

DTA AND X-RAY DIFFRACTION INVESTIGATIONS OF LASER-IRRADIATED CeO₂ POWDERS

E. Segal¹, A. Andrei² and V. Pârvulescu²

¹Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, B-dul Republicii 13, Sector 4, Bucuresti 70031, Roumania

²Institute for Nonferrous Metals Industry, B-dul Biruintei 102, Sector 2, Bucuresti 73951, Roumania

(Received July 23, 1992)

Abstract

The TG and DTA curves and diffractograms of powdered CeO₂ samples irradiated with a CO₂ laser beam with powers of 0.41–1.39 kW/cm² are presented. The laser treatment induced structural changes and probably generation of a metastable phase. X-ray diffraction coupled with thermal analysis was used to establish the structural modifications in the irradiated samples after heating.

Keywords: CeO₂ powders, DTA, X-ray

Introduction

IR laser photochemistry has mainly been concerned with the vibrational excitation of molecules [1] and clusters [2], and with the preparation of thin films [3]. The effects of the interaction of laser radiation with inorganic solid materials have been less well investigated.

The aim of this preliminary work was to provide evidence of the changes induced in CeO₂ powder by continuous-wave CO₂ laser radiation.

Experimental

CeO₂ powder was obtained from laboratory-synthesized cerium nitrate of 99.991% purity, by precipitation at *pH* 8.0 with ammonium hydroxide (Merck). After washing, the precipitate was heated at 120°C for 8 h.

The crystalline structure of the resulting and irradiated CeO₂ powder was checked by comparing its X-ray diffractogram with that given in ASTM for the same compound.

The heating curves (TG and DTA) of the CeO_2 powder were recorded with a Q-1500D derivatograph (MOM, Budapest, type Paulik-Paulik) at a heating rate of $10 \text{ deg}\cdot\text{min}^{-1}$. In all experiments, the same mass of powder, $m_p = 550 \text{ mg}$, was used.

The X-ray diffractograms were recorded with the DRON-2 equipment, using $\text{CuK}\alpha$ radiation. Since the samples were obtained under identical conditions, the degree of crystallinity was directly proportional to the X-ray peaks heights.

For laser treatment, GT-1200 CO_2 laser equipment was used. The samples were irradiated at incident beam powers in the range $0.41\text{--}1.39 \text{ kW}/\text{cm}^2$ for exposure times between 7 and 14 s. The laser beam was focussed on a surface area of 39 mm^2 . The thickness of the layer submitted to irradiation was 1.5 mm. The pressure of the gas mixture was 24 torr ($p_{\text{He}} = 13 \text{ torr}$, $p_{\text{N}_2} = 9 \text{ torr}$, $p_{\text{CO}_2} = 2 \text{ torr}$).

Results

Thermal analysis

Figure 1 shows the TG and DTA curves of a non-irradiated CeO_2 powder sample relative to those for a sample of CeO_2 powder calcined at 1000°C (this latter sample was used as an inert material for DTA). Two endothermic effects associated with a loss in mass were observed at 149 and 260°C , as was a strong exothermic effect at 290°C , followed by a weak one at 326°C .

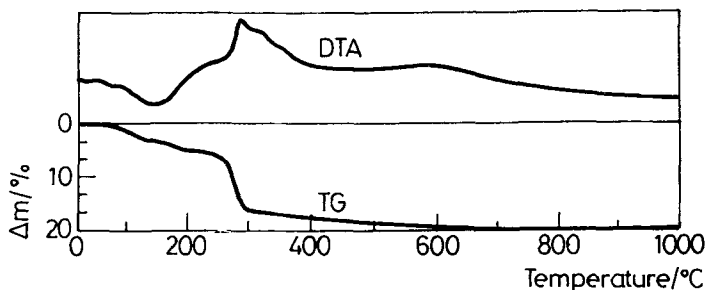


Fig. 1 The TG and DTA curves of a CeO_2 powder sample heated at 120°C for 8 h; as reference, a CeO_2 powder heated for 3 h at 1000°C was used

The thermal curves of CeO_2 samples irradiated at $0.55 \text{ kW}/\text{cm}^2$ or $1 \text{ kW}/\text{cm}^2$ for 7 s are given in Figs 2 and 3. The DTA curves were recorded relative to a CeO_2 sample treated at 120°C for 8 h as inert material. These curves still reveal losses in mass accompanied by an exothermic effect, followed

by the same weak endothermic and exothermic phase changes. The sharpness of these effects decreases with increase of the irradiation powder.

