.008	-3.058
ρ (gr/cm ³)	4.27	4.33	4.28	4.17

Table 1. Piezoelectric and ferroelectric properties of KNN.

k_p	d_{33} (pC/N)	$-d_{31}$ (pC/N)	ϵ_r	ρ (g/cm ³)	$\tan \delta$ (%)	T_C (°C)	Reference
0.36	80	32	290(100 kHz)	4.24	2(100 kHz)	---	Egerton & Dillon, 1959
0.45	160	49	420(100 kHz)	---	1.4(100 kHz)	---	Jaeger & Egerton, 1962
0.32	107	---	264(1 kHz)	4.09	---	---	Maeda et al., 2010
0.40	120	---	500(1 kHz)	4.4	---	400	Du et al., 2006
0.39	70 – 90	45	400(1 kHz)	4.28	2.5 (1 kHz)	390	Ringgaard & Wurlitzer, 2005
---	---	---	----	---	1.3 (10 kHz)	395	Singh et al., 2001
0.34	---	46.2	453(1 kHz)	---	35(1 kHz)	402	L. Liu et al., 2009
0.36	117 ¹	30	309(100 kHz)	4.33	1.6(100 kHz)	419	López et al., 2011a

Table 2. Piezoelectric and dielectric properties of $K_{0.5}Na_{0.5}NbO_3$ ceramics reported by several authors.

It is obvious the wide range of values of the piezoelectric properties, even when most authors use the conventional ceramic method for the production of ferroelectric ceramics. This remarks the sensitiveness of these materials to any small processing variation, the moisture sensitivity of alkaline carbonates, the calcination temperature, the heating time and, finally, the temperature at the sintering stage. All these steps considered together influence the poling process and then and final performance of the ceramics.

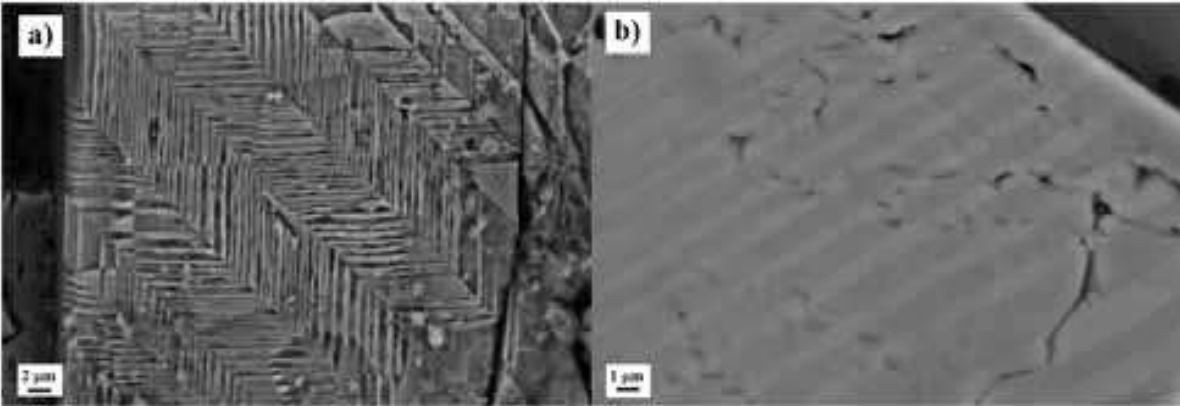


Fig. 10. Ferroelectric domains in KNN synthesized by microwave-hydrothermal method and sintered at 1080°C.

