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Properties of Piezoelectric Ceramics Nanofilm from Sol-Gel Process

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This paper aims to prepare lead-free piezoelectric ceramics with excellent properties by sol-gel process. There are some parameters such as structure, dielectricitypiezoelectricity and ferroelectricity for the ceramic materials as prepared, all of which have been analyzed herein. Design a new annealing method, i.e. a distributed annealing, compared with the traditional single-step annealing, this method greatly improves the film properties since it treats with every laminar layer by annealing in the film preparation process. There is an optimal temperature 700°C when using stepwise annealing. Experimental analysis reveals that the thicker the film, the greater the dielectric constant, and the lower the dielectric loss; the dielectric constant of the film heaves with the increase of the temperature. The thickness of the ceramic film is proportional to its polarization intensity, but inversely to the remnant polarization.

1. Introduction

Piezoelectric ceramics as a representative of piezoelectric materials features good piezoelectricity and dielectric properties. It has been finding wider and wider applications in medicine, acoustics, sensors, and in other fields (Saito et al, 2004; Takenaka and Nagata, 2005; Shrout and Zhang, 2007). The existing piezoelectric ceramics are mostly lead-based piezoelectric ceramics (lead oxides account for 70%), which, during production and use, will generate plenty of toxic substances that are seriously detrimental to the ecological and social environment.

Leadfree piezoelectric ceramics (BNT-, KNN-based, etc.), as new piezoceramic materials invented in recent years, features good piezoelectricity, low chemical pollution, and low anisotropy (Zhao et al, 2008; Leontsev and Eitel, 2010; Safari and Abazari, 2010; Xiao et al, 2008; Xiao et al, 2007; Xiao et al, 2006). However, due to the ceaseless volatilization of potassium and sodium ions when preparing BNT- and KNN-based films, the leakage inductance of piezoceramic films gets higher, and the high cost of lead-free piezoceramics prepared based on metal alkoxides is not conducive to its popularization on a large scale (Pisitpipathsin et al, 2008; Lu et al, 2009; Berksoy and Mensur, 2012; Belhadj et al., 2017).

In view of the above issues, scholars have attempted to suppress the cost of lead-free piezoceramics and particle volatilization during the preparation by various technologies (Lei et al, 2009; Hansen, Astafiev and Zawada, 2009), such as vapor phase, pulsed laser and magnetron sputtering deposition methods, as well as sol-gel process. Among them, the sol-gel process is superior to others because it takes chemical solution as reaction medium to prepare ceramic film with complex ingredients. In the presence of this solution, it can suppress the effect of high temperature during the preparation of the thin film and effectively reduce the volatilization of potassium and sodium ions (Cheng et al, 2015; Jin et al, 2014; Pang, Qiu and Zhu, 2011). Relevant studies suggest that the sol-gel process consumes less chemical admixtures when preparing ceramic films, utilizes raw material at a higher rate and lower overall production cost (Watcharapasorn and Jiansirisomboon, 2008).

This paper prepares lead-free piezoceramics with excellent properties by sol-gel process, and analyzes the parameters such as structure, dielectricity, piezoelectricity and ferroelectricity of the ceramic materials as prepared. The findings can provide a new clue to the preparation of lead-free piezoelectric ceramics.

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2. Preparation of sodium bismuth titanate (NBT) lead-free piezoceramics

NBT lead-free piezoceramics is a new ceramic nanometer proposed in recent years. In this paper, NBT lead-free piezoceramic film materials are prepared by sol-gel process.

