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Characterization of $Bi_{4-x}R_xTi_3O_{12}$ (R_x = Pr, Nd, Gd, Dy, $x = 0.8$) layered electroceramics by a photoacoustic method

A. Huanosta-Tera[a], R. Castañeda-Guzmán[b,*], J.L. Pineda-Flores[a]

[a]*Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Aptdo. Postal 70-360, C.P. 04510, México D.F., Mexico*

[b]*Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Aptdo. Postal 70-186, C.P. 04510, México D.F., Mexico*

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Abstract

We have carried out photoacoustic experiments to study the layered electroceramics $Bi_{4-x}R_xTi_3O_{12}$ (R_x = Pr, Nd, Gd, Dy), with $x = 0.8$. Results are shown in terms of successive analyses performed on functions, PA(t, T_i), which result from the interaction of the laser beam with the crystalline lattice. Previous permittivity experiments performed in the materials suggested anomalous ferroelectric behavior. Using a pulsed Nd:YAG laser (10 Hz, 5 ns pulse width), photoacoustic experiments were run from room temperature up to 800 °C. Perturbations in the resultant correlation curves can be interpreted as the existence of a wide set of different transition temperatures in the material, such as are believed to occur in relaxors. From these experiments, we conclude that the temperature dependence of non-classical ferroelectrics can be more closely monitored.

Keywords: A. Ceramics; D. Dielectric properties; C. Ferroelectricity; C. Phase transition

1. Introduction

A good understanding of the fundamental physical behavior of new ceramic materials for practical applications in solid state devices is required. The physical behavior required depends on the sensitivity of the research technique to be used to obtain the appropriate experimental information. For example, in the case of ferroelectric materials, the temperature dependence of the interconnected physical parameters heat capacity, volume compressibility or volume thermal expansion are some of the most helpful variables for investigating the transition temperature. Also, the temperature dependence of

* Corresponding author. Tel.: +52-5-622-8614x115; fax: +52-5-622-8651.
E-mail addresses: huanosta@servidor.unam.mx (A. Huanosta-Tera), castanr@aleph.cinstrum.unam.mx (R. Castañeda-Guzmán).

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permittivity has been widely used to determine dielectric properties of materials, particularly ferroelectrics. In the last case a sharp peak in the curve ε' versus T can be taken as the signature of a well-behaved ferroelectric. Location of the peak gives the Curie temperature. It is also known that when ferroelectric properties are investigated, ε' versus T curves may not be sensitive enough to detect the presence of small variations of permittivity in the temperature interval investigated. This is important in the case of relaxor materials, characterized by a diffuse phase transition.

Recently, photoacoustic experiments have been used to study phase transitions in a variety of materials [1–3]. These authors have carried out photoacoustic experiments with $BaTiO_3$, which is a classical ferroelectric, to determine its T_c. Their results perfectly agree with those in the literature. Using photoacoustic experiments of pulsed laser, it has been recently established [4] that valuable information related to diffuse phase transitions can also be obtained.

2. Photoacoustic method

In the thermoelastic regimen (no ablation), the acoustic waves generated after the irradiation of the sample with laser pulses, is detected with a piezoelectric sensor. The interaction laser beam-lattice produces a function [3,5] say $\mathrm{PA}(t, T_i)$, where i indicates the size of the temporal signal, and T_i describe different temperatures. Once the functions are obtained they can be mathematically manipulated to extract the important physical information.

In the direct coupling method, isotropic case, the acoustic wave is related to the thermal expansion ΔV_{th} of the irradiated volume V_{o}. In this case ΔV_{th} can be written as $\Delta V_{\mathrm{th}} = \beta H/C_p\rho$, where β is the volume expansion coefficient or compressibility, C_p is the specific heat at constant pressure, ρ is the density, and H is the heat deposited in the volume V_{o}. This expansion creates a pressure wave which travels outwards at the velocity of sound. The electrical signal generated in the transducer is proportional to pressure, and it was stated [1] that, for phase transitions, $\mathrm{PA}(t, T_i)$ is proportional to the ratio (β/C_p). All the other parameters are practically constant, thus allowing characteristic temperature determinations.

