Synthesis and characterization of micrometric ceramic powders for electro-rheological fluids

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Abstract.

Micrometric lamellar ceramic powders of the displacive ferroelectric oxide $Bi_4Ti_3O_{12}$ were synthesized by coprecipitation of bismuth nitrate and ammonia titanyl solutions followed by a heat treatment. It was found that a complete thermal decomposition is reached at 1000°C. Structural and thermal evolution of these ceramic powders were studied by X ray diffraction, thermogravimetry and differential thermal analysis. The homogeneity in size and morphology of these ferroelectric particles are appropriate to prepare electro-rheological fluids. One of these fluids was prepared by dispersing the powders in silicon oil; the complex cluster structure formed by the particles, under an applied AC electric field, was observed.

1. Introduction

Electro-rheological fluids (ER) are materials formed by micrometric (0.1 to 100 μm) polarizable particles, dispersed in an inert fluid (low conductivity and high dielectric breakdown strength), usually a mineral oil [1]. The rheological properties of these complex materials change drastically under the application of the electric field (AC and /or DC), this change can be as strong that the system undergoes a reversible liquid-to-solid transition.

This is due to the complex structure formed by the particles. Micrometric powders of aluminium [2], glass [3], ceramics like potassium niobate, lithium niobate, barium titanate, strontium titanate [4], or even polymers like polyacrylonitrile [5,6] have been used to prepare ER fluids.

The Brownian motion effects become negligible in this wide range of particle sizes, therefore, it prevails the electrostatic force between the particles [7]. Eventhough, there has been a great interest and many publications on this subject there still remain several open questions, one of them regarding the role of the dielectric properties and morphology of the particles on the structure formation. In order to explore these points, we prepared ferroelectric microcrystals, uniform in shape and size.

Ferroelectric particles are interesting in this application due to the presence of spontaneous polarization and high dielectric constants. One might expect that these particles dispersed in an oil, in the presence of an electric field must produce a tighter bond structure than those particles with relatively weaker interactions. There are few reports concerning the use of ferroelectric materials for ER fluids, most of them are focused on barium titanate [4]. Bismuth titanate, $Bi_4Ti_3O_{12}$ (BTO), is a displacive bidimensional ferroelectric, the transition from the paraelectric tetragonal phase (4/mmm) to the ferroelectric monoclinic phase (m) ocurrs at 675°C [8,9], this ferroelectric phase is easily described as pseudo-orthorhombic, by point group 2mm. At room temperature, the lattice parameters are $a_o = 5.450$ Å, $b_o = 5.4059$ Å and $c_o = 32.832$ Å, consequently, the typical morphology of these crystals is lamellar.

In this report we focus our attention on the preparation of micrometric plate-like ceramic powders, uniform in size and shape, of bismuth titanate by a coprecipitation method. With

an adequate heat treatment of the precipitate at 1000°C during one hour, it is possible to obtain the desired particles, as shown by our studies done by X-ray diffraction (XRD), scanning electron microscopy (SEM) and simultaneous differential thermal analysis and thermogravimetry (SDT).

2. Experimental procedure

Powders of bismuth titanate were prepared by coprecipitation from a stoichiometric mixture of bismuth nitrate, $Bi(NO_3)_3$ (Aldrich,99.999%) and ammonia titanyl, $(NH_4)_2TiO_4$ aqueous solutions, followed by thermal decomposition of products. In a first step we proceed according to the guidelines reported for this coprecipitation reaction in [10], ammonia titanyl is obtained by ammonia addition to the hydrate titanium oxide (Aldrich,99.999%) in the presence of an oxidant, in our case we use nitric acid (Merck,65%) under continuous agitation and adjusting the pH to 8.5. Then, we add this solution to an acid solution of bismuth nitrate also under continuous agitation. The last step is a thermal treatment up to 600°C according to reference [10]. XRD patterns were obtained in a D5000 Powder Diffractometer (Bruker AXS), Cu–Kα radiation, $\lambda = 1.5406$ Å, 2θ range from 5° to 70°, step scan 0.02 deg, at room temperature. SEM microphotographs were obtained in a JSM 5400 LV (Jeol) system. DTA and TG studies were performed in a simultaneous differential technique module (SDT–TA Instruments 2960), in a nitrogen atmosphere, with heating rate 10°C/min.

