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Novel hydroxide precursors for low temperature synthesis of selected ternary oxides

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Abstract

A novel method of using hydroxide precursors to reduce the synthesis temperature for few selected ternary oxides has been presented here. This technique is very useful and advantageous when the ternary oxides contain an alkaline earth element. The selected compositions for this method are $BaCeO_3$ (BC), $BaBiO_3$ (BB), $La_{0.7}Sr_{0.3}CoO_3$ (LSCO) and $BaBi_2Nb_2O_9$ (BBN). Commercially purchased strontium (or barium) hydroxide and freshly prepared lanthanum, cobalt, bismuth and niobium hydroxides were mixed thoroughly in stoichiometric ratio and heated at different temperatures ranging from 100 to 700 °C for 10 h for corresponding compositions. The sequence of the reaction and evolution of the product phase were studied by the X-ray diffraction (XRD) studies. The phase purity and lattice parameters were also determined by XRD investigations. All the product phases in each case were formed at relatively low temperature than when they were prepared by co-precipitation or solid state method. The morphology and average particle size of these powders were investigated by scanning electron microscopy (SEM).

Keywords: A. Ceramics; A. Oxides; B. Chemical synthesis; C. X-ray diffraction; C. Electron microscopy

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1. Introduction

The ABO_3-type, $BaBiO_3$ attracts special attention because it shows a metal–semiconductor transition and superconductivity in the metallic phase [1–11]. Pure $BaBiO_3$ also has potential application as a positive temperature coefficient (PTC) thermistor, whereas doped $BaBiO_3$ compounds show a negative temperature coefficient (NTC) effect over a wide temperature range and have prospective applications in electronics for the suppression of in-rush current, for temperature measurement and control, and for compensation for other circuit elements. Li-substituted $BaBiO_3$ acts as a catalyst action for the partial oxidation of methane. The compound, $BaCeO_3$ has been reported to have high ionic conductivity between 600 and 800 °C and considered as one of the best candidates to replace the YSZ electrolyte materials for solid oxide fuel cell (SOFC).

Perovskite type oxides comprised of a rare earth ion and d-transition metal ion such as $LaFeO_3$, $LaMnO_3$ and $LaCoO_3$ are being increasingly applied as electronic and magnetic materials. A considerable attention has been

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focused on the $La_{0.7}Sr_{0.3}CoO_3$ (LSCO) due to its excellent properties such as high electronic conductivity, magnetic susceptibility, large negative magnetoresistance, magnetohydrodynamic (MHD) generators, catalytic activity, cathode material with maximum electrochemical activity, extremely fast response thermocouple applications and low resistivity [12–27]. The low resistivity of these materials can be exploited for use as electrodes in several situations and the good catalytic activity for oxygen reduction in SOFCs for potential electric power generation because of the simplicity of system design in SOFC.

Recently, bismuth-based compounds with the Aurivillius type structure have attracted much attention because of their low operating voltage, fast switching speed, negligible fatigue after up to 10^{12} switching cycles, excellent retention characteristics and low leakage current density on Pt electrodes for integrated device applications in nonvolatile ferroelectric random access memories (FRAM) [28–32]. The Aurivillius family of compounds is represented by a formula (Bi_2O_2 ($A_nB_{n-1}O_{3n+1}$) where A (=Sr, Ba, Ca) is a larger cation in 12-fold coordination and B (=Nb, Ta) a small cation in 6-fold environment.

Both traditional solid state and wet-chemical methods (co-precipitation and sol–gel) are used for the preparation of these compounds. In all these techniques, the temperature for the formation of product is >700 °C. The solid state method requires high temperatures. And this leads to poor compositional homogeneity and high sintering temperature. The co-precipitation method also yields these powders only above 800 °C due to the fact that alkaline earth metal (Ba, Sr, Ca) carbonate or oxalate will decompose only at higher temperatures ($T > 800$ °C) and hence this method also does not produce this compound at low temperatures. Here we communicate a simple procedure to prepare all the above compounds at relatively low temperature. This method is not reported in the literature. This technique has been already used for the preparation of $LiNbO_3$, $KNbO_3$ and $NaNbO_3$ and reported by us [33,34]. The method is easily amenable for large-scale production and relatively economical.

