

Room temperature thermal properties of $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ ferroelectromagnetic ceramics

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The thermal properties of ferroelectromagnetic $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ ceramics obtained using the conventional ceramic method at different sintering temperatures between 850°C and 1000°C by stoichiometric mixing of the corresponding oxides and using different kinds of precursors, have been investigated for the first time. In particular the thermal conductivity was calculated from the measured values of thermal diffusivity and specific (volume) heat capacity using the photoacoustic technique and the temperature relaxation method, respectively. Whereas no influence of the kind of precursor used for sample preparation on the thermal conductivity (k) was observed, we have found that the value of k depends on sintering temperature and has a maximum for samples synthesized at 900°C, regardless of the use of precursors or not. This paper shows that such feature is determined by the competition of the thermal conductivity mechanisms inside the grains and those at the grain boundaries in combination with the morphologic features.

Keywords: Thermal diffusivity; thermal conductivity; specific heat capacity; ferroelectromagnetic; multiferroic; lead iron niobate (PFN).

Se determinan por primera vez las propiedades térmicas de la cerámica ferroelectromagnética $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ obtenida utilizando el método cerámico convencional a diferentes temperaturas de sinterización, entre 850°C y 1000°C, mezclando estequiométricamente los óxidos correspondientes y utilizando diferentes tipos de precursores. En particular, la conductividad térmica se calculó a partir de los valores medidos de la difusividad térmica y el calor específico (a volumen constante) utilizando la técnica fotoacústica y el método de relajación térmica, respectivamente. Aunque no se observó ninguna influencia del tipo de precursor utilizado en la preparación de la muestra sobre la conductividad térmica (k), se encontró que el valor de k depende de la temperatura de sinterización y alcanza su valor máximo para las muestras sinterizadas a 900°C, sin importar si se utilizaron precursores o no. Este artículo muestra que esta propiedad está determinada por una combinación de los mecanismos de conducción dentro del grano con los que suceden en la frontera de grano y las características morfológicas.

Descriptor: Difusividad térmica; conductividad térmica; calor específico; ferroelectromagnético; multiferroico; niobato de plomo y niobio (PFN).

PACS: 77.84.Dy; 78.20.Hp; 81.40.Rs

1. Introduction

Multiferroics are materials of great scientific and technological interest because they show coexisting features such as ferro- or antiferromagnetism, ferroelectricity, or ferroelasticity/shape memory effects [1-5]. In the last few years the ferroelectric and antiferromagnetic single phase compound with perovskite structure lead iron niobate [$\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$, PFN for short], in which electric and magnetic order coexist, has been widely investigated [6-16]. Although detailed, systematic studies about their physical properties have been reported before, to the best of the authors' knowledge, reports on their room temperature thermal properties are not yet available in the literature. Thus the main objective of this work is the evaluation of the thermal properties of PFN ceramics and we focus our attention on the influence of the sintering temperature and the effects of different kinds of precursors used for sample preparation on the thermal conductivity.

2. Experimental

The PFN ceramic samples studied here were obtained using the conventional ceramic method. One group of samples, labeled PFNoxides, were produced from calcined powders synthesized by solid state reaction of reagent grade iron, niobium and Pb oxides (Fe_2O_3 , Nb_2O_5 and PbO respectively) in stoichiometric amounts. The other two groups were obtained by the B-site precursor method using the ferrocolumbite (FeNbO_4) as precursor, which has been recognized as an effective way to obtain a pure perovskite phase in lead-based systems. They were labeled PFN1075 (when the monoclinic phase FeNbO_4 precursor synthesized at 1075°C was used) and PFN1200 (the orthorhombic phase FeNbO_4 precursor synthesized at 1200°C was used). The samples were sintered at different temperatures between 850°C and 1000°C. More details about the fabrication process are given in previous reports [7,9].

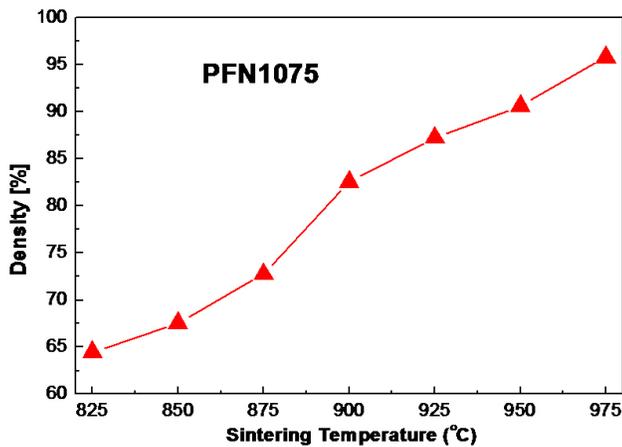


FIGURE 1. Average density values in percent of the theoretical value of the PFN1075 samples as function of the sintering temperature.

