Journal of Thermal Analysis, Vol. 44 (1995) 147-159

ON THE CHANGES INDUCED BY LASER IRRADIATION IN CrO_3 AND $K_2Cr_2O_7$ POWDERS

V. Pârvulescu[*], *D. Fătu*[**], *A. Andrei*[*] *and E. Segal*[**]

[*]Institute for Nonferrous Metals Industry, B-dul Biruintei 102, Sector 2
Bucureşti 73951, Roumania
[**]University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry
B-dul Republicii 13, Sector 4, Bucureşti 70031, Roumania

(Received December 3, 1993; in revised form January 30, 1994)

Abstract

Some results concerning the CO_2 laser induced changes in CrO_3 and $K_2Cr_2O_7$ powders, obtained from X-ray diffractograms and thermoanalytical curves are presented.

Keywords: CrO_3, $K_2Cr_2O_7$, laser induced decomposition

Introduction

The change CrO_3–Cr_2O_3 occurs usually at temperatures higher than 600°C with or without reducing agents. As far as the change $2K_2Cr_2O_7 \rightarrow Cr_2O_3 + 2K_2CrO_4 + 3/2O_2$ is concerned, it occurs in the absence of reducing agents at temperatures higher than 500°C with release of oxygen [1].

This paper presents the results of an investigation concerning the CO_2 laser induced decomposition of CrO_3 and $K_2Cr_2O_7$.

Experimental

Samples of powdered CrO_3 (Merck) and $K_2Cr_2O_7$ (Merck) have been submitted to irradiation with a CO_2 laser with a continuous wave equipment type GT-1200 at powers in the range 0.64 kW/cm^2–2.30 kW/cm^2. The exposure times were the range 0.7–28.0 s for CrO_3 and 14–180 s for $K_2Cr_2O_7$. The laser beam was rectangularly focalized on a surface area of 39 mm^2. The layer submitted to irradiation had a thickness of 1.5 mm. The total pressure of the gas mixture was 24 torr (He – 13 torr, N_2 – 9 torr and CO_2 – 2 torr).

The solid products of decomposition were analyzed by X-ray diffraction using DRON 2 and PHILIPS PW 1400 equipments. The X-ray diffractograms

0368–4466/95/ $ 4.00

John Wiley & Sons, Limited
Chichester

were recorded using the K_α radiation of copper. In order to identify the compounds the ASTM files were used. The degree of crystallinity of the samples prepared under identical conditions was estimated from the diffraction peak heights.

The thermoanalytical curves (TG and DTA) were recorded by means of a Q-1500 D MOM derivatograph type Paulik-Paulik-Erdey in static air atmosphere at a heating rate of 10 deg·min^{-1}.

Results and discussions

In Table 1 are listed the experiments concerning laser induced decomposition of CrO_3 and the corresponding working conditions.

Figure 1 shows the X-ray diffractogram of a Cr_2O_3 sample obtained by the thermal decomposition of CrO_3 kept at 900°C for 4 h. After reaction, the sample was cooled by water hardening and then dried at 120°C for 8 h, and then the diffractogram was recorded

Table 1 List of experiments and working conditions concerning the laser irradiation of CrO_3

No.	Laser beam power/W	Time of exposure/s	Supplied energy/kJ	Energy/ kJ·mol^{-1}
C1	250	10.5	2.6	1.3×10^3
C2	400	14.0	5.6	2.8×10^3
C3	500	14.0	7.0	3.5×10^3
C4	600	14.0	8.4	4.2×10^3
C5	300	28.0	8.4	4.2×10^3
C6	400	28.0	11.2	5.2×10^3
C7	500	28.0	14.0	7.0×10^3
C8	850	2.8	2.38	1.19×10^3
C9	650	4.9	3.18	1.59×10^3
C10	750	4.9	3.67	1.84×10^3
C11	900	0.7	0.63	0.32×10^3

In Figs 2–4 the X-ray diffractograms of Cr_2O_3 samples obtained from CrO_3 exposed for 14 s to laser beams with irradiation powers in the range 0.4–0.6 kW are shown.

Figures 5–7 show the diffractograms of Cr_2O_3 samples obtained from CrO_3 exposed for 28 s to laser beams with powers in the range 0.3–0.5 kW.