The temporal profile of the acoustic pressure depends on the spatial properties and microscopic characteristics of those regions where the ultrasonic wave interacts with the physical system. Therefore this kind of experiments should be able to detect fundamental structural changes in the material as a consequence of the interaction of the modulated laser beam with the crystalline lattice.

The analysis performed involves two types of correlation, the first one over successive functions $\mathrm{PA}(t, T_i)$ and $\mathrm{PA}(t, T_{i+1})$, which will reveal those changes occurring in the specimen in the temperature interval $(T_{i+1} - T_i)$, where the correlation between $\mathrm{PA}(t, T_i)$ and $\mathrm{PA}(t, T_{i+1})$ will be one if they are identical functions, but less than one if any change occurs in the temperature interval $(T_{i+1} - T_i)$. This correlation is very sensitive to local crystalline changes in the material. This produces a temperature-dependent curve which exhibits noticeable resolution characteristics. With the second correlation, a comparison is carried out between $\mathrm{PA}(t, T_1)$ and every $\mathrm{PA}(t, T_i)$ function, where $i = 1, 2, 3, \ldots$, as performed in any standard correlation [6]. Then the appropriate conclusions can be reached by the analysis of the temperature dependence of one or both correlation types between events.

For example, using the first correlation type, plotted as a function of temperature, phase transition temperatures have been obtained with reliable accuracy [5]. In the specific case of ferroelectric transitions, crystalline changes caused by temperature variations have been obtained by photoacoustic

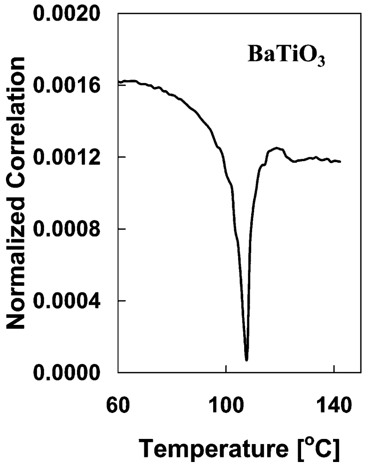

Fig. 1. Photoacoustic curve of correlation analysis for $BaTiO_3$.

experiments carried out as a function of temperature, and results have been compared with those from classical experiments to determine T_c. The agreement is exceptional in the case of $BaTiO_3$ [1] (Fig. 1), where it can be observed that there is a pronounced peak at the correct value of T_c. This means that, as a function of temperature, the curves obtained give quantitative information about the temperature where the ferro-paraelectric transition occurred.

3. On the studied materials

By normal solid state reaction we prepare layered electroceramics given by $Bi_{4-x}R_xTi_3O_{12}$ (R_x = Pr, Nd, Gd, Dy) details are given elsewhere [7]. These compounds belong to the Aurivillius phases, which are made up of constituted by a large family of layered compounds characterized by an intergrowth between $(Bi_2O_2)^{2+}$ sheets and $[M_{n-1}B_nO_{3n+1}]^{2-}$ perovskite-like layers, where n describes the number of octahedral stacked along the direction perpendicular to the sheets, M can be Bi^{3+}, Pb^{2+}, Ba^{2+}, Sr^{2+}, rare-earth elements, etc., and B can be Ti^{4+}, Nb^{5+}, Fe^{3+}, etc., where M and B occupy the 12- and 6-fold coordination sites, respectively, of the perovskite slab [8]. For the studied compounds it is considered that the rare-earth (R_x) has been introduced in the host lattice $Bi_4Ti_3O_{12}$, in which R_x occupy Bi sites. When ferroelectric materials do not present a successful phase transition at a strictly determined T_c, i.e., when they exhibit a diffuse permittivity maximum which is frequency dependent, they are called relaxors. A large number of Aurivillius phases are ferroelectric, but it is also possible to modify that behavior by doping them with the appropriate cations, which often produces relaxor materials.

