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PREPARATION OF $BaPbO_3$ FROM COPRECIPITATED BARIUM–LEAD OXALATE

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ABSTRACT

The barium–lead oxalate has been coprecipitated at about 310 K by adding an ethanol solution of oxalic acid to an aqueous solution containing (1 : 1) barium and lead ions. The coprecipitated oxalate has been examined by a multiple thermal analysis of thermogravimetry, differential thermal analysis and evolved gas analysis. The thermal decomposition of the oxalate around 500 K gives a mixture of anhydrous barium and lead oxalates. The resulting BaC_2O_4 and PbC_2O_4 decompose to $BaCO_3$ at 670 K and PbO at 720 K, respectively. The formation of $BaPbO_3$ starts at 840 K. The perovskite-type compound of $BaPbO_3$ has been obtained by calcining the coprecipitated oxalate at 1000 K for 50 ks.

INTRODUCTION

A perovskite-type compound of $BaPbO_3$ has been reported to have high electrical conductivity [1–3] and orthorhombic symmetry [3,4]. Since Sleight et al. [5] found the superconductivity of $BaPb_{1-x}Bi_xO_3$ in the range of $x = 0.05$–0.3 in 1975, increasing attention [6–9] has been focused on $BaPbO_3$ as a component of the material.

The method by Nitta et al. [1] has been commonly used [2–4] for the preparation of $BaPbO_3$ by calcining the mixture of barium carbonate and lead oxide. In this method, an excess amount of lead oxide is added to the starting mixture as PbO evaporates during preparation at high temperatures. Therefore, it is rather difficult to obtain $BaPbO_3$ with a stoichiometric composition. For preparing the stoichiometric compound, it is desirable to synthesize the compound from a stoichiometric mixture at a temperature as low as possible to avoid the evaporation of PbO.

In the present study, $BaPbO_3$ was prepared by calcining the coprecipitated oxalate at a relatively low temperature. The oxalate was obtained using the

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method employed by Yamamura et al. for the preparation of $BaTiO_3$ [10] and $Pb_{0.92}La_{0.08}Zr_{0.65}Ti_{0.35}O_3$ [11]. The characterization of the oxalates was undertaken using a multiple thermal analysis of thermogravimetry (TG), differential thermal analysis (DTA) and evolved gas analysis (EGA).

EXPERIMENTAL

Barium carbonate (99.99%, Rare Metallic Co., Ltd.) and lead monoxide (yellow, 99.99%, Rare Metallic Co., Ltd.) were each dissolved into dilute nitric acid. The solutions were denoted as Ba- and Pb-solutions. The Ba and Pb concentrations were approximately 100 mol m^{-3} as determined by atomic absorption analysis.

Barium and lead oxalates were prepared separately via the following procedure. The ethanol solution of oxalic acid of 5×10^{-4} m^3 was added dropwise to the Ba- and Pb-solutions of 1×10^{-4} m^3 for 1.2 ks, resulting in the precipitation of oxalates. The amount of oxalic acid was in excess of the stoichiometric ratio for each oxalate by 20%. The solutions were stirred and held at 310 K during the addition. The precipitates were aged for about 43 ks at room temperature, filtered, washed with ethanol and dried in air. For comparison, barium oxalate was also prepared by adding an aqueous solution of oxalic acid in the same manner.

The coprecipitated oxalate was prepared from the stoichiometric mixture (Ba/Pb = 1.00) of Ba- and Pb-solutions and ethanol solution of oxalic acid in the same procedure as described above.

Thermal decomposition of the oxalates was examined by the TG–DTA–EGA. Figure 1 shows the block diagram of the experimental setup. A commercially available apparatus (Seiko Industries and Electronics Ltd., SSC/560GH) was employed for TG and DTA. For EGA, laboratory-made equipment with thermal conductivity detectors [12] was attached to the apparatus. Magnesium perchlorate and ascarite were used as absorbers for H_2O and CO_2, respectively.

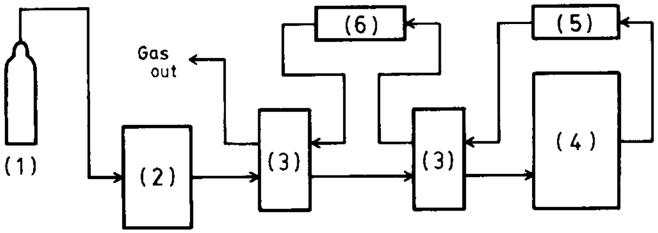

Fig. 1. Block diagram of the apparatus: (1) gas cylinder; (2) flow rate controller; (3) thermal conductivity detectors; (4) thermobalance; (5) $Mg(ClO_4)_2$; (6) ascarite.