Figures 8, 9 and 10 show the diffractograms of Cr_2O_3 samples irradiated at higher powers 0.65–0.85 kW but for shorter time, i.e. 4.9 and 2.8 s.

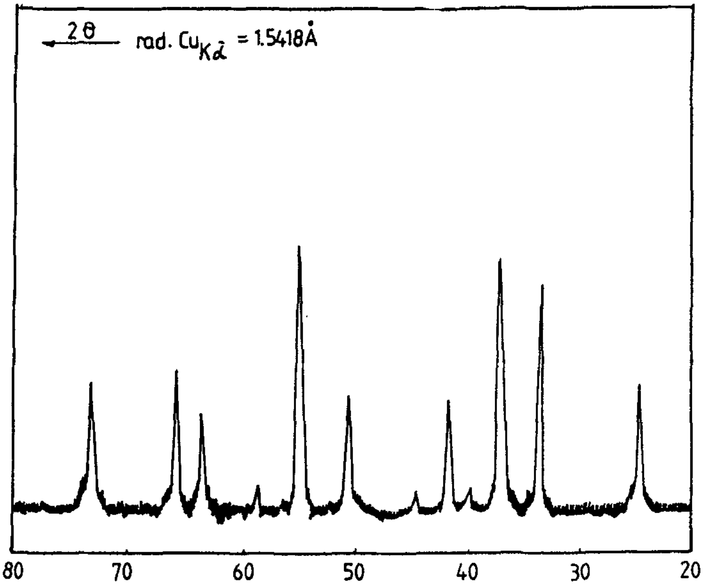


Fig. 1 The diffractogram of a Cr_2O_3 powder sample obtained by thermal decomposition of CrO_3 at 900°C for 4 h

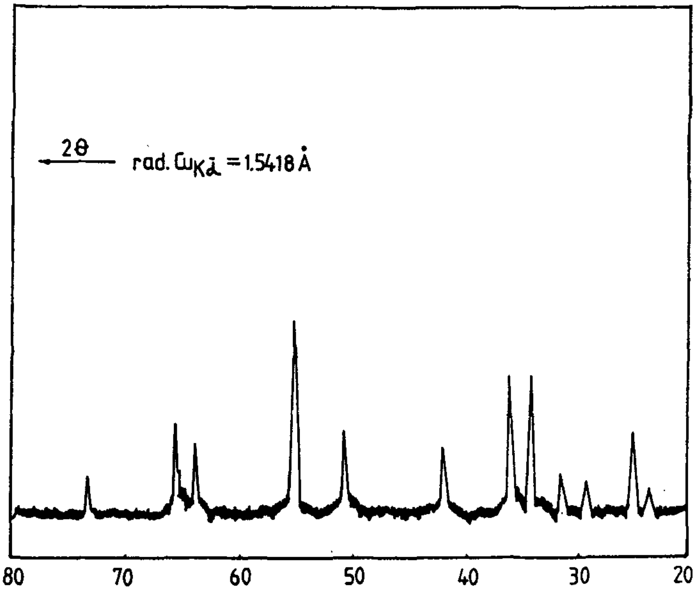


Fig. 2 The diffractogram of a Cr_2O_3 powder sample obtained by CO_2 laser irradiation of CrO_3 with a power of 0.4 kW for 14 s

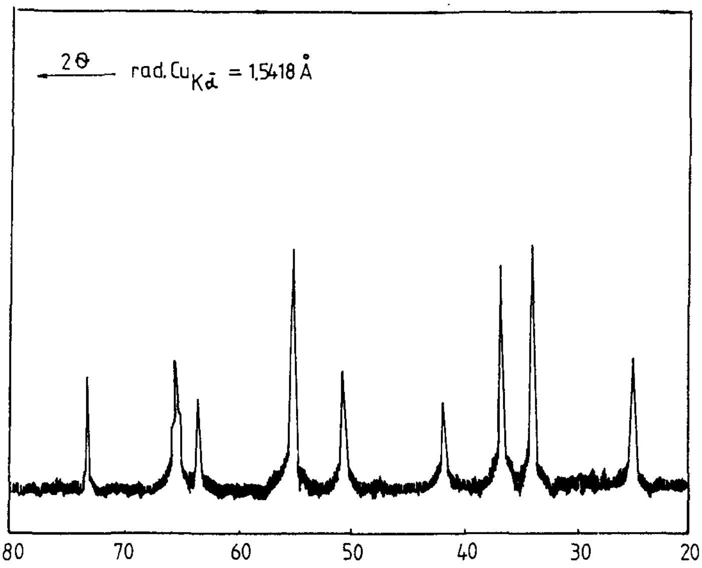


Fig. 3 The diffractogram of a Cr_2O_3 powder sample obtained by CO_2 laser irradiation of CrO_3 with a power of 0.5 kW for 14 s

