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Pulsed Photoacoustic: A Reliable Technique to Investigate Diffuse Phase Transitions and Associated Phenomena in Ferroelectrics

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Often permittivity against T curves do not provide a conclusive characterisation of dielectric features of ferroelectric materials. Particularly, when permittivity is obtained from impedance measurements, where to experimental data is gradually lost at high frequencies when the temperature rises. Here we show how a combination of permittivity measurements and photoacoustic experiments can give a much more complete characterization of the ferro-paraelectric phase transitions and associated phenomena than those obtained from permittivity data alone. Peaked correlation curves, obtained from photoacoustic experiments were interpreted to be a manifestation of large enough microscopic variations of the compressibility as the temperature changed. On one hand, using a classical ferroelectric ($BaTiO_3$) and a well-recognized relaxor ($Ba(Ti_{0.65}Zr_{0.35})O_3$) the main differences between their photoacoustic response are established. On the other hand, dielectric and photoacoustic results from the compounds Bi_2WO_6 and $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$, were combined to characterize the temperature dependence of their dielectric behavior. Results provide evidence of the presence of a diffuse phase transition in Bi_2WO_6 at 660°C similar to that corresponding to relaxor behavior. Additionally the occurrence of a classical ferro-paraelectric phase transition above 900°C was found. This last phenomenon is detectable only by photoacoustic experiments. In $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$ the presence of a well defined transition was not detected. Dielectric determinations throughout ac measurements were carried out in the frequency interval 5 Hz-13 MHz. A pulsed Nd:YAG laser (10 Hz, 5 ns pulse width) was used to perform the photoacoustic experiments, where the out-coming signal was detected by a piezoelectric transducer. Dielectric and photoacoustic experiments were performed in a temperature interval from 250°C up to 1000°C.

Keywords Pulsed photoacoustic; ferroelectrics; relaxors

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Introduction

Solid state devices designed and built by using new ceramic materials require a close understanding of the fundamental physical properties of the utilized materials. This may depend on the sensitivity of the used research technique. In the case of ferroelectrics, the temperature dependence of the interconnected physical parameters heat capacity, volume compressibility or volume thermal expansion are some of the most helpful variables to be considered. Also the temperature dependence of permittivity has been widely used to determine dielectric properties of materials, particularly to have information on the transition temperature of ferroelectrics. In this last case a sharp peak in the curve ε' vs T can be taken as the signature of a well-behaved ferroelectric. Location of the peak gives the temperature of the ferro-paraelectric transition. One problem with this type of determination is when only small permittivity variations occur in a given temperature interval, in this case the curve ε' versus T may not be sensitive enough to develop the presence of a not very well developed peak. This is important in the case of diffuse phase transitions and in relaxor materials, where the ε' versus T curve is characterized by a broad rather than a sharp peak.

Using photoacoustic experiments, it has been recently established that valuable information related to diffuse phase transitions can be obtained [1, 2]. By this technique the temperature dependence of fluctuations of physical properties that couple sufficiently strongly to the crystalline indicatrix can be investigated. This is the case for phase transitions, such as those occurring in a ferro-paraelectric transition.

In this work both, photoacoustic and permittivity experiments were carried out on the compound Bi_2WO_6 and in the derived one $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$, in order to follow the temperature dependence of the involved ferro-paraelectric transitions. Two ferroelectric transitions have been reported [3] in Bi_2WO_6, one of them at 660°, and the other one at 961°C, while in the new tantalum containing compound, $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$, that determination will be reported here.

Previously we compared the photoacoustic results for the classic ferroelectric $BaTiO_3$ and the relaxor $Ba(Ti_{0.65}Zr_{0.35})O_3$ [4].

Experimental Procedure

Compounds were prepared by solid state reaction of the constituent oxides. Strem Chemicals were used: Bi_2O_3 (99.9%), WO_3 (99.999%), Ta_2O_5 (99%). Mixing the appropriate amount of the reactants, Bi_2WO_6 and $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$ were obtained. The mixed powders were grinded under acetone, after that they were air-calcinated at 700°C for 4 h to drive off CO_2, then they were calcinated at 800°C for 20 h to react the Bi_2O_3, to avoid its melting. Fairing was accomplished at 950–1000°C during 3 days in covered Pt crucibles in a high temperature electric furnace.

