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THERMAL DECOMPOSITION OF PRASEODYMIUM-LANTHANUM MIXED OXALATE BY MULTIPLE THERMAL ANALYSIS

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ABSTRACT

Thermal decomposition of Pr-La mixed oxalate has been studied by multiple thermal analysis of TG, DTA and EGA in various atmospheres of $He+O_2$ (4:1), He and CO_2 up to 1200 K at a heating rate of 0.25 Ks^{-1}. In $He+O_2$, Pr^{3+} is partially oxidized to Pr^{4+}, and hence the decomposition process shows a wide variety of features depending on the mole fraction of Pr. In He and CO_2 the stability of the intermediates, especially dioxide carbonate, is markedly increased. In La-rich compositions, when the resultant oxide kept at 1200 K is cooled in CO_2, it absorbs CO_2 and gives dioxide carbonate which is stable at room temperature. Isothermal decomposition of $La_2O_2CO_3$ in CO_2 and $Ar+CO_2$(1%) shows that the decomposition process is apparently of the 1st order reaction. The activation energies obtained are 448 and 264 $kJmol^{-1}$ respectively.

INTRODUCTION

Lanthanide oxides play important roles in refractories, heat- and corrosion-resistant additions, electronic materials and many other industrial ramifications. These oxides are usually obtained by the decomposition of their salts. Properties of oxides thus obtained depend strongly on the kind of the starting salt and also on the decomposition process. From the above standpoint, the thermal decomposition of the lanthanide oxalates has been widely investigated [1], but that of the mixed lanthanide oxalates has not been thoroughly studied. As is well known, praseodymium offers extensively nonstoichiometric oxides depending on the oxygen pressures and the temperatures [2]. The nonstoichiometric feature is expected to vary with the addition of other lanthnide elements such as lanthanum. In order to obtain the praseodymium-lanthanum mixed oxide of definite property, authors have made a reseach on the thermal decomposition of praseodymium-lanthanum mixed oxalates in various atmospheres using multiple thermal analysis of TG, DTA and EGA.

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EXPERIMENTALS

Mixed oxalates were prepared by coprecipitation from the mixed nitrate solutions [3]. The thermal decomposition was carried out using a thermobalance SSC/560GH (Seiko Instruments and Electronics Ltd.) attaching the EGA equipment involving thermal conductivity detectors which was developed by one of the authors [4]. Experimental procedures were previously described [1].

RESULTS AND DISCUSSION

Thermal Analysis in $He+O_2$ (4:1) Atmosphere : Figures 1, 2 and 3 show TG, DTA and EGA curves of decahydrate oxalates in which the mole fraction of Pr, X, are 1, 0.5 and 0 and also those of 1:1 physical mixture. The dehydration process shows the same behavior in every sample and in all the atmospheres employed in this experiment. The decomposition of the anhydrous oxalate begins just after the completion of the dehydration process with a small exothermic peak in DTA and also a small but sharp evolution of the gas in EGA. As CO is not detected in EGA, evolved CO seems to be instantly oxidized to CO_2 in this atmosphere. In such an oxidizing atmosphere, Pr^{3+} is partially oxidized to Pr^{4+}. Praseodymium(IV) ion, Pr^{4+}, decreases the average basicity of the cations in carbonate and intermediate oxide carbonates, and hence makes them unstable. Thus, the decomposition process of the anhydrous oxalate differs markedly depending on the amount of Pr^{4+}, and the resultant oxide reveals a large nonstoichiometry. If the amount of Pr^{+4} is properly chosen, DTA and EGA curves will exhibit distinctly separated peaks each of which corresponds to a decomposition reaction step. This feature is well shown in the case of X=0.5 and is quite different from that of 1:1 physical mixture. This fact confirms that mixed oxalate obtained by the coprecipitation gives a homogeneous solid solution and this is also confirmed by the X-ray diffraction.