2. Experimental

All the reagents used in this work were of AR grade (Loba cheme, India). To prepare $BaCeO_3$ and $BaBiO_3$, reagent grade barium hydroxide ($Ba(OH)_2\cdot 8H_2O$), cerium nitrate ($Ce(NO)_3\cdot 6H_2O$), bismuth nitrate and sodium hydroxide were used as the starting materials. Fresh cerium hydroxide and bismuth hydroxide were prepared under basic conditions by adding an excess amount of sodium hydroxide to cerous (or bismuth) nitrate solution. The hydrated individual hydroxide precipitates was filtered, washed free of anions by distilled water and oven dried overnight at 100 °C. Required quantity of $Ce(OH)_2$ or $Bi(OH)_3$ and $Ba(OH)_2$ were mixed thoroughly and heated at different temperatures ranging from 100 to 700 °C for 10 h.

To prepare $La_{0.65}Sr_{0.35}CoO_3$, lanthanum oxide (La_2O_3), strontium hydroxide ($Sr(OH)_2\cdot 8H_2O$), cobalt nitrate ($Co(NO_3)_2\cdot 4H_2O$) and sodium hydroxide (NaOH) were used as starting materials. The required quantity of La_2O_3 was dissolved in minimum amount of hydrochloric acid and aqueous sodium hydroxide is added to it dropwise to precipitate lanthanum as hydroxide. Similarly, cobalt was precipitated as hydroxide under basic conditions. The addition of NaOH was continued until pH $\sim$ 11 to ensure completion of the precipitation. Then all the hydroxides were mixed thoroughly in stoichiometric ratio in an agate and mortar for more than 1 h with the aid of acetone and heated at different temperatures ranging from 100 to 700 °C for 10 h.

To prepare $BaBi_2Nb_2O_9$, niobium(V) oxide, bismuth(III) nitrate, barium hydroxide and sodium hydroxide were used as starting materials. First, commercial Nb_2O_5 was dissolved in minimum amount of HF after heating on a hot water bath maintained around 90 °C for 10 h. Then niobium hydroxide was produced by the addition of aqueous sodium hydroxide to the niobium fluoride solution. Bismuth hydroxide was precipitated by adding excess aqueous NaOH to 0.1 M solution of bismuth nitrate solution under basic conditions. Then commercial barium hydroxide (should be cautiously handled because of carbonate formation), freshly prepared dry bismuth and niobium hydroxides were mixed thoroughly in stoichiometric ratio and heated at 450 °C for 10 h.

The sequence of the reaction and evolution of the product phase as a function of calcination temperature were monitored by the X-ray diffraction (XRD) investigations. The phase purity and lattice parameters were also determined by the X-ray diffraction studies. For lattice parameter and interplanar distance (d) calculation, the samples were scanned in the 2θ range of 10–80° in the step scan mode. Silicon was used as an internal standard. A least squares method was employed to determine the lattice parameters. The scanning electron microscope (SEM) images were observed using a Leica Cambridge 440 microscope. All the powders were dispersed in amyl acetate for SEM studies.

3. Results and discussion

Fig. 1 shows the XRD pattern of $BaCeO_3$ precursor powder heated at different temperatures ranging from 100 to 350 °C. It is observed that at temperatures ~100 °C, the product phase was formed but with some intermediate phases. These peaks were authentically not indexed to any known compound but few peaks were for barium carbonate. All the extra peaks were vanished when these powders were calcined at 350 °C. This is the lowest temperature reported so far for the formation of $BaCeO_3$ in the literature. The conventional method forms this phase only at $T > 900$ °C. The $BaCeO_3$ is orthorhombic and all the d-lines pattern match with reported values (JCPDS: 22-0074). The calculated lattice parameters by least squares fit are $a = 8.779$ Å, $b = 6.214$ Å and $c = 6.236$ Å (SD 0.003 Å). When the sample was heated at 500 °C, no change in the XRD (not shown) was found indicating stability of the compound. Fig. 2 shows the XRD patterns of $BaBiO_3$ precursor powder heated at different temperatures. It is observed that at temperatures