In order to perform the electrical determinations, coin-shaped pellets of 10 mm in diameter and ∼1 mm thickness were fabricated. The applied pressure was 2.5 ton/cm^2, sintering them at 1000°C. To have a two-probe configuration, gold paste was applied on both flat faces to attach small gold foil strips, heating at 700°C in air to cure the paste. Impedance measurements were performed from 250°C to 1000°C in air, by using 10–15°C steps. An impedance analyzer HP4192A, controlled by a microcomputer was used to obtain the electrical response. The rms applied voltage was 1V, in the frequency interval 5 Hz to 13 MHz. The photoacoustic experimental set-up employed consisted of: a) a pulsed Nd:YAG laser (10 Hz, 5 ns pulse width); b) a beam splitter and a pyroelectric detector; c) a commercial electric tubular furnace connected to a PID temperature control; d) a

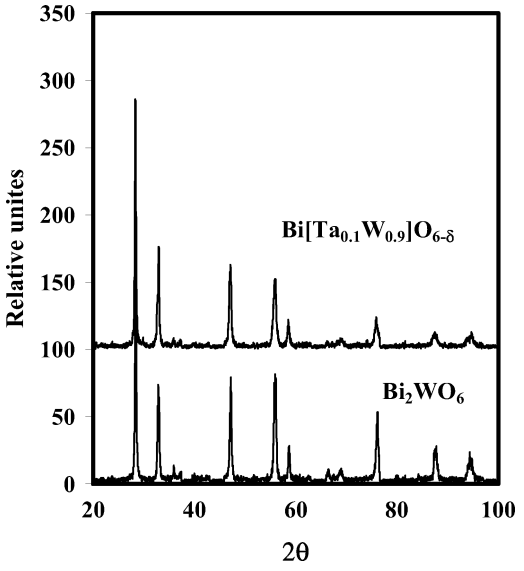


Figure 1. X-ray diffraction patterns of Bi_2WO_6 and $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$. Both correspond to the orthorrombic structure of Bi_2WO_6.

piezoelectric ceramic coupled to the sample through a quartz bar and the averaged signals (300 scans) were monitored with a digital oscilloscope.

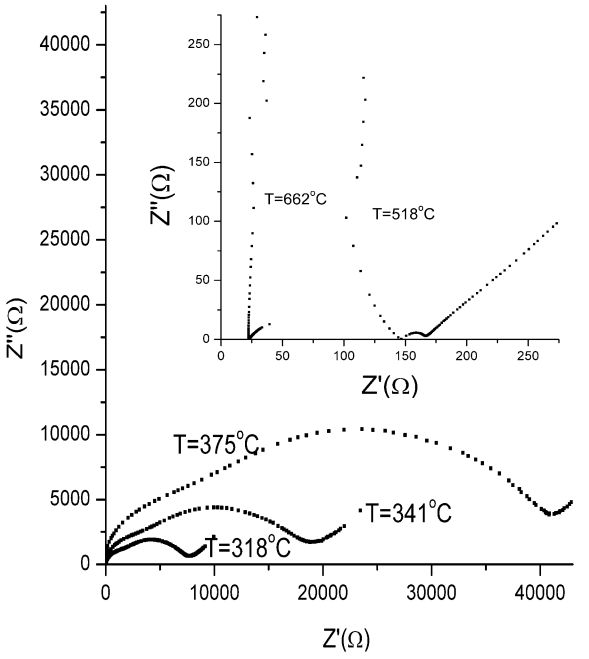
The out-coming acoustic signal, detected by a piezoelectric transducer was generated in samples which were used previously in conductivity experiments, without the gold paste. These last experiments were carried out at a heating rate so slow as to consider them temperature constant events.

Results and Discussion

X-ray diffraction patterns, Fig. 1, of both prepared compounds closely agree, which means that the orthorrombic structure of Bi_2WO_6 was not affected by the introduction in the structure of tantalum atoms.

