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Dielectric Properties of Ytterbium Yb^{2+} Substituted Barium Titanate Synthesized by Sol–gel Method

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Abstract

Ceramic powders of Yb doped Barium titanate ($BaYbTiO_3$) of a perovskite structure were prepared by the conventional solid state reaction route. The results of scanning electron microscopy (SEM) show that with increasing Yb rate, the sphericity of the grains increases while the average grain size decreases from from 1,7 µm for BT to 0.56 µm when the rate of Ytterbium reaches 21%. Characterization by X energy dispersive spectroscopy (EDS) confirms the incorporation of Yb in the barium titanate. The relationship between the dielectric properties and percentage of Yb in BT for different frequency measurements has been studied.

1. Introduction

The barium titanate is a ferroelectric material which is known for nonlinear properties. The latter may be developed for the realization of new frequency converters by frequency doubling by phase matching. The potential of $BaTiO_3$ is linked particularly to the existence of several crystalline phases. Its optical, electrical and piezoelectric properties are very promising technologically such as the mirror conjugation pumper phase, the linear resonator, the phasing of laser sources and the active waveguides. We therefore focused our choice on barium titanate $BaTiO_3$ as the material which when adequately doped may exhibit ferroelectric features at temperatures near the room temperature and as this material meets the environmental requirements and is regarded as standard material for studies of dielectric, piezoelectric and pyroelectric properties [1-3], and hence the development of dielectric and piezoelectric devices. In this sense the dielectric behaviour of pure and doped barium titanate has been extensively studied [4-8]. However effects of ytterbium (Yb) on the dielectric properties of $BaYbTiO_3$ ceramics have rarely been studied. Therefore, the development of free lead-electric devices – considered as next generation- is necessary to study the relationship between the dielectric properties and the rate of incorporation of elements in BT, sach as Yb for different frequency measurement. The technique that we have used to prepare these materials is the sol-gel route.

2. Experimental

2. 1. *Materials synthesis*

To elaborate the samples we used barium acetate trihydrate ($Ba(CH_3COO)_2{,}3H_2O$), titanium alkoxide $Ti[OCH(CH_3)_2]4$ and Ytterbium Acetate $Yb(O_2C_2H_3)_3.xH_2O$ as precursors, lactic acid ($CH_3CH(OH)COOH$) as peptizing agent**,** Raw powder, after grinding, was calcined in air at temperature 1050 °C for 10h, in a programmable oven. These compositions were then pressed into pellets of 12 mm diameter and a thickness of 1 mm under a uniaxially pressure equal to 10 tons/cm2. The pelletized samples were finally sintered at 1250 °C for 6 h in a programmable furnace.

2. 2. *Material characterization*

The obtained powders were characterized by X energy dispersive spectroscopy and Scanning Electron Microscopy (SEM) using a JEOLT330 microscope. Dielectric characterization was performed as a function of frequency from 1 kHz to 2 MHz. These dielectric measurements were carried out in the temperature range 30-225 °C and under sub weak level of excitement (1v) using an Agilent 4294A precision impedance analyzer (Hewlett-Packard, Palo Alto, CA).

3. Results and discussion

3.1. *Microstructure study*

The results of characterization by X energy dispersive spectroscopy (EDS) of $Ba_{1-x}Yb_xTiO_3$, sintered at 1050 °C for 10 hours, are given in table 1. These results show that all the chemical elements Ba, Yb, Ti and O are present; In particular, incorporation of Yb in A site is evidenced. It is also seen that percentages of Ti and O remain practically constants with increasing of Yb concentration. The SEM images obtained on the sintered pellets at 1250 °C (figure 1) show that for the pure BT sample the formed particles have a relatively uniform size and have a substantially regular spherical shape (elongated), while doping by Ytterbium affects the shape of the grains. Indeed, when the concentration of Yb increases, the sphericity of grains increases, reflecting a new rearrangement at the unit cell. On the other hand the average grain size decreases with addition of Yb. Indeed the average size of BT grains in BT powder is 1,7 µm and decreased to an average value of about 0.56 µm when the rate of Ytterbium increases to 21%.