3. Results and discussion

The product obtained following the reported procedure [10] is a light yellow powder, its XRD pattern is shown in Fig. 1, the phase identification by comparison of the diffractogram with the JCPDS files lead us to identify the presence of $Bi_2Ti_4O_{11}$, TiO_2 and hydrated $Bi(NO_3)_3$, meaning that the thermal decomposition is still incomplete at 600°C, this is a different result to that asserted in [10]. Additionally, the obtained powders by this procedure show highly inhomogeneous morphologies and sizes, as it can be observed in Fig. 2. That corresponds to a SEM picture of one of the typical obtained agglomerates. They are extremely fragile and have irregular granular aspect.

In order to determine the temperature at which the precipitates must be treated to achieve the complete thermal decomposition, namely, obtaining only the phase $Bi_3Ti_4O_{12}$, we performed DTA-TG studies with the precipitates. Fig. 3 shows the results of these measurements. The DTA curve clearly indicates that there exist two endothermic reactions, with onset point at 765°C and 844°C respectively. It can be observed also in the TG curve, that the process of decomposition starts at 750° C and ends at 793°C. At approximately 900°C, the loss weight becomes negligible. Considering these data, we may assure that the decomposition reaction has completely finished with a heat treatment at 1000°C. In this way we have obtained our ceramic powders. Additional evidence of the full decomposition of the precipitates was obtained by XRD experiments. Fig. 4 shows the pattern of thermally treated precipitates under the conditions above mentioned. The phases found were mainly BTO and traces corresponding to $Bi_2Ti_2O_7$, this time there are any traces of TiO_2 and hydrated $Bi(NO_3)_3$. Also, in order to have some insight about the kinetics of the solid state reaction at 1000°C , the precipitates were heated during one and two hours, and we found that in any case, there is no change in XRD patterns.

Fig. 5 shows a micrograph of our ceramic powders, these can be described as a stacking of lamellae of BTO. Platelet-like morphology is typical of this bidimensional ferroelectric oxide, this was also observed in ceramic and single crystals [11]. Average size of particles is 20 μm. It is worthy of notice that both, morphology and size are very regular in our samples. DTA thermogram of our BTO ceramic powders is presented in Fig.6 , it is clearly visible the endothermic peak due to the paraelectric-ferroelectric transition of BTO at T_{onset} = 640°C.

Another coprecipitation procedure reported [12] to obtain BTO ceramic powders is based on the hydrolysis of titanium (III) or (IV) chloride in an aqueous solution of bismuth nitrate, they also found that at 600°C the phase $Bi_2Ti_4O_{11}$ is present and only it is possible to eliminate this phase, with a cold pressed processing at 50 MPa and sintering in air at 1100°C for 240 min. The method reported by us is a refinement of the process in [10] and it enables to obtain BTO particles uniform in size and morphology, under mild conditions.

Once obtained the particles, we could proceed to prepare the ER fluid. Electro-rheological fluid was prepared using silicon oil, with a viscosity equal to 90 cP and dielectric constant equal to 2.5. A volume fraction of 0.07 of BTO lamellae ceramics was added and introduced in a cell suitable to apply the electric field. Fig. 7 shows a photograph of the BTO complex cluster structure of particles developed under 25 kV applied voltage (120 Hz), at room temperature.

In a comparative study of high dielectric constant particles for ER fluids [13], including TiO_2, $SrTiO_3$, $BaTiO_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Bi_4Ti_3O_{12}$, it was shown that bismuth titanate had the highest yield stress under the same applied electric field, even though there

was no control on size and shape of the particles. A scanning electron micrograph of BTO particles in this paper shows a fibrilar structure.

The structure formed by the particles is fundamental in understanding the properties of ER fluids, it is expected that shear modulus must be higher when the structure is complex, i.e., when the aggregation of chains forms thick columns with a body centered tetragonal symmetry as observed in [14]. In our case, the structure of BTO particles under applied electric field is more complex than the fibrilar reported for some oxides [13], they form clusters, so that we expect a higher yield stress.

