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Microwave assisted preparation of binary oxide nanoparticles

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A group of binary oxide nanophase materials were prepared using a microwave assisted soft-chemical route. $BaTiO_3$, $Ba_6Ti_{17}O_{40}$, $BaZrO_3$ and $PbTiO_3$ were prepared from $BaCl_2$ hydrate, $Pb(Ac)_2$, $Ti(OPr^i)_4$ and $ZrOCl_2$. All reactions were performed in ethylene glycol, which acted as both a solvent and a growth regulating agent, under atmospheric pressure in a microwave reactor. The products that were obtained were analyzed by using XRD, TEM, XPS, EDX and FT-IR.

Introduction

Perovskite ferroelectrics are a special group of advanced electronic ceramics, which undergo spontaneous electric polarization and possess reversible polarization under an applied electric field.[1] These materials have already found applications in many areas, such as electro-optic devices, multilayer capacitors and others.[2] The growing demand for ferroelectric ceramics with nanometer dimensions has accelerated the development of new powder synthetic methods. Because the performances of such materials are determined by the characteristics of the starting powder, the dimensions and morphology of the nanoparticles could have a profound influence on the dielectric properties of the resulting electronic ceramic.[3]

Traditionally high temperature synthetic methods were used for the preparation of pervoskite electronic ceramics. In these methods many hours of high-temperature heating (1100–1400 °C) are needed, which leads to high agglomeration and partial sintering of the powder.[4] For example, for the synthesis of $BaZrO_3$ the starting materials are barium carbonate and zirconium oxide. This solid state reaction leads to powders of relatively large and varied grain sizes and varying impurity content.[5] In the past few decades considerable research has focused on the application of low temperature methods for ceramic synthesis. One of the leading methods is the hydrothermal method. This method was applied for the preparation of a large number of different ceramics from a variety of precursors. In the hydrothermal method, solvent, pressure and temperature can stabilize the desired product while inhibiting the formation of undesirable compounds. Because hydrothermal synthesis involves mostly reactions between heterogeneous precursors, the timescale of such a synthesis is very long (generally a few days) and only thermodynamically stable phases under specific conditions can be synthesized. Only recently a few reports appeared about the applications of such reactions to nonaqueous solvents.[6,7] For example, ethylene glycol as a solvent has been successfully applied to the synthesis of rare earth iron garnets.[8] Such reactions have a few advantages relative to hydrothermal reactions: lower reaction temperatures (when using 1,4-butanediol as a solvent, the reaction temperature could be 300 °C), lower reaction pressure, the reaction begins from a homogeneous phase (this is especially important if alkoxides are used as precursors). The use of alcohols as solvents also prevents the polymerization process, which occurs when water is used as a solvent. The polymerization process in water occurs through a sol–gel mechanism, which is slowed down considerably in alcohols. The microwave-assisted route is yet another novel method for the synthesis of electroceramic materials and has become a rapidly developing area of research.

Microwaves have been used for the acceleration of organic chemical reactions for some time, because the method is generally faster, simpler and very energy efficient.[9] Unfortunately the exact nature of the interaction of the microwaves with the reactants during the synthesis of materials is somewhat unclear and speculative. However, it is well known that the interaction of dielectric materials, liquids or solids, with microwaves leads to what is generally known as dielectric heating. Electric dipoles present in such materials respond to the applied electric field. In liquids, this constant reorientation leads to friction between molecules which subsequently generates heat.[10]

In the current study we report the synthesis of a group of inorganic materials in ethylene glycol. The reaction take place at the boiling point of ethylene glycol, and shows that binary oxides like $BaTiO_3$, $Ba_6Ti_{17}O_{40}$, $BaZrO_3$ and $PbTiO_3$ can be readily and rapidly synthesized as nanophase materials.