Thermal conductivity (k) was calculated from the measured values of thermal diffusivity (α), and specific (volume) heat capacity (C), by means of the well known relationship

$$k = \alpha C. \quad (1)$$

The thermal diffusivity was obtained using the photoacoustic (PA) technique in its open cell configuration [17-19], in which the sample is mounted directly on top of an electret microphone where the PA signal is detected, while the specific heat capacity was measured using a calorimetric technique, namely the temperature relaxation method [20,21]. This methodology has been successfully employed before by several authors for the characterization of a great variety of materials, such as semiconductors [22], foods [23], wood [24], among others, as well as other kinds of ferroelectric ceramics [25,26], therefore we will not give specific details here.

3. Results and discussion

The thermal diffusivity, studied as a function of the sintering temperatures for three groups of samples, exhibits a maximum value for the samples sintered at 900°C. On the other hand, we observe that the specific heat capacity, measured with the technique described in detail by E. Marín and H. Valiente [27], does not show an appreciable variation with respect to the sintering temperature, having an average value of $(1.50 \pm 0.10) \times 10^6 \text{ J/cm}^3 \text{ K}$. This constant value of C can be explained by taking into account its definition as the product of the density (ρ) and the specific heat (c). The specific heat is defined as the change in the internal energy per unit of temperature change; thus, if the density of a solid increases (or decreases) the solid can store less (or more) energy. Therefore, as the density increases with sintering temperature (see Fig. 1), the specific heat must decrease and then the product $C = \rho c$ stays constant for all sintering temperature values. As a consequence of C being constant, and according to Eq. (1), the behavior of the thermal conductivity is similar to that of

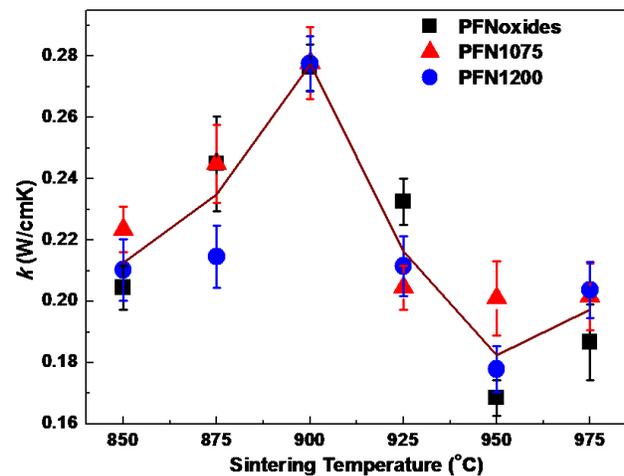


FIGURE 2. Thermal conductivity as function of the sintering temperature. Solid line links the average value for each temperature.

TABLE I. Values of average density and grain size, $\text{Fe}^{3+}/\text{Fe}^{2+}$ concentration ratio, maximum dielectric constant and diffuseness exponent for the PFN ceramics obtained by three different kinds of precursor at a sintering temperature of 900°C.

	Sample		
	PFNoxides	PFN1075	PFN1200
Average			
Density (g/cm^3)*	7.43(88)	6.77(80)	6.54(77)
Average			
Grain Size (μm)	1.9	1.8	2.1
$\text{Fe}^{3+}/\text{Fe}^{2+}$			
Concentration Ratio	0.66	0.57	0.56
Dielectric Constant			
Maximum, $\epsilon'_m \omega_i$ *	695	641	6790
Diffuseness Exponent α	1.65	1.86	1.73

*Values in parenthesis are average densities in percent of the theoretical value. *Values at 100 kHz

the diffusivity, as is illustrated in Fig. 2, showing a maximum at 900°C.

As can be seen in Fig. 2, the samples prepared with different precursors exhibit very similar values of thermal conductivity, regardless of the temperature at which they were sintered, although their dielectric and ferroelectric properties are significantly different according to previous studies. This is an understandable result if we take into account the structural and morphological characteristics of the different samples. As an example, let us examine the samples sintered at 900°C, previously studied in detail [9-11,14,16], which are those that also show the lowest dispersion in the k values compared with those obtained at different temperatures. Also, these samples obtained with different precursors, showed no structural differences, a uniform grain distribution, the same ferroelectric-paraelectric transition temperature of 110°C,

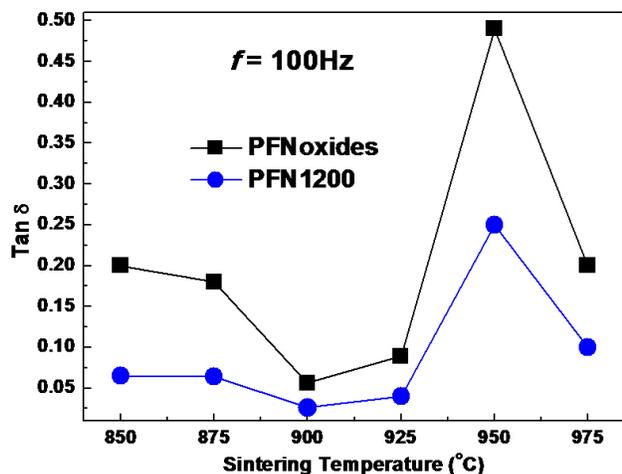


FIGURE 3. Dielectric loss as function of the sintering temperature for PFNOxides and PFN1200 samples at a frequency of 100 Hz.

and a normal diffuse phase transition (non-relaxor behavior), as summarized in Table I. We also see that among the samples sintered at 900°C, PFN1200 shows the best electrical behavior, meaning higher values of dielectric permittivity and remanent polarization, and the lowest dielectric losses [9-11,16]. Thus the following question arises: What is the origin of the maximum of thermal conductivity at the sintering temperature of 900°C, at which also a lower dispersion in the k values is observed?

