

Chemical Synthesis of Ba_2MnWO_6 by Polymerizable Complex Method

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Ordered perovskite oxide Ba_2MnWO_6 (BMW) was prepared by the polymerizable complex method, based upon the Pechini-type polyesterification between citric acid and ethylene glycol. Fine homogeneous BMW powders with an average particle size of 100 nm were prepared. The procedures for preparation became simpler and the required sintering temperature 800°C was much lower as compared with the conventional solid state reaction technique.

Key words: Double perovskites, Polymerizable complex method, Uniform fine particles, X-ray diffraction, Scanning electron microscopy

1. INTRODUCTION

Double perovskites with a general formula $\text{A}_2\text{BB}'\text{O}_6$ have been under continuous interest particularly due to their interesting magnetic properties since the pioneering studies by Patterson [1] and Blasse [2][3]. Double perovskites have conventionally been prepared through the solid-state reaction (SSR) technique. However, samples prepared through the SSR method often suffer from inhomogeneities, and occasionally the preparation of single phase samples has been difficult. This is the characteristic feature of the SSR technique: due to the long diffusion paths, high temperature and long sintering times are necessary. This results in large grain size, which may have additional effects. For example, Wada found that the Curie temperature of ferroelectric BaTiO_3 decreases with decreasing grain size once the grain size is of the order of 100 nm [4]. This phenomenon is more generally known as a grain size effect [5]. Various double perovskites were also applied as a reductants by Wei et al. [6]. This encouraged us to synthesize ordered double perovskites with large specific surface area suitable for industrial applications.

The preparation of high quality samples is an essential starting point prior to the detailed investigations. In this paper, we report the synthesis of Ba_2MnWO_6 (BMW) through a nontraditional chemical method. Cubic BMW can be considered as a prototype double perovskite, where the manganese and tungsten ions are ordered due to the large differences in valence and ionic radii: ionic radius of Mn^{2+} is 0.97 Å and that of W^{6+} is 0.74 Å [7]. BMW has an ideal structure to study 90° and 180° superexchange between paramagnetic Mn^{2+} cations over two O^{2-} anions and diamagnetic W^{6+} ion, where the angles are between $\text{O}^{2-}-\text{W}^{6+}-\text{O}^{2-}$ and $\text{O}^{2-}-\text{Mn}^{2+}-\text{O}^{2-}$ [2]. There are numerous chemical solution techniques, such as sol-gel, coprecipitation and hydrothermal method, which can yield fine and homogeneous particles [8]. In the synthesis of BMW the problem is that BaWO_4 is easily precipitated in case that manganese and tungsten ions coexist in solution. Therefore, for the synthesis of BMW, it is crucial that Ba, W, and Mn ions are stable in a solution. Since citric acid (CA) has three carboxyls in a one molecular unit, the polymerized complex (PC)

method based on the Pechini-type polyester reaction [9] allows cations to be finely dispersed. Thus, cations are restrained from forming compounds with each other while being homogeneously mixed in a solution, and the mixture can be sintered without losing its homogeneity. In a case of some solution techniques, toxic organic solvents are used or harmful gases, such as nitrogen or sulphur oxides or chlorides, are exhausted. Here we demonstrate the moderate (harmonious with environment) synthesis of BMW by the modified PC method. This allowed us to avoid environmental pollution due to the use of lesser amount of toxic organic solvents and exhaust gases.