Table 1: Percentage of chemical elements obtained by spectroscopy of fluorescence and values of the maximum of the permitivity (ε_{max})

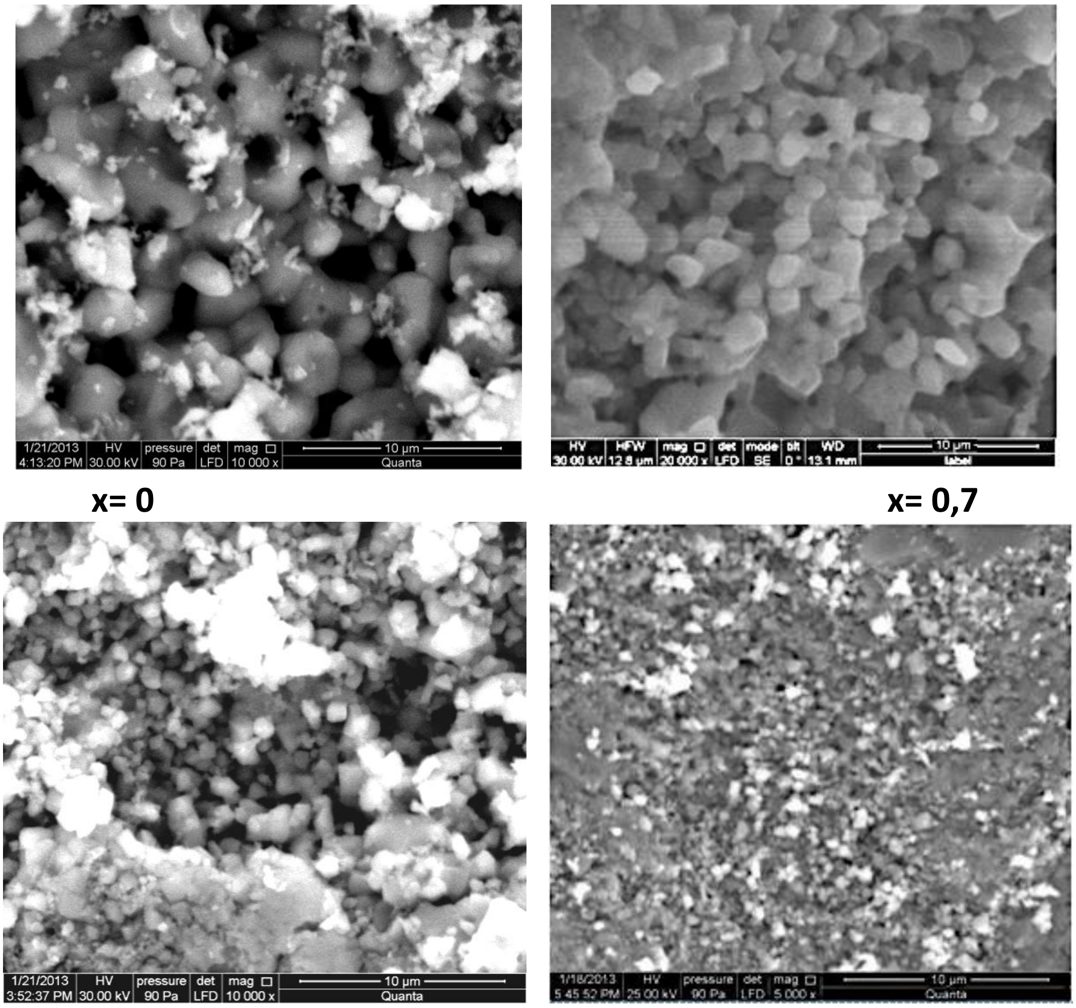
	% in mole				$\varepsilon_{r\ max}$
x%	Yb	Ba	Ti	O	
0	0	19,18	19,67	60,85	2854
7	1,34	18,33	20,10	60,23	3885
14	2,39	17,21	20,39	60,01	4465
21	3,99	16,20	20,41	59,39	5404

