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Preparation of Lead Zirconate Titanate (Pb(Zr_{0.52}Ti_{0.48})O₃) by Homogeneous Precipitation and Calcination

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ABSTRACT

Aqueous solutions of lead chloride (PbCl₂), zirconium oxychloride (ZrOCl₂·8H₂O) and titanium tetrachloride (TiCl₄), in appropriate volumetric amounts, were used as the starting materials in the synthesis of phase-pure Pb(Zr_{0.52}Ti_{0.48})O₃ powders. Preparation of the phase-pure PZT powders were achieved, in the presence of urea (CH₄N₂O), by the chemical powder synthesis route of homogeneous precipitation.

Calcination and phase evolution behaviors of PZT precursor powders were studied as a function of temperature by powder XRD (X-ray diffraction) in an air atmosphere, over the temperature range of 90 to 750°C. Morphological properties of the precipitated Pb(Zr_{0.52}Ti_{0.48})O₃ powders were investigated by the SEM (scanning electron microscopy) studies. Semi-quantitative chemical analysis of the samples were performed by EDXS (energy-dispersive X-ray spectroscopy).

INTRODUCTION

Lead zirconate titanate, PbZr_xTi_{1-x}O₃ (PZT), ceramics are of great technological interest due to their excellent piezoelectric and ferroelectric properties [1, 2]. PZT ceramics are extensively used as electromechanical transducer materials. The electromechanical response of these ceramics is maximum when x corresponds to the composition of the morphotropic phase boundary (MPB) which separates the tetragonal (T) and rhombohedral (R) phases towards Ti-rich and Zr-rich sides, respectively. The precise determination of the MPB composition range, which is believed to be quite narrow, has, therefore, attracted immense interest.

Conventionally, the PZT phase is prepared by solid state reactive firing of the constituent oxides (PbO, ZrO₂ and TiO₂). However, due to intermediate reactions which lead to the formation of PbTiO₃ (PT) and PbZrO₃ (PZ), the PZT formed by this method is chemically heterogeneous, including compositional fluctuations, which modify several electrical properties [3, 4].

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The variations in composition may lead to a diffuse MPB between the tetragonal and rhombohedral PZT phases. Another negative feature of such a practice is the production of agglomerated powders with low sinterability. Moreover, the completion of the reactions by long-range diffusion also requires temperatures in excess of 1000°C. A lower calcination temperature, on the other hand, is always desirable since it yields fine powders of improved surface reactivity.

PZT's synthesized by chemical methods have resulted in powders with low compositional fluctuations, narrow MPB and of high reactivity [5-7]. Among these chemical methods were the sol-gel technique [6], and the partial chemical methods as described by Kakegawa [5] and Yamamoto [8]. In the method proposed by Yamamoto [8], lead-oxalate was precipitated on ZT particles processed by hydrothermal reaction, or on ZrO₂ and TiO₂ particles. However, the use of zirconia and titania particles also resulted in intermediate reaction products and a consequent deviation in the PZT stoichiometry. It was also reported by Singh, *et al.* [9] that single-phase PbZr_xTi_{1-x}O₃ powders were synthesized at about 600°C by a semi-wet procedure.

In the present study, the experimental details of the synthesis of lead zirconate titanate phase from water-soluble salts of Pb-, Zr- and Ti-chlorides by homogeneous precipitation, via urea decomposition, were presented. The decomposition of urea in aqueous solutions was accompanied by the slow and controlled supply of ammonia and carbon dioxide into the solution [10]. The smooth pH increase obtained by the decomposition of urea, in unison with the steady supply of OH⁻ and CO₃²⁻ ions, typically leads to the precipitation of metal hydroxycarbonates of controlled particle morphology [11-13]. Homogeneous precipitation from aqueous solutions, in the presence of urea, has previously been used to produce dispersed spherical particles of basic lanthanide carbonates [14], CeO₂ [15], YAG (Y₃Al₅O₁₂) [16], LaAlO₃ [17], YIG (Y₃Fe₅O₁₂) [18], BaTiO₃ [19], and PbZrO₃ [20]. In this study homogeneous precipitation techniques, similar to those described in the literature [11-20], were employed and shown to be successful for the preparation of phase-pure PZT after calcination in air at 500°C.