To conclude this section it should be mentioned the efforts to achieve the low temperature synthesis of KNN powders as was underlined at the hydrothermal synthesis section. This method requires heat treatment for a long time at low temperature (<300°C) if the conventional hydrothermal method is used. But recently, the microwave-hydrothermal technique it is being explored for the synthesis of some inorganic materials. Although, the influence of microwaves on the reaction system it is not well understood until now. In the case of potassium-sodium niobate, the synthesis was proved to proceed faster with the aid of microwaves. The sintered powders experienced extremely grain growth with grain size

¹ This value was not reported in (López et al., 2011a).

average $> 60 \mu\text{m}$ where the ferroelectric domains were revealed easier. In Fig. 10 the ferroelectric domains are shown in the ceramics sintered at 1080°C for 4 hours in air. As it is observed, the ferroelectric domains are large enough to be revealed by contrast using backscattered electrons (at 1 pA and 20kV), and in etched samples with hydrofluoric acid. The domain structure was found to be constituted mostly by 90° and 180° ferroelectric domains, for more details refer to the work by López et al. (López et al., 2011c).

6.2.3 Sintering of KNLNT

The synthesized powders by spray drying with $(\text{K}_{0.48}\text{Na}_{0.52})_{0.96}\text{Li}_{0.04}\text{Nb}_{0.85}\text{Ta}_{0.15}\text{O}_3$ composition were pressed and sintered at 1100 - 1150°C in air for 2 hours. The SEM pictures of these samples are shown in Fig. 11. The grain size was smaller comparing with the KNN composition. It is reported that the addition of Ta^{+5} into the KNN structure inhibits grain growth (Saito & Takao, 2006). When the sintering temperature was set at 1100°C , the grains grow inhomogeneously, but increasing the temperature to 1120 and 1130°C , these are bigger with the characteristic cubic shape, and for 1150°C , the grains grew even more because the faster mass transport rate. The densities and other piezoelectric parameters are shown on table 3. As it was observed for KNN ceramics, here the behavior of density and piezoelectric properties first increase and then fall for samples sintered at higher temperature. The factors which affect the densification of KNN pellets are also present for KNLNT composition. Evidently, the high temperature used for the sintering is because of the Ta^{+5} content, and the low concentration of Li^{+1} on the system, despite that, it is well known that lithium aids densification at lower temperatures as compared with KNN.