Figures 4–8 depict TG and DTA curves of CeO_2 powders irradiated for 7 s at powers of 0.55, 0.69, 0.83, 1.11 and 1.39 kW/cm^2 . The DTA curves were recorded relative to a sample treated for 3 h at 400°C . Only small mass losses occurred at 0.55 and 0.69 kW/cm^2 . Attention should be drawn to the exotherm exhibited only by the DTA curve at 0.55 kW/cm^2 . At higher irradiation powers, this peak vanishes. High irradiation power generated an exotherm in the range $290\text{--}300^\circ\text{C}$.

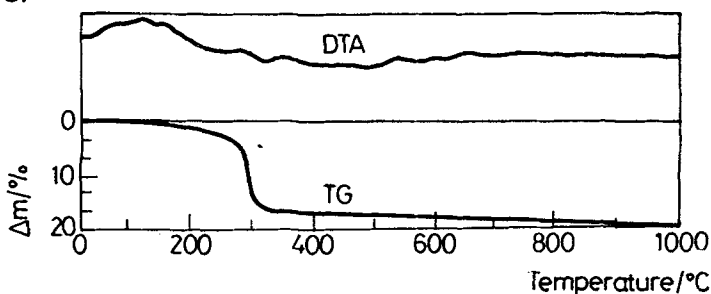


Fig. 2 The TG and DTA curves of a CeO_2 powder sample irradiated with 0.55 kW/cm^2 ; as reference, a CeO_2 powder heated at 120°C for 8 h was used

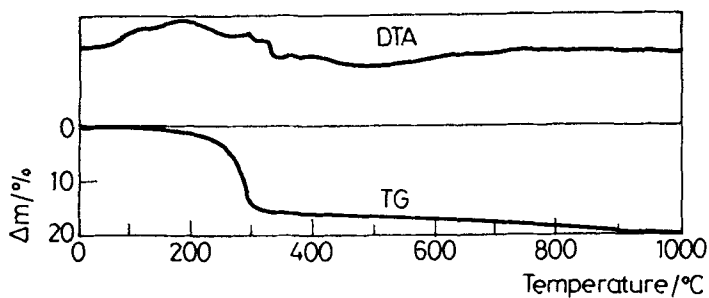


Fig. 3 The TG and DTA curves of a CeO_2 powder sample irradiated with 1.00 kW/cm^2 ; as reference, a CeO_2 powder heated at 120°C for 8 h was used

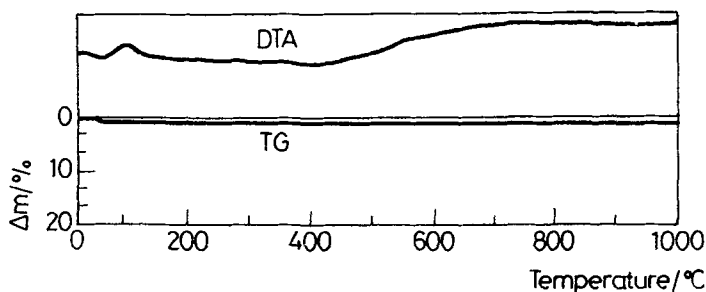


Fig. 4 The TG and DTA curves of a CeO_2 powder sample irradiated with 0.55 kW/cm^2 ; as reference, a CeO_2 powder heated at 400°C for 3 h was used

