Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: M. Yessari, A. Hajjaji, M. Rguiti, S. Aboubakr & A. Arbaoui (2016) Elaboration and characterization of BZT lead-free ceramic prepared in chemical way and with the addition of a sintering aid (LBCU), Molecular Crystals and Liquid Crystals, 628:1, 130-138, DOI: 10.1080/15421406.2015.1137150

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1137150

MOL. CRYST. LIQ. CRYST.
2016, VOL. 628, 130–138
http://dx.doi.org/10.1080/15421406.2015.1137150

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Elaboration and characterization of BZT lead-free ceramic prepared in chemical way and with the addition of a sintering aid (LBCU)

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ABSTRACT

The Barium Titanates are very promising materials ecologically, but still have poor piezoelectric properties compared to the Lead Zirconate Titanates. So in order to improve them, a substitution of the zirconium in our ceramic (BT) has been investigated by X-ray diffraction (XRD) and grain size distribution. After the preparation of the BZT powder in chemical way we have added a sintering aid (Li_2O_3 - Bi_2O_3-CuO) and we have tried to study our massive ceramic. The X-ray diffraction, grain size distribution and scanning electron microscope of the BZT with LBCu show a better particles arrangement and density. In other hand we have noticed an important improvement of the piezoelectric properties (d_{33} = 220 pC/N at 25°C) especially in comparison with other lead-free ceramics. These properties make BZT a lead-free high performance material for piezoelectric applications.

KEYWORDS

lead-free ceramic; chemical way; sintering aid; X-ray diffraction; piezoelectric properties; Barium Zirconate Titanate

I. Introduction

Through their properties of electromechanical conversion, piezoelectric materials are used increasingly as sensors, actuators, piezoelectric motors or transformers and in various fields such as medicine, aeronautics and electronics. There are also several research works on their use for energy harvesting [1–4]. Currently, the most used piezoelectric materials are ceramics and most of these ceramics are lead-based (PZT, PMN-PT …) because of the high properties (density, d33, k33, Qm) attributed to the presence of lead in the structure of these ceramics.

The lead Zirconate Titanates, $Pb(Zr_xTi_{1-x})O_3$ (PZT)are ceramics showing important piezoelectric properties[5, 6]. For many years, several studies have been done on these materials to optimize their electromechanical conversion: co-doping [7], addition of sintering aid [8] …etc.

However, one of the most critical disadvantages of PZT is that it contains more than 60 percent lead (Pb) by weight. This large lead content creates hazards during processing (lead volatilizes and is released into the atmosphere), limits applications (e.g., in vitro), and is potentially environmentally toxic during disposal [9]. Over the past few years, regulatory agencies

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world-wide began putting strict restrictions on the use of lead, with the exception of the electronics industry due to the lack of a suitable replacement to PZT [10].

The barium titanates are ferroelectric materials with a perovskite structure [11] used mainly for manufacturing multilayer ceramic capacitors and thermistors due to their high dielectric constant [12] and the absence of lead in these materials makes them very promising materials ecologically [13].

In order to approach the piezoelectric properties of Lead Zirconate Titanates, BT ceramics can be doped by substituting cations Ba^{2+} or Ti^{4+} by isovalent or heterovalent cations and by this modulate the properties of our ceramic [14]. However the substitution of the zirconium in our ceramic must be investigated in order to find the optimum rate of zirconium to add.

The use of sintering aids in small quantities to the ceramic powder has also been studied in this work. With their relatively low melting points, sometimes during sintering a liquid phase appears which helps the powder particles to rearrange. One of their drawbacks is to reduce electric and piezoelectric properties of the materials. The purpose of this work is to lower the melting temperature without much influencing the electrical and piezoelectric properties of the materials.

A wide range of sintering aids was reported in the literature, among them, fondants based on Lithium and Bismuth. Dong and al. [15–16] have shown that Bi_2O_3 oxide could reduce the sintering temperature of PZT massive ceramics. The mixture Li_2O_3 - Bi_2O_3 (LB) in equimolar proportion can also be used as fondant. Hayashi [17] notes that the addition of 1% LB on solid PZT doped with antimony lowers the sintering temperature of about 200°C with a good holding of ferroelectric properties. Chen [18] adds 4% of this fondant to thick films which reduces the sintering temperature.

