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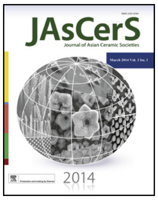

Letter

Synthesis of nano-sized perovskite-type oxide with the use of polyvinyl pyrrolidone

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ABSTRACT

A new easy-to-use process for obtaining fine powders of lanthanum-based perovskite-type oxides ($La_{1-x}Ae_xMO_3$: Ae = Ca, Sr, M = Mn, Co, Fe) with a high specific surface area was successfully developed by the use of polyvinyl pyrrolidone (PVP) as a dispersant. This approach made it possible to prepare a single phase of perovskite by calcining at a lower temperature (600 °C) compared to conventional synthetic processes such as a solid state reaction and citrate process. SEM observations revealed that the oxide prepared with PVP was ca. 20–30 nm in size, while those prepared by the citrate process and solid state reaction were ca. 50 nm and 1 μm, respectively. Furthermore, the results of a thermal analysis in which we heated the precursors for the different reactions support the idea that PVP plays an important role in the formation of the perovskite phase at low temperature.

1. Introduction

Lanthanum-based perovskite-type oxides are well-known functional materials with a wide range of applications, and are used as electrocatalysts for alkaline fuel cells (AFC) [1,2] and metal air batteries [3–5], and as environmental catalysts [6,7] (e.g., oxidation of hydrocarbon and CO, and the reduction of NOx). Generally, an increase in the specific surface area of a perovskite-type oxide improves its catalytic activity by increasing the contact area between the catalyst and gas. However, particles of perovskite-type oxides are still not small enough, largely because the conventional synthesis processes require calcination at high temperature. Thus, the obtained perovskite particles are heavily agglomerated and sintered.

To date, several methods for the preparation of nano-sized perovskite-type oxides have been proposed to enhance the catalytic activity. Among these, the reverse micelle method [8,9] is one of the most effective approaches for the synthesis of nanocrystalline perovskite-type oxides with a high specific surface area (ca. $50\,m^2\,g^{-1}$). However, this process is not particularly practical due to the low yield of the target material and the elaborate experimental conditions are required (surfactant, R_w value (molar ratio of $[H_2O]$ and [surfactant]), temperature, and calcination atmosphere). Thus, an easy-to-use approach for obtaining fine particles of perovskite-type oxides is required.

In addition, optimization of the constituent elements and their composition is also important for promoting catalytic activity because the perovskite-type structure is composed of a 12-coordinate cation (mainly, rare-earth or alkaline earth) site and a tetrahedrally coordinated transition metal cation site. Many studies have reported that the catalytic activity of La-based perovskite-type oxide ($LaMO_3$) is drastically improved by doping the La^{3+} site with alkaline-earth metals. At a transition metal cation site, partial substitutions with different metals are often attempted to adjust the catalytic activity. Therefore, the desired perovskite-type oxides with high catalytic activity could be composed of several elements. In the preparation of a perovskite-type oxide with a high specific surface area and a suitable composition, the formation of impurities (in particular alkaline earth carbonate) can become a serious problem due to the low-temperature calcination. In fact, it is not easy to synthesize such materials by conventional low-temperature processes (e.g., citrate process, co-precipitation method).

It has been reported that the use of polyvinyl pyrrolidone (PVP) for the preparation of ceramic films is effective for controlling condensation and promoting structural relaxation of the materials under heat-treatment [10]. This is also known to be advantageous for preparing materials with a high surface area and minimizing aggregation, and various oxides with a simple composition (i.e., ZnO [11], NiO [12], and CeO-based oxides [13]) have already been reported. Since PVP has relatively high decomposition temperature, it should also be able to control particle aggregation.