For the samples irradiated with energies higher than 2.8×10^3 kJ/mol CrO_3 the only product was Cr_2O_3, while for the samples irradiated with energies in the range $1-2.8\times10^3$ kJ/mol CrO_3, Cr_2O_5 was also evidenced.

As shown in Fig. 11, after irradiation with a beam of 0.9 kW but for 0.7 s only untransformed CrO_3 was evidenced.

Table 2 shows the experiments performed and the results concerning the laser irradiation of $K_2Cr_2O_7$.

Table 2 List of experiments and working conditions concerning laser irradiation of $K_2Cr_2O_7$

No.	Laser beam power/W	Time of exposure/ s	Supplied energy/ kJ	Energy/ kJ·mol^{-1}	hkl D(104) (Å)	D(110) (Å)	$\frac{D(110)}{D(104)}$
K1	900	20	18	9×10^3	370	557	1.51*
K2	900	120	108	54×10^3	558	556	0.99**

*asymmetrical crystallites
**symmetrical crystallites

For comparison, in Table 3 are presented the experiments on the thermal decomposition of $K_2Cr_2O_7$ with (K2T) and without (K1T) sulphur.

The X-ray diffractograms show that sample K1 contains the irradiation products Cr_2O_3 and K_2CrO_4 as well as unreacted $K_2Cr_2O_7$. Sample K2 irradiated for

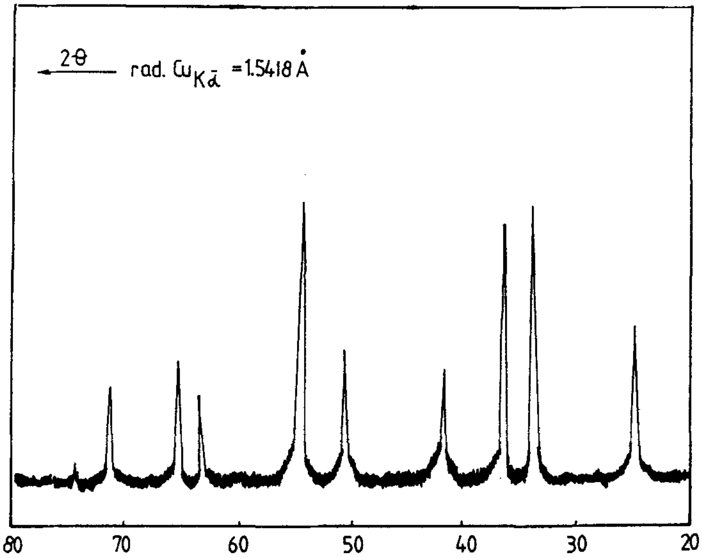


Fig. 4 The diffractogram of a Cr_2O_3 powder sample obtained by CO_2 laser irradiation of CrO_3 with a power of 0.6 kW for 14 s

a longer time as well as samples K1T and K2T thermally treated contain only the crystalline product Cr_2O_3. The samples irradiated with laser beam whose power was lower than 9×10^3 kJ/mol $K_2Cr_2O_7$ do not contain crystallised reaction products.

Table 3 List of experiments on the thermal decomposition of $K_2Cr_2O_7$

No.	Temperature/ °C	hkl		
		D(104) Å	D(110) Å	$\frac{D(110)}{D(104)}$
K1T	900	929	1200	1.29*
K2T	900	850	870	1.02**

*asymmetrical crystallites

**symmetrical crystallites

In Table 2 are listed the crystallite sized D(104) and D(110) as estimated from the diffraction lines corresponding to the planes (104) and (110) by Scherrer's formula [2]. The instrumental width of the diffraction maxima was corrected with respect to the width corresponding to a sample of α-SiO_2. In order to prove the asymmetry of crystallites the ratio D(104)/D(110) for the investigated samples is given.