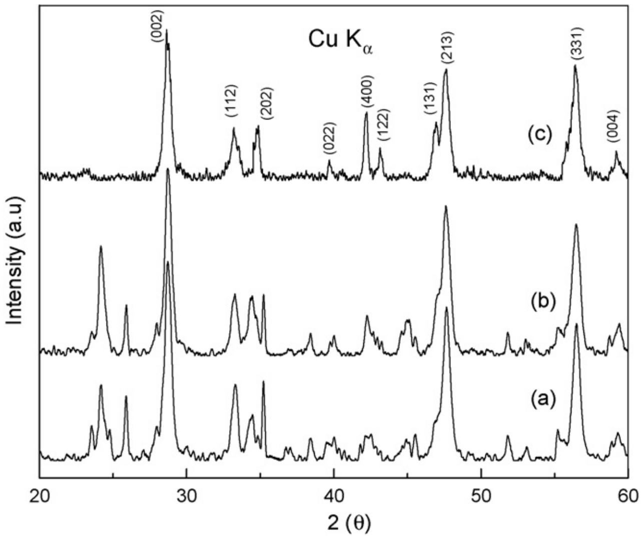

Fig. 1. The XRD of $BaCeO_3$ precursor heated at (a) 100 °C, (b) 300 °C and (c) 350 °C.

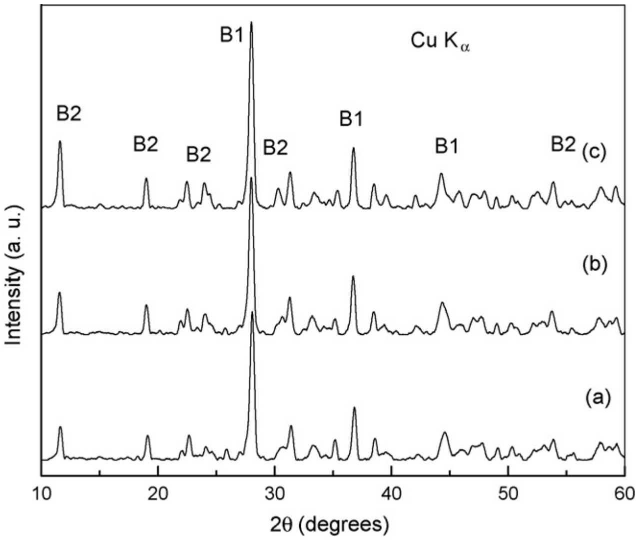

Fig. 2. The XRD of $BaBiO_3$ precursor powders heated at (a) 100 °C, (b) 200 °C and (c) 300 °C. The symbol 'B1' indicate Bi_2O_3 and 'B2' = $Ba(OH)_2 \cdot 8H_2O$.

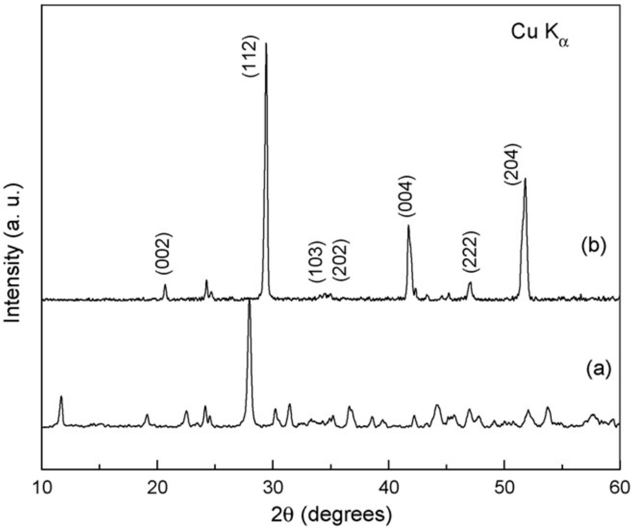

Fig. 3. The XRD of $BaBiO_3$ precursor powders heated at (a) 400 °C and (b) 550 °C.