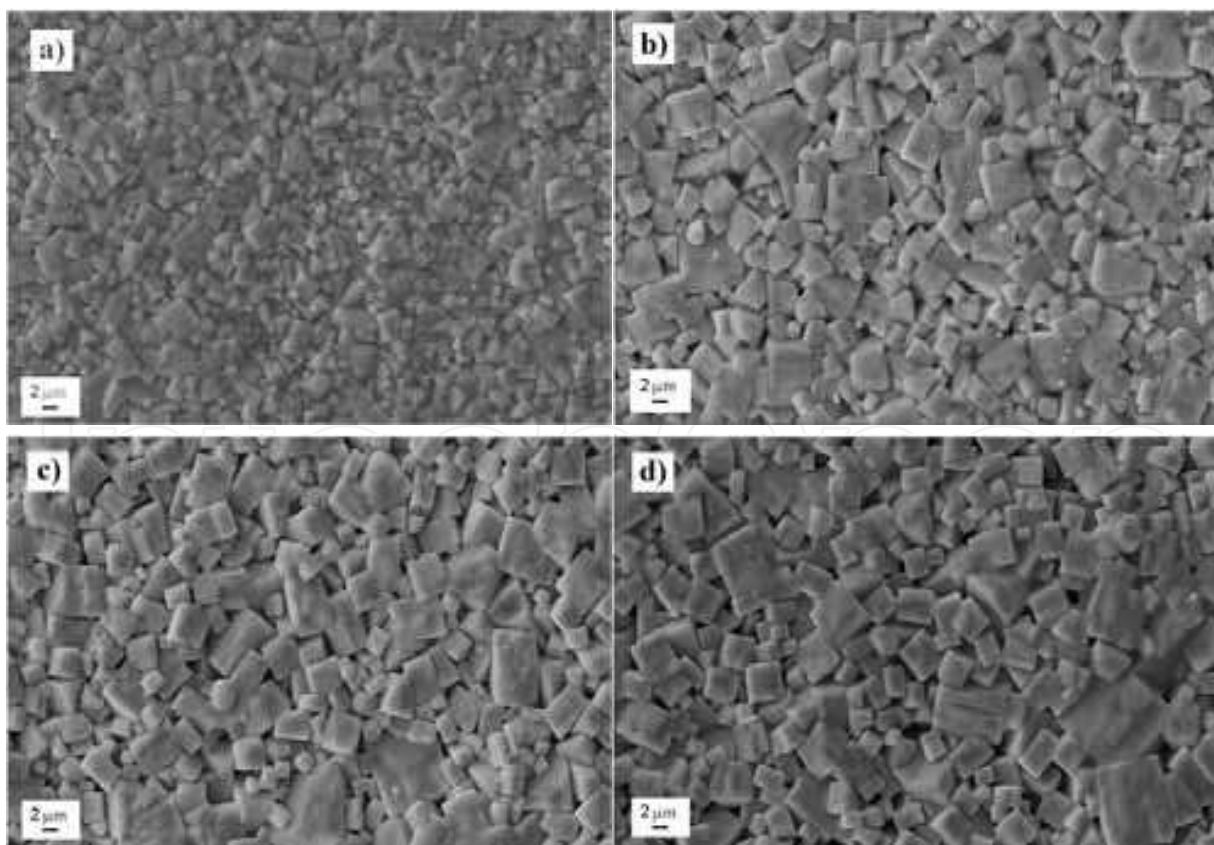


Fig. 11. SEM images of KNLNT sintered pellets, a) 1100°C , b) 1120°C and c) 1130°C (López et al., 2010), 1150°C for 2 h.

6.2.4 Piezoelectric, dielectric and ferroelectric properties of KNLNT

The KNLNT samples were processed and poled as reported before (López et al., 2010). In table 3, the properties obtained for the samples sintered at 1100 and 1150°C are also included. The values of piezoelectric properties increase with increasing sintering temperature, reaching maximum values for 1120°C, and then decrease for 1130 and 1150°C. In these materials is common to reach equilibrium between sintering temperature and piezoelectric properties. The temperature must be high enough to guarantee the diffusion of matter, eliminate pores and to promote grain growth, but not too high for avoiding the volatilization of alkaline elements and the formation of secondary phases, which degrades the piezoelectric properties. The presence of secondary phases, liquid phase or a high concentration of vacancies would result in incomplete poling because the leakage current leads to poor performance. Then the optimum sintering temperature of KNLNT ceramics was established at 1120°C. At this temperature the density, k_p and other parameters were improved. In Figs. 12 and 13 the dielectric constant and $\tan \delta$ are shown for samples sintered at 1120 and 1130°C. The ϵ_r curves for both samples are similar, except that the magnitude of ϵ_r is higher for 1120°C. Furthermore, only one phase transition is observed at 354°C, from tetragonal to cubic (T_C). In addition, the dielectric constant has no dispersion with frequency and temperature.

Parameter	Sintering temperature (°C)			
	1100	1120	1130	1150
k_p	0.30	0.41	0.40	0.29
$-d_{31}$ (pC/N)	49.01	55.86	50.55	37.12
$\tan\delta(\%)(100\text{kHz})$	0.7	1	1	1.2
T_C (°C)	360	354	354	350
$2P_r$ ($\mu\text{C}/\text{cm}^2$)	24.00	25.84	21.43	12.24
$2E_C$ (kV/cm)	20.92	25.70	26.77	19.82
$S_{11}^E(10^{-12}\text{ m}^2\text{ N}^{-1})$	12.33	11.80	12.24	13.12
$S_{12}^E(10^{-12}\text{ m}^2\text{ N}^{-1})$	-4.15	-2.786	-3.64	-4.271
ρ (gr/cm ³)	4.49	4.57	4.56	4.37

Table 3. Piezoelectric properties of KNLNT sintered ceramics.