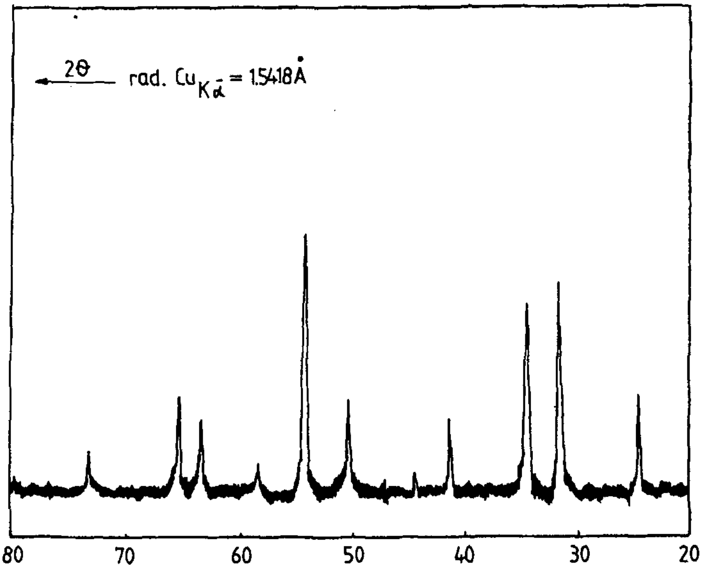


Fig. 5 The diffractogram of a Cr_2O_3 powder sample obtained by CO_2 laser irradiation of CrO_3 with a power of 0.3 kW for 28 s

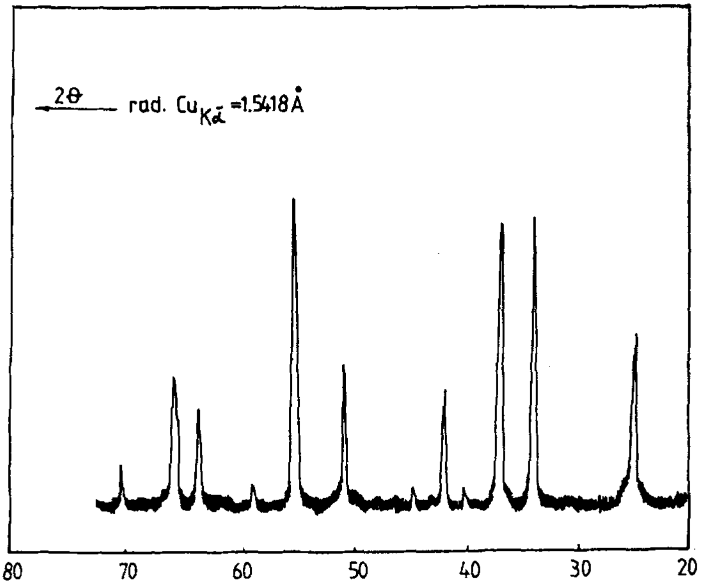


Fig. 6 The diffractogram of a Cr_2O_3 powder sample obtained by CO_2 laser irradiation of CrO_3 with a power of 0.4 kW for 28 s

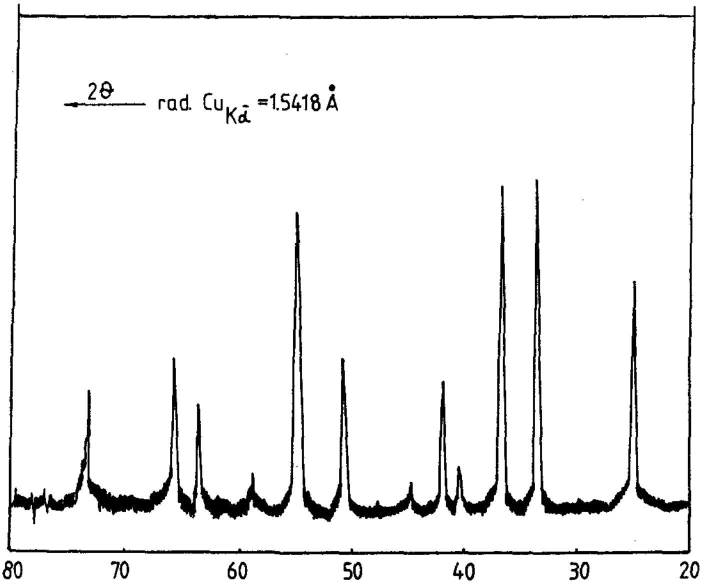


Fig. 7 The diffractogram of a Cr_2O_3 powder sample obtained by CO_2 laser irradiation of CrO_3 with a power of 0.5 kW for 28 s

