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In celebration of the 60th birthday of Dr. Andrew K. Galwey

THERMALLY INDUCED OXYGEN UPTAKE AND RELEASE IN THE Ba–Cr–O–SYSTEM

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Abstract

Dibarium-chromate(IV), Ba_2CrO_4, has been prepared and its thermal behaviour in different atmospheres has been studied. An unusual reversible mass change in oxygen reflects the uptake and release of oxygen in a cyclic thermal program for a product mixture obtained in a previous thermal decomposition step. Initial and product phases have been characterized by X-ray powder diffraction.

Keywords: Ba_2CrO_4, solid state decomposition, TG

Introduction

Mixed oxides of composition A_2BO_4 exist in a variety of structures, the best well known being spinel, K_2NiF_4, olivine and K_2SO_4 types. The specific structural type to which a compound belongs, may be estimated from the radii ratio A/B [1]. In the K_2SO_4 structure family [2], a number of peculiarities may be observed, e.g., for Ti^{4+}, the only well known compound with isolated TiO_4 tetrahedra, i.e. Ba_2TiO_4 in its polymorphic forms [3], belongs to this family. Its thermal behaviour, in particular relative to CO_2, has been studied earlier [4]. Ba_2CrO_4, as another example, represents one of the rare compounds with isolated $Cr(IV)O_4$ tetrahedra. The generally rather unstable tetravalent state of chromium is stabilized by the high lattice energy of this structure. Tetravalent chromium may obviously be both oxidized and reduced, and therefore it seemed to be of interest to study the redox behaviour of this phase in various atmospheres.

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Synthesis of samples

In the literature, there are a number of recipes for the preparation of Ba_2CrO_4, starting from various combinations of barium chromates with different valences of chromium, barium hydroxide, barium and chromium oxides and under different atmospheres [5–11]. All these methods were accompanied by a number of problems, since in most cases, hydroxy compounds were obtained as impurities if hydroxide ions were contained in the starting materials. By using dry barium chromate(VI), chromium(III) oxide and barium oxide and working under vacuum at 1000°C for 10 hours, these problems could be avoided. From the different thermogravimetric measurements, we estimate the impurities in this product to amount to less than 0.4%.

Experimental

The thermal behaviour of the samples was studied using a Mettler 2000C thermogravimetric system in different, defined atmospheres in the temperature range from room temperature to 1000°C, with a heating rate of 10 deg·min^{-1}, as well as Guinier-Lenné X-ray powder diffraction camera Y-909 (Nonius, NL-Delft) in oxygen.

Results

a) Under nitrogen

In a nitrogen atmosphere, pure Ba_2CrO_4 is completely inert, i.e. no mass gain or loss is observed over the whole temperature range investigated. This also confirms the absence of water in the samples.

b) Under carbon dioxide

In an atmosphere of CO_2, a mass gain in two steps is observed. Between 300 and 400°C, a small mass increase of about 1–2% can be attributed (after X-ray diffraction analysis of the products) to the carbonatization of remaining barium hydroxide impurities. Above 450°C, a continuous mass gain up to 800°C is observed, which is attributed to the formation of $BaCrO_4$, $BaCO_3$ and CO (detected by XRD and mass spectrometry, respectively) and further reaction of the two solid products to $Ba_3(CrO_4)_2$, CO_2 and O_2.