Thermal analysis was carried out from room temperature to 1100 K at a heating rate of 0.17 K s^{-1} in the stream of the He + O_2 (4 : 1) at a flow rate of 2×10^{-6} m^3 s^{-1}. The amount of the sample used for each experiment was about 20 mg. For the reference material in DTA, α-Al_2O_3 was used. X-ray (CuK_α) diffraction was conducted on the samples cooled from various temperatures for phase determination.

RESULTS AND DISCUSSION

Figure 2 shows TG, DTA and EGA curves of Ba-oxalates prepared from the aqueous (solid lines) and ethanol (broken lines) solutions. The evolution

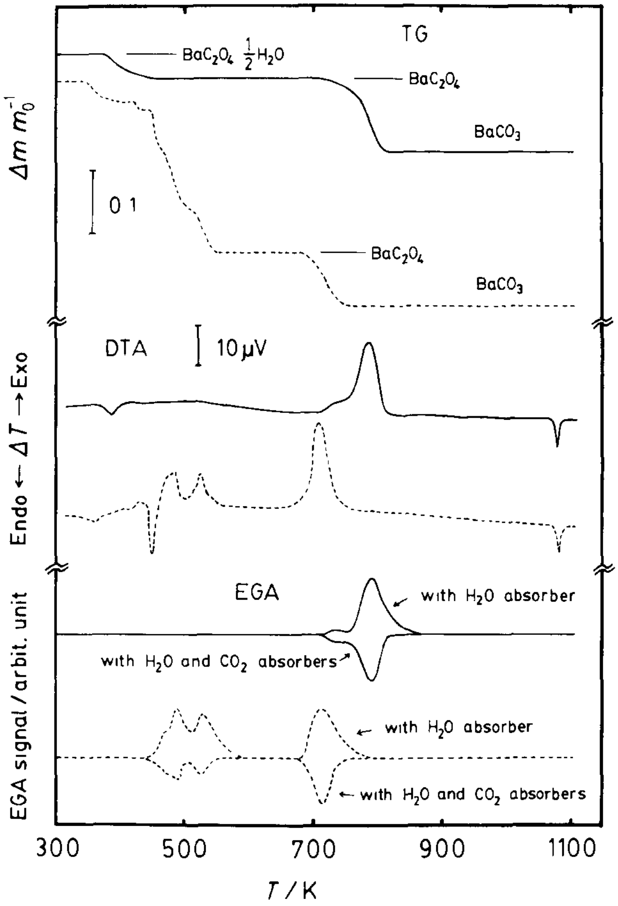

Fig. 2. TG, DTA and EGA curves of Ba-oxalate prepared from water (———) and Ba-oxalate from ethanol solution (- - - -) at a heating rate of 0.17 K s^{-1} in the He+O_2 (4:1) atmosphere.

of H_2O, CO and CO_2 was expected during the decomposition. The EGA curve obtained with the H_2O absorber shows the peaks for the evolution of CO and/or CO_2. When CO is evolved, it is oxidized by O_2 in the atmosphere, resulting in the formation of CO_2. Therefore, the peaks in the curve obtained with both H_2O and CO_2 absorbers suggest the evolution of CO, since the oxidation of CO consumes O_2 in the atmosphere.

The precipitate from the aqueous solution is a hemihydrate, and dehydration occurs at temperatures between 370 and 490 K, forming anhydrous barium oxalate. The barium oxalate decomposes to $BaCO_3$ at 710–810 K. The EGA reveals that CO is evolved and oxidized to CO_2. The DTA shows the corresponding exothermic peak. This result agrees well with that of Walter-Levy and Laniepce [13].

The barium oxalate from the ethanol solution exhibits two steps of mass loss due to dehydration at temperatures between 330 and 420 K. The subsequent three steps of mass loss are observed in the region of 440–550 K, accompanying the evolution of CO_2 and the consumption of O_2. This result suggests that the oxalate precipitated in the ethanol solution contains ethanol as well as water. Above 550 K, BaC_2O_4 is the product, which begins to decompose to $BaCO_3$ at 670 K. The decomposition temperature of this specimen is lower by 40 K than that of BaC_2O_4 prepared from the aqueous solution. In both cases, the phase transition in $BaCO_3$ is clearly detected at 1080 K by DTA.

