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Effect of atmosphere on decomposition of rare earth oxide-activated barium titanyl oxalate

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Abstract

The effects of atmosphere on the thermal decomposition of rare earth oxide-activated barium titanyl oxalates were investigated under various oxygen partial pressures. The fact that all of the oxygen partial pressures decrease indicates that oxidation of activated oxalates can occur under a lower oxygen partial pressure because the rare earth oxides behave as catalysts. The oxidation reactions are promoted significantly by the addition of empty (La^{3+}) or half-filled (Gd^{3+}) 4f rare earth oxides during the decomposition processes. The La- and Gd-activated barium titanyl oxalates showed a higher activity in oxidation than the others. The activation energies of oxalate decomposition by the addition of rare earth oxides were also determined.

1. Introduction

Barium titanate is of great interest for its ferroelectric and other electric properties. In recent years, the preparation of barium titanate powders from the decomposition of barium titanyl oxalate ($BaTiO(C_2O_4)\cdot4H_2O$) has been studied extensively. Clabaugh *et al.* [1] demonstrated that a highly pure barium titanate of nearly perfect stoichiometry can be prepared by precipitating barium titanyl oxalate and subsequently converting this material to the barium titanate by pyrolysis. Gallagher *et al.* [2,3] have modified the renowned three-step mechanism of the decomposition reactions in barium titanyl oxalate. Enomoto and Yamaji [4] have employed Clabaugh's method to prepare barium titanate powder by the thermal decomposition of oxalate in a flowing O_2 and N_2 mixture. It is well known that the substitution of rare earth for Ba^{2+} in the perovskite lattice produces n-type semi-insulating ferroelectric titanates [5,6] and increases oxidizing activity of the barium titanate [7–10].

In a previous study [11], the present authors found oxygen partial pressure of 0.04 atm as a characteristic that pure oxalate would decompose and follow the three-step mechanism, and undergo an oxidation above this pressure. The oxygen partial pressure required for Gd-activated oxalate was reduced to a value of 0.02 atm. This implied that oxidation occurred under lower oxygen partial pressure when the rare earth oxides were acting as catalysts.

In this work, the effects of atmosphere on the thermal decomposition of rare earth oxide activated-barium titanyl oxalate were investigated under various oxygen partial pressures. The purpose of this paper is to compare the oxidizing activities in the activated-barium titanyl oxalates in terms of the oxygen partial pressure and to determine an appropriate amount of the rare earth oxides which need to optimize the activity.

2. Experimental procedure

Reagent-grade barium chloride and titanium tetrachloride were chosen as starting materials. They were dissolved in distilled water. Since titanium tetrachloride reacts vigorously with water at room temperature, it was cooled, mixed carefully with cooled distilled water and then kept in a refrigerator. Titanium content in the titanium tetrachloride solution was determined by a gravimetric method [3] in which TiO_2 was used as a weighing form. Rare earth oxides (La_2O_3, Ce_2O_3, Pr_2O_3, Nd_2O_3, Sm_2O_3, Eu_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3 and Yb_2O_3) were dissolved in nitric acid. The mixed solutions of barium chloride, titanium tetrachloride and dissolved rare earth oxide were added to an aqueous solution of oxalic acid to obtain the rare earth-activated barium titanyl oxalates. The molar ratio of the components in the mixed solution was $[Ti^{4+}]/[Ba^{2+}]/[C_2O_4{}^{2-}]=1.0:1.05:2.2$ reported by Kudaka *et al.* [12]. The content of rare earth oxide ranged from 0.3 to 12.5 mol% of Ti^{4+}. The precipitated oxalates were filtered, washed with pure ethanol and distilled water several times and then dried at 100 °C for 8 h.

The thermal decompositions of rare earth-activated barium titanyl oxalates were monitored by differential

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thermal analysis (DTA). Each sample was heated to a desired temperature with a heating rate of 100 °C/min. The gas mixture contained O_2 and N_2 with the desired oxygen partial pressure controlled by adjusting the volume ratio of input gases.

3. Results and discussion

A three-step mechanism has been proposed for the thermal decomposition of barium titanyl oxalate by Gallagher *et al.* [3].