3.2. *Dielectric studies*

3.2. 1. *Compositional and frequency effects on the relative permittivity*

In figure 2, are reported the curves showing the thermal variation of the relative permittivity (ε_r) as a function of temperature for various compositions BYxT sintered at 1250 °C (for 6 h). For x = 0, ε , when the temperature increases, the relative permittivity increases and passes through a maximum, ε_{max} at the temperature T_c (the Curie, temperature) which is frequency independent. The shape of the curves ε_r (T) recorded on the BY_xT compounds (x> 0) is similar to that of $BaTiO_3$ (x=0), they differ from each other only by the position of the transition temperature (T_m) and by the diffuse nature of the ferro-to-paraelectric transition (FPT). Below the transition temperature (T_m), corresponding to the temperature of the maximum of $\varepsilon_{r,}$ the distortion of the perovskite structure under the influence of temperature is accompanied by a relative movement of the ions, which enhances the spontaneous polarization across the lattice cell. Thus, the Ti^{4+} and Yb^{2+} (or Ba^{2+}) no longer occupy the center and vertices of the cell respectively; they are displaced along the main directions of the crystal lattice. This gives rise to a spontaneous polarization increasingly important until it reaches a maximum value at T_m. These changes in polarization with T_m can explain the value of $\varepsilon_{r\ max}$ at this temperature. In the theory of

Cochran and Anderson [9,10], the ferroelectric phase transition is processed in terms of dynamics of the crystal lattice; it would correspond to the progressive decrease in the frequency of a vibration mode network, called soft mode. At T_C, clearing between short elastic interaction and long-range Coulomb interaction causes instability of the network. Thus the ions more easily move in the vicinity of T_m and hence the maximum of the permittivity is increased with increasing Yb rate (table 1).



x= 0 **x= 0,7**

x= 0,14 **x=0,21**.

Figure 1: SEM images of $Ba_{1-x}Yb_xTiO_3$ ceramics, sintered at 1250 °C

In addition, as mentioned above, the peak of the ferroelectric paraelectric phase transition located at T_m becomes diffuse. This broadening of the peaks is attributed to the diffuse nature of the transition, and may result from a more or less significant disorder in the cationic sites of the material. But some authors have shown that the phase transition behaviour was closely connected to the sub-microscopic chemical inhomogeneity in the material [11,12]. Based on this assumption, the ytterbium, when added to BT, promotes the formation of nanoregions of different chemical natures, breaking the long-range ferroelectric order [13]. Each monoregion contributes with its own Curie temperature upon cooling, the distribution of local transition temperatures reveals a diffuse maximum ε_{rmax}. If we assume that the size of nanoregions increases with the concentration of Yb^{2+}, we can explain the origin and evolution of the increasing spreading of the Curie peak as a function of the concentration, regardless of the size of the grains observed. Indeed, due to the short range of the chemical inhomogeneity, the BY_xT material is enough macroscopically homogeneous. However, from the microscopic point of view, a number of small nano-regions exist and have a concentration of barium/Ytterbium (Ba/Yb) different from the average concentration, resulting in a Curie peak broadening. As a guide, for all our samples, the value, $\varepsilon_{r\ max}$, decreases with increasing frequency in the range [1 kHz-100 kHz] and increases in the range [100kHz-1MHz]. To our knowledge this behavior was never mentioned in the literature.

