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PREPARATION OF $BaTiO_3$ BY THERMAL DECOMPOSITION OF BARIUM TITANYL OXALATE SIMULTANEOUSLY INVESTIGATED BY EMANATION THERMAL ANALYSIS, TG-DTA AND EGA

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ABSTRACT

The decomposition reactions of Ba-titanyl oxalate and behaviour of the reaction product - $BaTiO_3$ - during heating in oxygen, carbon dioxide, argon, and helium were studied during heating up to 1500 °C by Emanation Thermal Analysis, TG, DTA and EGA. The results are discussed and the ETA is recommended for the assessment of changes in the surface area, porosity and structure of the intermediate and final reaction products.

INTRODUCTION

The importance of Barium metatitanate and the scientific interest in it are due mainly to the specific electrical properties of the ceramics produced from this substance. For this application the thermal and chemical history of $BaTiO_3$ are controlling factors of its properties.

$BaTiO_3$ can be prepared e.g. by the solid-state reaction of a $BaCO_3$ and TiO_2 mixture at elevated temperatures or by the thermal decomposition of Barium Titanyloxalate, etc. The latter way of the preparation of the titanate results in the product of a high activity which is especially suitable for the fabrication of the dense ceramic material.

This work aims to show the possibilities of the emanation thermal analysis, simultaneously used with TG-DTA and EGA, for the study of the preparation of the $BaTiO_3$ by the thermal decomposition of Barium Titanyloxalate and for the assessment of the changes of active state of the product.

THE PRESENT STATE OF KNOWLEDGE OF $BaTiO_3$ PREPARATION

The thermal decomposition of Barium Titanyloxalate tetrahydrate $BaTiO(C_2O_4)_2 \cdot 4H_2O$ has been investigated by several authors (ref. 1 – 7). Although several dissociation mechanisms were suggested all results showed that $BaTiO_3$ was formed in the temperature range of 600 – 800 °C. There is a general agreement of the authors that the first step in the thermal decomposition is that 4 moles of water are lost at 20 – 250 °C.

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Gallagher and Thompson (ref. 7) suggested that after losing water of crystallization, oxygen is adsorbed to form active $BaCO_3$ and TiO_2 which react to form $BaTiO_3$ at temperatures of 500 – 700 °C and CO_2 is released.

The thermal behaviour of $BaTiO_3$ prepared at temperatures of 600 – 900 °C was studied by Swillam and Gadalla (ref. 6). They have shown that when lower temperatures are used for the calcination of $BaTiO_3$ compacts, samples with extremely fine pores are formed, whereas higher temperatures cause the agglomerates to shrink to much smaller particles, eliminating these pores. They have determined the optimum temperature for preparing active $BaTiO_3$ in air as high as 900 °C.

EXPERIMENTAL

Apparatus

The NETZSCH simultaneous thermoanalyzer STA 429 was used enabling the simultaneous performance of the emanation thermal analysis (ETA), TG, DTA, and EGA. For the description of the apparatus see (ref. 8).

Labelling of the samples for ETA

The powdered Barium Titanyloxalate tetrahydrate was labelled by ^{228}Th and ^{224}Ra by impregnation with an aqueous solution containing the trace amounts (10^5 s^{-1} ml^{-1}) of these nuclides. Radon atoms are formed by the spontaneous decay according to the scheme

$$^{228}Th \xrightarrow{\alpha} {}^{224}Ra \xrightarrow{\alpha} {}^{220}Rn \qquad (1)$$

and introduced by the recoil into the surface layers of the powder grains in the depth of approx. 70 nm.

Experimental conditions

The amount of 0.3 g of sample was used for the measurements carried out in the flow of a gas (oxygen, CO_2, argon, helium) with a heating rate of 5 °C min^{-1} (flow-rate was 50 cm^3 min^{-1}).

The results of the ETA measurements, expressed as the rate of radon release from the sample depend on the surface area, morphology of the sample and the radon diffusion coefficient of the sample. The changes in the radon release rate indicate the changes of these properties, even in the cases when no change of mass occured, volume or thermal effect are indicated by common methods of thermal analysis (ref. 9).

RESULTS AND DISCUSSION

In Fig. 1 DTA and ETA curves measured during the heating of Barium Titanyloxalate tetrahydrate in oxygen and carbon dioxide are shown. The loss of water is indicated both by DTA and ETA in the temperature range of 25 – – 225 °C. Whereas the endothermal DTA effects reflect two steps of the dehydration, only one sharp ETA effect was observed, indicating the temperature of the changes in the surface layers of the sample grains labelled by radon, due to the water evolution.

The anhydrous salt decomposed between 225–465 °C, and $BaCO_3$ and TiO_2 in a highly active form are formed. This process is accompanied (ref. 7) by the release of one CO mole and two CO_2 moles, being indicated by the endothermic effect (see the maximum at 350 °C in Fig. 1) in CO_2 and argon and helium atmosphere; in oxygen atmosphere the oxidation of CO takes place which is reflected by the exothermal effect on the DTA. The ETA curve indicated the decomposition of the anhydrous salt by a small effect only, showing that no remarkable change in the surface area takes place during this process.