EXPERIMENTAL PROCEDURE

PbCl₂ (99.5%, Merck, Darmstadt, Germany), ZrOCl₂·8H₂O (99%, Merck, Darmstadt, Germany), and TiCl₄ (Merck, Darmstadt, Germany) were used as the starting chemicals. 0.2 M ZrCl₄ and 0.02 M PbCl₂ aqueous stock solutions were first prepared in de-ionized water. The as-received TiCl₄ (9.1191M) was diluted to 2 M TiCl₄ by de-ionized water. Reagent-grade urea (CH₄N₂O, 99.5% Riedel-De Haen AG, Germany) was used as the precipitation agent.

A total of 160 mL of cation stock solutions (i.e., lead, zirconium and titanium chlorides) were thoroughly mixed in a glass beaker. 27 g of urea dissolved in de-ionized water (350 mL) was then mixed with the above solution. The resultant clear solution was slowly heated in 1 h to 90°C in a water bath. Precipitation started by the end of the next 70 min with a slight turbidity in the clear solution. Precipitates were aged for 2 hours at 90°C. pH-values were continuously recorded as a function of time.

Precipitation experiments were also repeated for varying urea/cation ratios (i.e., 75, 60, 45, 30, 15, and 10) and for different aging times (120, 60, 30, and 10 min). Following aging, the precursors were quenched to room temperature. Precipitates were then separated from the mother liquors by filtering. Recovered precursors were washed four times with deionized-water. The washed precipitates were oven-dried overnight at 90°C in an air atmosphere.

(2) Calcination

Dried precursors were slightly ground in an agate mortar and then calcined in an air atmosphere, in alumina boats or crucibles, over the temperature range of 100 to 750°C for calcination times of up to 6 hours at the peak temperatures.

(3) Powder Sample Characterization

Powder XRD spectra were obtained from the dried precipitates, as well as from powders heated at 100 to 750°C, in open alumina crucibles in a dry air atmosphere. An X-ray powder diffractometer (Rigaku, D-Max/B, Tokyo, Japan) was used in this study with CuK_α radiation at the step size of 0.02° and a preset time of 1 second to perform phase characterization, and to check the phase purity of the synthesized PZT powders.

Particle size and morphological characteristics of the powders were monitored through scanning electron microscopy (SEM) photomicrographs (Model ISM6400, JEOL, Tokyo, Japan). An ultrasonic disrupter (Misonix, Inc., Model: XL 2015, NY, USA) was used to form suspensions of PZT powders. 1 g of powder was ultrasonicated in 15 mL of isopropyl alcohol for 10 minutes, prior to evaporation to dryness on tiny glass slides. Energy dispersive X-ray spectroscopy (KeveX, Foster City, CA) analysis were performed on green PZT pellets to acquire semi-quantitative elemental-distribution information. The EDXS analysis were believed to be accurate to about ± 3 wt%.

The high temperature behavior of PZT precursors produced by homogeneous precipitation experiments were monitored by the XRD charts of the isothermally heated powder samples. Fig. 1 shows the phase distribution and crystallization paths of these powders as a function of increasing calcination temperature.

It was observed that the precursor powders calcined (in an air atmosphere) at 100 and 200°C were already crystalline, and composed of the phases of Cerussite (PbCO_3 ; ICDD PDF 5-417), Hydrocerussite ($\text{Pb}_2(\text{CO}_3)_2(\text{OH})_2$; ICDD 13-131) and Laurionite (PbClOH ; ICDD 31-680).

Following calcination at 300°C for 6 h, the PZT precursors were composed of the phases of litharge (PbO ; ICDD 5-561), zirconia (ZrO_2 ; ICDD 37-31), and titanium oxide (Ti_2O_3 ; ICDD 18-1403). This observation showed that over the temperature range of 200 to 300°C, lead hydroxycarbonate phases (i.e., Cerussite and Hydrocerussite) have totally been converted to their oxides (i.e., Litharge). It was also interesting to note that at this temperature the free phases of zirconium and titanium oxides did crystallize from the precursor powders. Upon calcination at 400°C, the phases of litharge and zirconia completely disappeared, and the formation of PbZrO_3 (ICDD 35-739 and 20-608) was observed, and a small amount of PZT ($\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$; ICDD 33-784) evolved. This temperature may be regarded as the starting temperature for the formation / crystallization of the PZT phase.