In the impedance plane, Fig. 2 shows the main features of the electrical response of Bi_2WO_6 and $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$. At low temperatures two well defined circular arcs can be appreciated in both studied compounds. As typically happens in ceramic materials, the high frequency arc in the impedance plots describes bulk properties. Also, as a function of temperature, bulk permittivity ε'_b(=gfC/ε_o, gf being a geometrical factor and $\varepsilon_o = 8.854 \times 10^{-14}$F/cm) frequently is obtained through impedance data. This last because bulk capacitance (C) can be determined using the relation $\omega_{max}RC = 1$, which holds at the maximum of each semicircular arc. Although this method is, very often, limited at high temperature mainly due to the fact that experimental information is gradually lost at high frequencies as the temperature rises. This last effect was present in the studied materials, as can be appreciated inset Fig. 2. Therefore, if ε'_b is calculated from the frequency independent capacitance on the maximum of the impedance plots, and the maximum on the curves tends to disappear at increasing temperatures, then it will become impossible to perform any permittivity calculation. Additionally, if in a studied material the occurrence of relatively high conductivity is registered, as is the case in the present

(a) Bi_2WO_6



(b) $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$

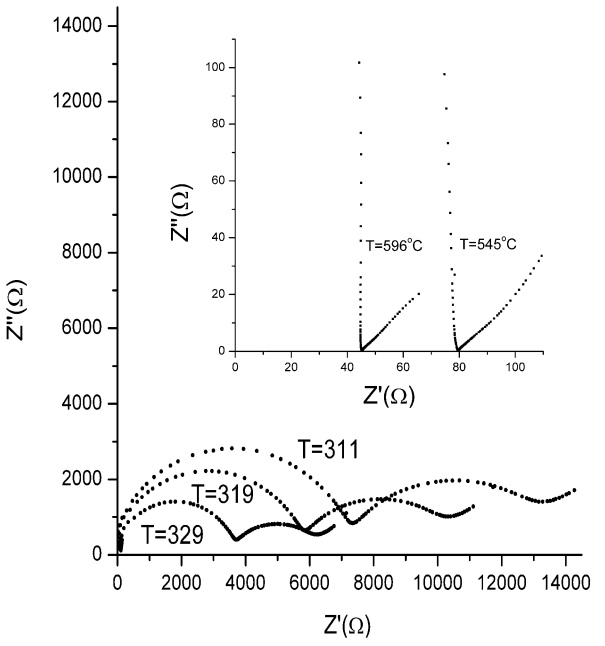


Figure 2. a, b) Low temperature impedance curves from Bi_2WO_6 and $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$. There are two semicircular arcs with their center located below the real axis. Inset curves, impedance data for the same compounds at high temperatures.

research, it makes that determination more difficult or simply impossible. Determinations of transition temperatures in ceramic materials where those types of problems are present deeply limit the reliability of this kind research.

For the compounds Bi_2WO_6 and $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$, from medium to high temperatures, there were problems to obtain correctly ε'_b values, then under these circumstances a complete bulk dielectric characterization can not be presented here throughout the studied temperature interval. Attempting to overcome this difficulty, and using the same impedance data, the frequency dependent permittivity, $\varepsilon'(\omega)$, can be worked out to have a better measure of the permittivity behavior. Permittivity in this last case is given by $\varepsilon'(\omega) = (g/\varepsilon_o)[\omega Z''\{1+(Z'/Z'')^2\}]^{-1}$, where $\omega = 2\pi f$, and f being the measuring frequency. In the case of Bi_2WO_6 the resultant curves are shown in Fig. 3a, b, where at around 600°C there exists a dispersive region in which data at 15 Hz is observed as a well formed peak. There is a moderate dispersion at around 800°C, but above this last temperature the data are so strongly dispersive that we decided to shut it out. For $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$, there is a broad but perfectly formed hill for the low frequency curves around 600°C, particularly at 15 Hz, this can be observed still up to 10 kHz. Also, the presence of additional dispersion above 700°C can be seen, where it is much more marked at the largest frequencies. Particularly at 100 kHz and 1 MHz $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$ exhibit the occurrence of a strong dispersion from around 500°C till the highest temperatures. In this last case, permittivity values are even larger than those for lower frequencies, which is an anomalous situation, as can be corroborated in Fig. 4b.