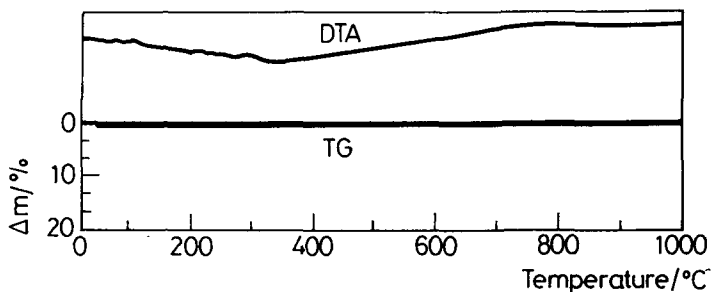


Fig. 5 The TG and DTA curves of a CeO_2 powder sample irradiated with 0.69 kW/cm^2 ; as reference, a CeO_2 powder heated at 400°C for 3 h was used

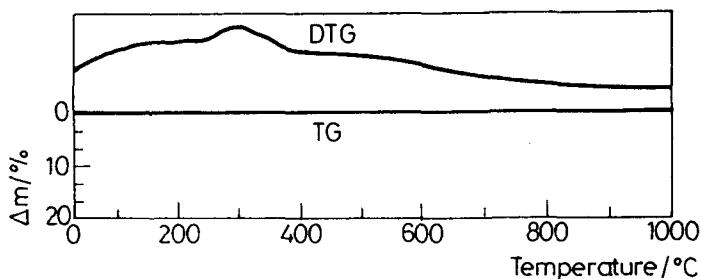


Fig. 6 The TG and DTA curves of a CeO_2 powder sample irradiated with 0.83 kW/cm^2 ; as reference, a CeO_2 powder heated at 400°C for 3 h was used

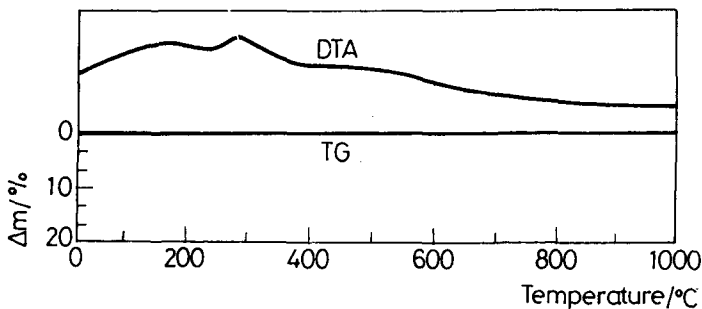


Fig. 7 The TG and DTA curves of a CeO_2 powder sample irradiated with 1.11 kW/cm^2 ; as reference, a CeO_2 powder heated at 400°C for 3 h was used

Figures 9 and 10 show the TG and DTA curves of samples irradiated at 0.41 and 1.11 kW/cm^2 relative to a sample heated at 1000°C for 3 h as inert material. The only significant peak is the exotherm at 298°C (1.11 kW/cm^2). The weak exotherms at 110 and 547°C are observed only at low irradiation power (0.41 kW/cm^2).

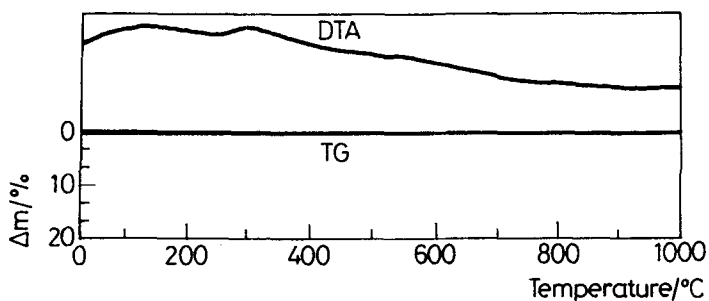


Fig. 8 The TG and DTA curves of a CeO_2 powder sample irradiated with 1.39 kW/cm^2 ; as reference, a CeO_2 powder heated at 400°C for 3 h was used

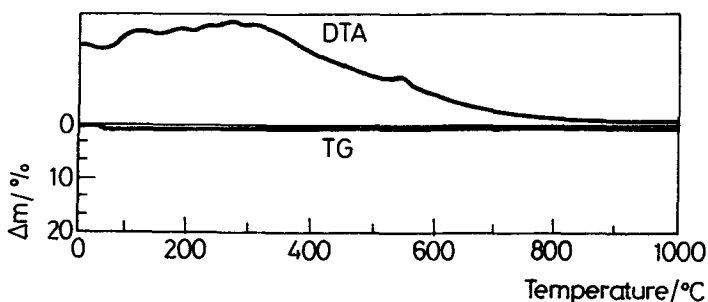


Fig. 9 The TG and DTA curves of a CeO_2 powder sample irradiated with 0.41 kW/cm^2 ; as reference, a CeO_2 powder heated at 1000°C for 3 h was used