Calcination of our precursor powders at temperatures higher than 400°C (in air atmosphere), as seen in Fig. 1 (urea/cation ratio = 45), all yielded single-phase PZT. A pyrochlore phase was not observed. Therefore, it can be stated that "500°C" is the temperature of formation for PZT powders prepared by homogeneous precipitation in aqueous solutions in the presence of urea. The EDXS analysis performed on the 700°C-calcined samples gave the mean atomic percentages of 20.04 : 10.29 : 9.67 (for Pb : Zr : Ti).

The XRD traces given in Fig. 2 show the phase formation behavior of precursor powders (all being heated at 700°C) as a function of changing "Urea/Cation" ratios in aqueous solutions. It was hereby shown that there must be a minimum level for this ratio for the formation of PZT phase. At the ratio of 10, the PZT phase can not be formed, and the resulting phases are a mixture of Cerussite and Hydrocerussite.

Figure 3 shows the solution "pH" versus "time" curves recorded in the precipitation solutions on a real-time basis. Various Urea/Cation ratios in the solutions have been studied and the final pH values required for the

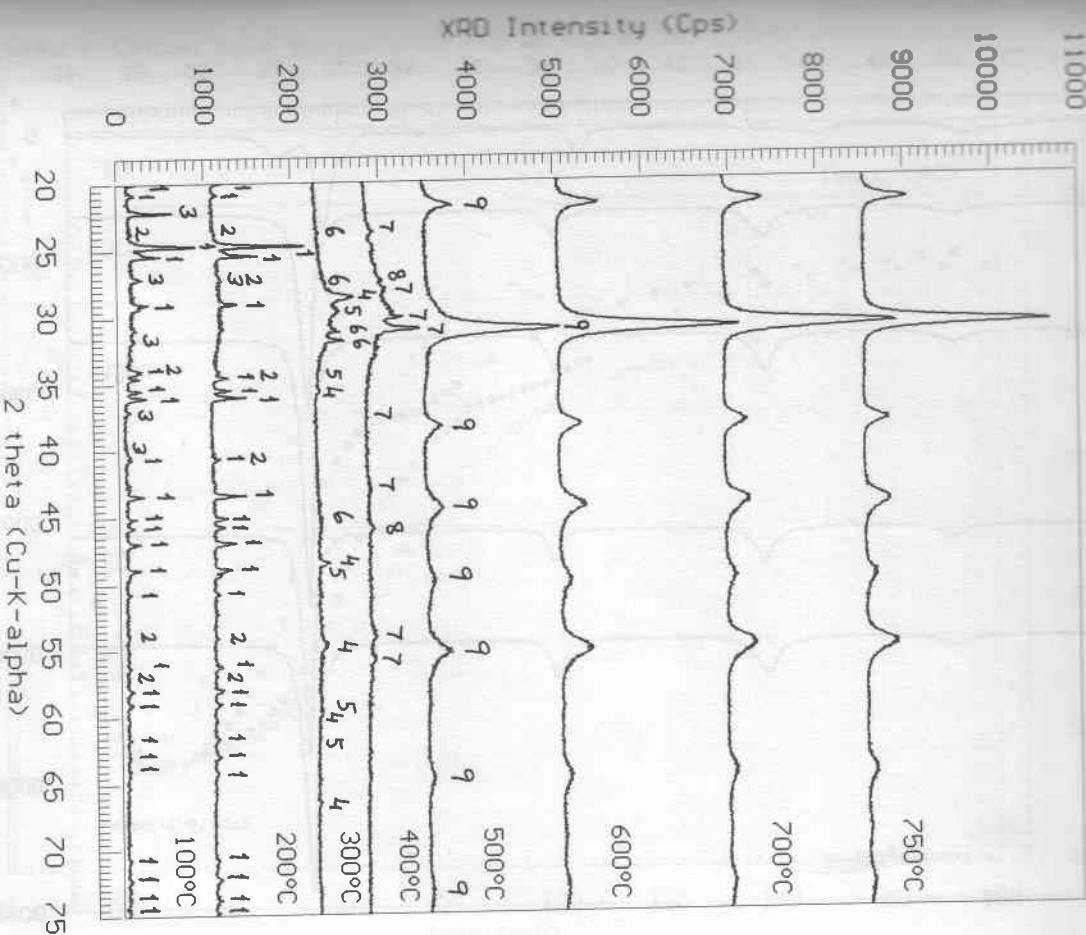


Fig. 1 XRD spectra of PZT precursor powders (urea/cation ratio = 45) heated at various temperatures for 6 h in an air atmosphere (ICDD PDF 1: 5-417, 2: 13-131, 3: 31-680, 4: 5-561, 5: 37-31, 6: 18-1403, 7: 35-739, 8: 20-608, 9: 33-784)