The fondant selected in our study is the LBCu2. LBCu2 fondant consists of Lithium, Bismuth and Copper. Garg [19] shows that the substitution of 2% of bismuth increases electric and piezoelectric properties of massive ceramics sintered at 1200°C. He estimates that 2/3 of bismuth are incorporated into the mesh and substituted in Site A (Bi^{3+}instead of Pb^{2+}). The density is improved in view of the presence of a liquid phase during sintering. And when the CuO oxide is added, it is reasonable to assume that the improved kinetics of sintering (and therefore the final density) is responsible for improving the properties.

In our study High Temperature X-ray Diffraction (XRD) and grain size distribution were used in order to follow the formation of the barium zirconate titanate. Then ceramics were made with the powder from chemical process. The LBCu was added to the powder to improve the density of the solid ceramic and lower sintering temperature.

II. Preparation and characterization of BZT

Several methods can be used for the synthesis of the barium zirconate titanate.

The chemical way has many advantages compared to the solid state one, among which we can mention the microstructural characteristic of the powder to be sintered, the stoichiometry and the reproducibility [20]. There is two main processes: sol-gel method [21] and the coprecipitation method [22]. The technique developed in the laboratory is based on the hydroxides coprecipitation and multiple oxalates with a definite pH [23–25].

1. Preparation of powders by coprecipitation

The precursors used are titanium butoxide [Ti (OC_4H_9)] (Huls) and the zirconium butoxyde [Zr(OC_4H_9)], Barium acetate [$(CH_3COO)_2Ba$] (Aldrich), oxalic acid[$H_2C_2O_4$] (Merck). The

titanium butoxide and zirconium butoxide are dissolved in an excess of oxalic acid to form a soluble complex. The reaction scheme is as follows:

a) Hydroxide precipitation

$$(C_4H_9O)_4\,Zr + 2H_2CO_4 + 4H_2O \rightarrow 4C_4H_9OH + 2H_2C_2O_4 + Zr(OH)_4 \quad (1)$$

$$C_4H_9O)_4Ti + 2H_2CO_4 + 4H_2O \rightarrow 4C_4H_9OH + 2H_2C_2O_4 + Ti(OH)_4 \quad (2)$$

b) Complex formation:

$$Ti(OH)_4 + 2H_2C_2O_4 \rightarrow TiOC_2O_4 + H_2C_2O_4 + 3H_2O \quad (3)$$

$$Zr(OH)_4 + 2H_2C_2O_4 \rightarrow ZrOC_2O_4 + H_2C_2O_4 + 3H_2O \quad (4)$$

When titanium solubilization is complete, we slowly add an aqueous solution of barium acetate. The addition of Ba^{2+} lead to the precipitation of the barium oxalate which then reacts with the soluble metal oxalate to yield insoluble oxalates.

$$TiOC_2O_4 + H_2C_2O_4 + Ba(CH_3OO)_2 + 4H_2O \rightarrow BaTiO(C_2O_4)_2,\, 4H_2O + 2CH_3COOH \quad (5)$$

$$ZrOC_2O_4 + H_2C_2O_4 + Ba(CH_3OO)_2 + 4H_2O \rightarrow BaZrO(C_2O_4)_2,\, 4H_2O + 2CH_3COOH \quad (6)$$

Thermal decomposition of the precursor powder provides the barium titanate zirconate.

2. Procedure

The tests are performed on quantities which provide1/3mole of BZT, 105.6 g of oxalic acids dissolved in 1330 g of distilled water, we add112.42goftitanium butoxide and zirconium butoxide solution. After an hour of stirring, a barium acetate solution is added to the reaction mixture slowly and steadily, stirring is maintained for 4 hours and sedimentation of the precipitate is performed all night. A first rinse consists in evacuating the supernatant water; the same amount of water is added. After two hours of stirring, the solution is left again to settle. Then the solution is filtered through a sintered glass of porosity4. Once dried, the powder is heat treated a fist time at 650°C for10 hours, then a second time at 800°C to adjust the grain size Fig. 1.

The addition of zirconium allows the piezoelectric properties of BZT to be modulated. However it is really important to figure out the optimum rate of the added zirconium. The figure above shows the variation of k_t and d_{33} according to the rate of Zirconium (Zr).

We clearly notice in the graph Fig. 2 that the piezoelectric constant decreases as Zr rate is increasing in the material while the electromechanical coupling factor k_t increases slightly from the value of 5%. It is this composition which is selected for further study.

3. X-ray diffraction and grain size distribution

X-ray diffraction data were obtained with a X'Pert Pro MPD Panalytical diffracto meter using Cu Kα radiation ($\lambda = 1{,}5406$ Å) with an incident-beam monochromator.

