VOL.39 Nº4 2022
https://doi.org/102279/jMECTA.9301.en

Microstructural characterization of sodium niobates by the sol-gel process for use in tissue engineering

Suzana Noronha Ferreira Ribeiro[a] Amal Elzubair Eltom, Marcelo Henrique Prado da Silva

Instituto Militar de Engenharia – IME
Sessão de Engenharia de Materiais

[a]suzananoronha13@ime.eb.br

RESUMO: Niobato de sódio é um material dielétrico potencialmente importante por suas propriedades piezoelétricas. Possui estrutura do tipo perovskita, na sua forma mais estável. Os recentes avanços na engenharia de tecidos têm se concentrado no uso de sinais bioquímicos e físico-químicos para desencadear respostas celulares específicas e incentivar uma melhor interação biológica entre o biomaterial e o tecido vivo. A cerâmica piezoelétrica pode ser a chave para a funcionalização dos enxertos atuais, pois exibem comportamento elétricos gerados mecanicamente. Neste trabalho, foi adotada a produção do niobato de sódio ($NaNbO_3$), um biomaterial piezoelétrico, em composições molares diferentes, pelo método sol-gel com o objetivo de observar as alterações na microestrutura utilizando técnicas microscopia eletrônica de varredura (MEV). A síntese foi eficiente e a microestrutura está de acordo com o que foi encontrado na literatura
PALAVRAS-CHAVE: Niobatos de sódio. Sol-gel. Piezoelétricos.

ABSTRACT: Sodium niobate is a potentially important dielectric material for its piezoelectric properties. It has a perovskite-like structure, in its most stable form. Recent advances in tissue engineering have focused on the use of biochemical and physicochemical signals to trigger specific cellular responses and encourage better biological interaction between the biomaterial and living tissue. Piezoelectric ceramics may be the key to the functionalization of current grafts, as they exhibit mechanically generated electrical behavior. In this work, the production of sodium niobate ($NaNbO_3$), a piezoelectric biomaterial, in different molar compositions, by the sol-gel method was adopted in order to observe the changes in the microstructure using scanning electron microscopy (SEM) techniques. The synthesis was efficient and the microstructure is in agreement with what was found in the literature.

KEYWORDS: Sodium niobates. Sol-gel. Piezoelectric

1. Introduction

Tissue engineering has focused on the study of biochemical and physicochemical signals, with the aim of obtaining specific cellular responses and encouraging a better interaction between living tissue and implanted materials. Studies in this area indicate that the use of electrical stimuli can promote an increase in the speed of healing and tissue regeneration [1, 2].

Studies led to the development and use of exogenous electrical stimuli in the treatment of bone fractures in different parts of the human skeletal system. However, the use of punctual and non-constant electrical stimuli does not lead to responses as efficient as reported in the literature. Because of this, the clinical efficacy and safety of these exogenous electrical stimulation methods are being considered inconsistent and inconclusive. Because there is a lack of a sufficient number of randomized and well-controlled clinical studies to prove its use [1,2,3].

The high demand for new intelligent materials that can favor the tissue regeneration process leads to the study of new materials containing electrically active components or materials that can be polarized. Piezoelectric ceramics that have a perovskite structure are the most suitable for this type of action [2,3,4,5].

Piezoelectric ceramics could be the key to the functionalization of current implant designs. They exhibit mechanically generated electrical behavior.

The piezoelectric ceramic most used so far is lead zirconate titanate $Pb[Zr(x)Ti_{(1-x)}]O_3$ (PZT), where the composition x is used to adjust specific properties for memory or piezoelectric devices. However, due to the toxicity of these lead-containing devices, much effort has been devoted in recent years to finding suitable lead-free alternatives to PZT. A promising alternative materials system is the sol-gel synthesis of sodium potassium niobate (Na,K) NbO_3. While the structural and electronic properties of one end member potassium niobate ($KNbO_3$) are relatively well known, this is much less the case for perovskite sodium niobate ($NaNbO_3$) [5, 6, 7].