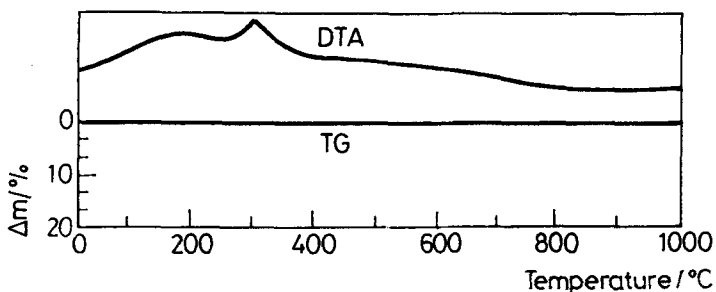


Fig. 10 The TG and DTA curves of a CeO_2 powder sample irradiated with 1.11 kW/cm^2 ; as reference, a CeO_2 powder heated at 1000°C for 3 h was used

X-ray investigations

Figures 11–13 show X-ray powder diffractograms of non-irradiated CeO_2 samples dried at 120°C or calcined at 325 or 1000°C . The diffractograms demonstrate that increase of the temperature of treatment leads to an increase in sample crystallinity.

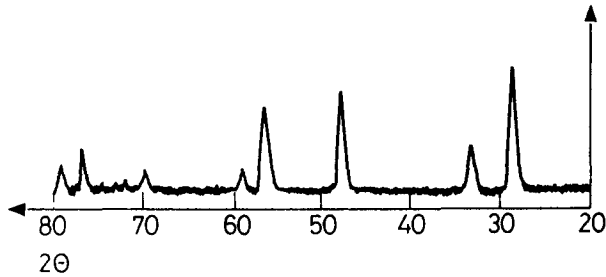


Fig. 11 The diffractogram of a CeO_2 powder sample heated at 120°C for 8 h

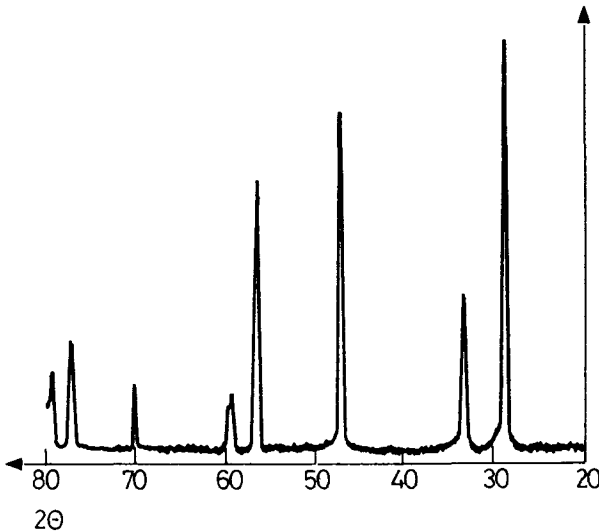


Fig. 12 The diffractogram of a CeO_2 powder sample heated at 325°C for 3 h

The diffractograms in Figs 14 and 15 are those of powdered CeO_2 samples irradiated with laser beam powers of 0.69 or 1.11 kW/cm^2 . Increase of the irradiation power similarly resulted in an increase in crystallinity.

Figures 16 and 17 show diffractograms of samples held for 2 min at 325 or 560°C after irradiation at 0.69 kW/cm^2 .

Comparison with Fig. 14 reveals that thermal treatment at 325°C causes a decrease in crystallinity. No difference is observed between the diffractograms of samples treated at 325 or 560°C .

The same behaviour is exhibited by CeO_2 samples irradiated at 0.83 kW/cm^2 and calcined at 325°C (Fig. 18), or irradiated at 1.39 kW/cm^2 and subsequently calcined at 560°C (Fig. 19).