In this study, a lanthanum-based perovskite-type oxide composed of 4 elements ($La_{0.6}Sr_{0.4}Mn_{0.6}Fe_{0.4}O_3$) was prepared in the presence of PVP to increase the surface area of the perovskite-type oxide. For comparison, $La_{0.6}Sr_{0.4}Mn_{0.6}Fe_{0.4}O_3$ was also synthesized by the conventional citrate process and solid state reaction. The characteristics of the resulting oxides were examined by BET (Brunauer–Emmett–Teller) specific surface area measurement, SEM observations and thermal analysis. Furthermore, perovskite-type oxides with various compositions ($La_{1-x}Ae_xMO_3$: Ae = Ca, Sr,

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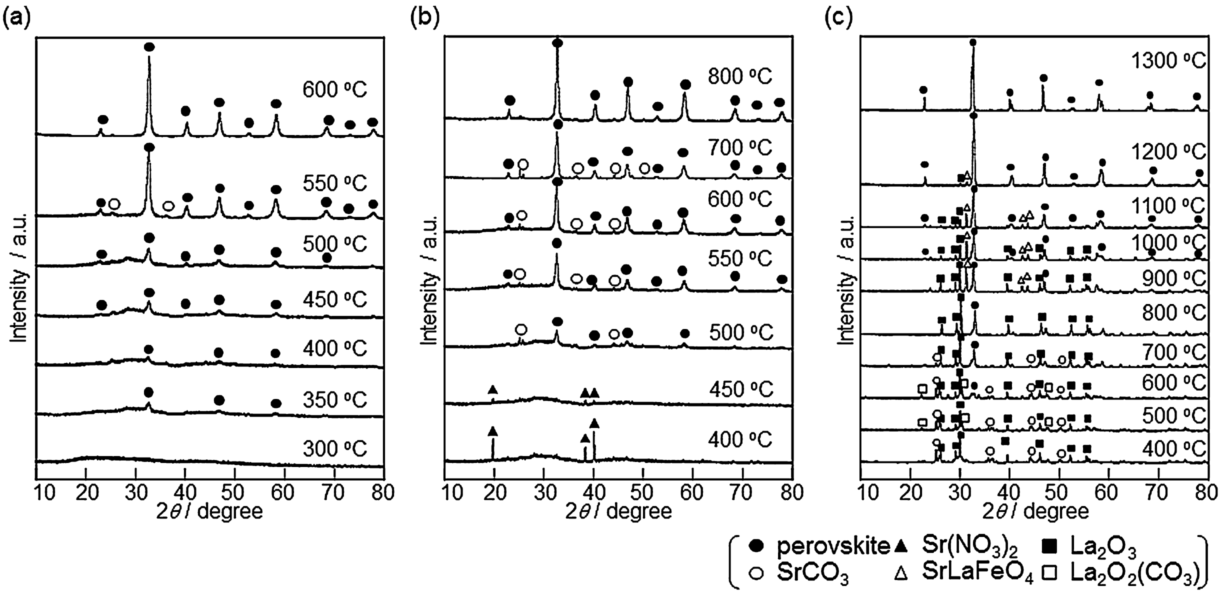

Fig. 1. XRD patterns of $La_{0.6}Sr_{0.4}Mn_{0.6}Fe_{0.4}O_3$ obtained by heating precursors at 300–1300 °C ((a) PVP addition, (b) citrate process and (c) solid state reaction).

M = Mn, Co, Fe) were prepared using PVP to confirm the superiority of the present method.