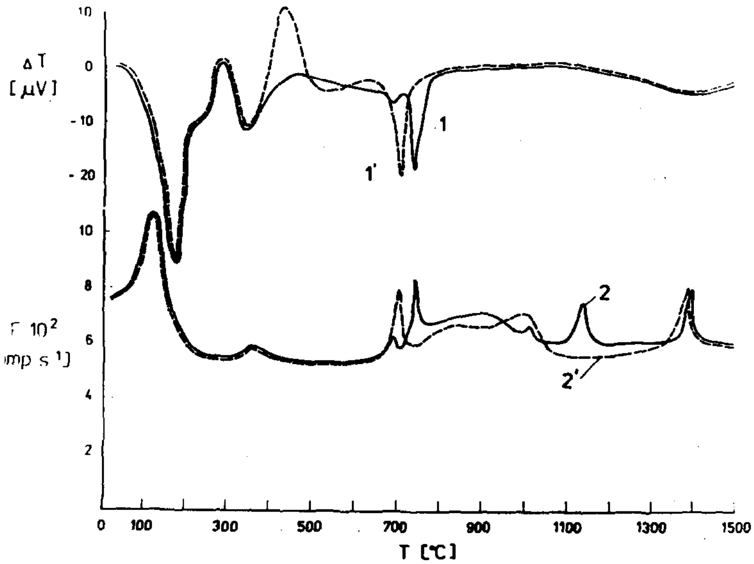

Fig. 1. DTA curves (1, 1′) and ETA curves (2, 2′) of Barium Titanyloxalate heated in oxygen and carbon dioxide at the rate of 5 °C/min. The curves 1′ and 2′ correspond to the heating in oxygen, the curves 1 and 2 correspond to the heating in CO_2.

The effects in the range of 670 – 770 °C correspond to the formation of $BaTiO_3$ in accordance with the reaction mechanism proposed by Gallagher and Thompson (ref. 7). This reaction is completed in oxygen at 720 °C whereas in carbon dioxide at 770 °C. Both DTA and ETA curves indicated these differences, the effects of CO_2 evolution were observed on the EGA curves.

During further heating the changes taking place in the $BaTiO_3$ formed are reflected by the ETA curves only. We can assume that the ETA effects correspond to the changes in the surface area, morphology and structure of the samples. Obviously, the changes in the reaction product of the Barium Titanyloxalate decomposition, taking place in the temperature range of 800 – – 1100 °C, cause the decrease in the highly active state of the reaction product.

The shrinkage of $BaTiO_3$ above 900 °C in air described by Swilam and Gadalla (ref. 6) is in good agreement with the results of this work (see the decrease of the radon release rate in curve 2', Fig. 1, above 1000 °C).

It is to note that these changes depend on the gas medium in which the thermal decomposition of the Barium Titanyloxalate took place. The sharp effect on the ETA curve at 1350 – 1390 °C corresponds to the 2nd order phase transition in $BaTiO_3$ (ref. 10), which is accompanied on the DTA curve by the shift of the base-line only.

CONCLUSIONS

The ETA simultaneously used with other methods of thermal analysis for the investigation of the thermal decomposition of Barium Titanyloxalate yields supplementary data about the surface and structure changes taking place during the respective thermal processes.

Moreover, the ETA enabled us to receive information about the changes in the decomposition product - $BaTiO_3$ - directly during its thermal treatment in the respective gas medium. In this way the ETA is suitable for the assessment of changes in the surface area, porosity and the structure which control the active state of the solid materials. The ETA can be recommended for the investigation of these changes also in other ceramic powders in cases when the common methods of thermal analysis are not sensitive enough.

REFERENCES

1 P.K. Gallagher, F. Schrey, J. Amer. Ceram. Soc., 46 (1963) 567.
2 B.V. Strizhkov, A.V. Lapitskii, L.G. Vlasov, Russ. Zh. Prikl. Khim., 34 (1961) 673.
3 D. Hoeffgen, H. Hoppert, L. Mönch, Ber. Dt. Keram. Ges., 55 (1978) 216.
4 K. Kiss, J. Magder, M.S. Vukasovigh, and R.J. Lockhart, J. Amer. Ceram. Soc., 49 (1966) 291.
5 O. Saburi, Experimental Researches in Semiconducting Barium Titanates, Murata Mfg. Co., Tech. Laboratory, Nagaoka-Cho, Japan, 1961.
6 M.N. Swilam, A.M. Gadalla, Trans. and J. Brit. Ceram. Soc., 74 (1975) 159.
7 P.K. Gallagher, J. Thompson, Jr., J. Amer. Ceram. Soc., 48 (1965) 644.
8 W.D. Emmerich, V. Balek, High Temp.-High Press., 5 (1973) 67.
9 V. Balek, Thermochim. Acta, 22 (1978) 1.
10 H. Kaiser, Z. Elektrochem., 58 (1954) 601.