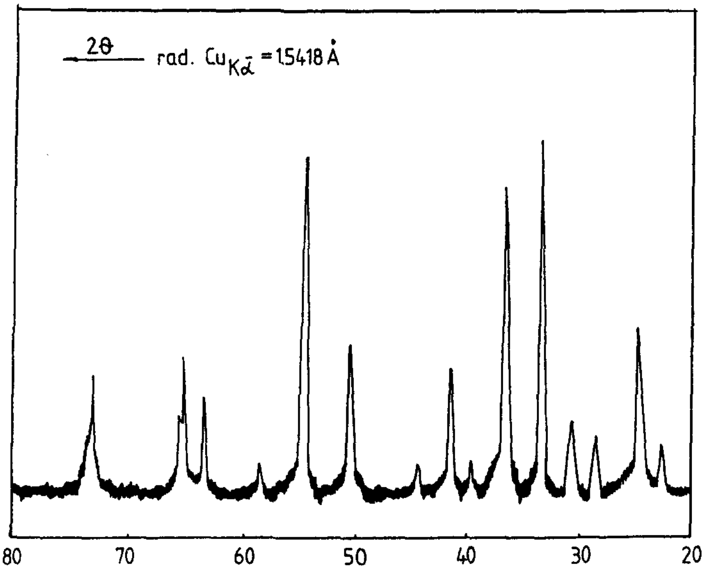


Fig. 8 The diffractogram of a Cr_2O_3 powder sample obtained by CO_2 laser irradiation of CrO_3 with a power of 0.65 kW for 4.9 s

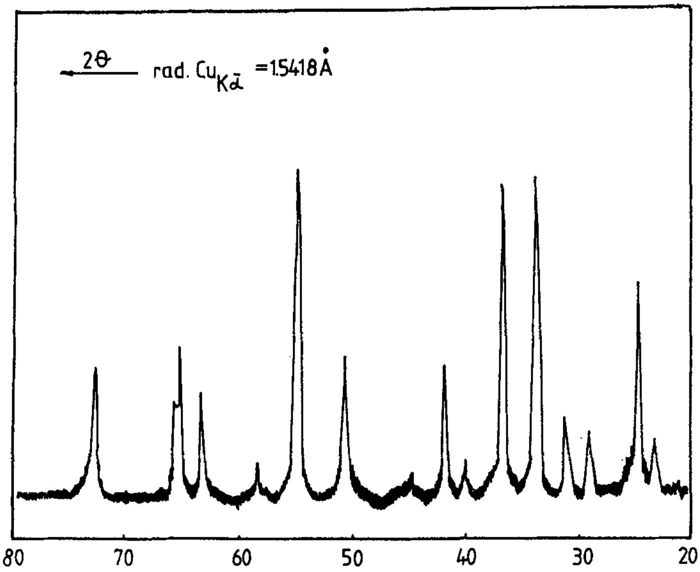


Fig. 9 The diffractogram of a Cr_2O_3 powder sample obtained by CO_2 laser irradiation of CrO_3 with a power of 0.75 kW for 4.9 s

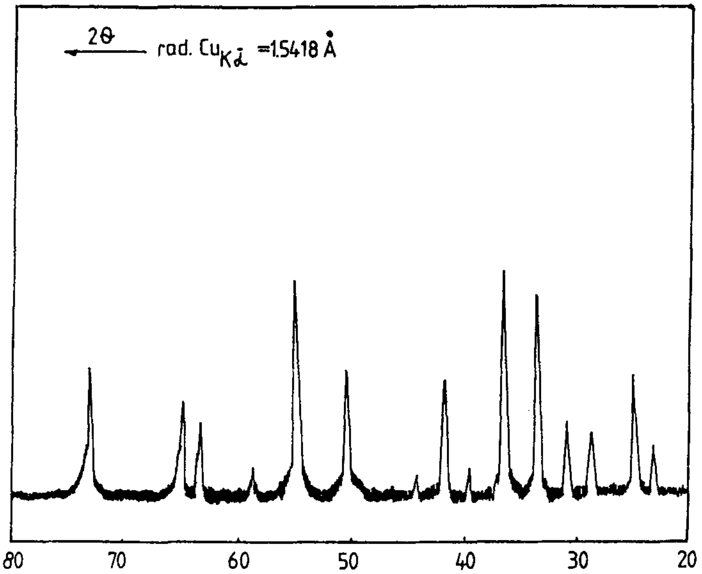


Fig. 10 The diffractogram of a Cr_2O_3 powder sample obtained by CO_2 laser irradiation of CrO_3 with a power of 0.85 kW for 2.8 s