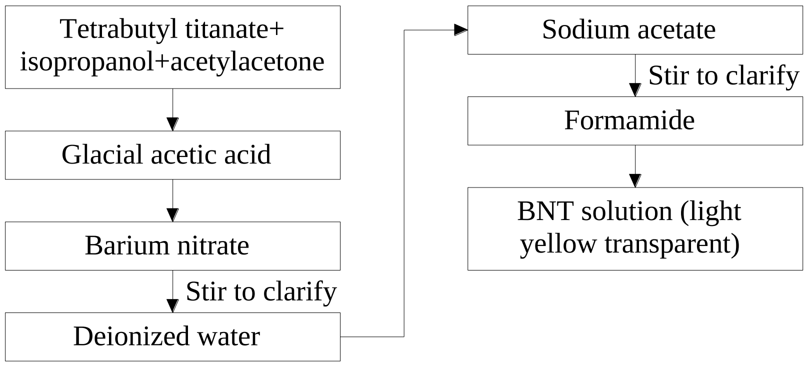


Figure 1: Preparation of NBT-based solution by sol-gel process

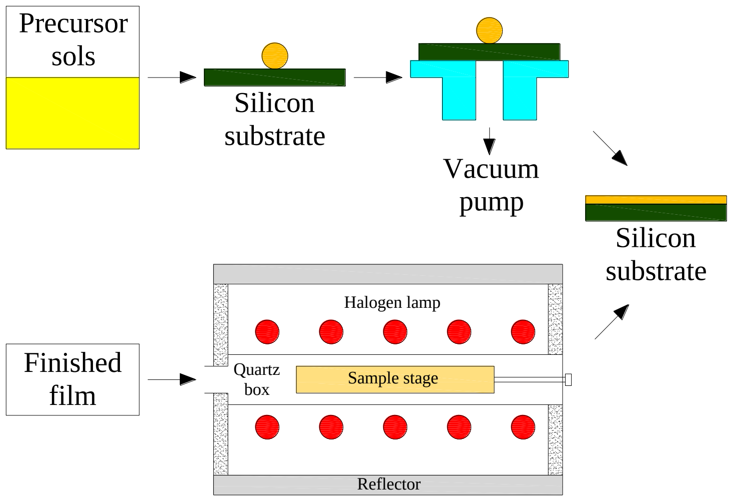


Figure 2: Preparation of NBT-based ceramic films by spin-coating process

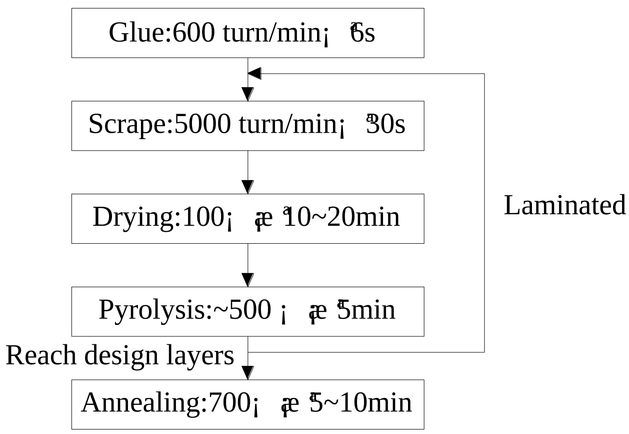


Figure 3: Heat treatment in the preparation of NBT-based ceramic films by sol-gel process

The preparation process of an NBT based solution using the sol-gel process herein is shown in Figure 1. In the test, the ambient temperature is controlled at 20°C; the reagent required in Figure 1 is sequentially added to the beaker and stirred with a magnetic stirrer. After the test, it is allowed to stand for 20 days in an incubator.

To further optimize the crystal structure of the NBT-based ceramic material film, the ceramic film is treated using the spin coating method, as shown in Figure 2. After the spin coating process, a layer of anti-passivation SiO2 coating is formed on the surface of the film. The whole process is performed at a high temperature (500 ℃~700℃).

After the ceramic film is smeared with SiO2, heat treatment is also required, as shown in Figure 3. First dry the NBT gel to remove excess moisture and other chemical substances from it, and then place it on a high-temperature heating stage to further remove organic compounds with high-melting point (boiling point). After the above pretreatment, the spin- and whirl coating (600 rpm), drying, pyrolysis, annealing and other processes are in turn performed.