It has been demonstrated that the magnitude of the dielectric constant is affected by extrinsic variables as the porosity (Fang et al., 1993), i.e. the air trapped within the samples has a low ϵ that is averaged in the measured signal. The grain size also influences the dielectric response (Fang et al., 1993; Hoshina et al., 2008), but there are the intrinsic effects due to the introduction of cations in the A and B sites of the ABO₃ structure. More precisely, when donor-type doping of KNN with La⁺³ and Ta⁺⁵ is performed (Hao et al., 2009) and in BaTiO₃ (Morrison et al., 1999), the dielectric constant at the T_C decreases and the transition became broad, this behavior it is not well understood but it is suggested that the many different transitions collapse at once resulting in the broad pick at T_C . In the KNLNT it

seems that the Ta⁺⁵ doping induces that the ϵ_r was lower at the transition compared with pure KNN, the contribution of grain size was discarded. The porosity of the sintered samples is of the same order and considering that well defined grain boundaries exist within them, the diminishment of ϵ_r is attributed to Ta⁺⁵ doping. The phenomena need more careful revision taking in mind the different ions introduced and the interactions among them as well as the type of bonding within the matrix atoms. Another important feature is the low dielectric losses in KNLNT (Fig. 13), in KNN it was found that high losses are related with high concentration of oxygen vacancies (Chen et al., 2007; Kizaki et al., 2007), then the high concentration of vacancies and the low activation energy needed to move them (Kizaki et al., 2007; L. Liu et al., 2009) increase the dielectric losses. This means that the KNLNT samples are thermally stable and have low conductivity due to vacancies. Fig. 14 shows the ferroelectric loops of the sintered samples. The four samples show saturated loops, the only difference between them are the remnant polarization and coercive field. The highest P_r is encountered for the sample sintered at 1120°C, and is reported in table 3. The other samples have lower P_r , finding the lowest value for the heat treatment at 1150°C.

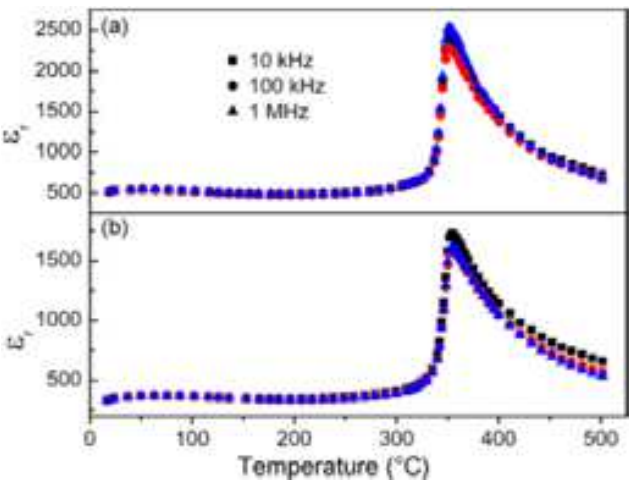


Fig. 12. Dielectric constant for KNLNT sintered samples, a) 1120 and b) 1130°C for 2 h.

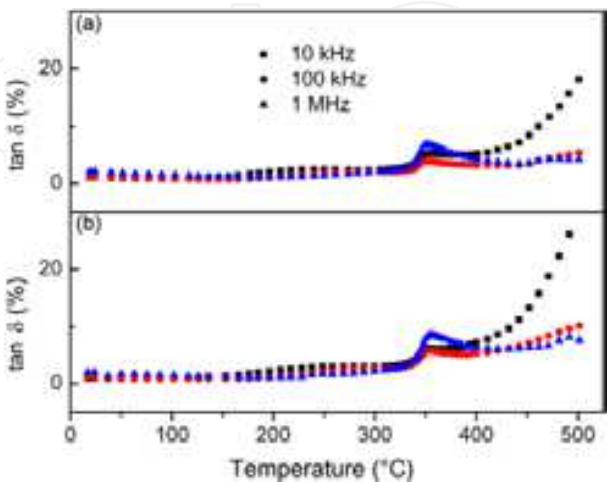


Fig. 13. Dielectric losses for KNLNT sintered samples, a) 1120 and b) 1130°C for 2h (López et al., 2010).