The fact the no $BaCrO_3$ was detected, as might be expected from the analogous formation of BaTiO3 in investigations on Ba_2TiO_4 [4], is not surprising, as this compound has so far only been synthesized at pressures above 3000 atm.

c) Under oxygen

The most interesting results have been obtained when Ba_2CrO_4 has been heated (10°/min) in oxygen (pure O_2 flow of 25 ml/min) (Fig. 1). The mass increases by 7% between about 200 and 350°C. This can be attributed to the reaction

$$Ba_2CrO_4 + O_2 \rightarrow BaCrO_4 + BaO_2.$$

On further heating to 700–800°C, a reverse process, i.e. a mass loss, half that of the previous mass increase occurs. Continuous high-temperature powder X-ray

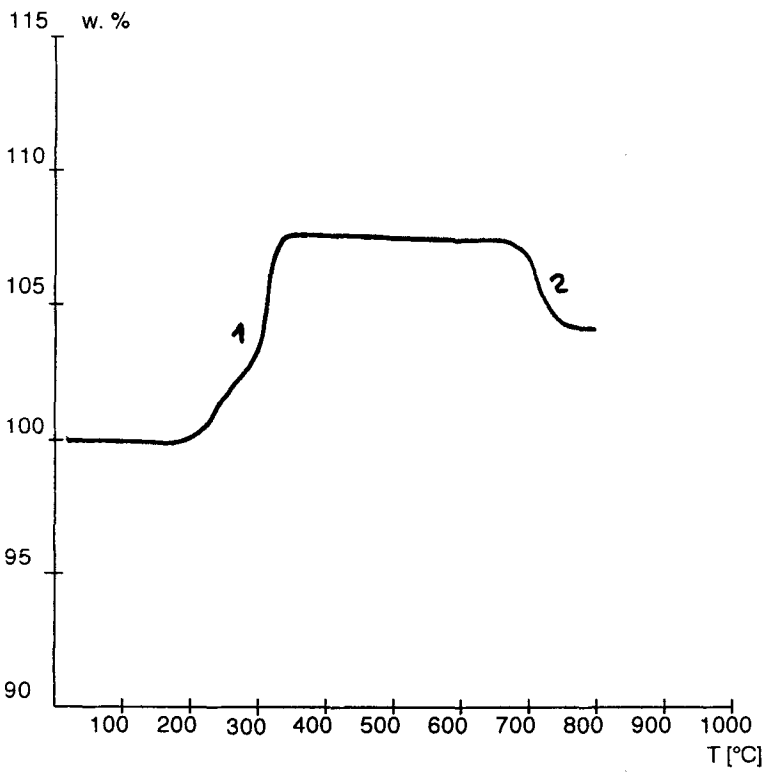

Fig. 1 Thermogravimetric curve of Ba_2CrO_4 under oxygen (heating rate 10 deg·min^{-1}, gas flow 25 ml/min)

diffraction by means of a Guinier-Lenné camera allowed us to identify the products of this reaction, and thus indicates this second step to be

$$2BaCrO_4 \rightarrow BaCr_2O_4 + BaO_2 + O_2.$$

If, after the first heating to 800°C, a cyclic temperature program between 600 and 800°C is applied, it becomes clear that the second of these reactions is completely reversible, and occurs in both directions in sharp steps (Fig. 2).