4. Conclusions

Micrometric lamellar ceramic powders of the displacive ferroelectric oxide $Bi_4Ti_3O_{12}$, were prepared by coprecipitation of bismuth nitrate and ammonia titanyl and thermal decomposition reaction at 1000°C. The particles were dispersed in silicon oil to prepare an electro-rheological fluid, under an AC electric field as low as 25 kV, the particles form complex cluster chains.

References

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FIGURE CAPTIONS

Fig.1 XRD powder pattern of products of coprecipitation reaction heated at 600°C. Peaks correspond mainly to $Bi_2Ti_4O_{11}$, those with asterisk correspond to $Bi(NO_3)_3 \cdot 5(H_2O)$ and TiO_2.

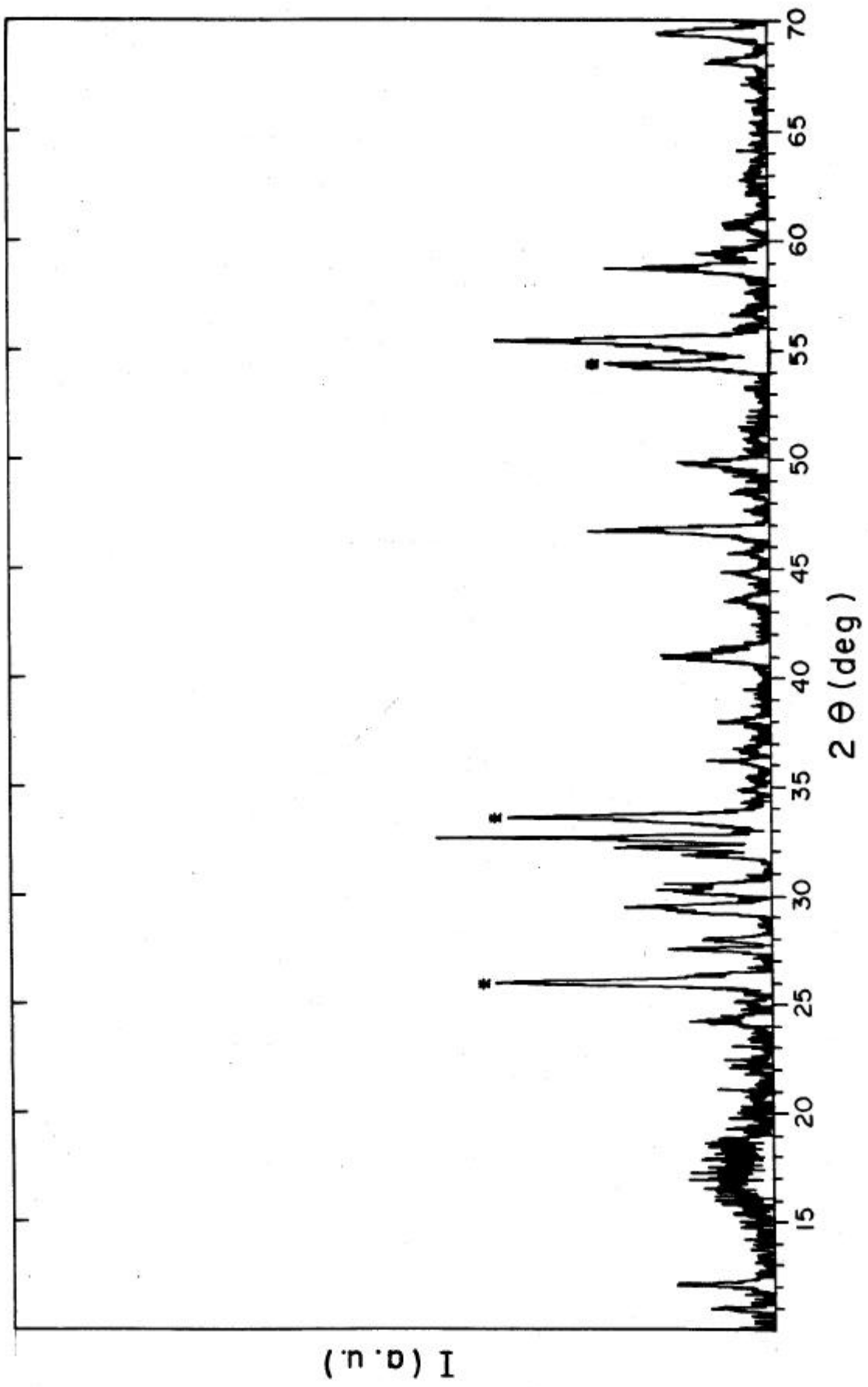Fig. 2 SEM microphotograph of powders with a heat treatment at 600°C.
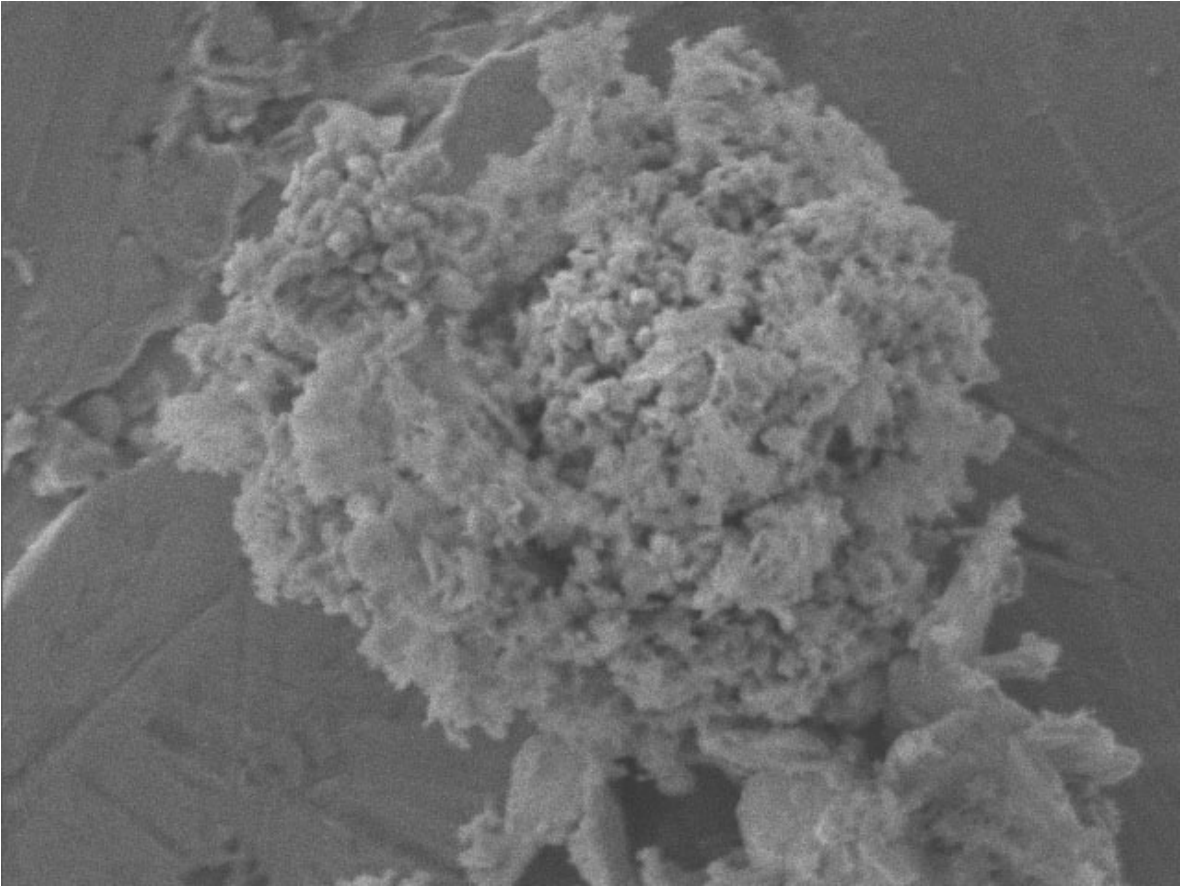
Fig.3 DTA–TG thermograms of precipitate.