Figure 3 presents TG, DTA and EGA curves of the lead oxalate precipitated in the ethanol solution. The oxalate decomposes to PbO at 570–660 K by a single step of mass loss, indicating that the precipitate is anhydrous lead oxalate. The decomposition proceeds as follows:

$$PbC_2O_4 \rightarrow PbO + CO + CO_2 \qquad (1)$$

The EGA curve confirms the consumption of O_2 due to the oxidation of the evolved CO. The heat evolution is detected in the DTA curve.

Figure 4 shows results of TG, DTA and EGA measurements made on a physical mixture (1 : 1) of barium and lead oxalates precipitated in the ethanol solutions. These curves can be considered as the superposition of the curves for barium and lead oxalates. The plateaux on the TG curve are designated by the letters A (540–580 K), B (650–690 K) and C (730–850 K). The sample cooled from the temperature indicated by the arrow in plateau A is the mixture of BaC_2O_4 and PbC_2O_4, as identified by X-ray diffraction. In the case of plateau B, BaC_2O_4 and PbO were detected, and the existence of $BaCO_3$ and PbO was observed in plateau C. The mass loss above 840 K is due to the following reaction:

$$BaCO_3 + PbO + \tfrac{1}{2}O_2 \rightarrow BaPbO_3 + CO_2 \qquad (2)$$

The EGA curves show the corresponding slow evolution of CO_2 and consumption of O_2. No anomaly corresponding to the phase transition in

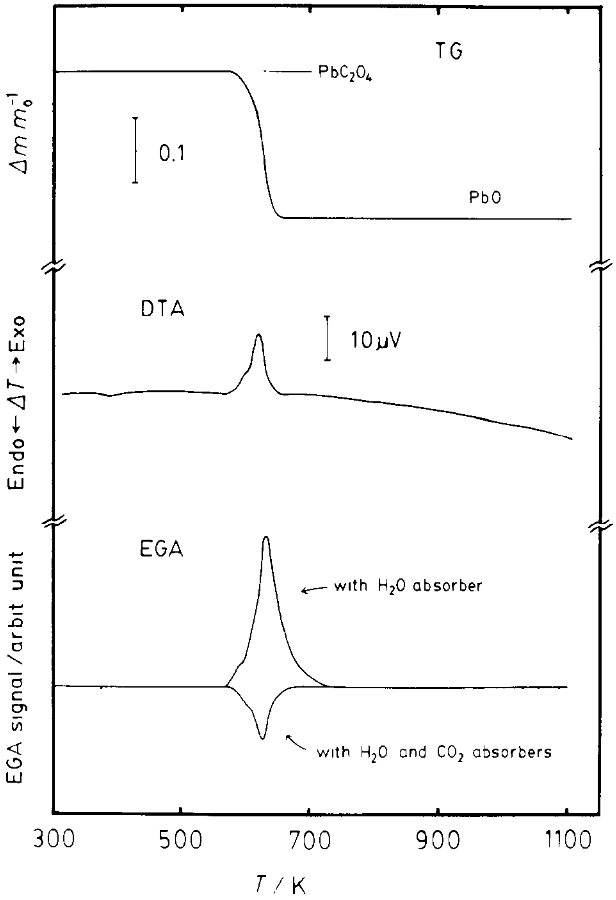

Fig. 3. TG, DTA and EGA curves of Pb-oxalate at a heating rate of 0.17 K s^{-1} in the He + O_2 (4 : 1) atmosphere.

$BaCO_3$ is observed in the DTA curve, which shows the formation of $BaPbO_3$.

Figure 5 presents TG, DTA and EGA curves of the coprecipitated Ba–Pb oxalate from the ethanol solution. The decomposition starts at 340 K. The first two steps of mass loss accompany endothermic peaks in DTA. These mass losses are ascribed to dehydration because no signal is observed in EGA. The subsequent two steps of mass loss commence at 450 and 470 K, accompanying exothermic peaks in DTA. In these steps the EGA curves show the evolution of CO_2 and consumption of O_2. The mass is constant between 500 and 620 K (plateau A). The product in plateau A consists of BaC_2O_4 and PbC_2O_4, as identified by X-ray diffraction of the quenched sample from the temperature indicated by the arrow. The decomposition behavior prior to the attainment of plateau A in the coprecipitated oxalate is different from that in the physical mixture of each oxalate. However, the