This is completely in agreement with the piezoelectric properties of the sintered ceramics. Probably, the most important issue is the crystal structure of the ceramics, if it is assumed that for KNLNT the polymorphic phase transition (PPT) is close to room temperature, and invoking the assumption that orthorhombic and tetragonal phases coexist at the PPT, then the polarization will be enhanced and the piezoelectric properties improved as well. This is evident when compared the properties found in KNN and KNLNT.

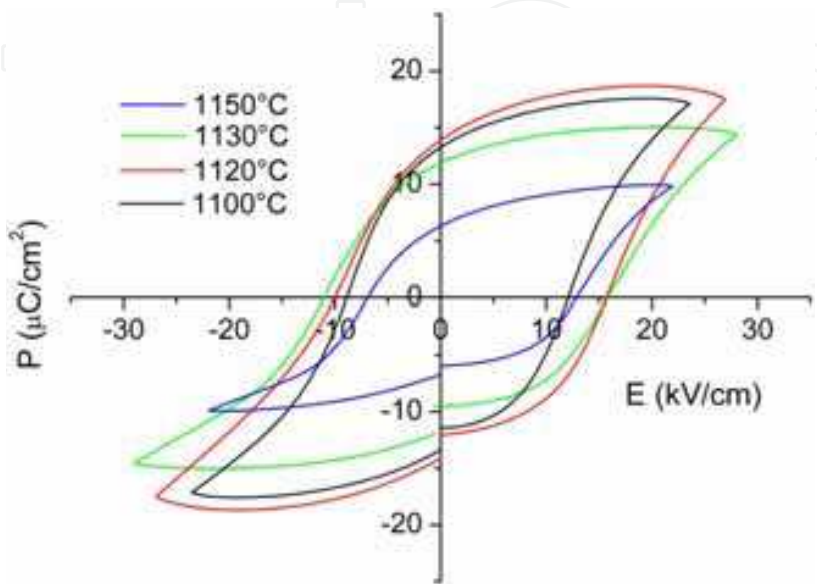


Fig. 14. Ferroelectric loops of KNLNT sintered ceramics.

In table 4, the comparison of several compositions is presented. In the same way as the results for pure KNN, the properties cover a wide range of values also for KNLNT and related compositions. It is observed that in compositions with BaTiO₃ k_p and d_{33} are reduced. On the other hand antimony increases these properties in general, but the T_C is shifted to lower values.

Composition	k_p	d_{33} (pC/N)	ϵ_r	$\tan \delta$ (%)	T_C (°C)	Reference
0.95(Na _{0.5} K _{0.5})NbO ₃ -0.05CaTiO ₃	0.41	241	1316(10 kHz)	9.0(10 kHz)	306	Park et al., 2007
(Na _{0.5} K _{0.5}) _{0.97} La _{0.01} Nb _{0.95} Ta _{0.05} O ₃	0.37	119	815(10 kHz)	4.5(10 kHz)	340	Hao et al., 2009
(K _{0.44} Na _{0.52} Li _{0.04})(Nb _{0.84} Ta _{0.10} Sb _{0.06})O ₃	0.48	299	1865(1 kHz)	2.1(1 kHz)	265	Hagh et al., 2007
(K _{0.5} Na _{0.5}) _{0.096} Li _{0.04} Nb _{0.775} Ta _{0.225} O ₃	0.48	208	1146	< 3	320	Lin et al., 2007
(Na _{0.52} K _{0.4375})(Nb _{0.9175} Sb _{0.04})O ₃ -0.0425LiTaO ₃	0.48	310	1644(10 kHz)	---	337	Fu et al., 2008
(K _{0.38} Na _{0.52} Li _{0.04})(Nb _{0.86} Ta _{0.10} Sb _{0.04})O _{2.97}	0.37	195	1060(1 MHz)	2.8(1 MHz)	276	Rubio-Marcos et al., 2007
(Li _{0.04} K _{0.44} Na _{0.52})(Nb _{0.85} Ta _{0.15})O ₃	0.38	200	---	---	---	Li et al., 2008
0.97Li _{0.06} (Na _{0.5} K _{0.5}) _{0.94} NbO ₃ -0.03BaTiO ₃	0.32	128	800(1 kHz)	---	370	Kakimoto et al., 2010
0.995(K _{0.5} Na _{0.5}) _{0.95} (LiSb) _{0.05} Nb _{0.95} O ₃ -0.005BaTiO ₃	0.42	209	1100(10 kHz)	2.6(10 kHz)	344	Zang et al., 2010
0.92(K _{0.5} Na _{0.5})NbO ₃ -0.08AgTaO ₃	0.41	183	683(10 kHz)	3.3(10 kHz)	356	Wang et al., 2010
(K _{0.48} Na _{0.52}) _{0.96} Li _{0.04} Nb _{0.85} Ta _{0.15} O ₃	0.41	186	465(10 kHz)	1.0(10 kHz)	354	López et al., 2010