Experimental

Lead acetate trihydrate, barium chloride dehydrate, zirconium perchlorate octahydrate, titanium isopropoxide ($Ti(OPr^i)_4$) were obtained from Aldrich Chemical Co. Ethylene glycol was received from J.T. Backer Co. The microwave refluxing apparatus has been described previously.[11] Transmission electron microscopy was performed using a JEOL-JEM 100SX instrument. EDX measurements were performed on an X-ray microanalyzer (Oxford Scientific) built on a JSM-840 scanning microscope (JEOL). The powder X-ray diffraction patterns were recorded using a Rigaku 2028 Cu-Kα X-ray diffractometer ($\lambda = 1.5418$ Å), nickel was used as the filter. X-Ray photoelectron spectroscopy (XPS) spectra were recorded using an AXIS, HIS, 165, ULTRA instrument (Kratos Analytical). FT-IR measurements were conducted using a Nicolet Impact 410 spectrophotometer using KBr pellets.

The general process used in the preparation of these ceramics is the following: the chloride or acetate salts were dissolved in ethylene glycol (EG) under static N_2 (in some cases the salt did not dissolve totally). Solid KOH was then added gradually to bring the pH to 11. $Ti(OPr^i)_4$ was added and immediately microwave assisted refluxing was turned on. All the reactions were conducted under a static pressure of nitrogen. The microwave power in all procedures was 80%. The times for each of the reactions are shown in Table 1. After the reaction was finished the resulting products were washed with doubly distilled and degassed water (this is important to prevent

Table 1 The dimensions of the produced particles as measured by various methods

Product	Reagents	Reaction time/h	Dimensions from TEM/nm	Dimensions from XRD/nm	EDX stoichiometry
$BaTiO_3$	$BaCl_2{\cdot}2H_2O$, $Ti(OPr^i)_4$, KOH	5	10 (as-prepared) 20–30 (heated)	9 (as-prepared) 18 (heated)	$Ba_{0.94}TiO_3$
$Ba_6Ti_{17}O_{40}$	Same as for $BaTiO_3$, but different molar ratios	5	15 (as-prepared) 40–50 (heated)	11 (as-prepared) 26 (heated)	$Ba_{5.7}Ti_{17}O_{40}$
$BaZrO_3$	$BaCl_2{\cdot}2H_2O$, $ZrOCl_2$, KOH	2	$\sim 200 \times 600$ (same for as-prepared and heated)	1.8 (as-prepared) 24 (heated)	$Ba_{0.92}ZrO_3$
$PbTiO_3$	$Pb(Ac)_2$, $Ti(OPr^i)_4$, KOH	1	5–7 (as-prepared) 20–30 (heated)	1.2 (as-prepared) 17 (heated)	$Pb_{0.9}TiO_3$

formation of $BaCO_3$ as a by-product) and centrifuged a few times. Then they were dried under vacuum at 70 °C.

Results and discussion

The phases of the as-prepared materials were in all cases semicrystalline as detected by X-ray and electron diffraction. A typical example is shown in Fig. 1 depicting the as-prepared $BaTiO_3$. It shows broad peaks that are attributed to cubic $BaTiO_3$. These broad diffraction peaks are the result of the small size of the as-prepared material. In Table 1 the sizes of the as-prepared and heated materials are presented as calculated from the TEM pictures and from the XRD by the Debye–Scherrer formula. For a better evaluation of the crystallographic structure, the as-prepared powder was heated to 700 °C under N_2 for a few hours. The resulting XRD and lattice parameters exactly match the cubic $BaTiO_3$ pattern (JCPDS 31-174). The XRD pattern of the as-prepared material shows an extra peak at $2\theta = 27.3°$ (Fig. 1a), which is attributed to the existence of a $BaCO_3$ impurity. This peak disappears, however, upon heating to 700 °C (Fig. 1b). Using different molar ratios and keeping all the other parameters unchanged led to the fabrication of $Ba_6Ti_{17}O_{40}$. The XRD for this as-prepared powder also shows very broad peaks. After heating (same conditions as for $BaTiO_3$) sharp peaks of $Ba_6Ti_{17}O_{40}$ appear with the presence of some $BaTiO_3$. The XRD of $PbTiO_3$ is shown in Fig. 2. In this case, the as-prepared product is either amorphous or an unidentified precursor (see Fig. 2a) whose broad nature is due to its small size (1–2 nm). After heating (see Fig. 2b) the pure tetragonal phase of $PbTiO_3$ is observed (JCPDS 06-0452). A semicrystalline product was obtained for the as-prepared $BaZrO_3$ (Fig. 3a). After heating (Fig. 3b) the as-prepared product a perfect match with the well-known pattern of $BaZrO_3$ (JCPDS 74-1299) is obtained. Stoichiometric ratios obtained using EDX measurements show small deviations from the theoretical values (see Table 1). The positions of the XRD diffraction peaks of all the products are compared with the database values. Calculation of the dimensions of the unit cell gives the following values (in Å): (a) for $BaTiO_3$: $a = 4.034$, $b = 4.034$, $c = 4.034$, cubic lattice; (b) for $PbTiO_3$: $a = 3.89$, $b = 3.89$, $c = 4.15$, tetragonal lattice; (c) for $BaZrO_3$: $a = 4.18$, $b = 4.18$, $c = 4.18$, cubic lattice. The measured results are in very good agreement with the published JCPDS data.