Sodium niobate is a ceramic that at room temperature has an orthorhombic structure, space group Pbma. The interest in this material is based on its perovskite phase which exhibits piezoelectric properties. There are a variety of $NaNbO_3$ preparation routes that mostly use niobium pentoxide. The synthesis using solid solution is well known, however, the sol-gel synthesis leads to obtaining materials with better homogeneity and with a shorter production time [8].

In this work, the production of sodium niobate ($NaNbO_3$) was adopted by the sol-gel method in different molar compositions, the heat treatment was carried out at a calcination temperature of 650°C and sintering at 1130°C with the objective of observing changes in the microstructure. With the control of these parameters, it will be possible to obtain an ideal synthesis prediction to guide further studies of application of this ceramic for bone regeneration.

2. Materials And Methods

The work consists of the synthesis of sodium niobate ($NaNbO^5$) by the sol-gel method following the steps used by Jigong (2010) [9]. The author took into account the phase diagram of sodium and potassium niobate **figure** 2, where, at one end there is the presence of sodium niobate and at the other, potassium niobate [10]. The reagents used are shown in Table 1 below.

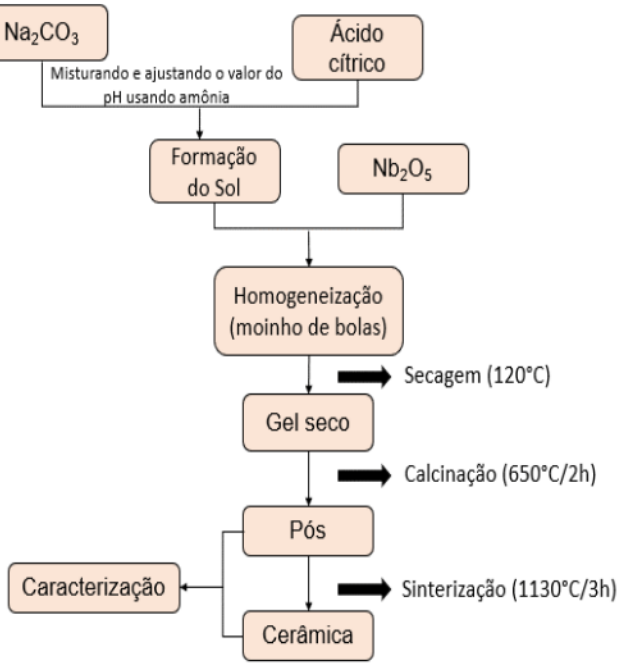
Tab. 1. Reagents used in the synthesis of NaNbO3 by the sol-gel method.

REAGENTS	PURITY (%)	MANUFACTURER
Na_2CO_3	99,8	Vetec
Nb_2O_5	99,96	--
Citric acid $C_6H_8O_7.H_2O$	99,5	Baker
Ammonia	--	Merck
Polyvinyl alcohol (PVA)	--	Merck

Source: Own authorship.

The precursors used as raw material were Na_2CO_3 (99.8%), Nb2O5 (99.96%) and citric acid ($C_6H_8O_7.H_2O$, 99.5%). The detailed scheme of the process is shown in the flowchart below **figure** 1. The heavy carbonate was dissolved in deionized water and stirred for 20 min. Citric acid (the molar ratio of citric acid to total cation content was 2 to 1) was dissolved in deionized water in a beaker and stirred for 20 min, then added to the carbonate solution. Then, small amounts of ammonia solution were added to adjust the pH value and form the sol. The Nb_2O_5 was added to the sol and the solution was stirred for 1h, after which it went through the homogenization process in the ball mill, containing alumina balls, for 8h. After milling, the slurry was dried at 120°C to form a xerogel. The resulting xerogel was calcined at 650°C for 2 h to obtain after sodium niobate. The calcined powders were pressed into tablets of approximately 3g and 12mm in diameter, using polyvinyl alcohol (PVA) as a binder. After firing the PVA, the pellets were finally sintered at 1130°C for 3h.

Fig.1 - Flowchart of NaNbO3 synthesis by the sol-gel method.