These observations serve to emphasize the difficulty of making reliable dielectric determinations at high temperatures by using impedance data. As mentioned above, this is frequently a limiting situation in studying dielectric properties of ferroelectric ceramic materials. Nevertheless, around the studied compounds, at least one important observation can be pointed out here: the permittivity data on the hills is distributed in a quite broad temperature interval. This, naturally, opens the possibility to consider the occurrence of a diffuse phase transition and/or a relaxor behavior. As has been recognized for a long time, diffuse phase transition is attributed to composition fluctuations on a microscopic scale [5], whereas in relaxor ferroelectrics [6, 7] a slow relaxation of the order parameter of the transition (the polarization P) is expected in a large temperature range around T_c. It is also considered that the occurrence of fluctuating polar nanoclusters at temperatures above T_c is distinctive of relaxor behavior [8].

The nano regions can be considered as the polarization units, the spatial limits of these must behave as domain walls, and the number of which may determine the broadness of the relaxation spectrum. Under a temperature field, local crystal chemistry may be affected, if so, a dynamic activity between nano regions and domain wall would be expected. Evidence for domain wall motion, as a function of temperature have been reported for $Pb(Mg_{1/3}Nb_{2/3})O_3$, which is a classical relaxor [9]. Authors found that the coercive field is a strong function of temperature and frequency. Also, if the associated microvolumes have slightly different transition temperatures for the onset of ferroelectric polarization, this would imply that a certain distribution of Curie temperatures would be expected along a permittivity versus temperature curve. The transition temperature generally lies in the upper range of T_{max}. Above the transition temperature the domains disintegrate and there is no longer a contribution from domain wall oscillation.

Those curves ($\varepsilon'(\omega)$ vs T) in Figs. 3 and 4, and despite of the very close steps in the temperature runs, are certainly broad, but it will be very difficult to say that such curves are composed of a set of small individual peaks. This rather emphasizes the fact that, although