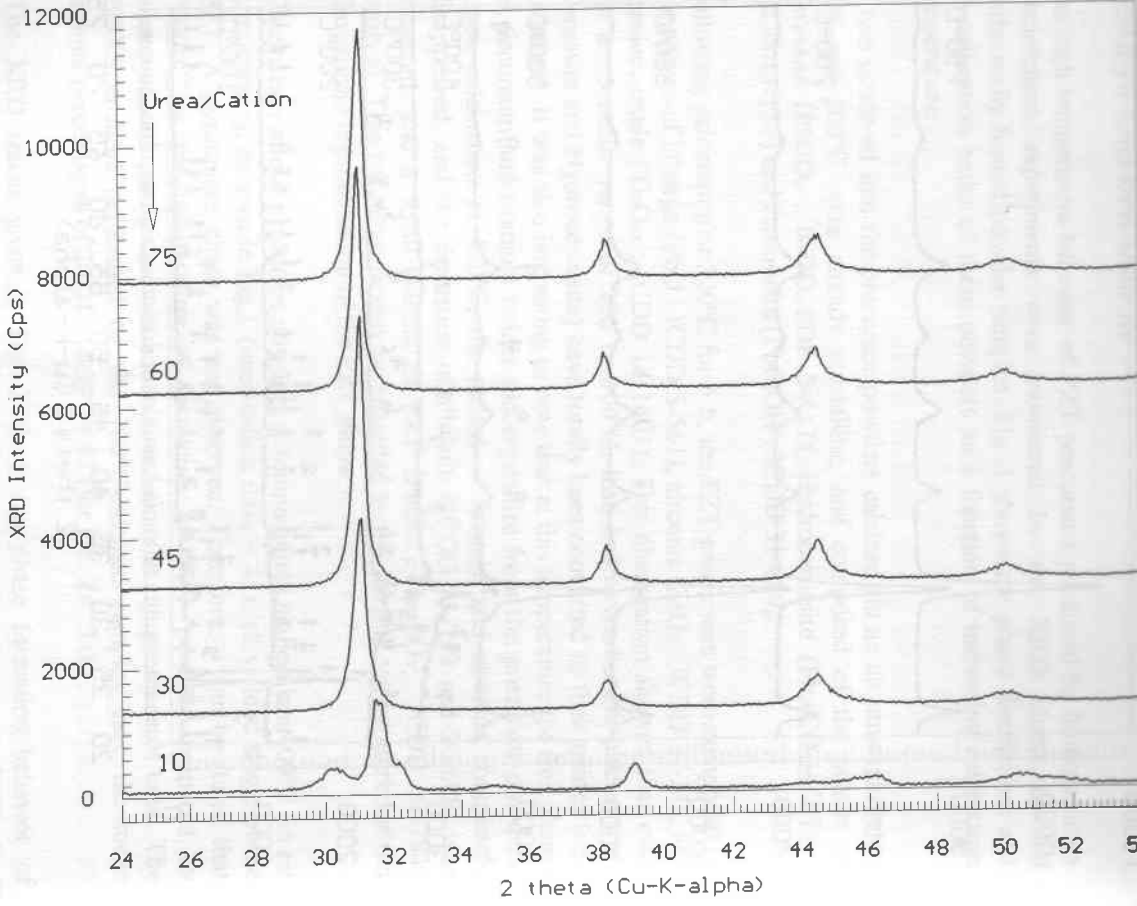


Fig. 2 XRD spectra of PZT precursor powders synthesized at different "Urea / Cation" ratios (calcination temperature : 700°C, 6 h)