The resulting graph (Fig. 3) shows the observed peaks corresponding to the lines of the perovskite phase. However a secondary phase is detected. This phase consists of BaZrO3.

After the thermal decomposition at 650°C, the powder prepared by the chemical way undergoes a second heat treatment at 800°C which has the effect of making the grains swell.

The particle size distribution of all prepared powders is determined using a laser granulometer COULTERLS 130 whose wave length is 750 nm. This device gives the parameters

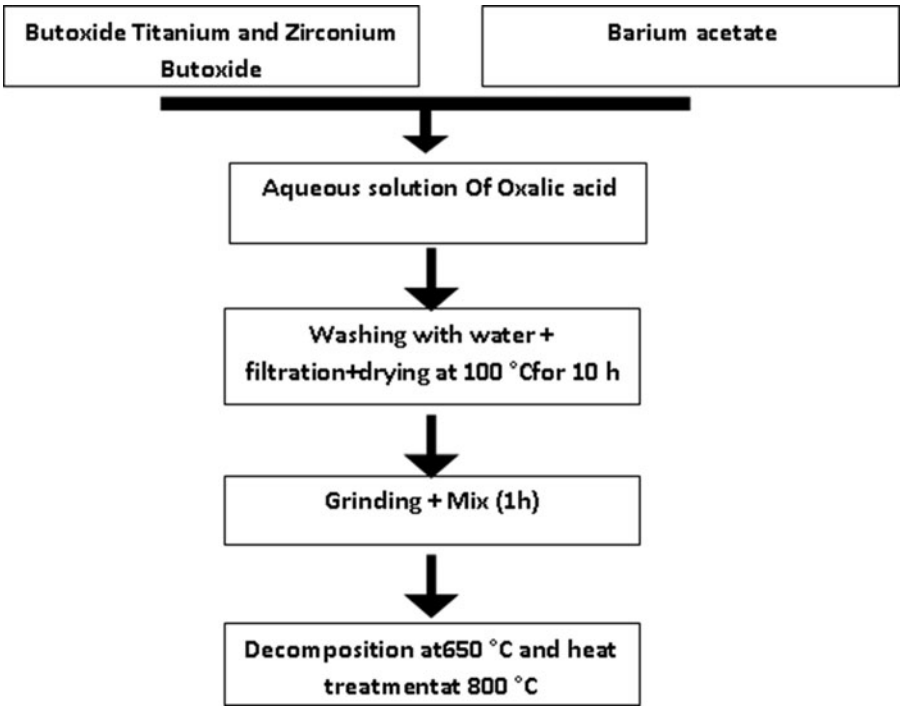

Figure 1. Synthesis of the powder by the coprecipitation method.

(diameters, means and medians, modes) by number or volume. The representation by volume makes it possible to detect the agglomerates presence, (they take up more volume than de-agglomerated particles). This representation gives an idea about the powders behavior, more agglomerates are, the more the dispersion of the powder is difficult to achieve.

The table above (Table 1) shows the granulometric characteristics by volume and number and the values of specific surface area determined with a specific surface analyzer Monosorb MS12 Quantachrome. Although powders made by the chemical way have a very high proportion of fine particles, the representation by volume highlights the presence of agglomerates,

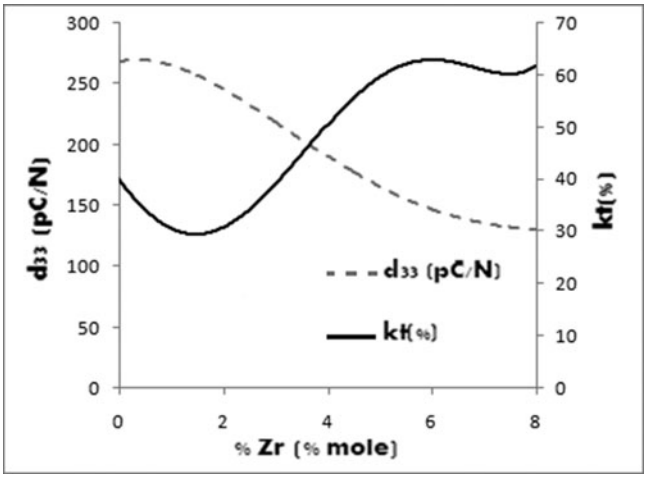

Figure 2. Evolution of d33 and Kt according to the rate of Zirconium.