The results are shown below through scanning electron microscopy (SEM) characterization. For comparison, sodium niobate was produced by two different compositions. The first composition has a stoichiometric ratio (A) one to one (1:1) of sodium carbonate and niobium oxide, and the second, a non-stoichiometric ratio (B) one to three quarters (1:3/4) of sodium carbonate. sodium and niobium oxide, respectively. The formula used to calculate the reagents was as follows:

$$Na_2CO_3 + Nb_2O_5 \rightarrow 2NaNbO_3 + CO_2$$

Table 2 shows the molar ratio used for comparison:

Tab. 2 - Molar ratio of compounds.

NOMENCLATURE OF SAMPLES	PROPORTION	
	Na2CO3	Nb2O5
$NaNbO_3$ - A	1	1
$NaNbO_3$ - B	1	3/4

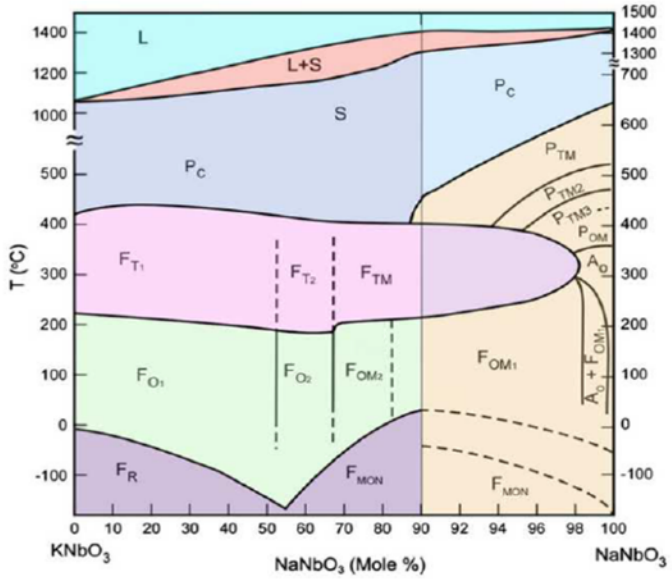
Fonte: Autoria própria.

The samples were characterized by scanning electron microscopy (SEM). The morphology of the calcined and sintered powders was investigated using a scanning electron microscope, model QUANTA 250 FEG, manufactured by FEI, installed in the Electron Microscopy laboratory of the Instituto Militar de Engenharia (IME) for analysis of microstructures via SE and BSE. In these analyses, secondary electron detectors – SE (brand SE Detector R580 from FEI) and backscattered – BSE (model 6 Channel BSD Amplifier MK 3.1 from FEI) associated with the Spirit 1.9 control software were used. The samples were covered with gold, deposited by a LEICA model EM ACE600 metallizer under a current of 50mA for 2 minutes.

3. Results And Discussion

Fig.2 presents the phase diagram of the $KNbO_3$ – $NaNbO_3$, system, where C, T, O and M indicate cubic, tetragonal, orthorhombic and monoclinic symmetry, respectively; F, A, P are the letters indicated to represent ferroelectric, anti-ferroelectric and para-electric behavior; S and L correspond to the solid and liquid states. It is possible to observe along the strip on the right side where the composition of sodium niobate is fully displayed. Esse material é totalmente dependente da sua composição e da temperatura de obtenção. Due to this, the process of obtaining sodium niobate is extremely important, since any difference in composition produces a different structure and, consequently, different properties.

Fig. 2 - System phase diagram $KNbO_3$ – $NaNbO_3$. . C, T, O and M indicate cubic, tetragonal, orthorhombic and monoclinic symmetry, respectively; F, A, P for ferroelectric, anti-ferroelectric and paraelectric behavior; S and L correspond to the solid and liquid states.