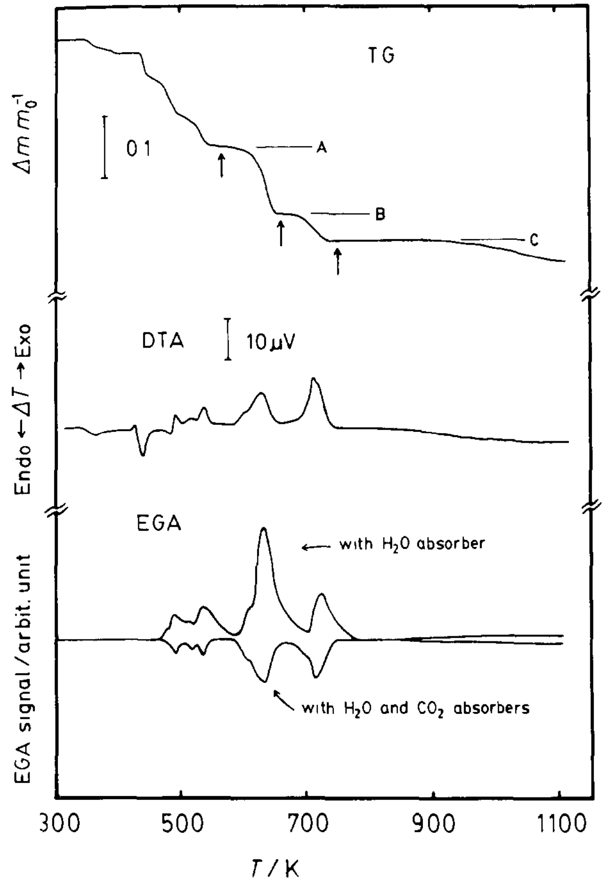

Fig. 4. TG, DTA and EGA curves for mixture of Ba- and Pb-oxalates at a heating rate of 0.17 K s^{-1} in the He + O_2 (4:1) atmosphere: (A) $BaC_2O_4 + PbC_2O_4$; (B) $BaC_2O_4 + PbO$; (C) $BaCO_3 + PbO$.

products in plateau A are the same in both cases. The further decompositions of the resulting oxalates proceed in a similar way to the physical mixture. The BaC_2O_4 and the PbC_2O_4 change to $BaCO_3$ at 670 K and PbO at 720 K, respectively. The formation of $BaPbO_3$ starts at 840 K.

Figure 6 presents X-ray diffraction patterns of the calcined samples of the coprecipitated oxalate (a) and the mixture of $BaCO_3$ and PbO (b), which have been heated at 1000 K for 50 ks in air. It can be seen that the formation of $BaPbO_3$ completes in the case of the coprecipitated oxalate, while small amounts of unreacted materials remain in the case of the mixture of $BaCO_3$ and PbO. This result indicates that the coprecipitated oxalate is preferable for synthesis of $BaPbO_3$ because the reaction completes at lower temperatures than the temperature at which the vaporization of PbO becomes significant. The formation of $BaPbO_3$ proceeds at lower temperatures in the coprecipitated oxalate than in the mixture of $BaCO_3$ and

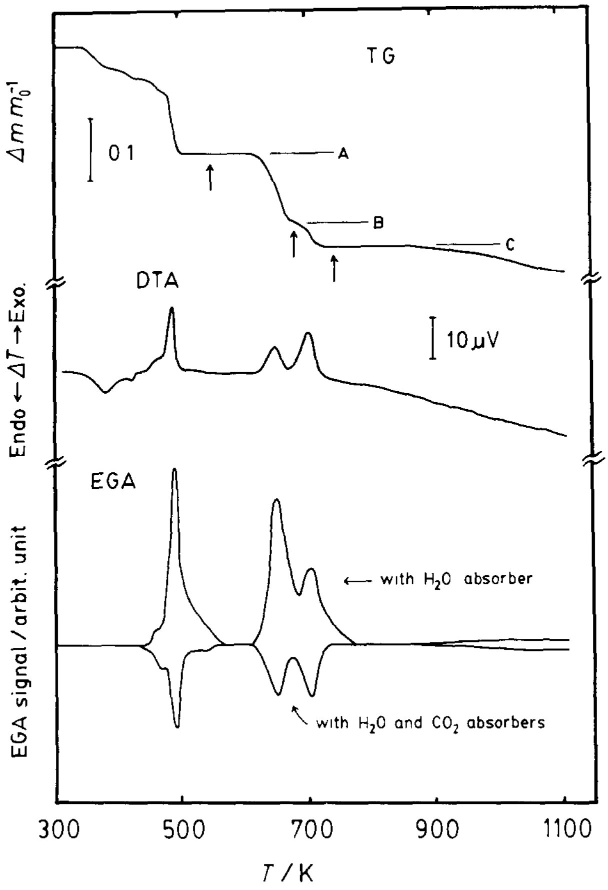

Fig. 5. TG, DTA and EGA curves of coprecipitated oxalate at a heating rate of 0.17 K s^{-1} in the He + O_2 (4 : 1) atmosphere: (A) $BaC_2O_4 + PbC_2O_4$; (B) $BaC_2O_4 + PbO$; (C) $BaCO_3 + PbO$.