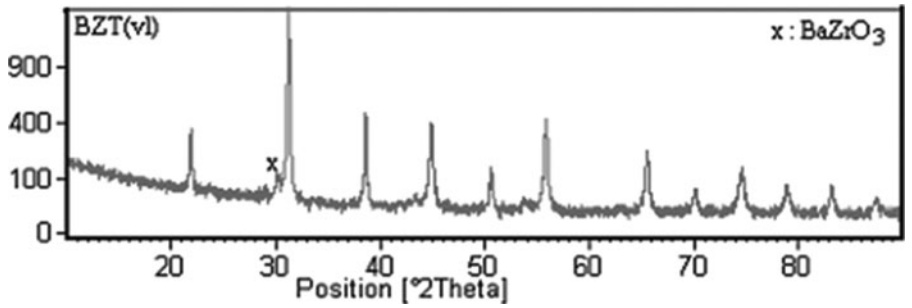

Figure 3. X-ray diffraction observed on BZT powder prepared by chemical way.

although they have indeed an important volume, they are low in quantity. The grain average volume has therefore increased owing to the presence of these piles of grains.

From a general point of view, in this type of material, particles obtained by a chemical way (800°C) are smaller and have different nature and form compared to those obtained by a solids state way.

4. Dielectric and piezoelectric properties

After the addition of 10% weight polyvinyl alcohol, the powder was pressed into pellets of the size Ø16 mm × 2 mm. Then, the samples were heated at 600°C for 4 h to eliminate the organic products. The sintering was done at temperatures between 1330 and 1370°C for 2 or 4 h with a 2°/min heating rate.

For dielectric measurements, silver electrodes were deposited onto both sides of the compacts. Poling was performed in a silicon oil batch at 110°C for a few minutes under an electric field of 2kV/mm which is also applied during cooling.

Densities (ρ) of the sintered ceramics were estimated from the mass and volume measurements in air. The dielectric losses (tgδ) and the permittivity (ε_r) were measured under low level (1 V/mm, 1 KHz) with an impedancemeter (HP 4284A).

The piezoelectric coefficient d33 was measured at a 100 Hz frequency with a Berlin courtmeter (Channel Products Inc).

III. Results

To enhance the densification rate of the BZT ceramic, a fondant was added to the powder in small quantities.

A ternary fondant Li_2CO_3-Bi_2O_3-CuO 30/25/45 (LBCu) was chosen for this work.

Lithium carbonate has a melting point at 723°C and a boiling point at 1310°C, the thermo gravimetric analysis indicates that the dissociation begins to 700°C and ends at 1310°C. The

Table 1. The granulometric characteristics by volume and number for BZT prepared in both chemical and solid way.

	AverageDiameter(μm)		MedianDiameter(μm)			
	By volume	By nombre	By volume	By nombre	Mode (μm)	Specific Surface (m^2/g)
BZT (vl)	2,924	0,511	2,156	0,389	2,313	13,96
BZT (vs)	1,09	0,546	1,005	0,470	1,019	3,07

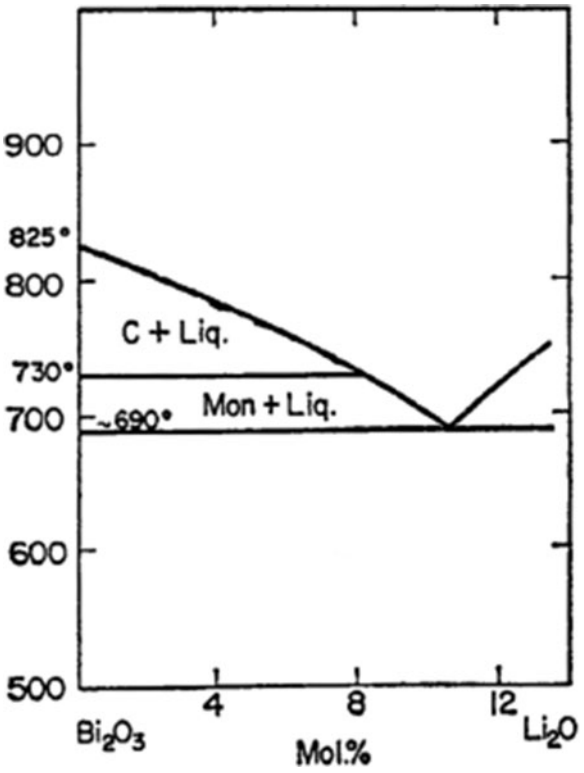

Figure 4. Phase diagramofBi2O3-Li2O system [23].

bismuth melting point is between 820 and 860°C, with a transition point at 704°C (Fig. 4). The melting point of the black oxide CuO is at 1326°C.