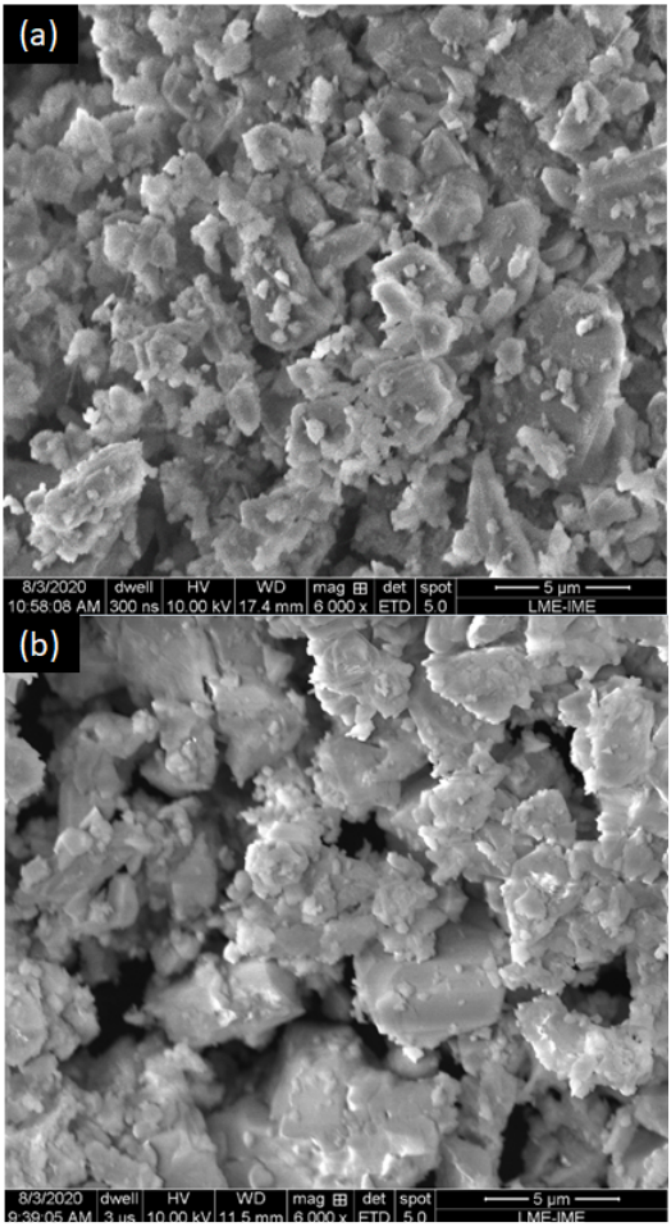


Source: LI (2013) [10].

3.1 Scanning Electron Microscopy (sem)

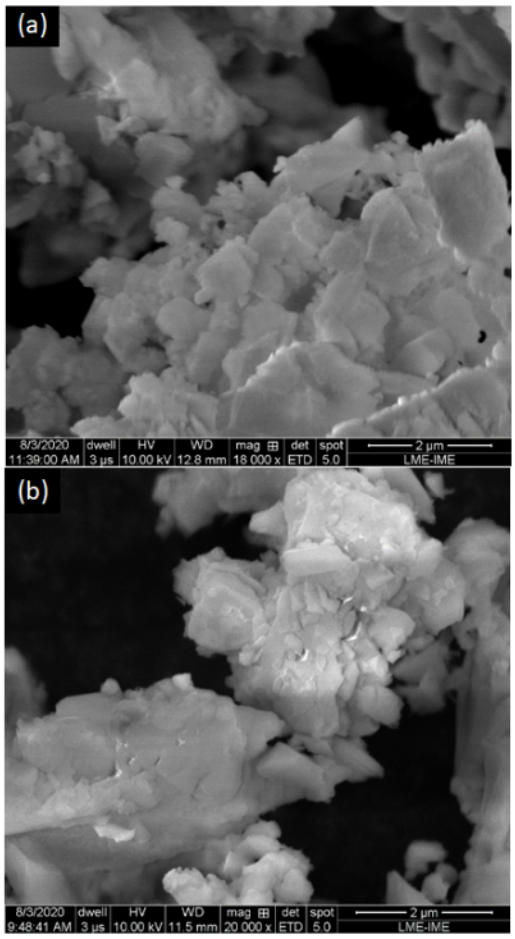
figure 3 and 4 show the micrographs obtained by scanning electron microscope (SEM) of samples of $NaNbO_3$ - A and $NaNbO_3$ - B, both calcined at 650°C for 2h. They denote how the variation in the microstructure equivalent to the compositional variation incited in this work occurs. SEM images show the formation of precipitates with irregular shapes. The calcined samples do not present a great variation in size, as can be easily noticed in the micrographs observed in **figure** 3 and 4. However, a greater compaction of the particles in the samples of $NaNbO_3$ – B compared to $NaNbO_3$ – A is remarkable.