4. Experimental set up

The photoacoustic experimental setup employed consisted of [1]: (a) a pulsed Nd:YAG laser (10 Hz, 5 ns pulse width); (b) a beam splitter and a pyroelectric detector with display for real time monitoring of the energy variations of the laser (<500 μJ); (c) a commercial electrically heated tubular furnace connected to a PID temperature control; (d) The acoustic response was detected using piezoelectric ceramics (resonance frequency at 240 kHz) coupled to the sample through a quartz bar, and the averaged signals (300 scans) were monitored with a digital oscilloscope. The signals without amplification were recorded in a digital oscilloscope and sent to a PC through a GPIB interface. Photoacoustic measurements were performed in a dry air atmosphere with a heating temperature rate of 5 °C/min, from room temperature up to 650 °C.

5. Results

In this paper we have selected the composition $x = 0.8$, from the synthesized compounds to perform photoacoustic experiments. In Fig. 2 we show a typical X-ray diffraction pattern from the studied materials and also that for $Bi_4Ti_3O_{12}$. Frequency-dependent permittivity against temperature curves, $\varepsilon'(\omega)$, obtained from these compounds were previously worked out. In Fig. 3 we present the permittivity results for $Bi_{3.2}Pr_{0.8}TiO_{12}$.

The permittivity peak is frequency dependent, and it is far from a sharp peak. Evidently, $\varepsilon'(\omega)$ decreases and the characteristic temperature increases, when the frequency increases. All of these features are the dielectric attributes of relaxor ferroelectrics.

Photoacoustic experiments carried out in the same specimens and at approximately the same temperature interval are presented in Fig. 4. For every compound studied, the correlation performed produced curves which detected the presence of various pronounced peaks distributed in a large temperature interval.

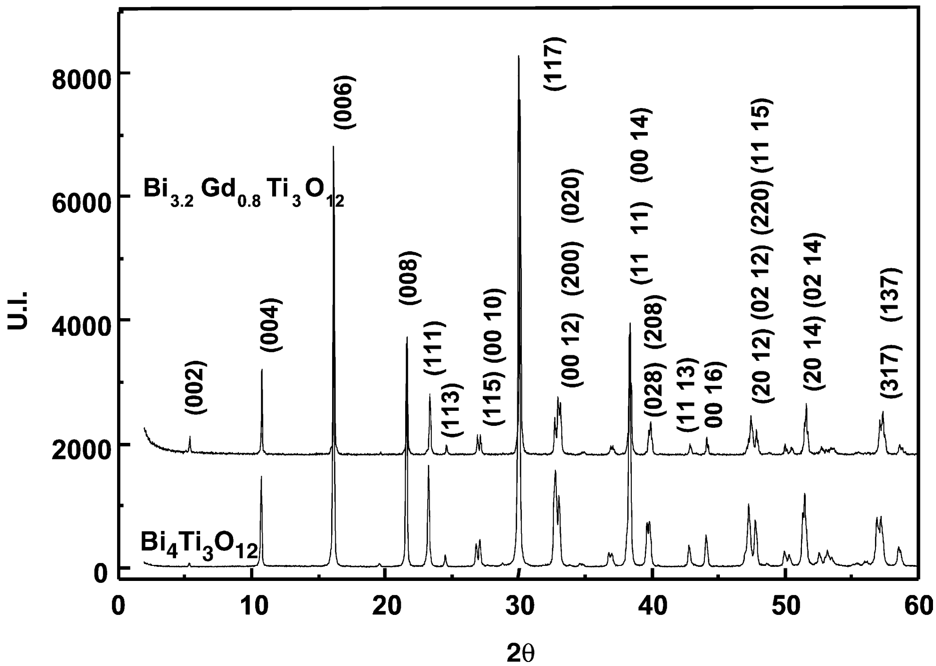

Fig. 2. Typical X-ray diffraction pattern for $Bi_{4-x}R_xTi_3O_{12}$ (R_x = Pr, Nd, Gd, Dy).