1. Density

Fondants have relatively low melting points; a liquid phase thus appears during sintering which helps the powder particles to rearrange (Fig. 5). This rearrangement helps to lower the sintering temperature of ceramic and improve their density (Table 2).

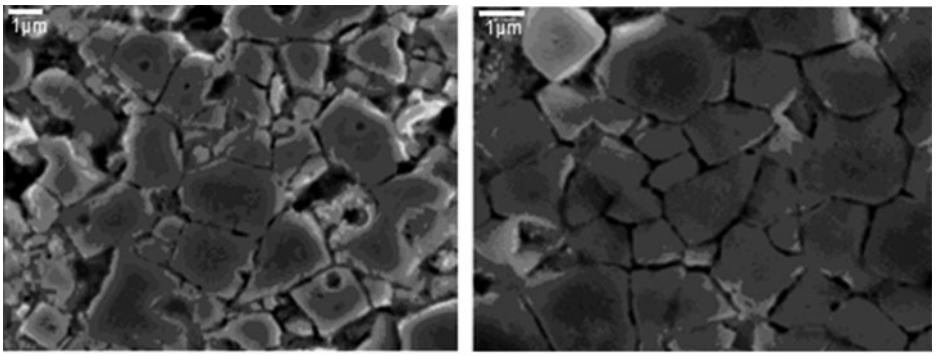

Figure 5. Scanning Electron Microscopy images of (a) BZT without fondant: grains average size 5µm, (b) BZT with fondant: grains average size 2 µm.

Table 2. The density of BZT with and without fondant in different sintering temperature.

Samples	BZT without fondant		BZTwith fondant		
Sinteringtemperature (°C)	1350	1370	1320	1350	1370
Density (g/cm^3)	4,80	5,00	5,20	5,53	5,50

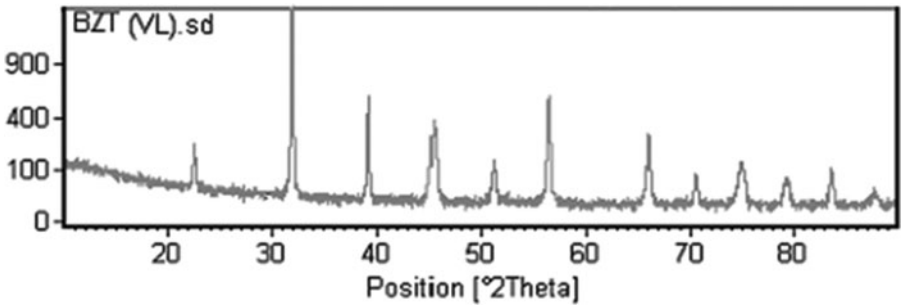

Figure 6. X-ray diffraction observed on BZT prepared in chemical way (after sintering).

A study of the BZT ceramic structural state is obtained using the laboratory diffractometer. This study allowed us to obtain a large amount of information on the sintered BZT (presence of phases and their crystal structures).

BZT is formed of solid solutions of BT with other materials, including antiferroelectric BaZrO3, the secondary phase x.

During the sintering process: heating, cooling and temperature holding, different mechanisms are involved: rearrangement of particles, densification and elimination of intergranular porosity and grain growth and elimination of closed porosities. During this process our material undergoes several phase transitions: cubic above 127°C, quadratic between 127° and 5°, orthorhombic between 5° and −3° and rhomboedric below −3°C . The disappearance of the secondary phase x (Fig. 6) noticed using R-X diffractions therefore correspond to a phase transition to an orthorhombic system.

2. *Influence of the rate of sintering aid*

Three fondant rates (LBCu) (1; 2 and 3%) were chosen and tested.

Table 3 shows an important improvement of the load constant in the presence of the fondant, the optimum rate is determined at 2% at a temperature of 1350°C.

The effect of sintering temperature on these ceramics made with 2% of fondant was tested. The table below shows the properties of BZT ceramics (with fondant) obtained after sintering for 4 hours at 1320°C, 1350°C and 1370°C. The use of fondant has lowered the sintering temperature compared to pure BZT. From 1320°C the dielectric and piezoelectric properties are correct.