(1) 25–225 °C: loss of water

$$BaTiO(C_2O_4)_2 \cdot 4H_2O \longrightarrow BaTiO(C_2O_4)_2 + 4H_2O$$

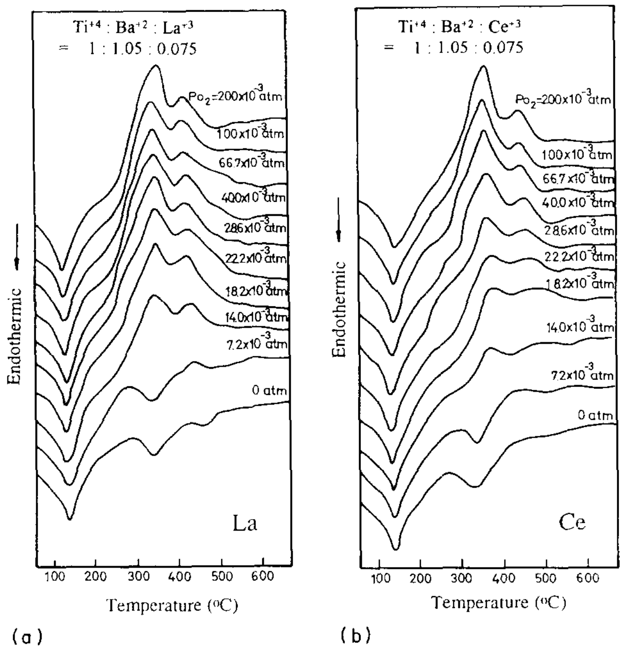
(2) 225–465 °C: oxalate decomposition

$$BaTiO(C_2O_4)_2 + 1/2O_2 \longrightarrow BaCO_3 + TiO_2 + CO + 2CO_2$$

(3) 465–700 °C: barium titanate crystallization

$$BaCO_3 + TiO_2 \longrightarrow BaTiO_3 + CO_2$$

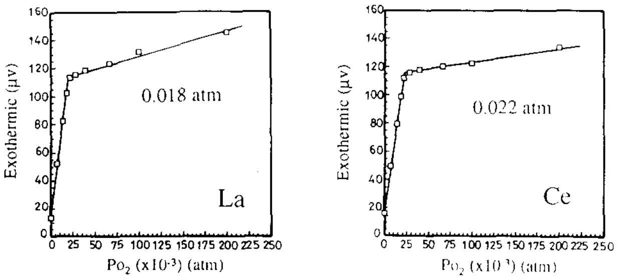
In the second step, the anhydrous compound decomposes and produces a barium carbonate and a titanium oxide as a result of oxidation. It has previously been reported [11] that the formation of anhydrous compound progresses in an oxidation reaction under an oxygen partial pressure of 0.04 atm. In the industrial process, the oxygen must be kept at a higher pressure to prevent failure from insufficient oxygen environment.



(a) (b)

Fig. 1. DTA curves of rare earth-activated oxalate decompositions at various oxygen partial pressures: (a) La (b) Ce.

The DTA curves of the La and Ce-activated oxalates, decomposed under various oxygen partial pressures, are shown in Fig. 1(a) and (b). It is evident that the exothermic reaction changes slowly to an endothermic reaction as oxygen partial pressure reduces from 0.2 atm to 0 atm near 350 °C. The first step (loss of water) and final step (barium titanate crystallization) appear to be independent of oxygen partial pressure. The relationships between the oxygen partial pressures and the values of exothermic energy (in μv) at 350 °C are given in Fig. 2(a) and (b). The critical oxygen partial pressures of rare earth-activated oxalate oxidation reaction are derived from the intersection of the DTA curves in Fig. 1 and determined by a least squares method. The critical oxygen partial pressures are 0.018 atm for La-activated oxalate and 0.022 atm for Ce-activated oxalate. The decomposition of the other rare earth-activated oxalates such as Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er and Yb were also measured. Figure 3 shows the oxygen partial pressures required for rare earth-activated oxalate to decompose. Obviously, all of the oxygen partial pressures for rare earth-activated oxalate are lower than that for the pure oxalate decomposition and show that the doped oxalates allow the oxidation reaction



(a) (b)

Fig. 2. Exothermic value of DTA curves of rare earth-activated oxalate decompositions at various oxygen partial pressures and at 350 °C: (a) La (b) Ce.

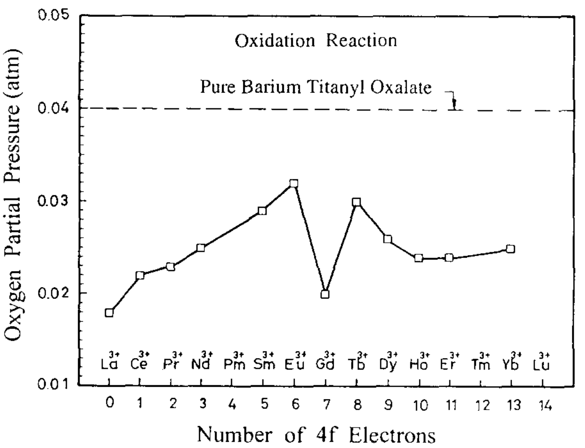


Fig. 3. Oxygen partial pressures of rare earth-activated oxalate decomposition.

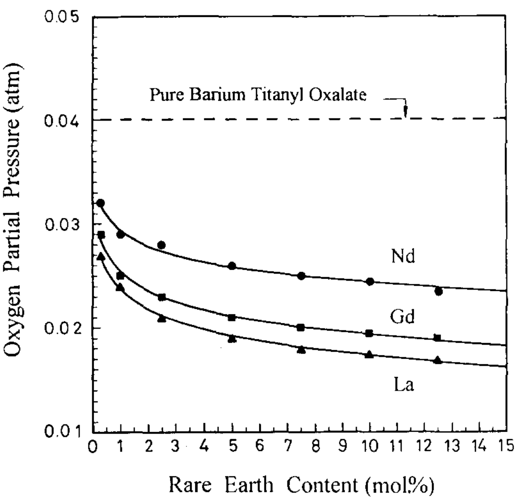


Fig. 4. Oxygen partial pressures of rare earth-activated oxalate decomposition as a function of rare earth content.