3. Properties of NBT leadless piezoceramic film

3.1 Effect of annealing temperature on properties of ceramic films

First, we focus on the effect of annealing temperature on the properties of ceramic films. As shown in Figure 4, the X-ray diffraction spectrum of NBT ceramic films is available at three annealing temperatures (650~750°C). It can be seen that when the annealing temperature is too high (750°C), a mass of sodium and Bi will volatilize, and a second phase occurred in the XRD spectrum will accelerate the deterioration of the film properties.

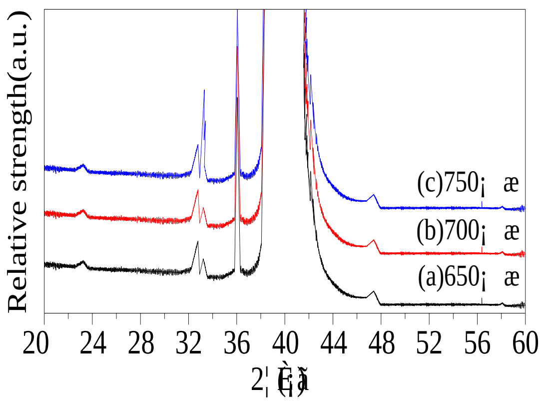


Figure 4: XRD spectrums of NBT ceramic films at three temps

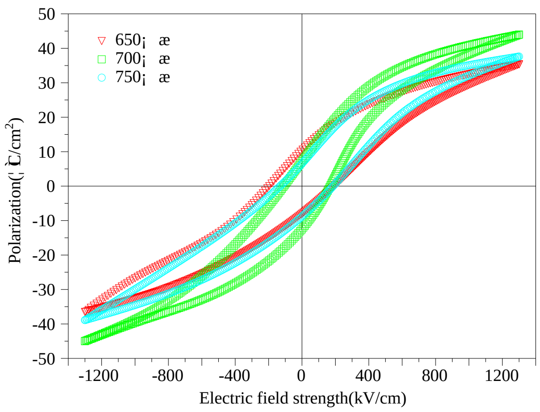


Figure 5: FHL of NBT ceramic film at three temperatures

As shown in Figure 5, the ferroelectric hysteresis loops of NBT ceramic films at three temperatures are obtained. As can be seen from the figure, when the temperature is at 650°C, the overall orthogon degree and remnant polarization of FHL are poor; when the temperature reaches 700°C, both parameters increase in different degree; at 750°C, the ferroelectric properties of the NBT ceramic film are best, but the sodium and Bi elements, etc., will volatile at overtop temperature, the annealing temperature can be set to be 700° C.

3.2 Effect of annealing process on the ceramic film properties

Most existing studies adopt one-step annealing process to treat with lead-free piezoceramic films. In view of the fact that the films prepared by this method contain plentiful pyrochlore, and the bottom laminar layer has insufficient reaction, we design the stepwise annealing, a new annealing process, herein. As shown in Figure 6, the traditional one-step annealing process (a) and the stepwise annealing algorithm (b) proposed herein play an effect on the electron spectrum of NBT ceramic films. It can be seen from the figure that the film prepared by the conventional annealing algorithm contains more pyrochlore, and for the annealing algorithm proposed herein, due to the annealing treatment performed on each layer, the pyrochlore further reacts to generate the perovskite phase. Reflected from the electron spectrum, the intensity of the spectral half-peaks of each element is higher and the peak width is minor.