2. Experimental

2.1. Sample preparation

The synthetic method of perovskite-type oxides using polyvinyl pyrrolidone (PVP) is as follows. A gel was obtained by stirring an aqueous solution of stoichiometric metal nitrates ($La(NO_3)_3{\cdot}6H_2O$ (Wako, 99.9%), $Sr(NO_3)_2$ (Aldrich, 99.95%), $Mn(NO_3)_2{\cdot}6H_2O$ (Wako, 99.9%), and $Fe(NO_3)_3{\cdot}9H_2O$ (Wako, 99.9%)) and polyvinyl pyrrolidone (PVP; 3 times the total moles of cations) at 100 °C. By subsequently drying at 150 °C for 1 h, a precursor of perovskite-type oxide was obtained. The polymerized precursors were fired in air at 300–600 °C for 6 h in air, and perovskite-type oxides ($La_{1-x}A_xMO_3$: A = Ca, Sr, M = Mn, Co, Fe) were obtained. In addition to the PVP method, $La_{0.6}Sr_{0.4}Mn_{0.6}Fe_{0.4}O_3$ was also synthesized by conventional solid state reaction and citrate process for comparison. For the solid state reaction, La_2O_3 (Wako, 99. 5%), $SrCO_3$ (Wako, 99. 9%), MnO_2 (Aldrich, 99.99%), and Fe_2O_3 (Aldrich, 99.99%) were used as starting materials. The powders were thoroughly mixed in an agate mortar, and the mixture was sintered at 400–1300 °C for 10 h in air. For the citrate process, metal nitrates and citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$ (Wako); 2 times the total moles of cations) were dissolved in water, and the solution was stirred at 100 °C until a gel was formed. After drying the gel at 150 °C for 1 h, a precursor was obtained. The precursor was calcined in air at 400–800 °C for 10 h in air. For calcination, the temperature was increased at a constant rate of 20 °C min^{-1}.

2.2. Characterization

The prepared perovskite-type oxides were identified by X-ray powder diffraction (XRD) analysis using Cu Kα radiation (RINT-Ultima$^+$, Rigaku). The crystalline diameter was calculated from Scherrer's equation (Eq. (1)):

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where D is the crystalline diameter (Å), K the Scherrer constant, λ the wavelength (m) and β is the FWHM.

The samples were also analyzed by scanning electron microscopy (SEM; JSM-6700F, JEOL), and wavelength dispersive X-ray fluorescence (XRF; Supermini, Rigaku). The specific surface areas of the oxides were calculated by the Brunauer–Emmett–Teller (BET) method (Bellsorp mini II, Bell Japan). Thermal analysis (TG-DTA) for the precursors of $La_{0.6}Sr_{0.4}Mn_{0.6}Fe_{0.4}O_3$ was carried out in air (TG-DTA-200SA, Bruker) at a heating rate of 20 °C min^{-1}.

3. Results and discussion

To determine the temperature at which a single phase of $La_{0.6}Sr_{0.4}Mn_{0.6}Fe_{0.4}O_3$ forms completely, XRD patterns were measured for precursors of $La_{0.6}Sr_{0.4}Mn_{0.6}Fe_{0.4}O_3$ after calcination at 300–1300 °C (Fig. 1). For the sample prepared using PVP, diffraction patterns of the perovskite structure can be observed over 350 °C, and the sample obtained by calcination of the precursor at 600 °C for 6 h was a single phase of the perovskite-type oxide. In contrast, the samples prepared by the citrate process and solid state reaction showed a perovskite structure and impurity phases such as $SrCO_3$ and metal oxides after calcination at 600 °C for 10 h. For the citrate process and solid state reaction under the conditions in this study, a single-phase sample was confirmed after calcination at 800 °C for

Table 1
Sample composition, BET surface area, and crystalline diameter for $La_{0.6}Sr_{0.4}Mn_{0.6}Fe_{0.4}O_3$ prepared by different processes.

	Composition	BET surface area (m^2 g^{-1})	Crystalline diameter (nm) (as prepared)
PVP (600 °C)	$(La_{0.62}Sr_{0.38})_{1.00}(Mn_{0.62}Fe_{0.38})_{0.96}O_{3-\delta}$	31.1	23.5
Citrate process (800 °C)	$(La_{0.65}Sr_{0.35})_{1.00}(Mn_{0.61}Fe_{0.39})_{0.94}O_{3-\delta}$	13.4	53.8
Solid state reaction (1300 °C)	$(La_{0.57}Sr_{0.43})_{1.00}(Mn_{0.60}Fe_{0.40})_{1.02}O_{3-\delta}$	0.384	121.8