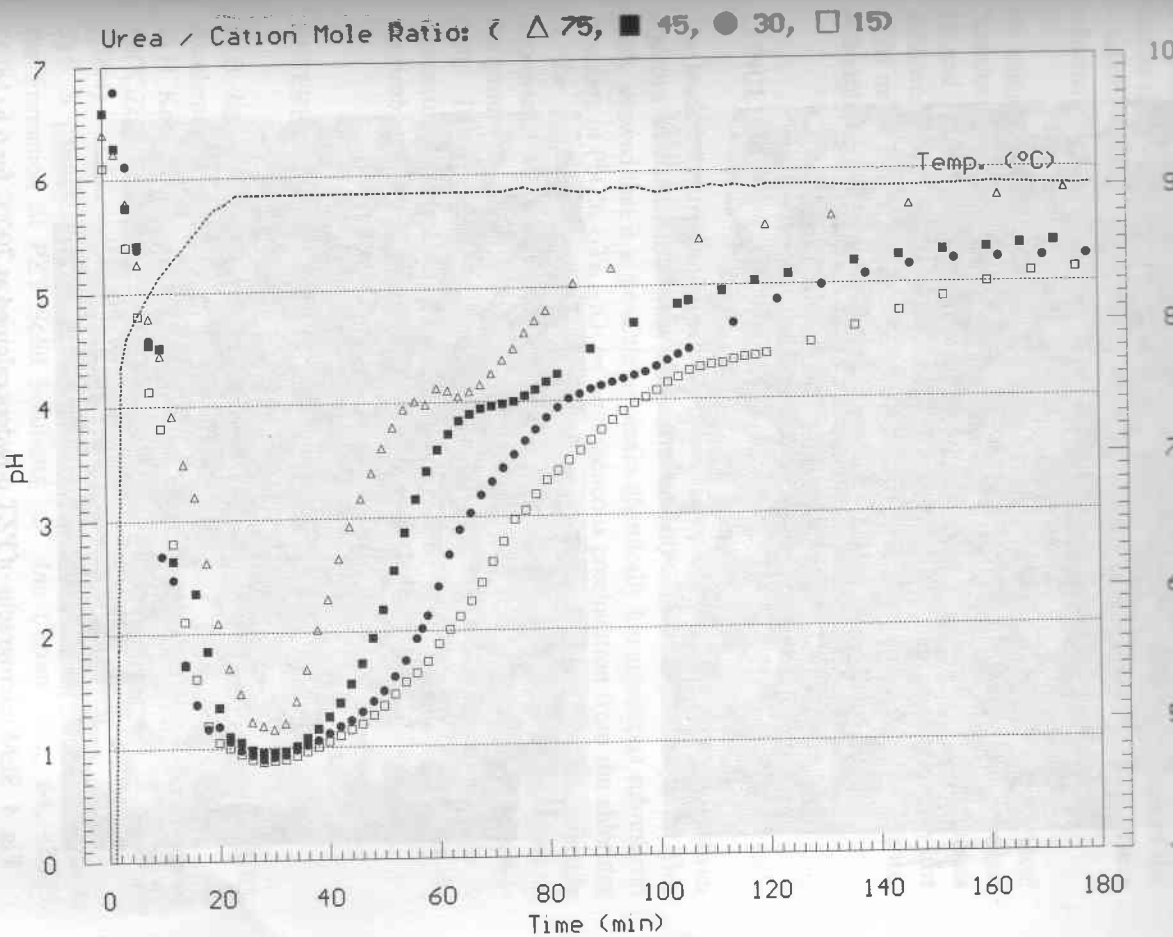


Fig. 3 "pH" vs. "time" plots of PZT precursor powders aged at different "Urea / Cation" ratios