Fig.4 XRD powder pattern of ceramic powders heated at 1000°C, it corresponds to $Bi_4Ti_3O_{12}$, dashed lines are from PDF file of BTO.
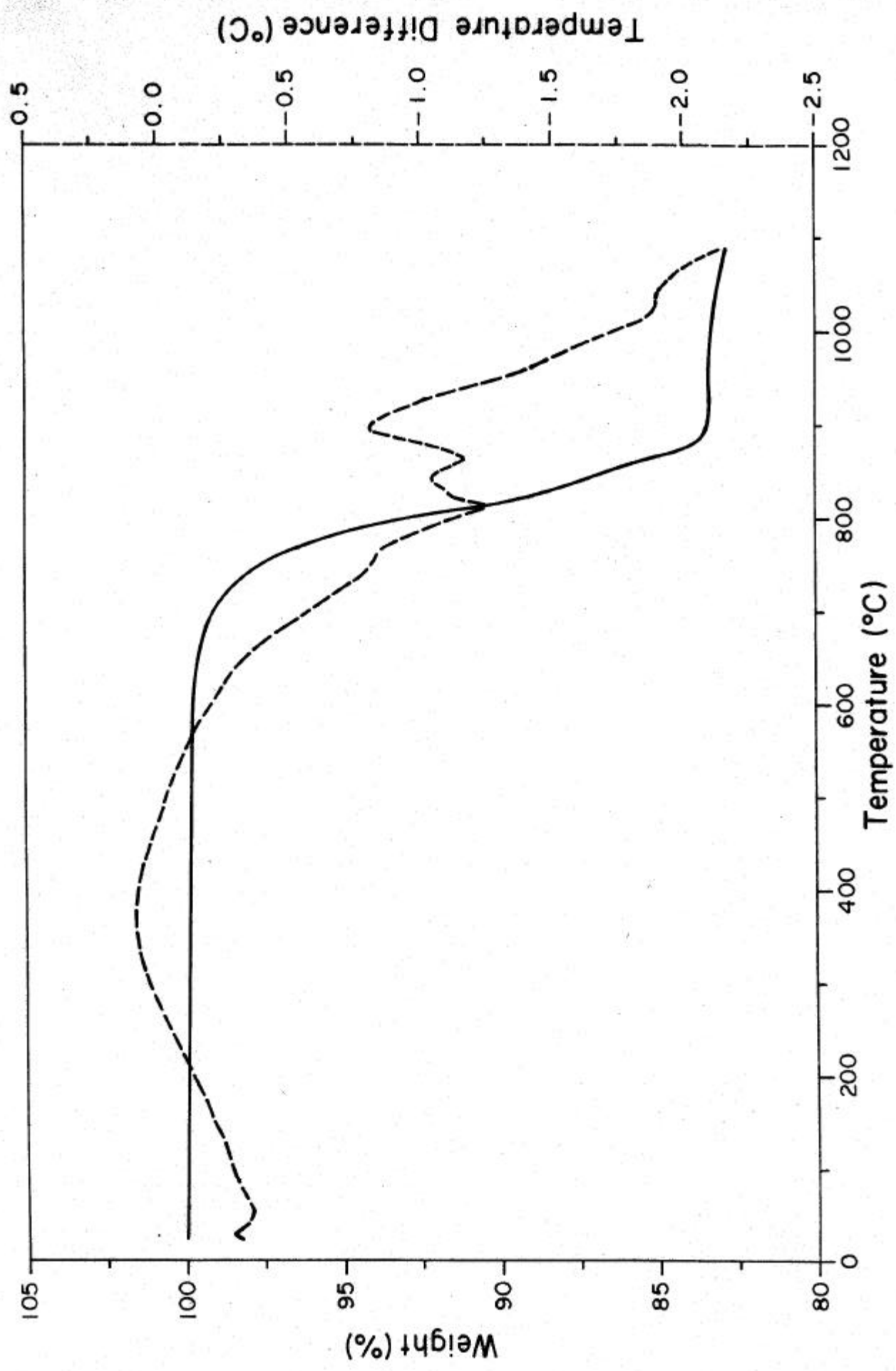
Fig.5 SEM microphotograph of $Bi_4Ti_3O_{12}$ powders.

Fig. 6 DTA of $Bi_4Ti_3O_{12}$ ceramic powders showing the peak associate to the paraelectric-ferroelectric transition.

Fig.7 Electro-rheological fluid prepared using $Bi_4Ti_3O_{12}$ ceramic powders.

I (a.u.)

2 Θ (deg)