Table 4. Piezoelectric properties of KNLNT and related compositions.

7. Conclusion

In the last few years several researches were performed in the lead-free ferroelectric materials for piezoelectric applications. These works were focused in the improvement of the piezoelectric properties by doping potassium-sodium niobate ceramics. The dopants are those of the A and B occupancy within the perovskite structure. Most of them shift the T_C and the polymorphic phase boundary (T_{O-T}) to room temperature, thus improving the piezoelectric performance. It is believed that this is due to the coexistence of the orthorhombic-tetragonal phases at room temperature, and this allows a better poling process because of the existence of more crystallographic directions for the polarization. Despite the improvement in properties, there are troubles in the synthesis, processing and poling of the sintered ceramics. The high volatilization of potassium, sodium and lithium is one of the most notable drawbacks of lead-free ferroelectric ceramics based in the KNN solid solution. For this reason, there is also a great search for low temperature synthesis and sintering of these materials. Then, the microwave-hydrothermal, sol-gel and Pechini synthesis methods are being proved, which in combination with the spark plasma sintering are some alternatives for processing KNN and related ceramics; nevertheless, these need more investigation to find appropriate conditions.

In this work, the spray drying synthesis method was used to synthesize KNN and KNLNT ceramics. The obtained results pointed out that this method is a promising option for avoiding inhomogeneous distribution of cations within the ceramics, and the losses of alkaline elements. This was possible because the temperature and time at the calcination stage were reduced. The sintered ceramics shown good piezoelectric and ferroelectric properties, i.e. high k_p , low $\tan \delta$ and ε , and moderate E_C and P_r . In the case of KNLNT the ideal sintering temperature, depends greatly upon the doping elements. In the KNLNT the improvement of the piezoelectric properties was attributed to the polymorphic phase transition close to room temperature.

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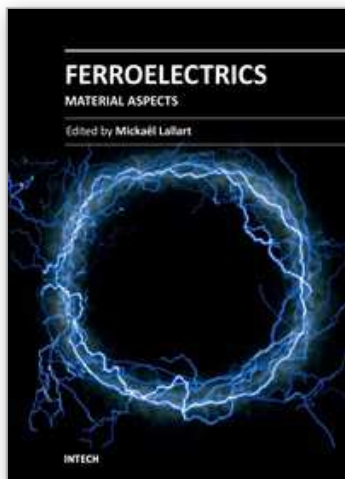
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Ferroelectric materials have been and still are widely used in many applications, that have moved from sonar towards breakthrough technologies such as memories or optical devices. This book is a part of a four volume collection (covering material aspects, physical effects, characterization and modeling, and applications) and focuses on ways to obtain high-quality materials exhibiting large ferroelectric activity. The book covers the aspect of material synthesis and growth, doping and composites, lead-free devices, and thin film synthesis. The aim of this book is to provide an up-to-date review of recent scientific findings and recent advances in the field of ferroelectric materials, allowing a deep understanding of the material aspects of ferroelectricity.

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