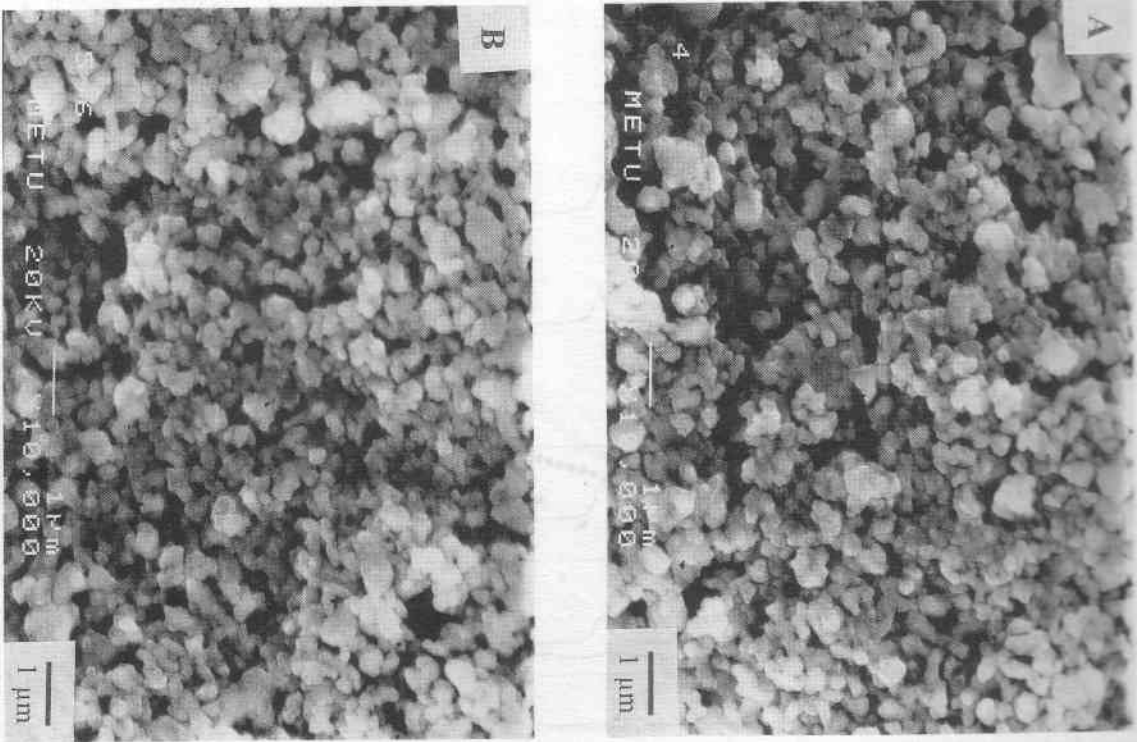


Fig. 4 SEM micrographs of PZT powders calcined at 700°C for 6 h
Urea/Cation ratio: (A) 45, (B) 30

precipitation reactions to proceed were determined. It was apparent from Fig. 3 that as the amount of urea in the solutions increased, the final pH values of the solutions were also increased. The "shoulders" displayed in these charts indicated the precipitation-start points, as a function of pH and aging time.

By using the data obtained in Figs. 2 and 3, it can be stated that the critical "urea/cation ratio" in the mother liquors must be located somewhere between 10 and 15, for the homogeneous precipitation of PZT powders in aqueous solutions. The morphology of the produced powders were examined by the SEM micrographs given in Fig. 4. The PZT powders had sub-micron particles, although they were highly agglomerated.

CONCLUSIONS

The lead zirconate titanate ($\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$) phase has been synthesized from aqueous solutions, following calcination at 500°C in an air atmosphere. This study showed that it is possible to obtain chemically homogeneous sub-micron powders of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ by homogeneous precipitation from the chlorides of the respective cations via the decomposition of urea. A considerable decrease in the processing temperature may thus be obtained in comparison to the processes which involve powder mixing and reactive firing in the solid-state. This decrease in synthesis temperature is also believed to help in eliminating the need for the strict use of atmosphere control to compensate for the problems of lead volatilization in large-scale manufacturing processes.

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PREPARATION AND LOW-FREQUENCY ELECTRICAL PROPERTIES OF $LaFeO_3$ BY CHEMICAL COPRECIPITATION

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ABSTRACT

Various mole ratios of $La(NO_3)_3 \cdot 6 H_2O$ and $Fe(NO_3)_3 \cdot 9 H_2O$ aqueous solutions with sodium hydroxide solution were used to prepare the precursors with OH ligands by using chemical coprecipitation for controlling stoichiometry accurately. After freeze drying, the precursors were calcined in the oven with a heating rate of 10 K/min to 1073 K for 4 h to obtain the corresponding compounds. Then the powders were sintered in the different atmosphere (air or nitrogen) and temperature (1373, 1473 or 1573 K) for 8 h. XRD, FTIR, SEM and XPS(ESCA) were used to analyze the crystallinity and microstructure of the calcined powders and the sintered bodies.

The DC resistivity decreases with increasing charged voltage. And $LaFeO_3$ is a semiconductor. The DC resistivity increases with increasing doping amount of ZrO_2 . But the resistivity and dielectric constant are smaller in sintering atmosphere of air than that in nitrogen. The dielectric constant increases with increasing temperature.

INTRODUCTION

Kao et al. have studied the preparation and characterization of fine La-Cr-Zr oxides ceramics by chemical coprecipitation at high temperatures[1]. $LaBO_3$ (B= transition metal element, such as Cr, Fe, Mn, Co etc.) is a perovskite-type oxide, having the specific properties of highly nonstoichiometry and mixed conductivity by both ionic

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