Ferroparaelectric transitions in relaxor materials studied by a photoacoustic technique

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Photoacoustic experiments were carried out in two ceramic compounds to present a promising way to study relaxor materials. This technique has been shown to have some advantages in the investigation of phase transitions in a variety of materials. We use the temperature-dependent data of both dielectric and photoacoustic responses from the ceramic compound $Bi_{4-x}R_xTi_3O_{12}$, with $R_x=Pr$, $x=0$ and 1.6, to illustrate this work. We establish definitely that $Bi_4Ti_3O_{12}$ is a relaxor. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1394950]

As ferroelectric properties are related to dielectric, acoustic, and optical parameters, in this work we use a photoacoustic technique to follow ferroparaelectric transitions in relaxor ferroelectric materials. Generation of sound by using modulated light or laser pulses, when it is absorbed by the sample, is what is known as the photoacoustic effect. So, in photoacoustic experiments relevant information is obtained by analyzing the acoustic signal excited by the laser pulse, in our case, on the surface of the material under study.

The laser beam induces a pressure wave, which is detected outwardly as an acoustic wave by using a piezoelectric transducer. The temporal profile of the acoustic pressure depends particularly on the spatial properties and characteristics of the microscopic region where the ultrasonic wave interacts with the material. This means that any change in the lattice should be shown by a change in the photoacoustic signal emerging from the physical system. This is important particularly for those cases where crystalline changes caused by temperature variations must be monitored. Therefore, this technique has been successfully used to study phase transitions.[1–3]

Different opinions exist[4] about ceramic $Bi_4Ti_3O_{12}$, namely, is it a ferroelectric material or is it a relaxor?

One of the objectives of this study is to clarify this controversy, another is to show some advantages in using this technique to investigate relaxor materials in particular.

For this purpose we will compare the temperature dependence of dielectric data from $Bi_{4-x}R_xTi_3O_{12}$, $R_x=Pr$, $x=0$ and 1.6, and data from photoacoustic experiments performed on the same sample. Incidentally, these materials are members of the so-called *Aurivillius* family built up by perovskite-like $M_{n-1}B_nO_{3n+1}$ slabs sandwiched by fluorite-like Bi_2O_2 layers, $n=1-5$, where M and B are ions with suitable chemical valence and ionic radii.[5]

Sample preparation was by the conventional solid-state process, full details will be given elsewhere.[6] In the experiments reported here, disk-shaped, 13-mm-diam, and 1-mm-thick samples of $Bi_4Ti_3O_{12}$ and $Bi_{2.4}Pr_{1.6}Ti_3O_{12}$, sintered at 1000 °C for 19 h, were used. The composition was controlled by x-ray powder diffraction techniques. To perform the photoacoustic measurements, a Nd:YAG laser (Continuum, model Surelite I) at 10 Hz, with a pulse width of 7 ns, was used and the transducer was PZT with 240 kHz resonance frequency. The laser beam was expanded and collimated with a pair of glass lenses and focused onto the sample in a 2 mm spot. More information about the experimental setup can be found in Ref. 1.

Heating experiments were carried out in normal laboratory conditions from 300 to 900 °C, using a well-controlled electrical tubular furnace. The analyzed measurements are the result of averaging at least 200 photoacoustic signals for a given temperature.

Dielectric data as a function of temperature are used to determine the ferroelectric transition temperature T_c. Data studied here come from compounds which are members of a wide set of compounds ($Bi_{4-x}R_xTi_3O_{12}$, $R_x=Pr$, Gd, Nd, Dy, and $x<2$) synthesized to study their dielectric characteristics by impedance spectroscopy methods. Following the temperature dependence of the dielectric constants we have found[6] a well-defined T_c for various prepared materials. We found that parameter x determines the ferroelectric behavior of the resultant compounds; low rare-earth concentrations ($x<0.8$) favor properly formed ferroelectrics, which produce sharp permittivity peaks at true transition temperatures, but large concentrations ($x>0.8$) favor the occurrence of relaxor materials, whose permittivity curves do not exhibit sharp peaks.

Dielectric data presented in Figs. 1 and 2, open circles,

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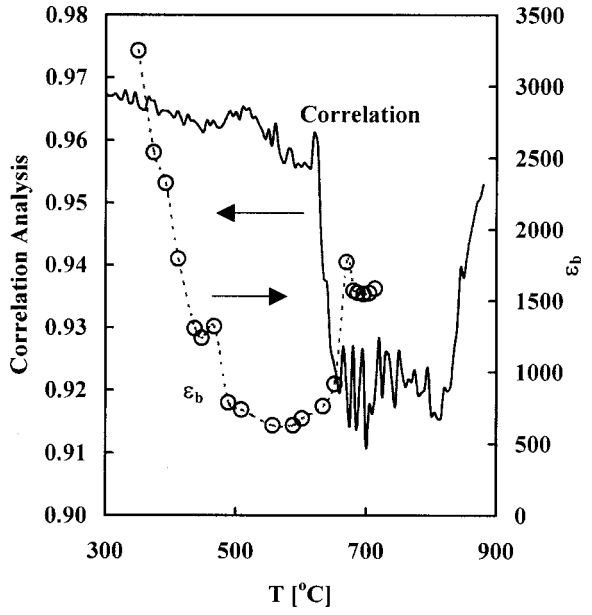