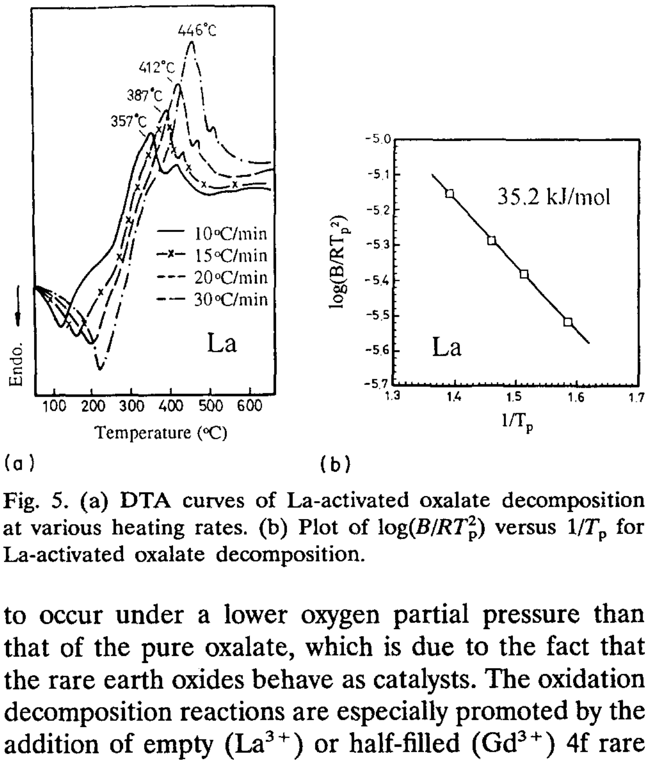


Fig. 5. (a) DTA curves of La-activated oxalate decomposition at various heating rates. (b) Plot of $\log(B/RT_p^2)$ versus $1/T_p$ for La-activated oxalate decomposition.

to occur under a lower oxygen partial pressure than that of the pure oxalate, which is due to the fact that the rare earth oxides behave as catalysts. The oxidation decomposition reactions are especially promoted by the addition of empty (La^{3+}) or half-filled (Gd^{3+}) 4f rare earth oxides. The La- and Gd-activated oxalates have higher oxidizing activities than those of the others. Figure 4 shows the dependence of the oxygen partial pressures upon La, Gd and Nd content. The oxygen partial pressures decrease with increasing rare earth content. When the amount of rare earth oxide exceeds 7.5 mol%, however, the oxygen partial pressures decrease slowly. Kissinger [13] has calculated the reaction activation energy for different heating rates and obtained peak temperatures (T_p). The kinetic energy of La-activated oxalate decomposition is evaluated using the DTA data (Fig. 5(a)) at heating rates from 10 °C/min to 30 °C/min. Plotting the $\log(B/RT_p^2)$ versus $1/T_p$ yields a straight line as shown in Fig. 5(b). The B appearing in the log term is the heating rate and R is the gas constant. The activation energy is calculated to be 35.2 kJ mol^{-1} from the slope of this line. Activation energies of the rare earth-activated oxalate decomposition are shown in Fig. 6. The activation energies for rare earth-activated oxalates are lower than that for the pure oxalate, 50 kJ mol^{-1}.

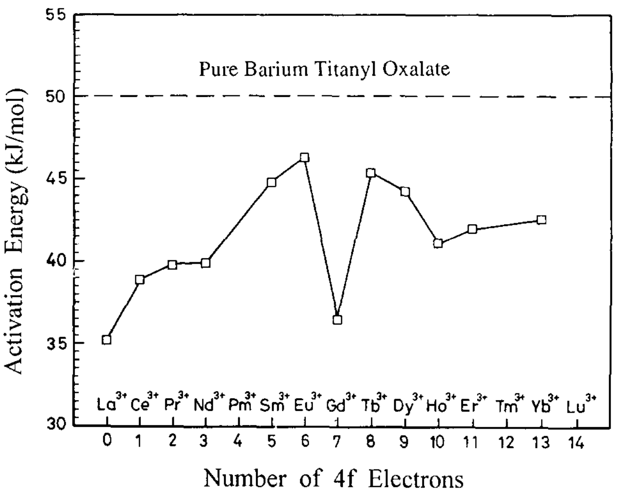


Fig. 6. Activation energies of rare earth-activated oxalate decomposition.

4. Conclusions

The rare earth-activated barium titanyl oxalates have higher oxidizing activity than that of pure oxalate during the process of decomposition. The oxidation reactions are promoted considerably by the addition of empty (La^{3+}) or half-filled (Gd^{3+}) 4f rare earth oxides in the decomposition processes. The oxygen partial pressures decreased with increase in the content of rare earth oxides. The activation energies of rare earth-activated oxalates are lower than those obtained in pure oxalate.

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