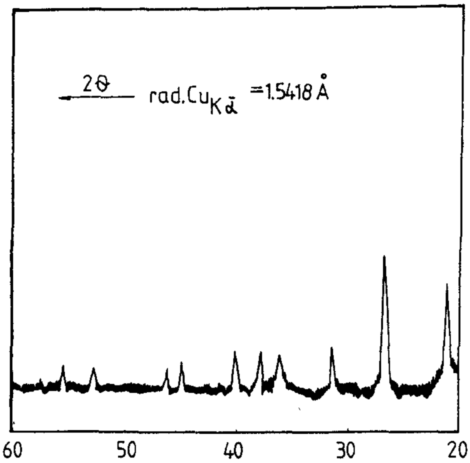
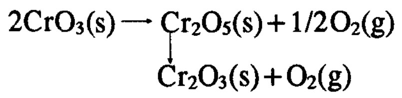


Fig. 11 The diffractogram of a Cr_2O_3 powder sample obtained by CO_2 laser irradiation of CrO_3 with a power of 0.9 kW for 0.7 s

As seen from the data in Tables 2 and 3 there is a preferential growth of crystallites in the direction of the normal to the planes (110) in samples K1 and K1T. By increasing the time of irradiation a trend of symmetrization leading to isometric forms can be noticed. The presence of sulphur determines the decomposition of $K_2Cr_2O_7$ only to Cr_2O_3 and identical growth rates according to the two previously mentioned directions.

Figure 12 shows the derivatogram of sample C9. This derivatogram is almost identical with the derivatograms of samples C8 and C10. The weight loss is 5.5%. According to the reaction scheme (1) the weight loss should be 24% if the reaction is total and 8% if



$$\begin{array}{l} 2CrO_3(s) \rightarrow Cr_2O_5(s) + 1/2O_2(g) \\ \qquad\qquad\quad \downarrow \\ \qquad\qquad\quad Cr_2O_3(s) + O_2(g) \end{array}$$

Scheme 1 A general picture of the changes undergone by CrO_3

the reaction occurs only in the first step. If the second step is taken into account the weight loss should be 17.4%. The experimental results are in agreement with the previously mentioned X-ray diffraction data which evidenced a percent of untransformed Cr_2O_5.

Figure 13 shows the TG and DTA curves for the samples submitted to energy values higher than 2.8×10^3 kJ/mol CrO_3. No matter of the values of energy per mole the only significant effect is the endothermic one at 475°C corresponding to the same value of the heat of change (constant area of the DTA peak). This is

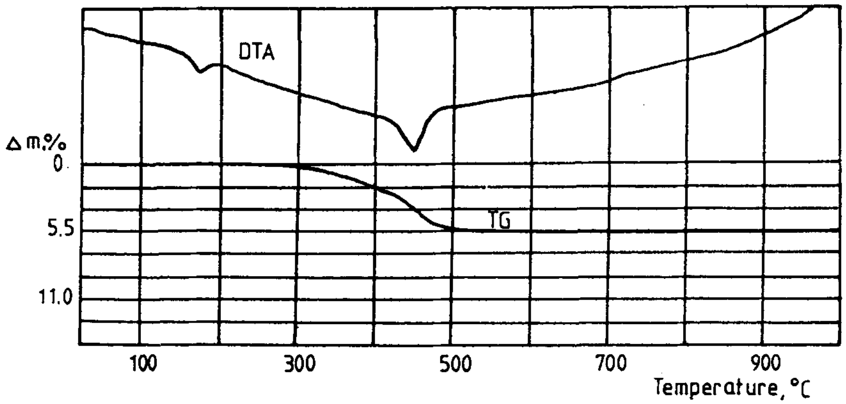


Fig. 12 The DTA and TG curves of a CrO_3 sample irradiated with a power of 650 W for 4.9 s using as standard a Cr_2O_3 sample calcined at 1000°C for 4 h

to the same value of the heat of change (constant area of the DTA peak). This is not a reversible effect as at the cooling of the sample no exothermic effect was recorded.