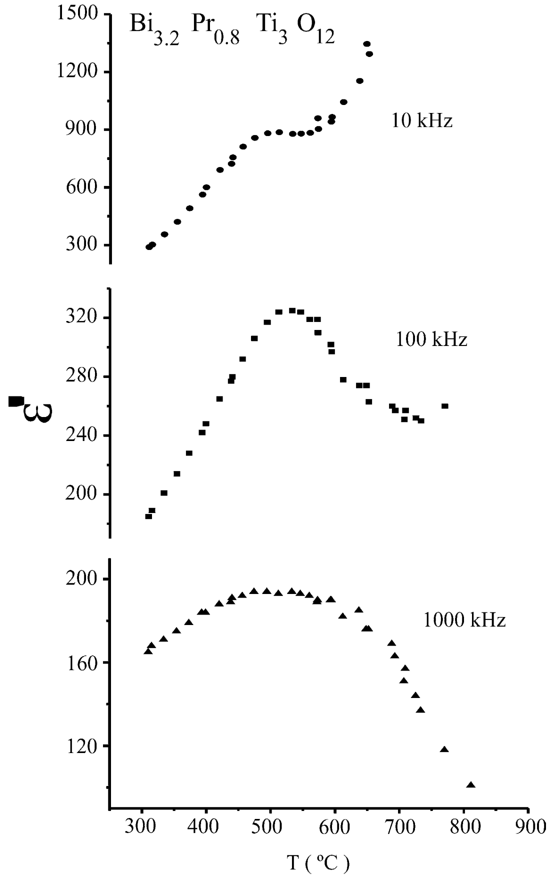

Fig. 3. Permittivity curve at three frequencies for $Bi_{3.2}Pr_{0.8}O_{12}$.

6. Discussion

As is known, in displacive ferroelectrics their properties arise by the occurrence of a displacement Δz of certain atoms from their higher temperature positions in the material. Atomic displacement dependence of the Curie temperature can be given by $T_c = (K/2k)(\Delta z)^2$ [9], where K has the dimensions of a force constant, k is the Boltzmann's constant, and T_c in absolute units. This expression establishes the equivalence between the lattice vibrational energy and the displacive energy of the ferroelectric state.

The nature of the physical properties of relaxors is still waiting for a definite explanation, but it seems to be related to a break of the traslational invariance of the polarization, present in a classical ferroelectric, which leads to microscopic charged compositional fluctuations [10]. This suggest the possibility of considering relaxors as made up of ferroelectric micro-regions possessing different transition Curie temperatures. In the materials studied, the substitution of Bi^{3+} by smaller ions, such as the rare-earth elements Pr, Nd, Gd, and Dy, seems to be favorable to the formation of micro regions with different transition temperatures, and in which the unit cell size and the polarization dynamics should be different as well. This is the source of the multi-peaked curves obtained by photoacoustic experiments (Fig. 4).