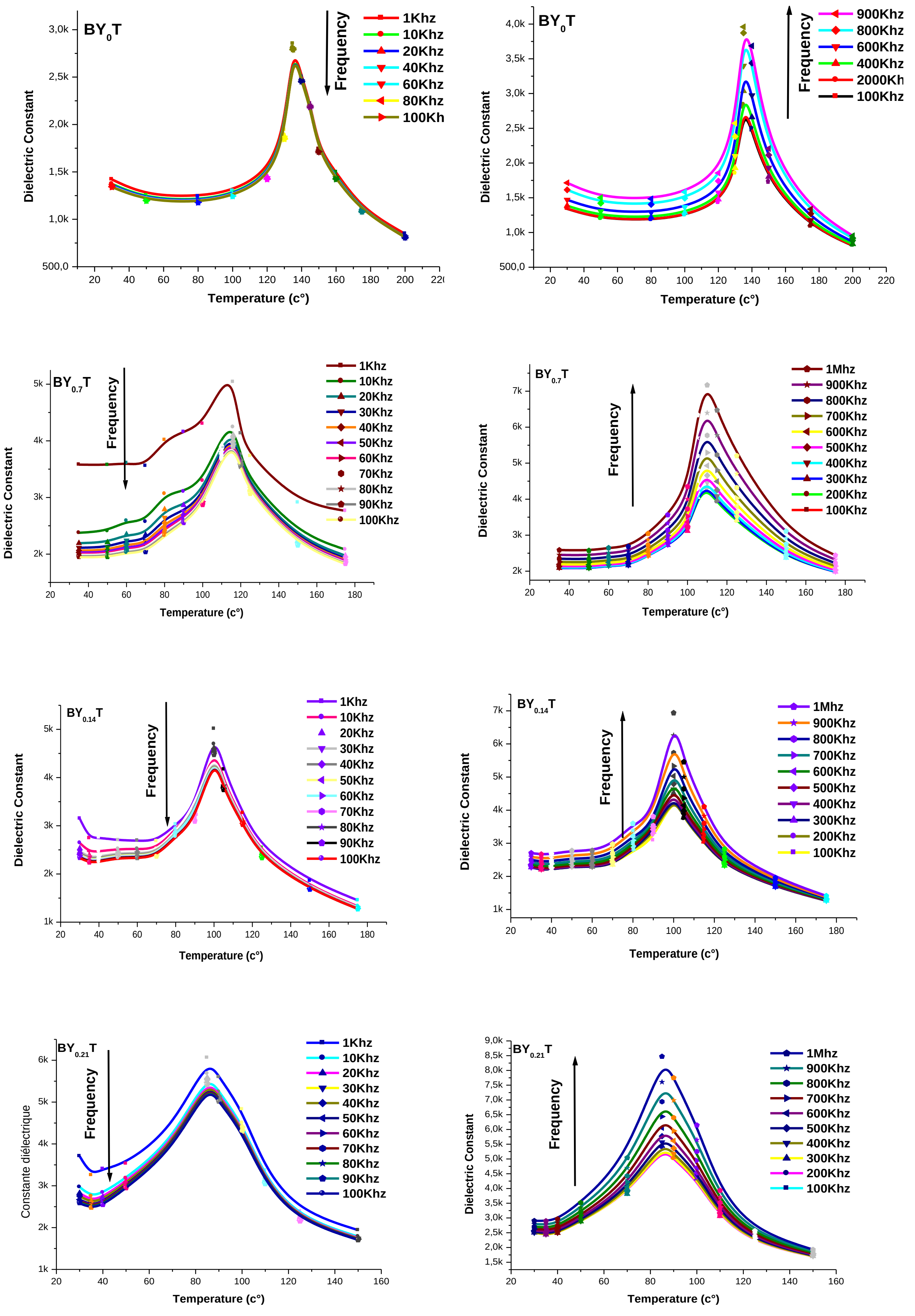


Figure 2: Temperature dependence of the dielectric constant of BY$_X$T, as a function of frequency

3.2. 2. *Dielectric loss*

The variation of the dissipation factor (x = 0 and 0.21) depending on the temperature at different frequencies is illustrated in the curves of figure 3. In BYxT samples and in the frequency interval [1kHz-100kHz], it can be clearly observed the existence of a FPT phase transition, indicated by a sudden change in dielectric loss (tgδ). Below T_m, the decrease in dielectric loss caused by the increase in temperature leads to a deterioration of the material properties that are related to the movement of domain walls [14,15]. Moreover, we note that this loss increases significantly and becomes frequency dispersive above 175 °C for $BaTiO_3$. This increase in tgδ, which is usually observed in the BT-based ceramics, is mainly due to the increased mobility of the defects and in particular the oxygen vacancies and also, the sample driver character in this region of temperature. Changes in tgδ for other samples (BY_xT) keep the same behaviour. In the meantime [100kHz-1MHz], we observe an opposite evolution of dielectric losses with increasing frequency. It is therefore interesting that the evolution of losses versus temperature for frequencies above 100 kHz is similar to that of the dielectric permittivity. This confirms that intrinsic losses contribute significantly to total losses in these materials. On the other hand for x = 21% in Ytterbium, changes in losses as functions of temperature confirm that the ferroelectric to paraelectric phase transition becomes diffuse. Indeed the peaks of losses become wider. moreover we have observed a decrease of losses above Tm, which may be explained as due to existence of polar nanoregions above this temperature that contribute to a non vanishing polarization even if $T>T_m$ [16].