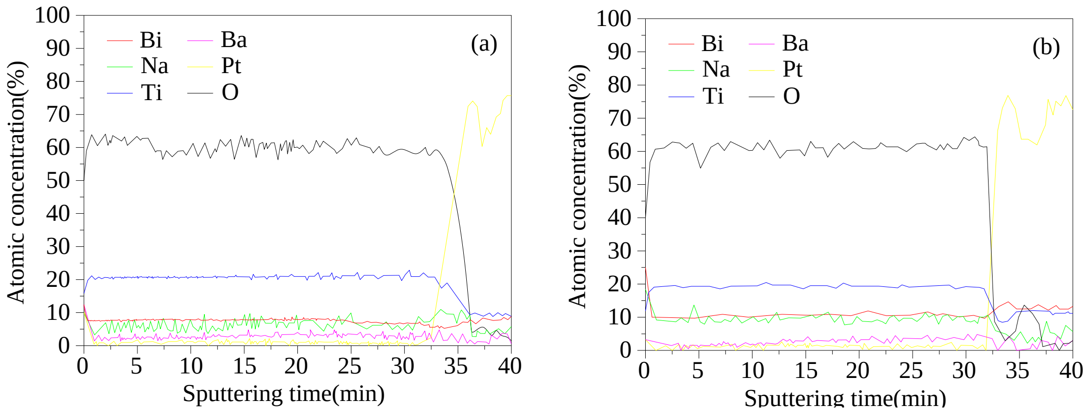


Figure 6: Effect of two annealing algorithms on electron spectrum of NBT ceramic films

3.3 Effect of ceramic film thickness on the film properties

As shown in Figure 7, the thickness of the ceramic film has an impact on its dielectric constant and losses. For the sake of easy comparison, a total of 4 types of ceramic films with different thicknesses from 120 nm to 560 nm are prepared herein. The effect of the thickness of the ceramic film on its dielectric constant and loss values is shown in Figure 7. As can be seen from the figure, the thicker the film, the higher the dielectric constant and the lesser the dielectric loss.

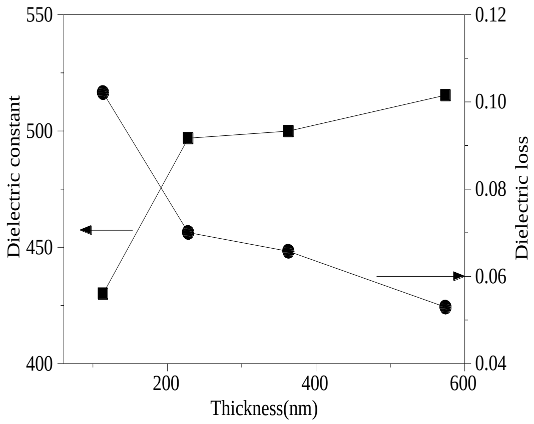


Figure 7: Effect of the ceramic film thickness on its dielectric constant and losses

Ceramic film capacitors can be expressed by the Eq. 1.

$$1/C = 1/C_f + 1/C_d \tag{1}$$

The dielectric constant and ceramic film capacitor have the following relationship:

$$\varepsilon = C \cdot d / \varepsilon_0 S \tag{2}$$

$$1/C = d_f / \varepsilon_0 \varepsilon_f S + d_d / \varepsilon_0 \varepsilon_d S \tag{3}$$

$$\varepsilon_r = \left(d_f / d_d + 1\right) / \left(d_f / \varepsilon_f d_d + 1/\varepsilon_d\right) \tag{4}$$

In theory, according to Eqs. 1~4, the film thickness is proportional to the dielectric constant.
As shown in Figure 8, there is a relationship between the dielectric constants and the temperatures of 4 types of ceramic films with different thicknesses. It can be seen from the figure that the dielectric constant of the film increases with the rise of temperature as a function of the thickness of 4 types of ceramic films, and when the ambient temperature is lower (below -150°C), the diviation in their dielectric constants is already very tiny.