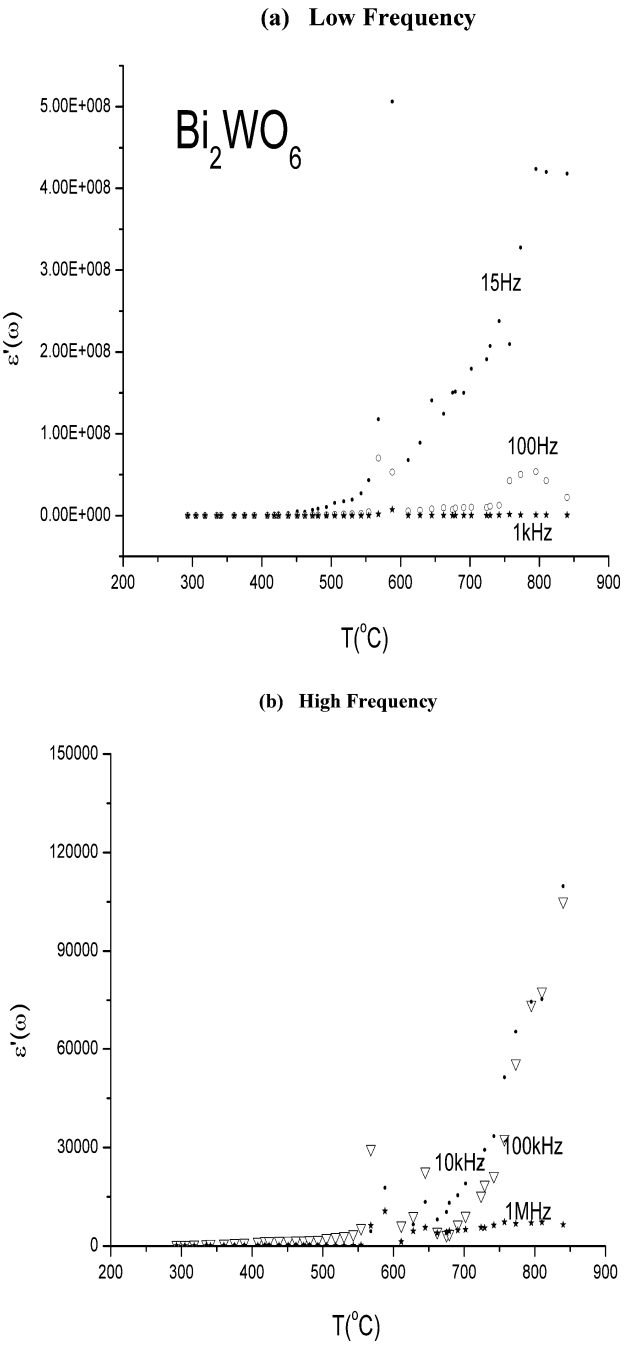


Figure 3. Permittivity against temperature curves for Bi_2WO_6, presented at selected frequencies.

overall permittivity properties can be easily obtained, it is quite difficult to correlate them with microscopic characteristics.

As is known, generation of sound by using modulated light, or laser pulses, when it is absorbed by a physical system, is what is called the photoacoustic effect. The acoustic

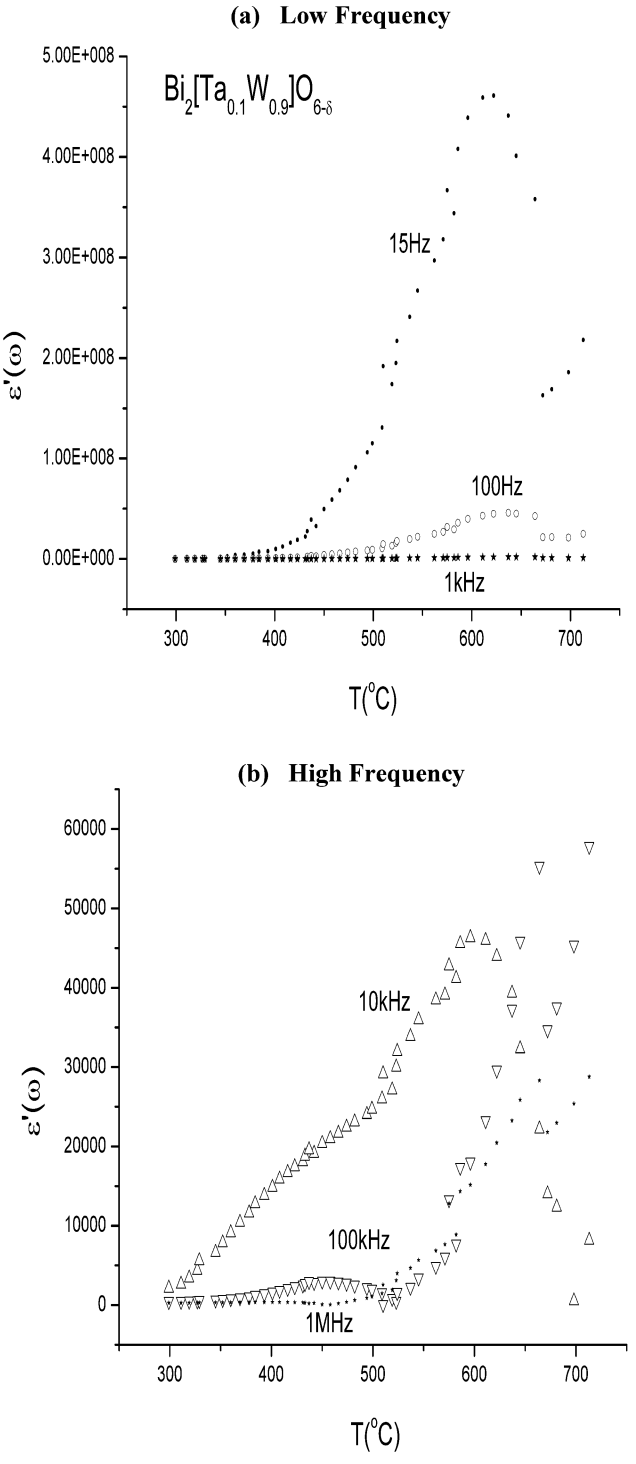


Figure 4. At selected frequencies, permittivity against temperature curves of $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$.