The TEM pictures of the as-prepared $BaTiO_3$ and $Ba_6Ti_{17}O_{40}$ are shown in Fig. 4a–c. It is possible to see that the $BaTiO_3$ powder consists of particles with average diameter close to 10 nm and that they are strongly aggregated. After heating the sample of the nanoparticles some growth to 20–30 nm diameter is observed. This is probably the reason why,

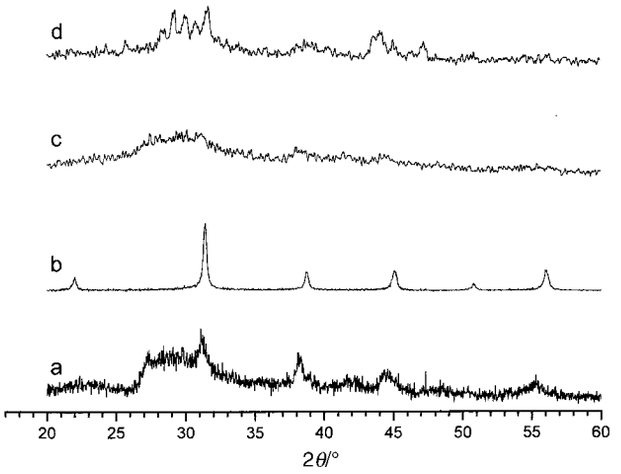

Fig. 1 Powder XRD: (a) as-prepared amorphous $BaTiO_3$; (b) crystalline $BaTiO_3$, heated to 700 °C; (c) as-prepared amorphous $Ba_6Ti_{17}O_{40}$; (d) $Ba_6Ti_{17}O_{40}$ heated to 700 °C.

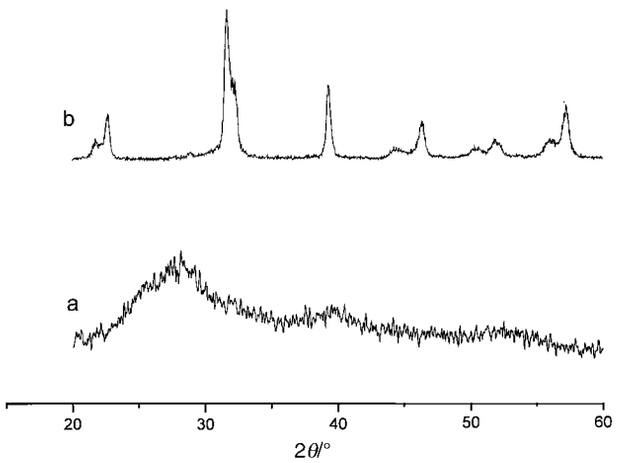

Fig. 2 Powder XRD: (a) as-prepared amorphous $PbTiO_3$; (b) crystalline $PbZrO_3$ heated to 700 °C.