FIG. 1. Photoacoustic signal and dielectric behavior (open circles) of $Bi_4Ti_3O_{12}$, against temperature.

show the temperature dependence of both $Bi_4Ti_3O_{12}$, and $Bi_{2.4}Pr_{1.6}Ti_3O_{12}$ ceramic compounds. The first compound exhibits a Curie temperature of 675 °C, whereas the second one shows a widely depressed and less smooth curve. Apparently, there is no maximum in the temperature dependence of the dielectric constant in the second case.

Dispersive behavior in dielectric properties is typical of the well-known class of relaxor ferroelectrics materials. There are several[7] models which attempt to explain the physical properties of these materials. These materials are technologically important for multilayer capacitors, sonar listening devices, etc. Presumably, its behavior is attributable to the presence of microscopic composition fluctuations.[8] Thus, physical interpretation of relaxor behavior is related to an unsuccessful phase transition at a strictly determined T_c. It is considered[9,10] that relaxors are those ferroelectric materials where micropolar regions switch between a variety of orientations, rather than in a preferential one, far below and above the transition temperature. This dynamical disorder, caused by thermal motion, is responsible for the lack of sharp peaks at a well-defined temperature in the dielectric constant against temperature curves.

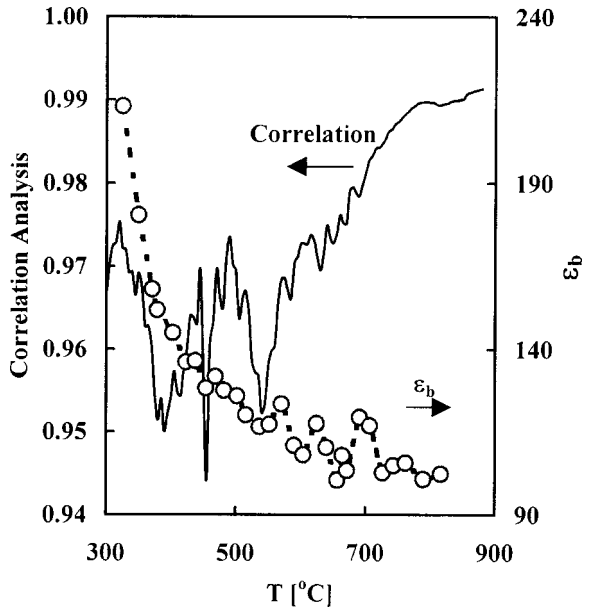

FIG. 2. Photoacoustic signal and dielectric behavior (open circles) of $Bi_{2.4}Pr_{1.6}Ti_3O_{12}$, as a function of temperature.

Generally speaking, in photoacoustic (PA) experiments the interaction between the laser beam and the lattice produces a function $PA(t,T_i)$,[3] which contains phenomenological information from the interior of the material. The index t in $PA(t,T_i)$ indicates the size of the temporal signal, while T_i is used to describe different temperatures. So, the correlation between functions $PA(t,T_i)$ and $PA(t,T_{i+1})$ will reveal those changes occurring in the sample at the temperature interval $T_{i+1}-T_i$. Furthermore, the correlation between $PA(t,T_i)$ and $PA(t,T_{i+1})$ will be 1 if both functions are similar, but less than 1 if any change occurs between successive signals.

As is known, compressibility is a sensitive parameter for ferroelectric/paraelectric transitions and its associated phenomenology. On the other hand, acoustic waves can be affected by compressibility changes along the wave propagation trajectory, such changes may behave as a source of dispersion for the waves. So, compressibility is probably the most important parameter affecting PA (t,T_i).

To establish a comparison with the dielectric results, samples of $Bi_4Ti_3O_{12}$ and $Bi_{2.4}Pr_{1.6}Ti_3O_{12}$ were used in photoacoustic correlation experiments. The continuous curve in Fig. 1 shows the correlation analysis of photoacoustic signals from $Bi_4Ti_3O_{12}$ as a function of temperature. In this curve no sharp peak is observed as would be expected from a ferroelectric transition, which was already verified in $BaTiO_3$.[1,11] The correlation exhibits a set of peaks distributed at the temperature interval ~650–830 °C. Thus, in $Bi_4Ti_3O_{12}$ a real massive transition is not occurring, therefore, it is evident that its behavior does not correspond to a classical ferroelectric material, but a relaxor.