The calcination of the irradiated samples does not change the degree of crystallinity exhibited by the samples after irradiation.

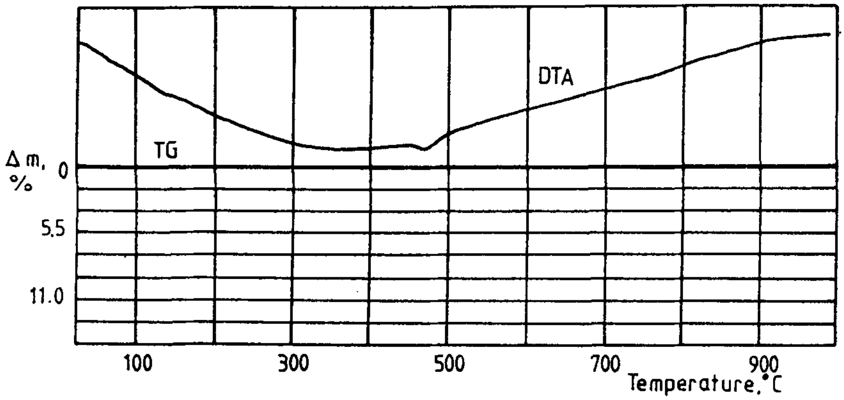


Fig. 13 The DTA and TG curves of a CrO_3 sample irradiated with a power of 400 W for 14 s using as standard a Cr_2O_3 sample calcined at 1000°C for 4 h

As already shown for energy values higher than 10^3 kJ/mol CrO_3, CrO_3 is totally changed into Cr_2O_3 while for energy values lower than 5×10^3 kJ/mol CrO_3, the change practically does not occur, as shown by the diffractograms which exhibit only the lines of CrO_3.

For exposure times of 14 s, the degree of crystallinity of the samples exposed to 0.4 kW is lower than for the thermally treated samples. At 0.5 kW the degree of crystallinity is comparable to the degree of crystallinity of the thermally treated sample while at 0.6 kW the degree of crystallinity is higher.

The same trend of increase of the degree of crystallinity with the irradiation power can be noticed for the exposure time of 28 s. In this case the degree of crystallinity of the thermally treated sample is reached at 0.3 kW, for 0.5 kW the degree of crystallinity being higher. It should be noticed that according to Table 1 the energy supplied in this case is 7×10^3 kJ/mol CrO_3 which can be considered as a quite high value.

The increase of the irradiation power to values in the range 0.65–0.75 kW determines for the irradiated samples a degree of crystallinity quite close to that obtained for the energy of 7×10^3 kJ/mol CrO_3 supplied to the samples of CrO_3 but with shorter times of exposure and consequently for energies in the range 1.59×10^3 kJ/mol CrO_3–1.84×10^3 kJ/mol CrO_3.

This increase of irradiation power and corresponding decrease of the exposure time is limited by the same amount of energy required by the induced transformation. Thus the decrease of the exposure time to 2.8 s, even if the power is increased to 0.85 kW leads to a sample of Cr_2O_3 with a degree of crystallinity comparable to that of a sample submitted to a thermal treatment. For 0.7 s and 0.9 kW only less than 5% of CrO_3 is transformed.

From the presented and discussed data it is obvious that the transformation of CrO_3 requires 10^3 kJ/mol CrO_3. If higher energies are supplied the excess is used to increase the degree of crystallinity.