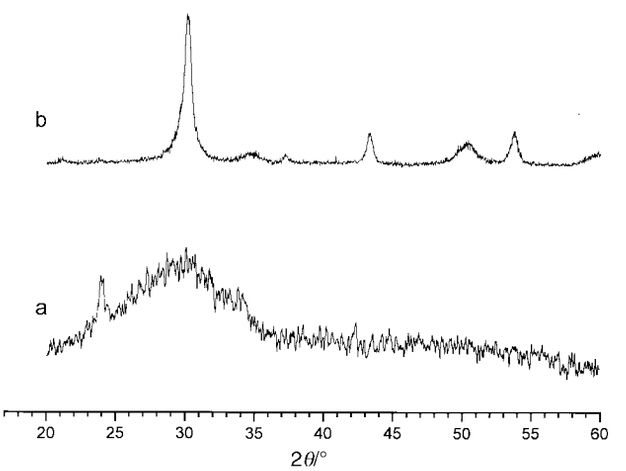

Fig. 3 Powder XRD: (a) as-prepared amorphous $BaZrO_3$; (b) crystalline $BaZrO_3$ heated to 700 °C.

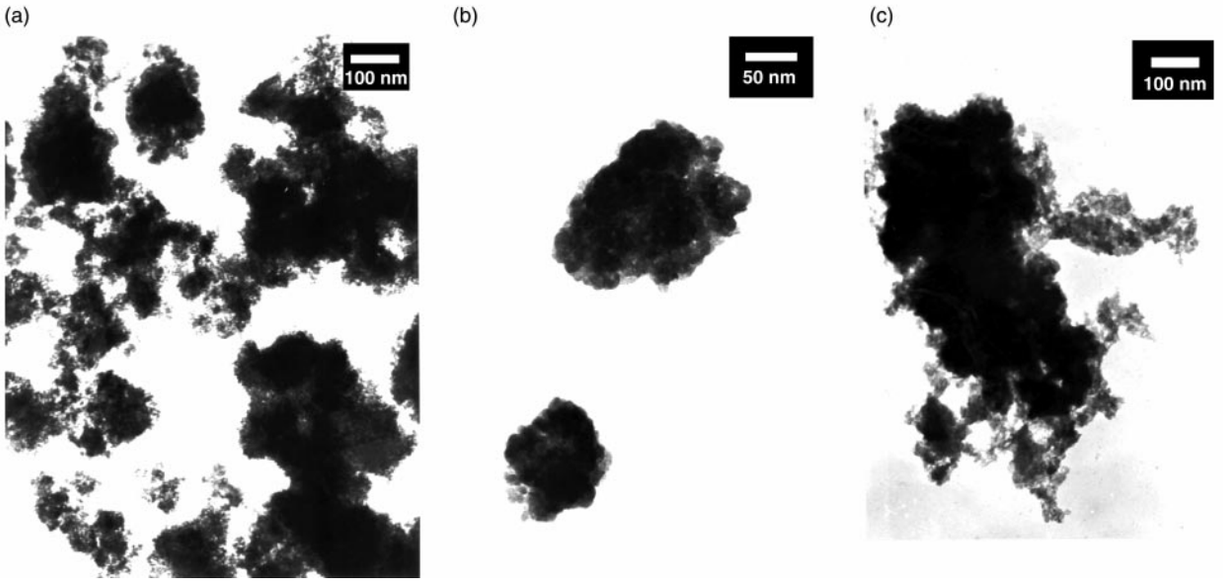

Fig. 4 TEM patterns: (a) as-prepared amorphous $BaTiO_3$ (bar = 100 nm); (b) same as (a) but with higher magnification (bar = 50 nm); (c) as-prepared amorphous $Ba_6Ti_{17}O_{40}$ (bar = 100 nm).

after heating, only the cubic crystallographic form was observed, and not the tetragonal form. The tetragonal form is stable at dimensions equal to or larger than 50 nm. The decrease in diameter of the nanoparticles leads to a transition to a "pseudo-cubic" structure.[12] The TEM micrograph of $Ba_6Ti_{17}O_{40}$ is shown in Fig. 4c. The average diameter of these nanoparticles is about 15 nm, which is slightly larger than that of $BaTiO_3$, and this material is also aggregated. The dimensions of the as-prepared nanoparticles of $PbTiO_3$ are about 5–7 nm (see Fig. 5a). They are heavily aggregated in spheres (diameter close to 300 nm, see Fig. 5b). Unlike the previous cases where heavily aggregated, small spherical individual particles were observed, for $BaZrO_3$ we did not observe such morphologies. The TEM picture of $BaZrO_3$ reveals rectangular shaped aggregates with dimensions of a few hundred nanometers. The size of these aggregates is extremely different from the XRD calculated size (as-prepared 1.8 nm, after heating 24 nm). This discrepancy will be explained as originating from the special order demonstrated in this aggregation, where the individual undetected particles (24 nm size) organize into these rectangles.