Photoacoustic correlation experiments performed in $Bi_{2.4}Pr_{1.6}Ti_3O_{12}$ are shown by the curve in Fig. 2. There are several pronounced peaks distributed between 300 and 700 °C. An immediate observation is that the acoustic response is far from that corresponding to a proper ferroelectric transition.

Additional analysis of the same signals is shown in Figs. 1 and 2, where a correlation between successive signals was performed. The purpose of this analysis is to show differences in temperature behavior, and the results are presented in Fig. 3. These curves can also be used as stability criteria;[3] the system is much less stable as the correlation value moves away from 1. So, $Bi_4Ti_3O_{12}$ is quite stable below 650 °C, while $Bi_{2.4}Pr_{1.6}Ti_3O_{12}$ exhibits instabilities in a large temperature interval (~450–700 °C). In the case of $Bi_4Ti_3O_{12}$, there is a large peak around 860 °C. One possibility for the interpretation of this peak is that it indicates the end of the temperature interval where the relaxor behavior is occurring. But it is also possible that the peak is due to the presence of a separate transition temperature. In dielectric experiments this peak is difficult to observe, because at such temperatures dielectric information is strongly influenced by the presence of a relatively large conductivity.

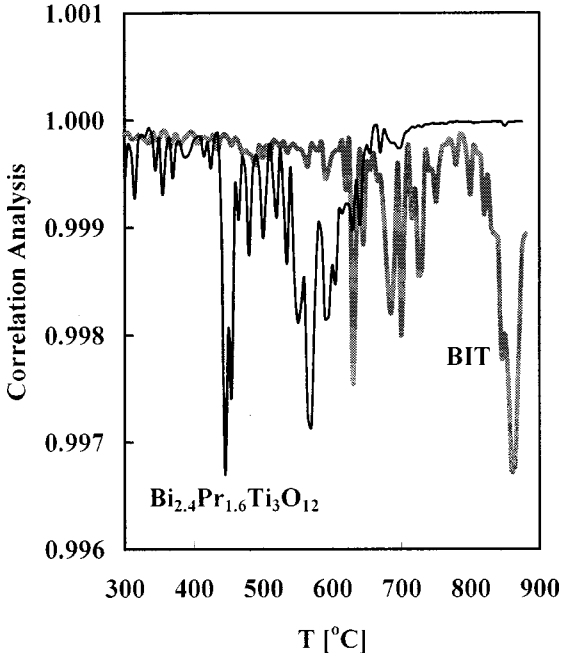

FIG. 3. Temperature dependence of the successive correlation of $Bi_4Ti_3O_{12}$ and $Bi_{2.4}Pr_{1.6}Ti_3O_{12}$.

The lack of a successful phase transition is understandable because the microstructure is actually considered as made up of ferroelectric microregions, which possess different transition Curie temperatures. This explains not only the presence of peaks distributed over a wide range of temperatures but also the coincidence of various peaks.

In terms of the polar microregions, we can explain the correlation curves as follows. The existing microregions undergo switching between different orientation states in the material, affecting the compressibility and, consequently, the acoustic wave traveling in the compound. This gives rise to a set of different PA (t,T_i) signals, whose correlations have a dramatic effect on the correlation curve, which cannot behave regularly. In other words, the presence of dynamical disorder on a nanoscale strongly affects successive PA (t,T_i) functions and, consequently, their correlation and its stability, Fig. 3, and for this reason the curves are not smooth. So, we consider both $Bi_4Ti_3O_{12}$, and $Bi_{2.4}Pr_{1.6}Ti_3O_{12}$, as relaxor materials.

The presence of numerous dispersion peaks in the acoustic response of a relaxor must be linked with the probability for groups of nanopolar regions to reach their own T_c. Then, materials under the influence of dynamic behavior of polar nanodomains have an associated temperature-dependent acoustic signal on a curve with several peaks. Consequently, the continuous curve for $Bi_4Ti_3O_{12}$, shown in Fig. 1, describes a relaxor. In conclusion, the results in this work allow us to establish definitely that $Bi_4Ti_3O_{12}$ and $Bi_{2.4}Pr_{1.6}Ti_3O_{12}$ are relaxors.

Then, the temperature dependence of the correlation between successive events of the interaction of a modulated laser beam with a crystalline lattice has proved to be a powerful method to detect fundamental structural changes in the evolution of any relaxor material under study.

Thus, the photoacoustic technique may represent an advantageous alternative to follow complex phase transitions such as those having a heterogeneous nature. Particularly, the technique produces a well-defined signal at the transformation interval, opening the possibility of more direct interpretation of relaxor behavior. It is also important that one of the advantages with this technique is that special sample preparation is not required.

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