Fig. 3 - Scanning electron micrograph (SEM) of samples of (a) $NaNbO_3$ - A and (b) NaNbO3 - B both calcined. Magnifications of (a and b) 6,000X.



Source: Own authorship.

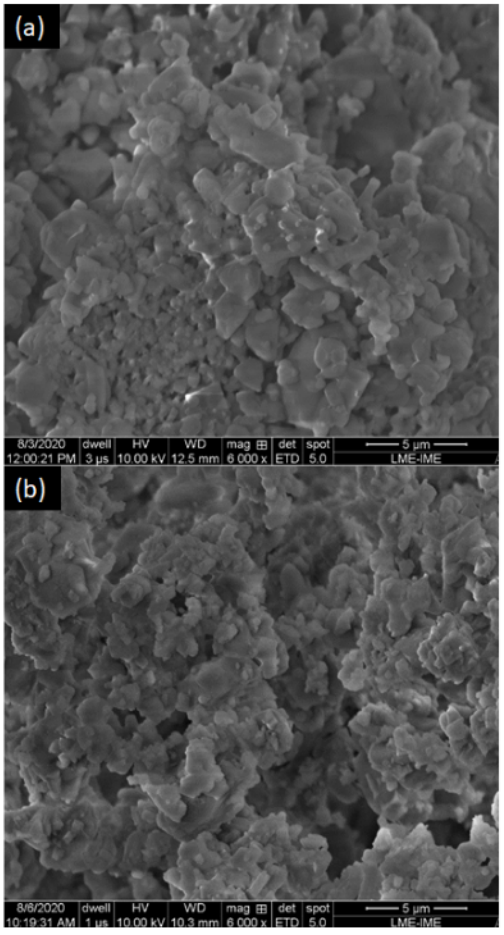
Fig. 4 - Scanning electron micrograph (SEM) of samples of (a) $NaNbO_3$ - A and (b) $NaNbO_3$ - B both calcined. Magnifications of (a) 18.000X and (b) 20.000X.



Source: Own authorship.