signal is a consequence of a pressure wave traveling in the crystal, induced by the incidence of the laser beam. The mechanically stressed state in the crystal, created by the wave pressure activates stress and strain in the lattice in such a way that changes of volume as a function of the pressure should be expected. The compliance of the system's volume with respect to the pressure is what characterizes the volume compressibility. This physical parameter is relatively small in solids. However as microscopic characteristics of the laser beam illuminated material determine the temporal profile of the acoustic pressure, then any microscopic change in the crystal would be reflected by some appropriately constructed correlation curve, via the out-coming photoacoustic signal. Now, if in a material, presumably ferroelectric, a photoacoustic experiment is carried out as a function of temperature, and the out-coming response can be used to evaluate changes in a physical parameter, then as explained below this might be the point where photoacoustic experiments can be shown to be much more appropriate to determine transition temperatures as well as to detect different types of phenomena such as the presence of diffuse phase transitions.

In a photoacoustic experiment, if PA(t, T_i) represents the interaction between the laser beam and the lattice, where different temperatures are described by T_i and the size of the temporal signal is indicated by the index t in PA(t, T_i), then we construct a correlation between successive functions [PA(t, T_i), PA(t, T_{i+1})] (call it "stability analysis" for their differentiation), whose correlation will show evidence of any change in the physical system. In the resultant correlated curves of a studied material it will be possible to locate those temperature intervals where the major structural instability exists, this evidenced by multipeaked curves or even by very sharp peaks. It has been demonstrated [10] that the PA(t, T_i) function can be written in terms of the volumetric expansion coefficient, which in turn is directly related to the volume compressibility. As already pointed out, this last is an appropriate parameter to follow ferroelectric transitions. Other types of correlations can be established, for example a standard correlation, in which comparison is made between a particular run, say PA(t, T_1) and every PA(t, T_i) function, where $i = 2, 3, \ldots$ [11]. Once again, in this second kind of correlation multipeaked curves are obtained, whose maxima closely correspond to those in the first correlation. This pair of correlations have been established as the most important to be handled in this type of experiments [1, 2, 12, 13]. However the first one is particularly useful, because this is particularly sensitive to the presence of different phases [12].

In order to provide a reasonable base to the following discussion, we present first correlation curves of the first type of photoacoustic experiments performed in a classical ferroelectric, $BaTiO_3$, and then those corresponding to a well recognized relaxor, $Ba(Ti_{0.65}Zr_{0.35})O_3$ [4]. Results are presented in Fig. 5, where the curves show the typical temperature dependent photoacoustic behavior of ferroelectrics and relaxors. Now, in a temperature dependent experiment, wide or small fluctuations between successive photoacoustic signals would produce peaks at the correlated curves in a determined temperature interval, such as those in Fig. 5. On the other hand, far away from any important change of the fundamental physical properties only extremely small fluctuations of the system can be expected as a function of temperature and the corresponding correlated curve would behave as a base line. It follows that, the correlation will be 1 when both PA(t, T_i) and PA(t, T_{i+1}) are identical, but less than one if any change occurs between them. The temperature dependence of a determined physical parameter will stamp specific features to the resultant curves. The most profound differences in the compressibility arise when the material changes from the ferroelectric regime to the paraelectric one, then sharp peaked correlation curves coming from photoacoustic experiments characterize well behaved ferroelectric