Fig. 6a,b show infrared spectra of the as-prepared $BaTiO_3$ and the heated sample, respectively. Two broad bands around 560 and 431 cm^{-1} are observed. The measured frequencies agree with those reported in the literature,[13] which have been assigned to surface modes.[14] The substructure of the peak at 560 cm^{-1} probably results from the presence of some organic impurities on the surface of the nanoparticles. This peak disappears after heating the sample.

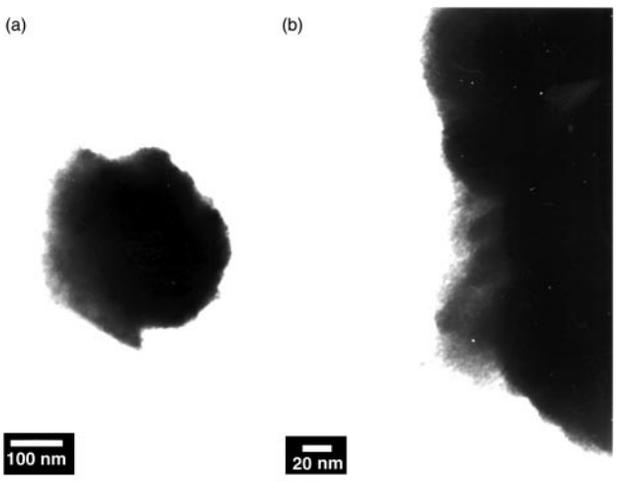

Fig. 5 TEM patterns: (a) as-prepared amorphous $PbTiO_3$ (bar = 100 nm); (b) same as (a) but with higher magnification (bar = 20 nm), it is possible to see aggregated nanoparticles.

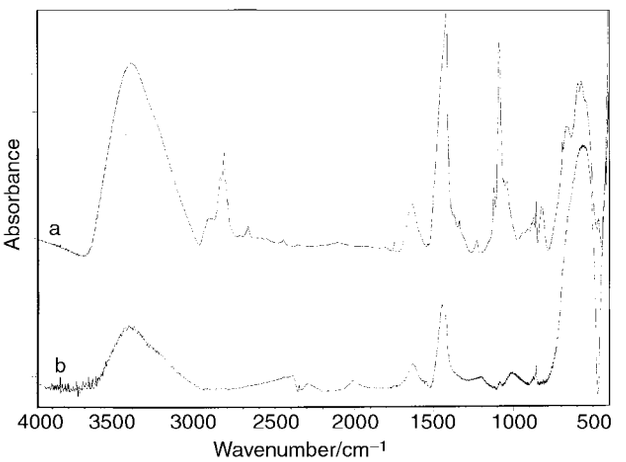

Fig. 6 FT-IR spectra: (a) as-prepared amorphous $BaTiO_3$; (b) crystalline $BaTiO_3$ heated to 700 °C.

Fig. 7 gives wide-scan XPS spectra of $BaTiO_3$ nanoparticles before (curve a) and after (curve b) heating. The spectrum is in general agreement with previous results.[15] The stoichiometric ratio found from the area under the XPS peak reveals that the atomic ratio of elements is close to the theoretical value with a slight excess of oxygen, which we attribute to the water molecules absorbed on the surface of the particles. Taking into account that the XPS probes only surface layers we consider this as another indication for the identification of the product as $BaTiO_3$. In both cases a C 1s peak at 284–288 eV is observed, which we attribute to the presence of $BaCO_3$ (288 eV) and carbon of other organic contaminants absorbed from the air (285 eV). The O 1s signal appears at 530 eV. Deconvolution analysis (not shown here) reveals that the peak of the as-prepared $BaTiO_3$ consists of two peaks, assigned to oxygen in $BaTiO_3$ (528. eV), and to CO_3^{2-} from $BaCO_3$ (529. eV). In the case of heated $BaTiO_3$ the O 1s signal appears to be