Table 3. The influence of the rate of sintering aid on d_{33} and density of BZT.

% Fondant	d_{33} (pC/N)	% Density
0	140	83
1	200	90
2	220	94
3	215	96

Table 4. Properties of BZT with fondant according to different sintering conditions.

Sintering Temperature (°C)	d_{33} (pC/N)	Qm	kp	kt	εr	Dielectric losses (%)
1320	222	283	0.340	0.471	1802	0.81
1350	220	969	0.325	0.503	1911	0.99
1370	235	451	0.331	0.422	2235	0.57

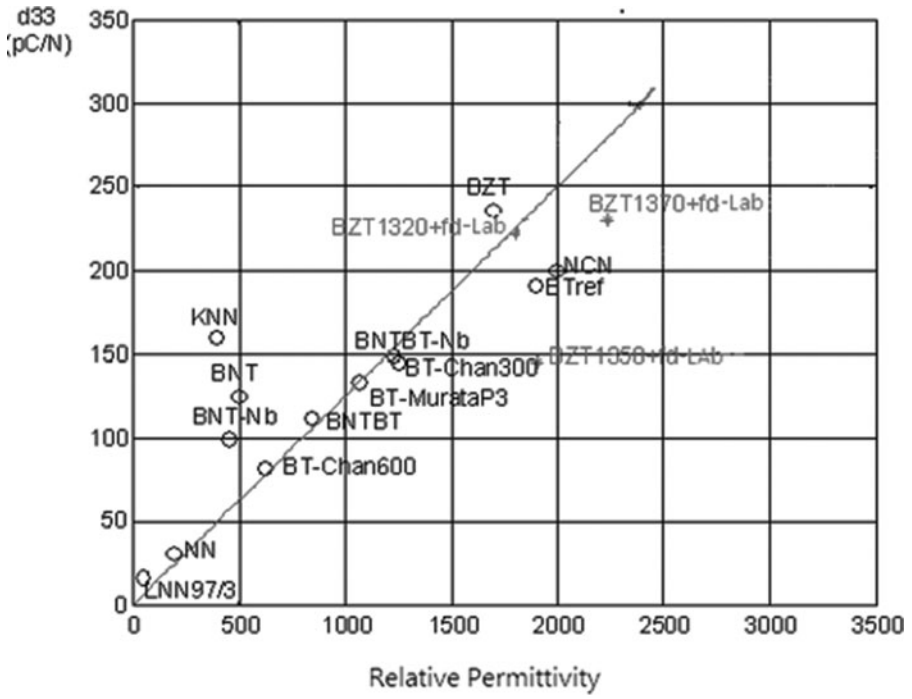

Figure 7. Piezoelectric properties of lead-free ceramics and materials prepared in our study.

At 1370°C, we obtain a d_{33} of 235 pC / N and ε_r of 2235. This study allowed us to optimize the sintering conditions ($T_{sintering} = 1370°C$) BZT ceramics with fondant (Table 4).

3. Comparison with other lead free materials

Figure 7 presents some piezoelectric properties of lead-free ceramics like alkaline niobates (NN: NaNbO3, LNN: LiNbO3-NaNbO3, KNN: KNbO3–NaNbO3), bismuth sodium titanates (BNT) and other barium titanate based compositions. The quasi-linear relation found between d_{33} and ε_r corresponds to a g_{33}value of 14×10^{-3}V m/N. BZT ceramics prepared from chemical process with the use of LBCu sintering aid shows dielectric and piezoelectric coefficients superior to those of other lead free materials.

IV. Conclusions

From high temperature X-ray diffraction data and grain size analysis, the Barium Zirconate Titanate formation has been studied and it is shown that an intermediate phase BaZrO3 was formed during the calcination of the precursor's powder. The powder from this chemical process is made of finer grains and leads to ceramics with very good properties and the intermediate phase had disappeared after sintering. The piezoelectric constant$d_{33}$was measured after

the use of **LBCu** sintering aid, at 25°C, and its value was around220 pC/N. This value is higher than the ones usually published for barium titanate ceramics: classically room temperature ε_r (1kHz) and d_{33} values are respectively around 1700 and 190 pC/N [26]. The use of fondant has lowered the sintering temperature compared to pure BZT; from 1320°C the dielectric and piezoelectric properties are correct. The electrical and piezoelectric properties are also largely superior to the other perovkite lead-free materials.

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