2. EXPERIMENTAL

2.1. Synthesis of Ba_2MnWO_6 fine powders

Figure 1 summarizes the preparation of BMW samples through the PC method. Barium carbonate (BaCO_3 , Kanto chemical Co., 99.9%) and manganese oxide (MnO , High purity chemicals, 99.9%) were added in an aqueous solution of CA ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, Wako, 98%) and ethylene glycol (EG, $\text{C}_2\text{H}_6\text{O}_2$, Kanto chemical Co., 99.5%) with a molar ratio of $[\text{CA}]:[\text{EG}]=1:4$, and the solution was heated up to 80°C while stirred. Metal tungsten is not likely to be oxidized and to allow the stoichiometry to be preserved. Tungsten powder (High purity chemicals, 99.999%) was dissolved in 30% hydrogen peroxide solution (Kanto chemical Co.) to form a tungsten-peroxo complex [10][11]. This solution was almost colourless and strongly acidic. After a complete dissolution was achieved, tungsten peroxo solution was added in the CA solution. This resulted in transparent and yellowish solution which was heated and magnetically stirred at 130°C for a several hours to promote esterification between CA and EG. First, a highly viscous, deep orange solution was formed, after which a brown glassy resin was gelled. Charring this resin up to 450°C in a mantle heater resulted in a black powder, which is hereafter referred to as 'precursor'. The precursor was calcined at 600°C for 12h in vacuum furnace. Calcined powders were annealed at 700 or 800°C for 12 hours in an encapsulated quartz tube containing tantalum foil (Nilaco Co., 99.9%) to absorb the possible residual oxygen inside the tube. Final products were pale-green fine powders.

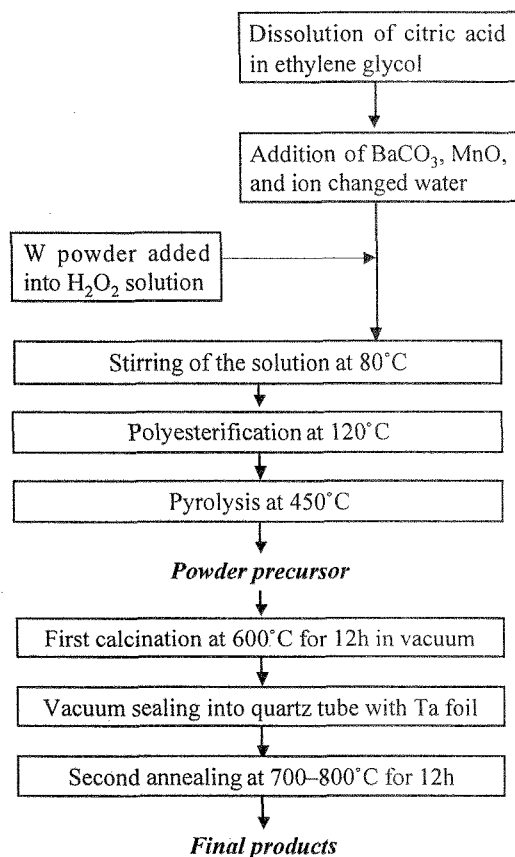


Fig. 1 Flow chart for the synthesis of BMW samples by the PC method. The molar ratio of [CA]: [EG] was 1:4.

2.2. Characterizations

X-ray diffraction (XRD) patterns were collected using a conventional X-ray diffractometer (MXP^{3VA}, MAC Science, Tokyo, Japan) with a diffracted beam graphite monochromator. A $\text{CuK}\alpha$ radiation was used (acceleration voltage and current were 40 kV and 40 mA, respectively). Step scan size was 0.02 degrees and the acquisition time was 4 s per step. Silicon powder (NIST 640c) was used as an external standard. Powder morphology was studied by a field emission scanning electron microscope (FE-SEM S-4500 Hitachi, Japan).

3. RESULTS AND DISCUSSION

The FE-SEM picture taken from the BMW sample is shown in Fig. 2. The average particle size was estimated to be between 120 and 180 nm. From the point of view of morphology, the powders were found as homogeneous, with a small deviation from the mean particle size.