<400 °C, bismuth oxide (JCPDS; 273-50) (marked 'B1') and barium hydroxide (JCPDS: 26-0155) (marked 'B2') peaks are seen in XRDs. However, at the calcination temperature ~550 °C, the product phase was found to be formed (Fig. 3). This is the lowest temperature reported so far for the formation of $BaBiO_3$ in the literature. The crystal structure of $BaBiO_3$ is monoclinic and all the d-lines pattern match with reported values (JCPDS: 35-1020). The calculated lattice parameters by least squares fit are $a = 6.182$ Å, $b = 6.136$ Å, $c = 8.669$ Å and $\beta = 90°$ 17 (SD 0.003 Å). When the sample was heated at 700 °C, no change in the XRD (not shown) was found indicating stability of the compound.

Fig. 4 shows the XRD pattern recorded for the LSCO samples heated at different temperatures ranging from 200 to 400 °C for 10 h. At 400 °C, in addition to lanthanum oxide (JCPDS: 43-1003) and cobalt oxide peaks (JCPDS: 42-1467), there are few more strong lines, which could not be indexed authentically and they may correspond to intermediate phases formed during calcination. At 500 °C, XRD shows (Fig. 5) the d-lines pattern similar to that

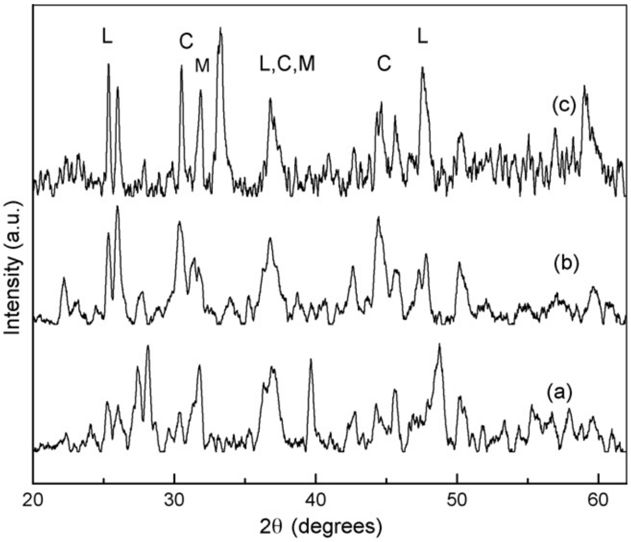

Fig. 4. The XRD of $La_{0.65}Sr_{0.35}CoO_3$ precursor powders heated at (a) 200 °C, (b) 300 °C and (c) 400 °C for 10 h. The symbol 'L' indicates La_2O_3, C = Co_3O_4.

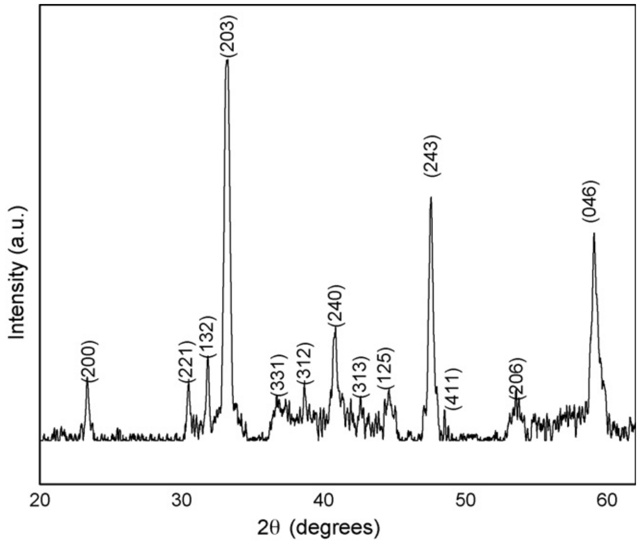

Fig. 5. The XRD of $La_{0.65}Sr_{0.35}CoO_3$ at 500 °C.