The lines corresponding to Cr_2O_5 which appear in the diffractograms obtained for energies lower than 2.8×10^3 kJ/mol CrO_3 show that the transforma-

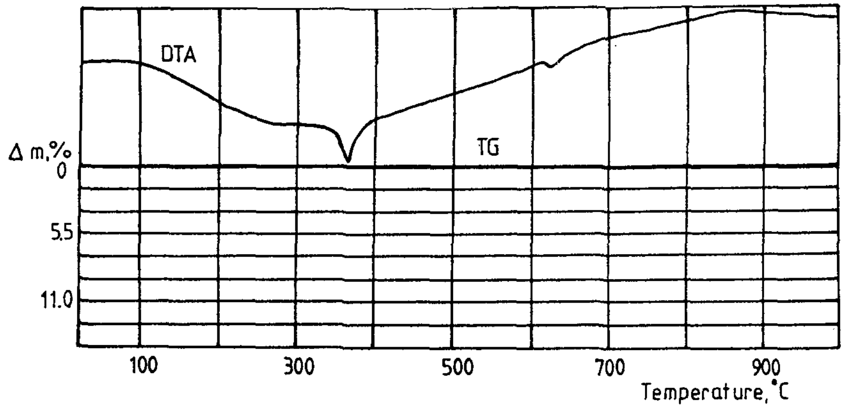


Fig. 14 The DTA and TG curves of a $K_2Cr_2O_7$ sample irradiated with a power of 54×10^3 kJ/mol $K_2Cr_2O_7$ using as standard a Cr_2O_3 sample calcined at 1000°C for 4 h

tion of CrO_3 into Cr_2O_3 occurs according to scheme (1). This statement is confirmed by the absence of Cr_2O_5 lines in the diffractograms of the CrO_3 samples irradiated with energy higher than 2.8×10^3 kJ/mol CrO_3. The derivatogram presented in Fig. 12 shows also that under the given conditions Cr_2O_5 is formed as a decomposition product. Up to 2.8×10^3 kJ/mol CrO_3 almost 32% of Cr_2O_5 is transformed into Cr_2O_3. This amount was also evidenced by the derivatograms. At higher energies Cr_2O_5 was not evidenced by the derivatograms.

Figure 14 shows the derivatogram of the product of the laser induced decomposition of $K_2Cr_2O_7$ irradiated with 54×10^3 kJ/mol $K_2Cr_2O_7$. As shown by the TG curve no change of weight was recorded. The thermoanalytical curves of nonirradiated $K_2Cr_2O_7$ exhibit an exothermic effect at 300°C associated with a weight loss and another endothermic effect at 430°C without weight loss associated with melting [3]. None of these effects is exhibited by the irradiated sample, thus showing that the change has taken place.

The decomposition of $K_2Cr_2O_7$ occurs according to the reaction:

$$2K_2Cr_2O_7(s) \rightarrow Cr_2O_3(s) + 2K_2CrO_4(s) + 3/2O_2(g)$$

As previously shown, for an energy of 9×10^3 kJ/mol $K_2Cr_2O_7$ the decomposition is not complete, unreacted $K_2Cr_2O_7$ being still present. At longer exposure times the transformation is complete, without further weight loss on the TG curves.

It is interesting to notice that at 54×10^3 kJ/mol $K_2Cr_2O_7$ although the molar ratio K_2CrO_4/Cr_2O_3 equals 2/1, the diffraction lines of K_2CrO_4 are not found but only those of Cr_2O_3. At lower energies (9×10^3 kJ/mol $K_2Cr_2O_7$) the diffraction lines of both K_2CrO_4 and Cr_2O_3 were observed.

The endothermic effects exhibited by the irradiated samples of CrO_3 (at 475°C) and $K_2Cr_2O_7$ (at 370°C) are due to the changes induced by CO_2 laser irradiation.

Conclusions

The investigations concerning the transformations of CrO_3 and $K_2Cr_2O_7$ under laser irradiation showed the existence of energetic thresholds for the decomposition. If the systems under investigation are supplied with higher energies, the amount of energy exceeding the threshold is used in order to increase the degree of crystallinity. In such a way the degree of crystallinity can reach even higher values than those obtained through thermal treatment.

References

1 N. Akhmetov, General and Inorganic Chemistry, Mir Publishers, Moscow 1987, p. 564.

2 D. Halliday and R. Resnick, Physics, John Wiley & Sons, Inc., New York, London, Sydney 1966, Part II.
3 Atlas of thermoanalytical curves (TG, DTG, DTA, curves measured simultaneously), Edited by G. Liptay, London, Heyden & Son Ltd., 1971–1974.

Zusammenfassung — Es werden einige Resultate (aus Röntgendiffraktogrammen und thermoanalytischen Kurven) bezüglich der CO_2-laserinduzierten Veränderungen in CrO_3- und $K_2Cr_2O_7$-Pulvern beschrieben.