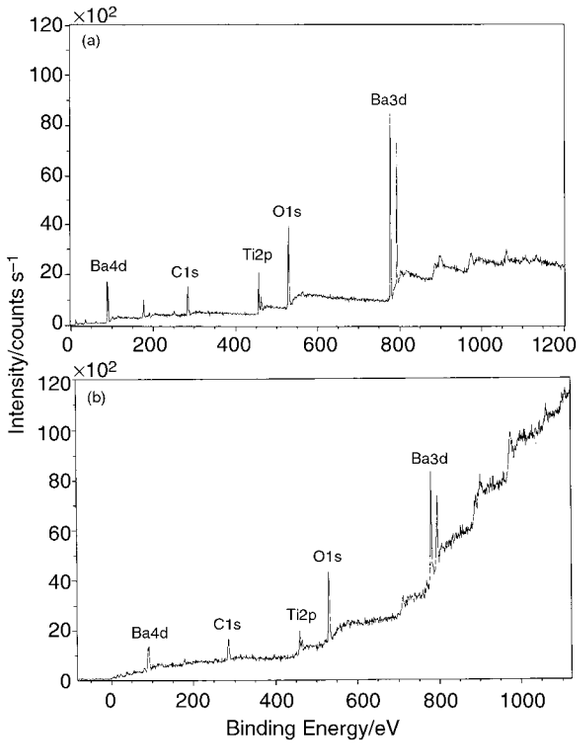

Fig. 7 XPS spectra: (a) as-prepared amorphous $BaTiO_3$; (b) crystalline $BaTiO_3$ heated to 700 °C (deconvolution results not shown).

symmetrical with a much smaller peak, characteristic of CO_3^{2-} groups. This is probably the result of the thermal decomposition of $BaCO_3$. Peaks of Ba 3d and Ba 4d appear at 779 and 90 eV, respectively. Also in this case it is possible to see a small contribution from the presence of $BaCO_3$ (by deconvolution, the $BaCO_3$ peak is generally 2–3 eV higher than $BaTiO_3$ peaks). This peak is drastically reduced upon heating. The Ba 3d and 4d and the Ti 2p peaks are doublets and are not related to impurities.

It is widely known that pH has a profound influence on the formation of the products in hydrothermal reactions. In the case of microwave assisted glycothermal reactions we observe that the optimal pH for the formation of oxides is close to 11. At higher pH we observe the reduction of Ti. The mechanism for the formation of particles in the glycothermal reaction is probably similar to that of the hydrothermal reaction: dissolution and crystallization. In the case of $PbTiO_3$ the reaction begins when not all the $Pb(Ac)_2$ is dissolved. However during the reaction it dissolves as expected from the Le Chatelier principle. In recent publications regarding glycothermal reactions,[16] Moon and coworkers stated that glycothermal reaction have very slow crystallization kinetics. We concur with this statement when microwave heating is not operated. However, with the application of microwave heating this problem is overcome, even without high pressure. Ethylene glycol reacts not only as a solvent but also plays the role of a complexing agent, and capping regulator of the growth of the nanoparticles. Because of its complexing power it reacts with titanium alkoxide producing a soluble complex which further reacts with Ba in solution, producing an intimately mixed intermediate between Ba (or Pb) and Ti (or Zr), which subsequently polymerizes to produce ceramics. Because salt hydrates are used in all cases as precursors, some quantities of water are present in the reaction mixture, and this equalizes hydrolysis rates of the precursors, which eliminates ion diffusion problems during synthesis.

Conclusions

A low temperature microwave assisted method for the preparation of $BaTiO_3$, $Ba_6Ti_{17}O_{40}$, $BaZrO_3$ and $PbTiO_3$ has been developed with ethylene glycol as a solvent. Playing a triple role as a solvent, capping agent and complexing agent, ethylene glycol makes possible the preparation of very small nanoparticles from water sensitive precursors. As in the case of the hydrothermal reaction, the glycothermal reaction is found to be sensitive to pH. The optimal pH is 11, and at higher pH we observe the reduction of the precursors. The sluggish kinetics of glycothermal synthesis is overcome by using microwave heating, which enhances the reaction rate considerably. This improvement shortens the reaction time and eliminates the need for high pressure as well.

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