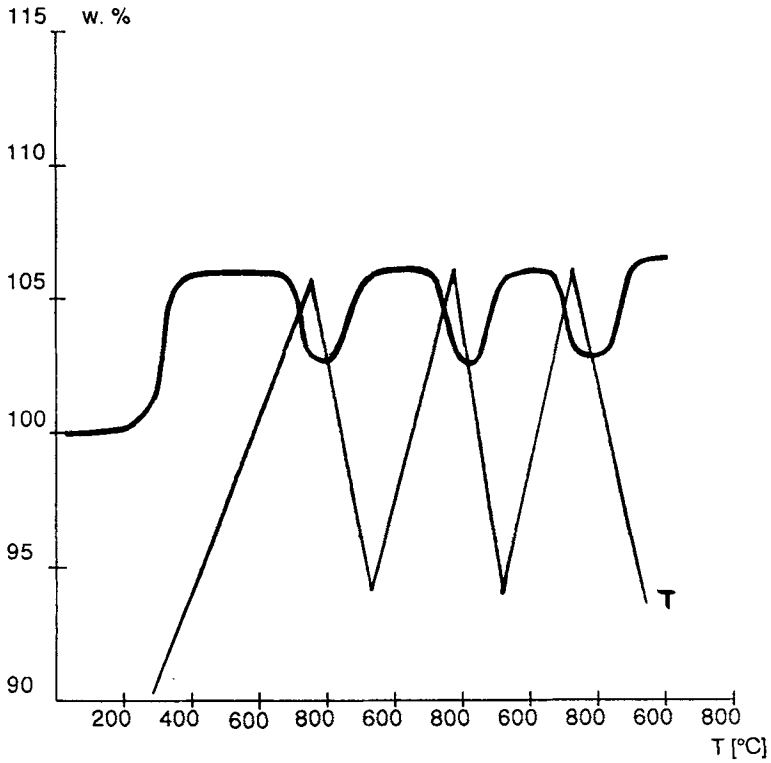

Fig. 2 Thermogravimetric curve of Ba_2CrO_4 subjected to a cyclic heating program under oxygen (other conditions the same as in Fig. 1)

Barium peroxide alone does not lose oxygen considerably below 800°C according to our own experiments under identical conditions and to the latest literature [12], and also barium chromate(VI) alone is inert under the given conditions. However, a mechanical mixture of the two compounds shows a similar cyclic behaviour to that of the product prepared by thermal decomposition of Ba_2CrO_4, but the steps of the TG curve are not as sharp. We assume that the 'catalytic effect' of barium peroxide on the barium chromate(VI) decompo-

sition is especially pronounced if the two phases are closely intergrown. A similar, intergrowth dependent redox behaviour has been observed in the Adkin's catalyst copper chromate [13]. The intergrowth in the present system will be studied by high-resolution electron microscopy in the near future, since this may be a promising substance for catalytic or sensor applications.

References

1 O. Müller, R. Roy, The Major Ternary Structural Families, 76, Springer Verlag, New York 1974.
2 Gmelin's Handbuch der Anorganischen Chemie, 8. Aufl., Band 22, Lieferung 1938, p. 708.
3 J. R. Günter and G. B. Jameson, Acta Crystallogr., C 40 (1984) 207.
4 O. Marks and J. R. Günter, Reactivity of Solids, 6 (1988) 217.
5 R. Scholder and G. Sperka, Z. Anorg. Allg. Chem., 285 (1956) 49.
6 R. Scholder, Angewandte Chemie, 65 (1953) 240.
7 R. Scholder and W. Klemm, Angewandte Chemie, 66 (1954) 461.
8 Gmelin's Handbuch der Anorganischen Chemie, 8. Aufl., Band 52, Teil B 1968, p. 834.
9 Hj. Mattausch and Hk. Müller-Buschbaum, Z. Anorg. Allg. Chem., 407 (1974) 129.
10 B. L. Chamberland, M. P. Herrero-Fernandez and T. A. Hewston, J. Solid State Chem., 59 (1985) 111.
11 R. Olazcuaga, J. M. Reau and G. Le Flem, Comptes Rendus, C275 (1972) 135.
12 A. F. Mayorova, S. N. Mudretsova, M. N. Mamontov, P. A. Levashov and A. D. Rusin, Thermochim. Acta, 217 (1993) 241.
13 O. Marks and J. R. Günter, J. Solid State Chem., 77 (1988) 15.

Zusammenfassung — Es wurde Dibariumchromat(IV), Ba_2CrO_4 dargestellt und sein thermisches Verhalten in verschiedenen Atmosphären untersucht. Eine ungewöhnliche, reversible Mass-enänderung in Sauerstoff spiegelt in einem cyclischen thermischen Programm die Aufnahme und Abgabe von Sauerstoff für ein Produktgemisch wieder, welches in einem vorangehenden thermischen Zersetzungsschritt gewonnen wurde. Ausgangs- und Produktephasen wurden anhand von Debye-Scherrer-Aufnahmen charakterisiert.