Figure 3 shows the XRD patterns of the precursor and BMW samples annealed at various temperatures. For comparison, the Bragg reflection positions corresponding to the ordered cubic structure of the BMW (space group $Fm\bar{3}m$) and BaWO_4 (PDF43-0643) are shown. Distinction between the space groups $Pm\bar{3}m$ (no ordering among the B-cations) and $Fm\bar{3}m$ (ordered phase) was straightforward to do, as there are several Bragg reflections characteristic only to the $Fm\bar{3}m$ phase, such as 111, 311, 331. It is seen that the ordered cubic BMW was the only phase in the case of the sample annealed at 800 °C. However, small

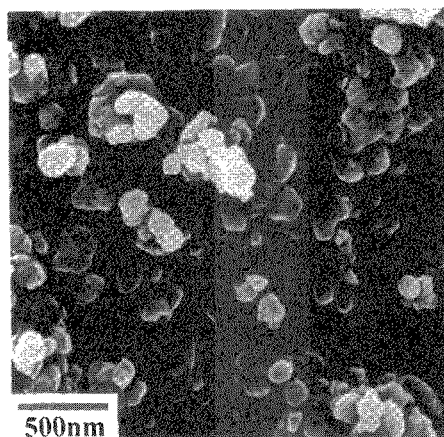


Fig. 2 FE-SEM micrograph of BMW synthesized by the PC method at 800°C.

amount of impurity phases, most notably BaWO_4 , were also observed in the case of the samples annealed at lower temperatures.

Single phase BMW samples were successfully prepared by the PC method without producing harmful exhaust gases (such as halide gas or nitrogen oxide). As other merits of our method, the use of hydrogen peroxide as an oxidizing agent results in only water as a by-product, the 30 % hydrogen peroxide is cheap and easy to handle without a risk of explosion. Thus, it should be useful for the industrial applications [12]. Oxidizing reaction between hydrogen peroxide and tungsten formed stable metal chelate complexes into the solution, which was a critical step once the single phase BMW samples were prepared.

Efficient reducing atmosphere was produced by encapsulating the pellets into a quartz tube during annealing. This technique has previously been combined with the SSR technique [13]. However, the problem was that quartz cannot sustain the high temperatures necessary to obtain solid state reaction and approximately 5 % impurity phase was contained in samples prepared by SSR method [13]. In the present method, this problem was removed with the use of fine particles, which react easily and do not necessitate such high temperatures.

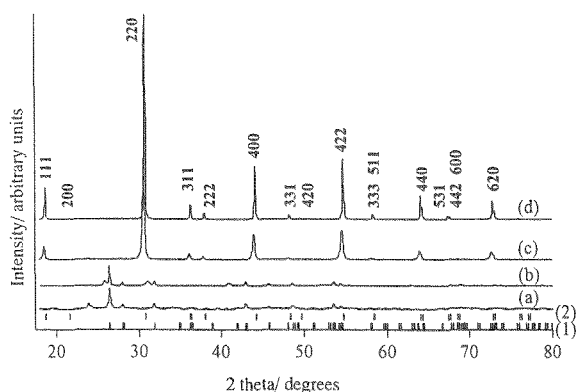


Fig. 3 X-ray diffraction patterns of the (a) precursor, (b) calcined at 600°C, (c) final products annealed at 700°C, and (d) 800°C for 12h into sealed quartz tube. The (1) and (2) rows of tick marks correspond to the positions of all reflections from BaWO_4 (PDF 43-0643) and the cubic Ba_2MnWO_6 ($Fm\bar{3}m$), respectively.

Although single phase samples can be prepared through the SSR method, this often necessitates repeated sintering and milling steps and substantial sintering time and temperature. For example, Azad et al. had to use 183h with a maximum temperature of 1250°C in order to prepare single phase BMW samples [14]. Single phase BMW fine powders were successfully obtained through the present chemical technique sintered at 800°C, which is 450°C lower than the temperature required to the SSR method.

4. CONCLUSIONS

Single phase BMW samples were successfully synthesized by the PC method. The final products were fine powders with an average particle size of 100 nm. The procedures for preparation became simpler and the required sintering temperature was much lower as compared with the conventional solid state reaction technique. XRD revealed that the correct space group was $Fm\bar{3}m$, instead of the space group $Pm\bar{3}m$, and correspondingly the BMW samples were ordered double perovskites.

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