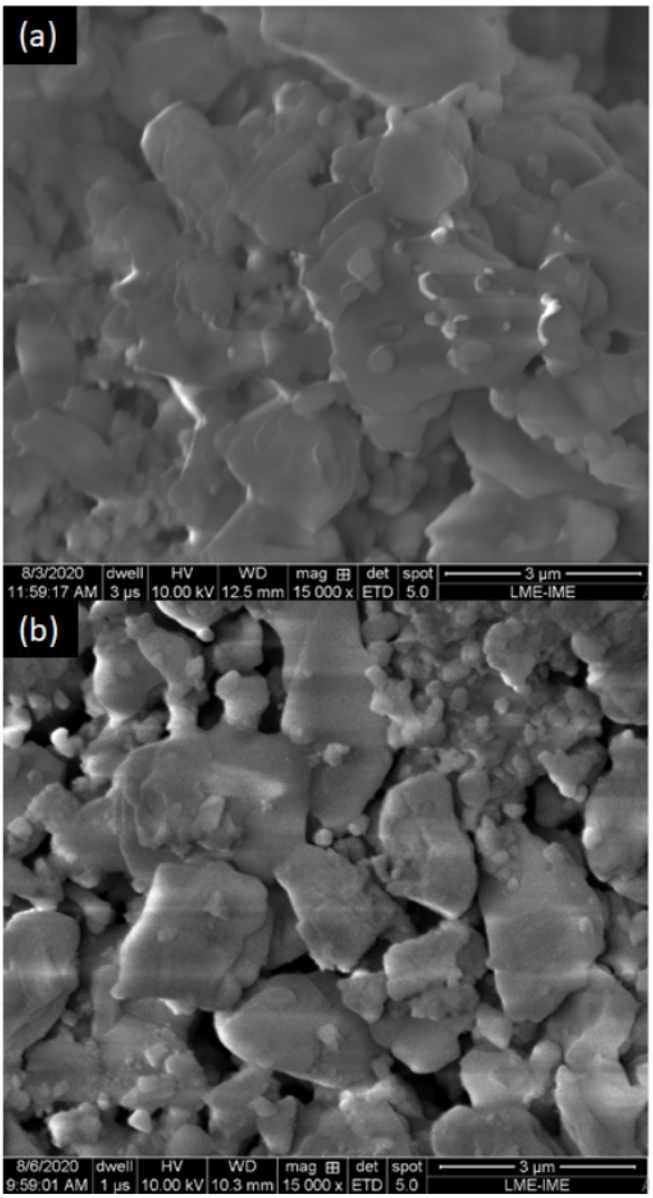
Figure 5 and 6 show the micrographs obtained by scanning electron microscope (SEM) of $NaNbO_3$ – A and $NaNbO_3$ – B samples, both calcined at 650°C for 2h and sintered at 1130°C for 3h. They denote how the variation in the microstructure equivalent to the compositional variation incited in this work occurs. SEM images show the formation of precipitates with irregular shapes. **Figure** 5(b) shows better homogeneity of the agglomerates compared to **figure** 5(a). In **figure** 6(b) it is possible to observe that some particles presented grain size with greater growth than the others observed in **figure** 6(a), which presented grains with homogeneous sizes. It may be possible to observe the presence of needles, they tend to appear when they are synthesized in low molar concentrations, therefore, the acicular and irregular shapes observed in these samples are understood. The two compositions can be compared by observing the variation in grain size for the slightly larger $NaNbO_3$ – B sample in relation to the $NaNbO_3$ – A sample. In addition, they present greater compaction observed in **figure** 5(b) and 6(b).

Fig. 5 – Scanning electron micrograph (SEM) of samples of (a) NaNbO3 - A and (b) NaNbO3 - B, both sintered. Magnifications of (a and b) 6.000X



Source: Own authorship.

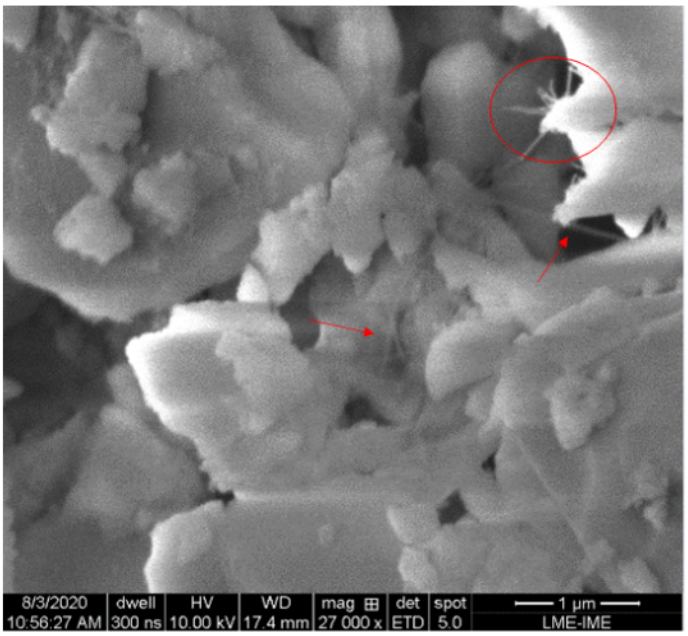
Fig. 6 – Scanning electron micrograph (SEM) of samples of (a) NaNbO3 - A and (b) NaNbO3 - B, both sintered. Magnifications of (a and b) 15.000X.



Source: Own authorship.

Fig. 7 shows the sample $NaNbO_3$ – – A calcined at 650°C for 2h. In these samples it is possible to observe the presence of precipitates in the form of sub micrometric threads. This result is interesting since, according to the literature, needles or nanoneedles are only obtained in lower molar concentrations, as shown by the formation of small needles noted only in this composition and in the thermal treatment of calcination [11].