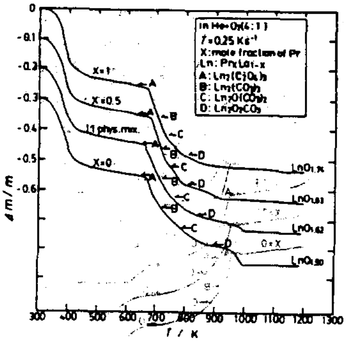

Fig. 1 TG curves in $He+O_2$

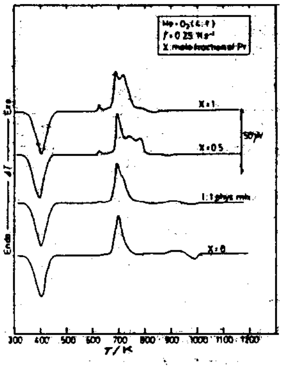

Fig. 2 DTA curves in $He+O_2$

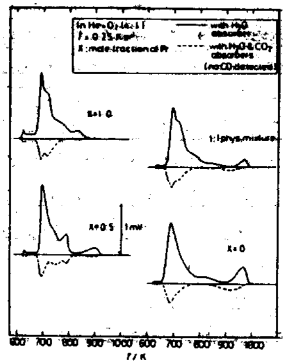

Fig. 3 EGA curves in $He+O_2$

Thermal Analysis in He Atmosphere : Praseodymium(III), Pr^{3+}, is hardly oxidized in He atmosphere. Thus, the decomposition process differs slightly depending on the small discrepancy between the basicities of Pr^{3+} and La^{3+}. Figures 4 and 5 show TG and EGA curves. Compared with in $He+O_2$ (4:1), the stability of the dioxide carbonate increases especially in La-rich composition range. The dioxide carbonate decomposes around 1000 K with CO evolution as shown in EGA curves. This CO evolution comes from the reaction between CO_2 and C deposited in the preceding stage. The color of the resultant sesquioxide became darker in Pr rich composition due to the finely divided residual carbon.

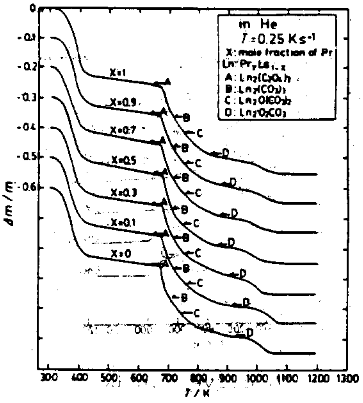

Fig. 4 TG curves in He.

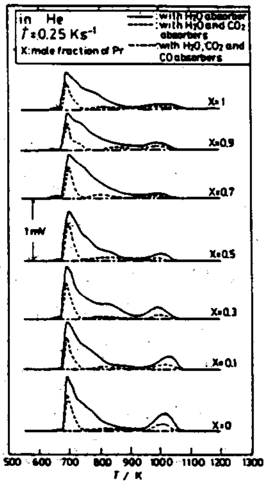

Fig. 5 EGA curves in He.

Thermal Analysis in CO_2 Atmosphere : Figures 6 and 7 show TG and DTA curves. TG curves display more distinct breaks and plateaus in the formation of intermediates. The final product of the decomposition is estimated to be sesquioxide. When this oxide is cooled in CO_2, in La-rich composition, it absorbs CO_2 and gives dioxide carbonate which is stable at room temperature.

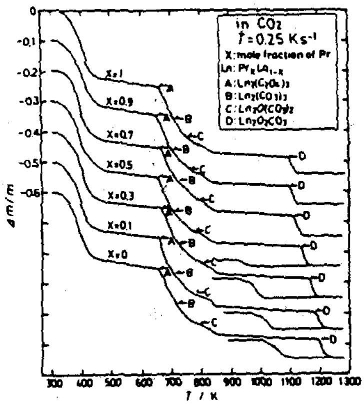

Fig. 6 TG curves in CO_2.

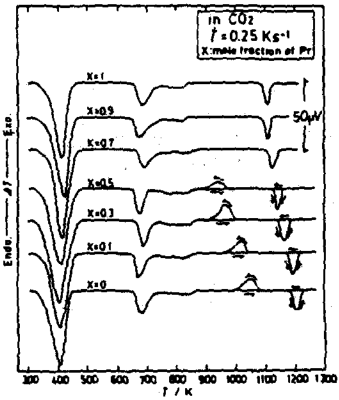

Fig. 7 DTA curves in CO_2.

Isothermal Decomposition of $La_2O_2CO_3$: order to obtain the thermochemical data of $La_2O_2CO_3$, isothermal decomposition has been performed in CO_2 and $Ar+CO_2$(1%). The decomposition process was apparently of the first order reaction. The values of rate constant, *k*, are shown in Table-1. The activation energies obtained were 448 and 264 kJmol^{-1} in CO_2 and $Ar+CO_2$(1%), respectively.

Table 1

in CO_2

Temperature/K	1179	1194	1210	1214
$k \times 10^3/s^{-1}$	2.26	4.22	7.35	8.38

in $Ar+CO_2$(1%)

Temperature/K	1020	1032	1046	1054
$k \times 10^3/s^{-1}$	0.85	1.38	1.83	2.42

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