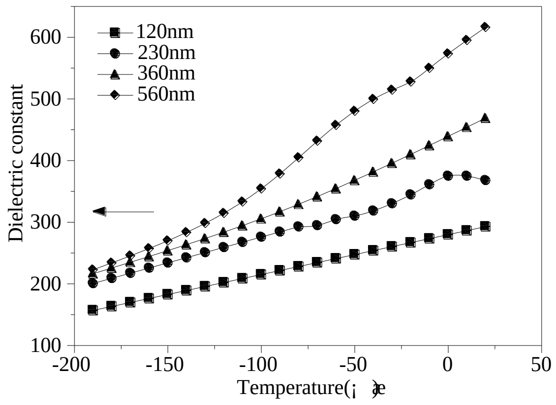
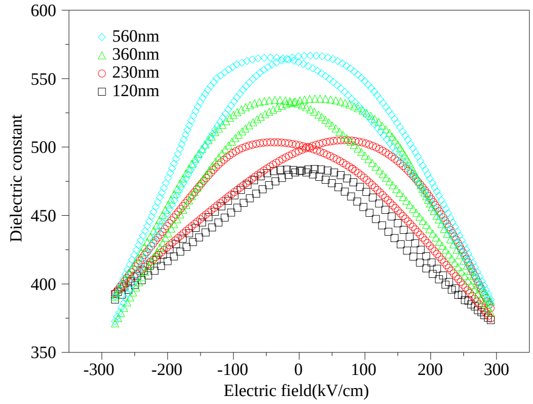


Figure 8: Relationship between dielectric constant and temperature of ceramic films with 4 thicknesses

As shown in Figure 9, there is a relationship between the dielectric constant of the film and the DC bias field as a function of the thickness of four ceramic films. The FHL of ceramic films evolves at different thicknesses as shown in Figure 10. It can be seen from Figure 9, the curves of the four ceramic films in the DC bias field are not distributed symmetrically, and as the field intensity increases, the difference in the dielectric constant of in the four films also gradually diminishes. It is known from Figure 10 that the thickness of the ceramic film is proportional to its polarization, and the remnant polarization is inversely proportional to the film thickness.



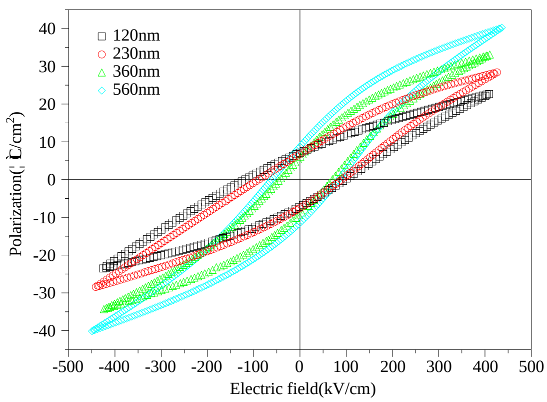


Figure 9: Relationship between dielectric constant and DC bias field as a function of thickness of four ceramic films

Figure 10: FHLs of 4 types of ceramic films

4. Conclusions

Here, lead-free piezoelectric ceramics with excellent properties are prepared by sol-gel process, and the parameters such as structure, dielectricity, piezoelectricity and ferroelectricity of the prepared ceramics get analyzed. Several conclusions are derived as follows:

(1) A new annealing method, distributed annealing, is designed, and compared with the traditional single-step annealing, it performs annealing treatment on every laminar layer in the film preparation process and causes pyrochlore contained in the film completely react to generate the perovskite phase so as to greatly improve the film properties.

(2) When the annealing temperature of the ceramic film reaches 750 °C, a mass of sodium (Na) and Bi will volatilize, which will accelerate the deterioration of the film performance. When the temperature is 650 °C, the integrated rectangular degree and the residual polarization of the ferroelectric hysteresis loop of ceramics are all poor; it is considered that the annealing temperature of the ceramic nano-film is 700°C.

(3) The thicker the film, the greater the dielectric constant, and the lower the dielectric loss; the dielectric constant of the film will build up with the increase of temperature.

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