Fig. 10 - Scanning electron micrograph (SEM) of the calcined NaNbO3 - A sample. Magnifications of 27.000X.



Source: Own authorship.

4. Conclusion

Sol-gel synthesis of sodium niobate was effective in producing the sodium niobate phase ($NaNbO_3$) with the presence of a small percentage of niobium oxide. The microstructure showed irregular grain size and pores in the calcined samples and good densification in the sintered samples. Thus, the study of sodium niobate is valid for its use in applications in biomaterials such as ceramics that present the phenomenon of piezoelectricity, where the tests will be carried out in later works.

Thanks

The authors would like to thank IME for the resources used to carry out this work, as well as for funding from CNPq, CAPES and FAPERJ.

References

[1] BAHAREH A.; MILAZZO M.; LAZZERI A.; BERRETTINI S.UDDIN M. J.; QIN Z. BUEHLER M. J.; DANTI S. Electrospinning piezoelectric fibers for biocompatible devices. Advanced healthcare materials. P. 1901287- 1901287, 2019.

[2] POON, K. K.; MATTHIAS, C.; WURM, EVANS, D. M.; EINARSRUD, M. A.; LUTZ, R.; GLAUM, J. Biocompatibility of (Ba,Ca)(Zr,Ti)O3 piezoelectric ceramics for bone replacement materials. J Biomed Mater Res. v.108, p.1295–1303, 2020. https://doi.org/10.1002/jbm.b.34477

[3] TOFAIL, A. M. S.; BAUER J. Electrically polarized biomaterials. Advanced materials. V.28, n.27, p.5470-5484, 2016.

[4] BODHAK, S.; BOSE, S.; BANDYOPADHYAY, A. Role of surface charge and wettability on early stage mineralization and bone cell–materials interactions of polarized hydroxyapatite. Acta Biomaterialia. v.5, p.2178–2188, 2009.

[5] SHROUT, T. R.; ZHANG, S. J. Lead-free piezoelectric ceramics: Alternatives for PZT? J. Electr. v.19, p.113–126, 2007.

[6] Y. Saito, H. Takao, T. Tani et al., "Lead-free piezoceramics," Nature, vol. 432, no. 7013, p. 84, 2004.

[7] X. Tan, C. Ma, J. Frederick, S. Beckman, and K. G. Webber, "The antiferroelectric ↔ ferroelectric phase transition in lead-containing and lead-free perovskite ceramics," Journal of the American Ceramic Society, vol. 94, no. 12, pp. 4091–4107, 2011.

[8] C. I. Cheon, H. W. Joo, K.-W. Chae et al., "Monoclinic ferroelectric NaNbO3 at room temperature: crystal structure solved by using super high resolution neutron powder diffraction," Materials Letters, vol. 156, pp. 214–219, 2015.

[9] JIGONG HAO; ZHIJUN XU; RUIQING CHU; YANJIE ZHANG; QIAN CHEN; PENG FU; WEI, LI.; GUORONG, LI.; QINGRUI, YIN. Characterization of (K0.5Na0.5)NbO3 powders and ceramics prepared by a novel hybrid method of sol–gel and ultrasonic atomization. Materials and Design v.31, p.3146–3150, 2010.

[10] Li, J.-F., Wang, K., Zhu, F.-Y., Cheng, L.-Q., & Yao, F.-Z. (2013). (K,Na)NbO3-Based Lead-Free Piezoceramics: Fundamental Aspects, Processing Technologies, and Remaining Challenges. Journal of the American Ceramic Society, 96(12), 3677–3696. doi:10.1111/jace.12715

[11] TSUNG-YING, KE; HSIANG-AN CHEN, HWO-SHUENN SHEU, JIEN-WEI YEH, HEH-NAN LIN, CHI-YOUNG LEE, HSIN-TIEN CHIU. Sodium Niobate Nanowire and Its Piezoelectricity. The Journal of Physical Chemistry. 2008 112 (24), 8827-8831