reported to LSCO (JCPDS Card No. 46-0704). This is the lowest temperature reported so far for the formation of LSCO. All other wet chemical method requires temperature above 800 °C for the orthorhombic phase LSCO. The calculated lattice parameters by least squares method are $a = 7.73$ Å, $b = 10.87$ Å and $c = 11.58$ Å (SD 0.003 Å). The traditional solid state method forms LSCO only at 900 °C with some minor secondary phases. Fig. 6 shows the XRD of BBN hydroxides precursor mixture heated at 450 °C. The formation of BBN phase is confirmed by X-ray diffraction studies (Fig. 6) (JCPDS: 86-1191). This is the lowest temperature reported so far for the preparation of these compounds. It is very advantageous to use this technique to prepare single phase compound in large scale without the involvement of carbonates.

The average particle size and morphology of the calcined powders were examined by scanning electron microscopy. Particle morphology of these calcined powders prepared by this technique were irregular in shape and agglomerated, with an average primary particle size around 50 nm (Figs. 7–10). The particle size (calculated from Scherrer's formula ($t = K\lambda/B\cos\theta_B$), where t is the average size of the particles, assuming particles are spherical,

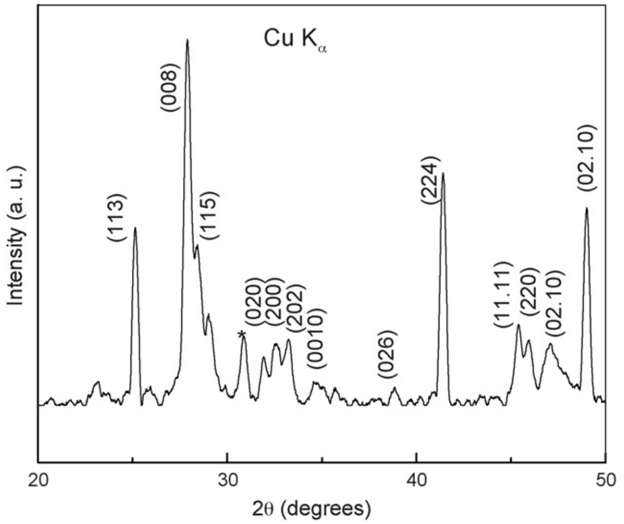

Fig. 6. The XRD of BBN powders heated at 450 °C.

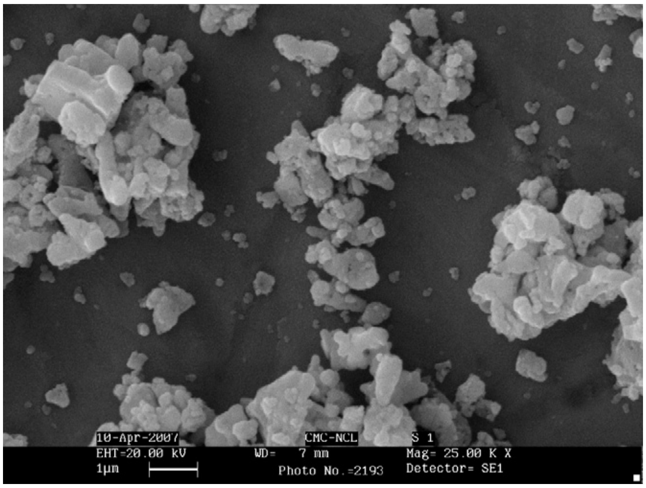

Fig. 7. The SEM micrograph of $BaCeO_3$ powders.