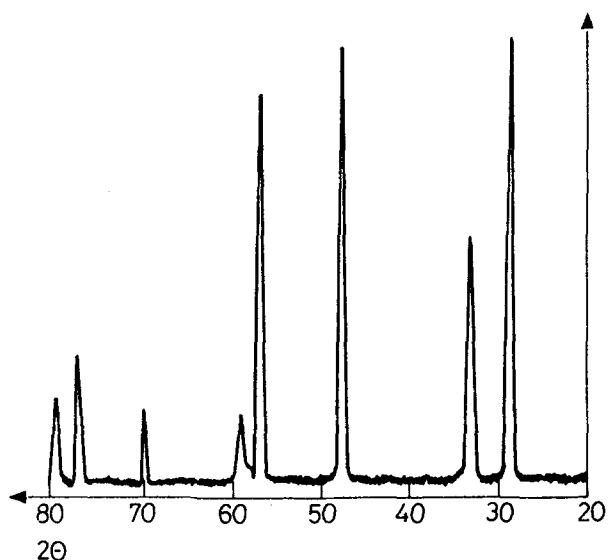


Fig. 13 The diffractogram of a CeO_2 powder sample heated at 1000°C for 3 h

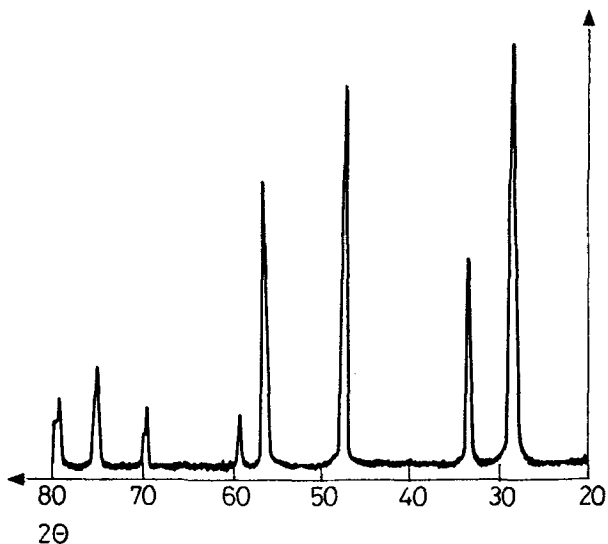


Fig. 14 The diffractogram of a CeO_2 powder sample irradiated with 0.69 kW/cm^2

Increase of the temperature of thermal treatment of the irradiated samples decreased the crystallinity with respect to the samples calcined at 325 or 560°C (Fig. 20).