Making a simple inspection of Fig. 2, we note that for temperatures below 900°C the thermal conductivity is higher than for temperatures above that value. From this fact, one is lead to believe, according to the above discussion, that possible causes of this behavior may be attributed to the relationship between the morphologic features of the samples and the strong competition between the thermal transport mechanisms inside the grains and those at the grain boundaries, as functions of the sintering temperature. It is known that, in general, near room temperature, the two principal thermal conduction mechanisms in solids are due to conduction electrons (especially in metals) and lattice vibration (phonons) (especially in insulators, such as ceramics) [28]. From previous dc and ac conductivity analyses in the samples here studied in the temperature range from room temperature to 300°C [7,9-11], we found that all observed conduction and relaxation processes were assumed to take place inside the grains, conditioned by the grain and ferroelectric domain sizes, the degree of deformation of the lattice and the crystallites, as well as the potential barriers in the grain boundaries due to space charge accumulated at these interfaces. Four contributions of electrical conduction mechanisms were identified in the studied temperature range for the three kinds of samples: n and/or p type hopping charge, small polarons, oxygen vacancy conduction, and the intrinsic ionic conduction which occurs at higher temperatures. The $n - p$ hopping charge and small polarons mechanisms were associated to Fe^{2+} presence and the other two to oxygen vacancies, both generated during the sintering processes. The small polarons,

defined as a coupling of lattice deformations with n or p -type charges (electron-phonon interaction), is a characteristic mechanism of these ferroelectric materials under electrical and thermal fields, in correspondence with their piezo- and pyroelectric properties [9-11]. Consequently, polarons result in suitable transport carriers for thermal energy.

With this picture in mind, the behavior of the thermal conductivity in Fig. 2 can be explained using the following arguments: At low sintering temperatures the samples look like pressed powders, with smaller grain size and very high porosity that hinders the intergrain heat transfer rate by the effects of interfacial thermal resistance; moreover, this phenomenon is favored in a similar way, by the very small crystallite size inside the grains which decreases the intragrain (intercrystallite) long range electrical conductivity. The latter situation is illustrated in Fig. 3 where, for PFNOxides samples (with smaller crystallite size), dielectric loss is more pronounced compared to that of PFN1200, due to a higher chaotic conduction along crystallite boundaries [11].

When the sintering temperature increases and approaches 900°C, the density of the sample increases (see Fig. 1); however, the density is not high enough to make the electrical conduction along grain boundaries the preponderant mechanism. On the contrary, in these cases the dielectric behavior is determined by the polarization and short range conduction processes taking place inside the grains. At 900°C the samples exhibit the best dielectric properties, as is illustrated in Fig. 3, showing the lowest values of the dielectric loss. From a previous study it was demonstrated that the higher contributions come from small polarons, so that heat transfer and therefore thermal conductivity are enhanced, thus justifying the maximum in Fig. 2.

For samples sintered at temperatures above 900°C we observed that the density approaches the theoretical value due to a higher intergrain fusion. Additionally, the ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ and the number of oxygen vacancies increase; consequently, a higher concentration of free charge carriers develops and the long range conduction mechanisms become predominant both inside the grains and along the grain boundaries with a consequent increase in the dielectric losses as can be seen in Fig. 3 for the PFN1200 and PFNOxides samples. However, this high mobility of charges at the grain boundaries leads to a higher chaotic thermal conduction in detriment of directional energy transport, reducing thus the thermal conductivity. This last effect is more pronounced for samples obtained at 950°C, where a minimum of k is observed in correspondence with the maximum of the dielectric loss at this temperature (see Fig. 3); moreover, this is enhanced for PFNOxides samples due to their small crystallite sizes, as was discussed above.

4. Conclusions

In summary, the thermal conductivity behavior in PFN ceramics is not affected by the kind of precursor used for their preparation; it is determined instead by the morphological

features and the competition between the thermal and electrical transport mechanisms (preponderantly small polarons) inside the grains and across the grain boundaries, and the conduction processes along the grain boundaries. The samples sintered at 900°C show the highest value of the thermal conductivity in correspondence with its best dielectric properties facts that are explained in terms of conduction and polarization processes by small polarons and short range conduction mechanisms taking place inside the grains, and not the long range conduction mechanisms occurring along the grain boundaries. This work shows the potential of the PA technique, aided with specific heat capacity measurements, to study the heat transport mechanisms in PFN ceramics and

similar materials. For a more comprehensive analysis of these mechanisms, temperature dependent measurements of thermal properties are necessary. Work in this direction is under way.

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