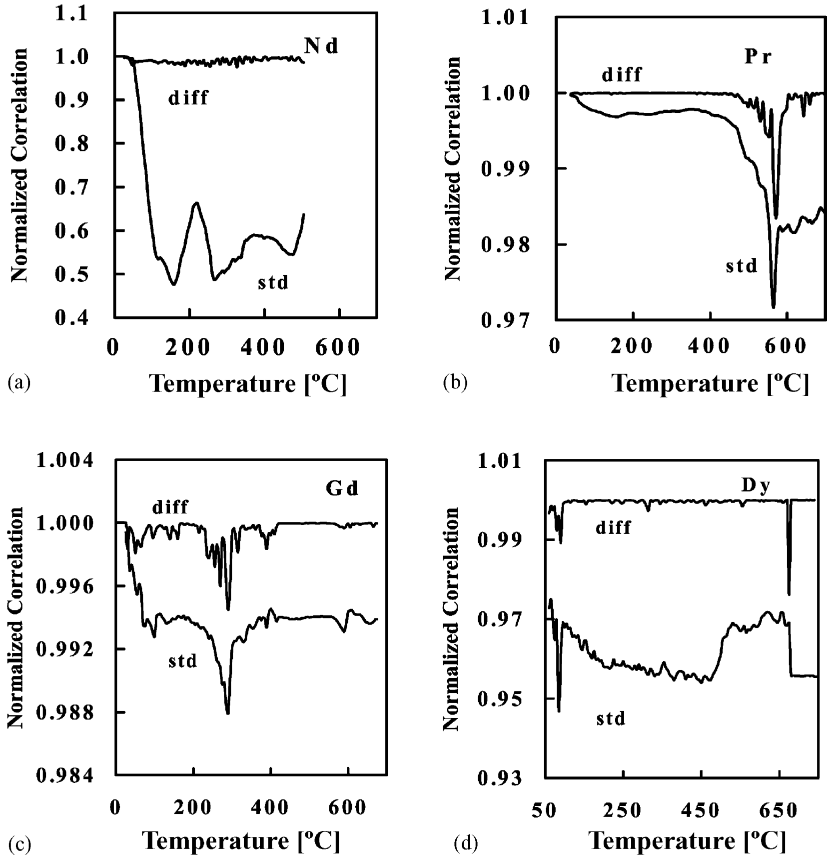

Fig. 4. Photoacoustic curves of correlation analysis, for standard (std) and differential (diff) analysis for $Bi_{4-x}R_xTi_3O_{12}$, R_x = Pr, Nd, Gd, Dy, $x = 0.8$: (a) Nd, (b) Pr, (c) Gd, (d) Dy.

We have suggested [4] the idea that differences in the differential variation of volume with the pressure wave travelling through the medium, which is essentially the compressibility, is what strongly affects the correlation curves in Fig. 4.

The frequency-dependent permittivity curves depict a very broad peak (Fig. 3), from around 400 °C till above 600 °C. At the same time, the correlation performed ('std' curve in Fig. 4b) between PA(t, T_1) and PA(t, T_i), suggests the occurrence of physical changes in the analyzed system. The broad peak in Fig. 3, and the peaked correlation in Fig. 4b, both occur approximately at the same temperature interval. Similar observations has been made for the other compounds. Permittivity curves (not shown) exhibit frequency-dependent broad peaks at similar temperature intervals as the peaked correlated curves are observed in the a, c, and d curves in Fig. 4. None of the curves in Fig. 4 exhibits a single sharp peak as would be expected from a proper ferroelectric to paraelectric transition. Obviously, the materials are not classical ferroelectrics, a real massive transition is not occurring in them.

We point to the presence of a sharp peak around 560 °C in the 'std' curve in Fig. 4b. So, as well as the relaxor behavior, this seems to announce the presence of a normal ferroelectric transition in the case of $Bi_{3.2}Pr_{0.8}TiO_{12}$.

Photoacoustic experiments can give reliable information about complex behavior, as in relaxors, however, up to now we have no mathematical expressions to establish a relationship between the parameters affecting T_c and the various peaks appearing in curves like those in Fig. 4.

Curves in Fig. 4 (marked 'diff') show the results of the successive analysis mentioned in Section 2. These curves have been interpreted [3] as a description of the dynamical stability occurring in the system. Stability will be altered if the curve moves away from 1. Then, as long as the curves are temperature independent, the material will be more stable. From this point of view, the compound $Bi_{3.2}Pr_{0.8}O_{12}$ would be the most stable, before the transition, of all studied compounds.

In conclusion, with photoacoustic experiments phenomenological information was obtained by analysing the acoustic signal excited by a modulated laser pulse. The pressure wave induced by the laser beam was detected as an acoustic wave by using a piezoelectric transducer. Differences in the photoacoustic response, determined from variations in amplitude and/or phase at the receiver provided enough information to conclude that the studied compounds behave as relaxor materials. Naturally, this type of experiment can be advantageously used to obtain quantitative information on transition temperatures of ferroelectric materials. Further, in the photoacoustic technique, the combination of pulsed laser and piezoelectric detection results in simplicity of the experimental set up, very compact devices and very high acoustic coupling, avoiding the requirement of signal amplification.

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