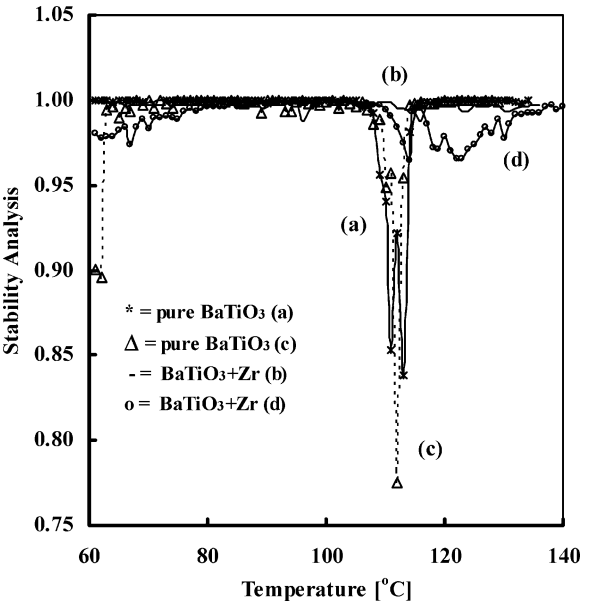


Figure 5. Correlation between successive photoacoustic functions from the classical ferroelectric $BaTiO_3$ and the well recognized relaxor $Ba(Ti_{0.65}Zr_{0.35})O_3$. The curves also illustrate the experiment of successive runs, (a, c) for $BaTiO_3$, (b, d) for $Ba(Ti_{0.65}Zr_{0.35})O_3$.

materials. That behavior is what the curve (a) in Fig. 5 is exhibiting, which corresponds to $BaTiO_3$ [14].

As the temperature is the parameter which drives phase transitions at any scale, it seems to be natural to consider that the number of nano regions in a relaxor, with a particular transition temperature, determines the height of the peaks in the correlation curves. This brings changes in the local physical properties as well. Consequently, the individual peaks can be ascribed to large enough microscopic variations of the compressibility. Therefore, we will expect a dented curve for the overall properties of a material consisting of a wide distribution of microvolumes with different Curie temperature, as relaxors are. So, broad multi-peaked curves would describe a deviated behavior of a classical ferroelectric, as illustrated in Fig. 5, curve (c), for the relaxor $Ba(Ti_{0.65}Zr_{0.35})O_3$.

Also, as a function of temperature, we expect a dynamic behavior of the number of micro regions and domain walls in the crystal. In order to have an insight to this, we have performed successive photoacoustic experiments to corroborate the hypothesis that, when a specimen is tested several times the number of nano clusters may change. That means, cycling thermal treatments should bring attached microscopic changes. Consequently, after the successive runs we must obtain different correlation curves, in which both the number and height of the peaks may vary. Successive runs were carried out in both $BaTiO_3$ and $Ba(Ti_{0.65}\ Zr_{0.35})O_3$, curves (b) and (d), respectively (Fig. 5). Runs were performed without any change in the experimental device. For the successive runs, results for the typical ferroelectric remain essentially similar, while differences of the relaxor curves are evident. In the first case PA correlations behave very close to the starting thermal run, while in the last one each new thermal treatment affects the features of the dispersive entities, modifying the correlations between the PA functions. We also present the standard correlation curves for $BaTiO_3$ and $Ba(Ti_{0.65}\ Zr_{0.35})O_3$, Fig. 6, for the same conditions as those mentioned

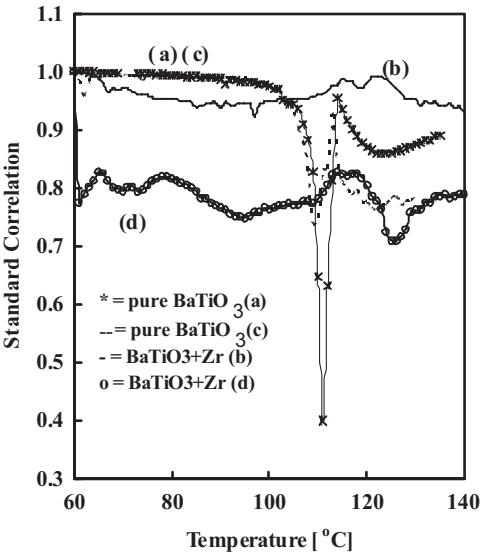


Figure 6. Standard correlation of photoacoustic functions for $BaTiO_3$ and $Ba(Ti_{0.65}Zr_{0.35})O_3$. The curves correspond to the same conditions as curves in Figure 5.

for the curves in Fig. 5. Curves (a) and (b) are for $BaTiO_3$ at different runs and curves (c, d) corresponds to the relaxor $Ba(Ti_{0.65}\ Zr_{0.35})O_3$. In the curves for the relaxor those temperature intervals where instability in the system is provoked by the diffuse phase transition in progress stand out remarkably well. Results are powerful; we believe they strengthen the nano cluster model. This also leads us to the conclusion that the density of nano domains fluctuates with the repeated heat treatment.