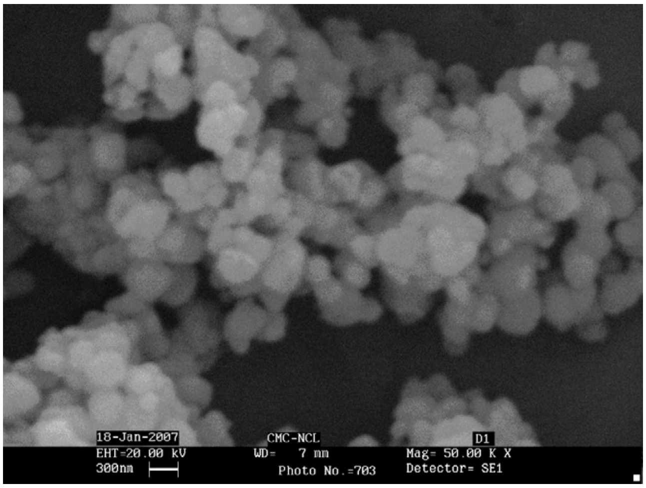

Fig. 8. The SEM micrograph of $BaBiO_3$ powders.

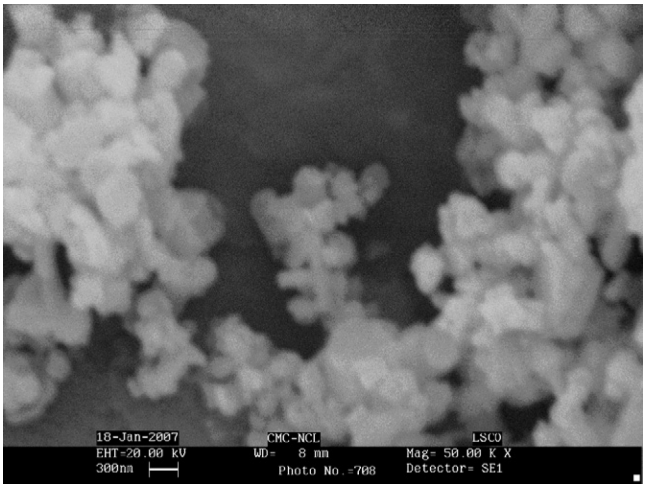

Fig. 9. The SEM micrograph $La_{0.65}Sr_{0.35}MnO_3$ powders.

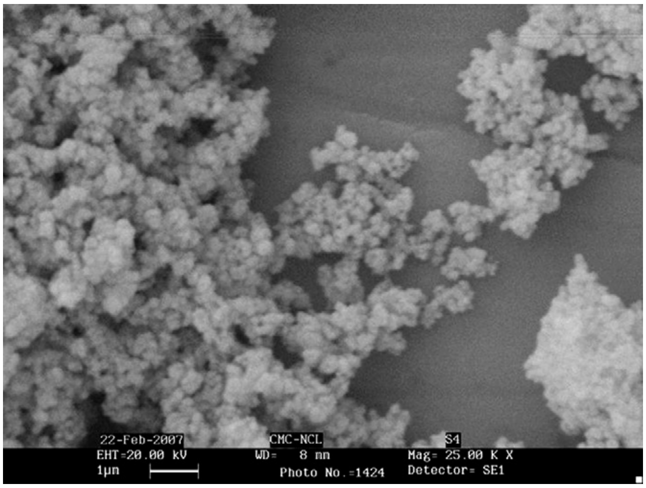

Fig. 10. The SEM micrograph of BBN powders.

$K = 0.9$, λ is the wavelength of X-ray radiation, B is the full width at half maximum of the diffracted peak and θ_B is the angle of diffraction) were in the range of 40–60 nm for these powders.

4. Conclusions

A simple two-step process is described for the preparation of ultrafine powders of ternary oxides which have alkaline earth element in their compositions. This process produces the final product relatively at low temperatures as compared to all other methods. The sequence of reaction was monitored by gradually heating samples over a temperature range and analyzing the XRD pattern at every stage. The average particle size and morphology of these powders were investigated by SEM.

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