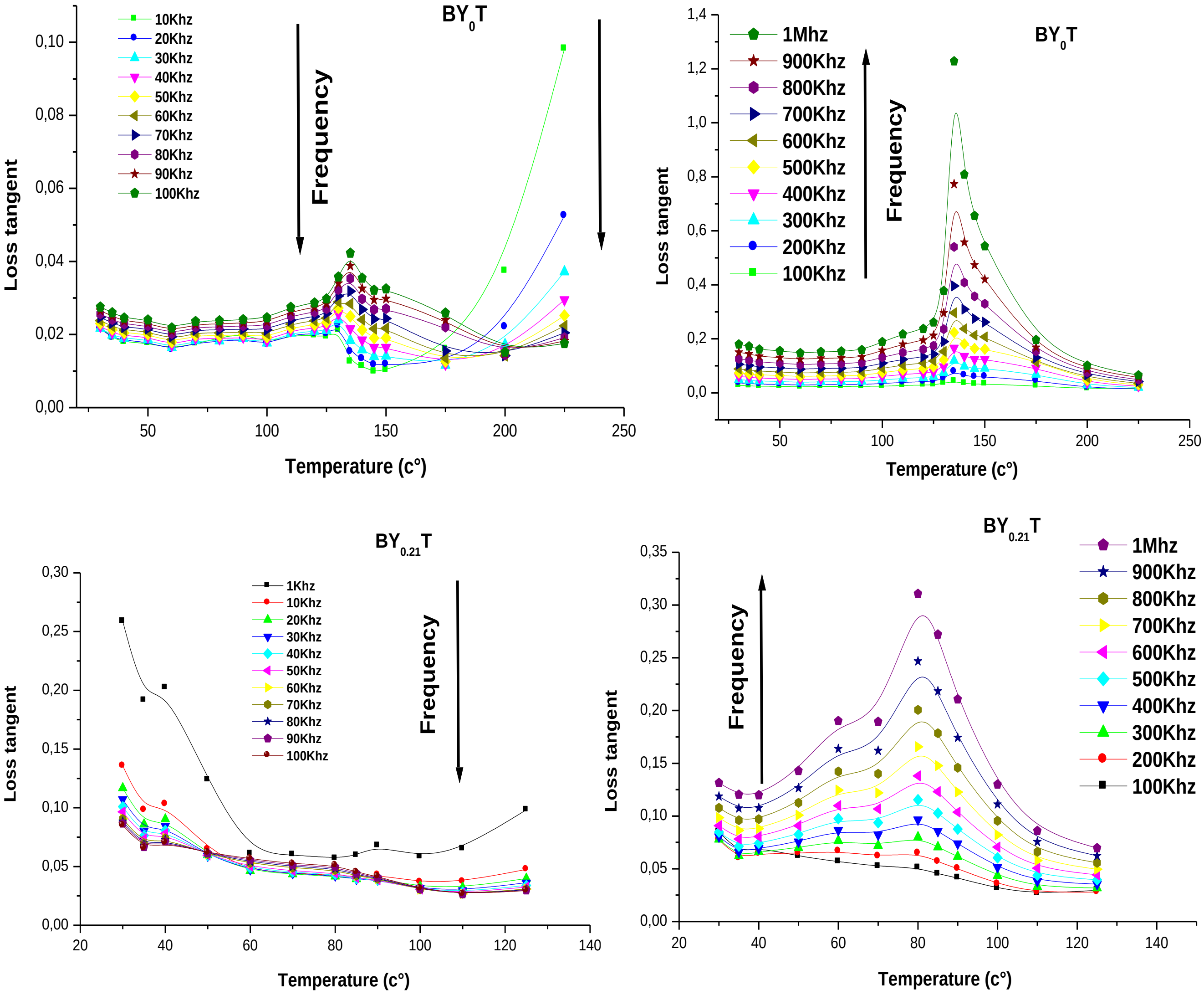


Figure 3: Temperature and frequency dependences of loss tangent of BY_xT sintered at 1250 ° C for 6 h

Conclusion

Microstructural and dielectric properties of solgel processed Yb doped $BaTiO_3$ powders were investigated. The results revealed a complete incorporation of Yb ions in the BT matrix, confirmed by EDS spectroscopy and that Yb influences parameters related to the microstrucure and dielectric behavior. Indeed, concerning the microstructure addition of Yb ameliorates do sphericity of the particles and diminishes their size. The temperature of the maximum of the permittivity shifted to lower values accompanied with an increase of the maximum of the permittivity. Incorporation of Yb gives rise to a diffuse character of the ferro to paraelectric transition at T_m.

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