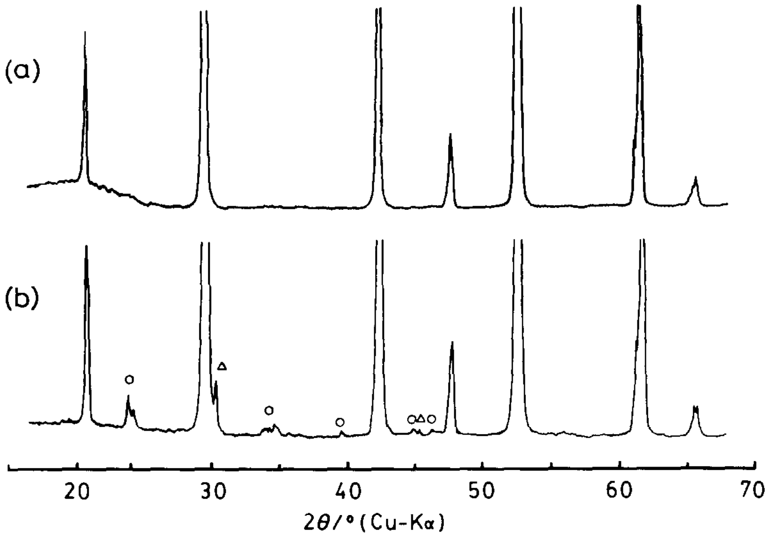

Fig. 6. X-ray diffraction patterns of coprecipitated oxalate (a) and mixture of $BaCO_3$ and PbO (b) after heating at 1000 K for about 50 ks: ○, $BaCO_3$; △, PbO.

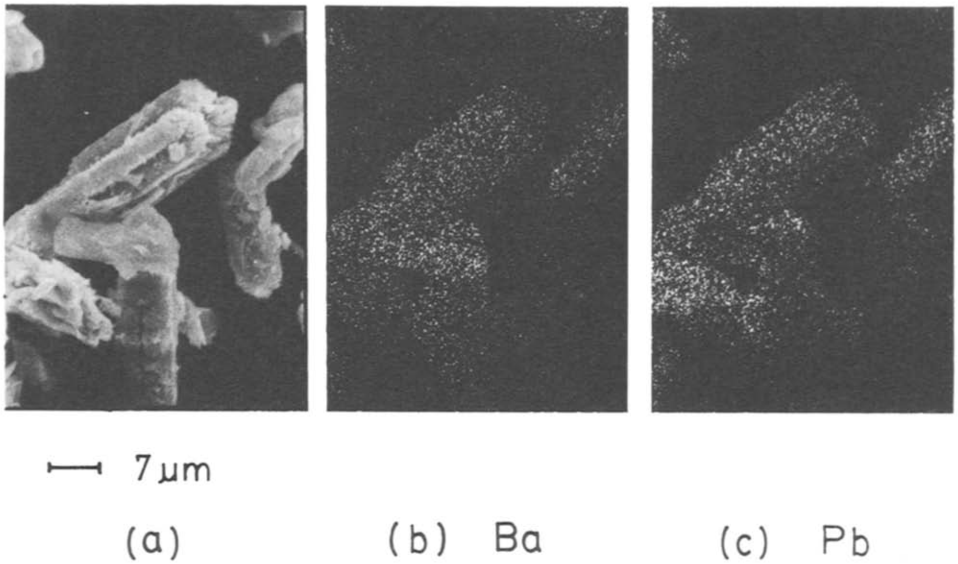

Fig. 7. Scanning electron micrograph and corresponding EDX images of coprecipitated oxalate after heating at 725 K: (a) secondary electron image; (b) X-ray image of Ba; (c) X-ray image of Pb.

PbO. The result implies that the mixing of $BaCO_3$ and PbO is performed more homogeneously in the decomposition products of the coprecipitated oxalate than in the mixture of each material. Figure 7 shows the SEM photograph and corresponding EDX images of the product in plateau C in Fig. 5. As clearly seen in Fig. 7, Ba and Pb distribute homogeneously in a powder particle.

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