Now we present photoacoustic results for Bi_2WO_6 and $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$. The corresponding photoacoustic curves are, in general, multipeaked curves as observed in Fig. 7. In fact, the resultant curves from the first constructed correlation relation can be used as thermodynamic equilibrium criteria [12], it follows that the studied samples exhibit relatively large instability in some determined temperature interval in each case. Bi_2WO_6 exhibits a slight instability around 500°C and another one starts above 600°C whose permanence is still registered above 800°C, Fig. 7a. That behavior seems to be linked in the literature to the mentioned ferroelectric transition at 660°C. However, our photoacoustic results indicate a possible relation with a diffuse phase transition, as in a relaxor material. Next, located at 930°C, an impressive sharp peak appears, like the one associated with a well-behaved ferro-paraelectric phase transition. We believe that the peak at this last temperature can be identified with the reported [3] ferroelectric transition at 961°C. The correlation curve for $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$ shows structural instability almost throughout the temperature interval investigated, Fig. 7b. In particular, a maximum seems to be formed around 450°C, which is also suggested in the $\varepsilon'(\omega)$ curves of figure 4b, obtained by permittivity experiments. Another peak appears close to 600°C, once again in a similar form as that in Fig. 4b. Approximately between 750–860°C there is an other strong instability, which may corresponds to the ferroelectric transition at 961°C in Bi_2WO_6. What is true here is that, from the photoacoustic experiments only a classical ferro-paraelectric transition has been localized, this in Bi_2WO_6 at 930°C, the other instabilities seem to be diffuse in character. There is not at all a typical ferro-paraelectric transition in the case of $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$. From these,

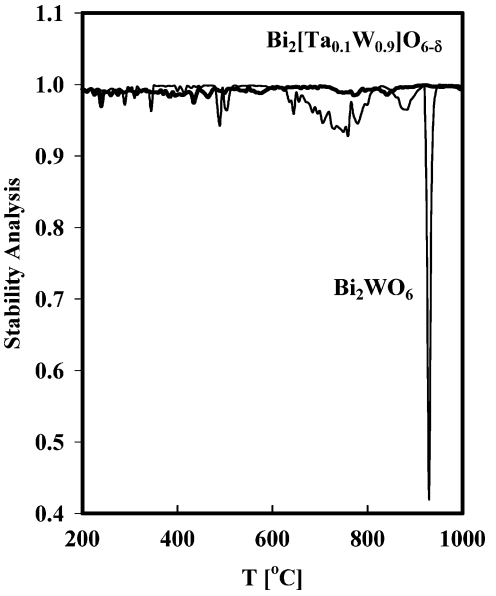


Figure 7. Correlation between successive photoacoustic functions from Bi_2WO_6 (curve a) and $Bi_2[Ta_{0.1}W_{0.9}]O_{6-\delta}$ (curve b).

there are some important things to be pointed out here; one of them is that the presence of Ta in the structure of Bi_2WO_6 strongly modifies the photoacoustic response. An other one is that the structural instabilities slightly shift toward lower temperatures. Also, in the reported temperature dependent photoacoustic experiments, compared with that obtained by permittivity determinations, results from photoacoustics have revealed in a better way important features of the ferroelectric transitions.

Conclusions

In photoacoustic experiments, results suggest that those extremely small shifts of ions involved in ferro-paraelectric phase transformations, which modify elemental volume characteristics, determine the resultant correlations coming from diffuse phase transitions. Index fluctuations are adequate enough to fulfill detection requirements of the technique. This can be considered important if we recognize that relatively tiny fluctuations of the dielectric constant are barely detectable by normal electric characterizations. The fine sensitivity of photoacoustic experiments make the technique useful to study fluctuations of the polar nanoclusters existing in relaxors. The dynamic behavior will be monitored by following the microscopic compressibility fluctuations, linked to the polarization/depolarization process involved in a ferro-paraelectric phase transition. It can be continuously correlated as a function of temperature to have an insight into the dynamic character of the phase transition in the Curie range of relaxors. Therefore, a much more complete description of a diffuse phase transition, or a ferroelectric relaxor, is exhibited by a correlated curve obtained via photoacoustic experiments compared with those obtained by conventional permittivity vs. temperature curves.

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