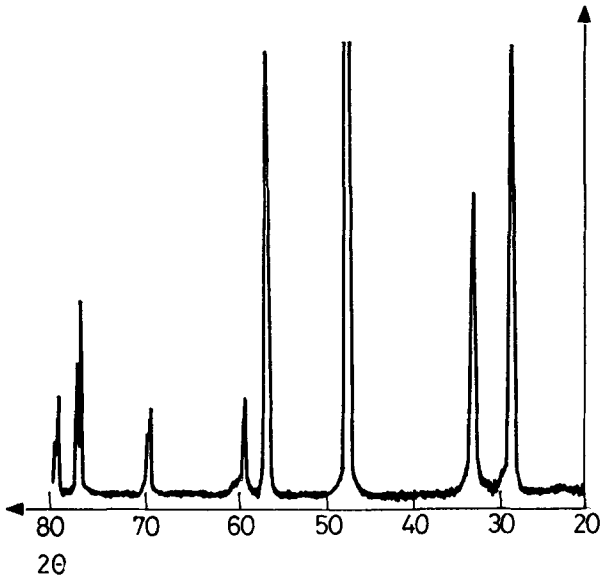


Fig. 15 The diffractogram of a CeO_2 powder sample irradiated with 1.11 kW/cm^2

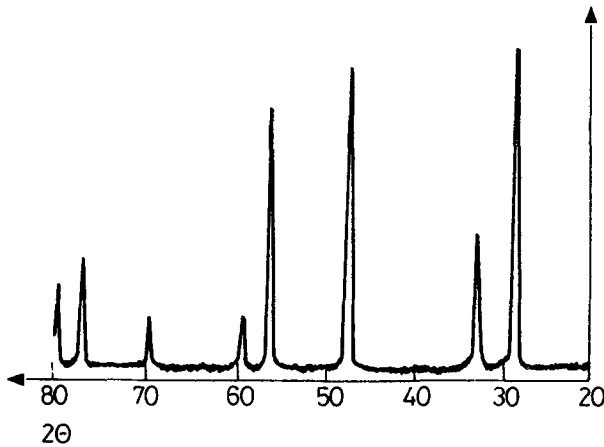


Fig. 16 The diffractogram of a CeO_2 powder sample irradiated with 0.69 kW/cm^2 and then heated for 2 min at 325°C

Discussion

The non-irradiated samples exhibit as main effects endotherms associated with loss in mass at 149 and 260°C and an exotherm at 290°C , probably associated with a structural change (crystallization). This assumption is confirmed

by the X-ray diffractograms, which show a higher degree of crystallization of samples calcined at 325°C relative to those not treated thermally.

In the temperature range 30–300°C, the DTA curves of samples irradiated at 0.55 or 1.00 kW/cm² relative to those of a sample heated at 120°C show a reverse picture with respect to that in Fig. 1, but with a lower intensity due to the irradiation effect.

At low irradiation powers, with samples calcined at 400 or 1000°C, as references a loss in mass was observed at 54°C, followed at 110°C by an exothermic effect associated with a structural change. The loss in mass and the thermal ef-

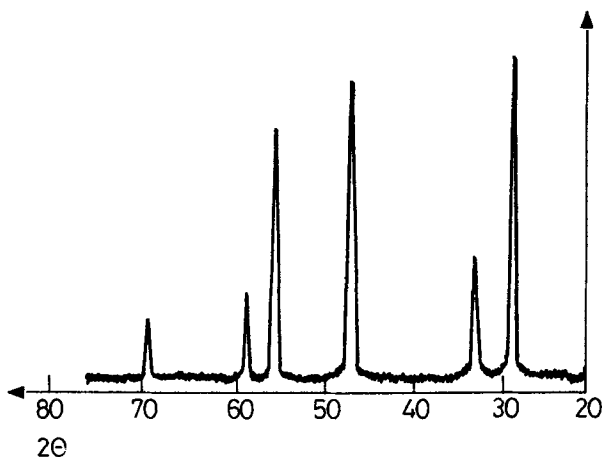


Fig. 17 The diffractogram of a CeO₂ powder sample irradiated with 0.69 kW/cm² and then heated for 2 min at 560°C

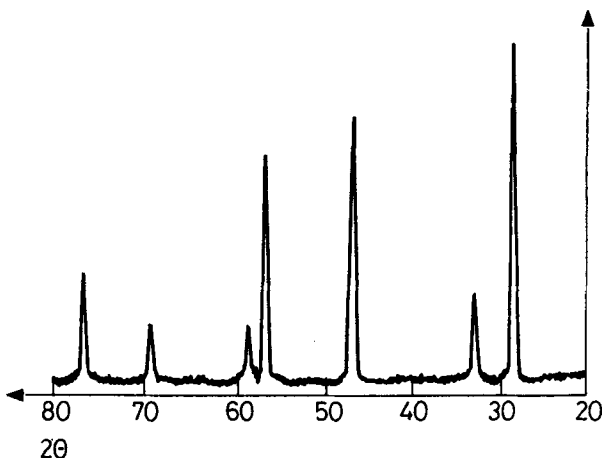


Fig. 18 The diffractogram of a CeO₂ powder sample irradiated with 0.83 kW/cm² and then heated for 2 min at 325°C

facts seem unusual as even the samples submitted to irradiation were kept at 120°C for 8 h. Since these effects were manifested at low irradiation powers (0.55 and 0.69 kW/cm²), they may be assigned to an incomplete laser effect. Increase of the irradiation power eliminated the exothermic effect in the temperature range 540–550°C and intensified the exothermic effect in the temperature range 290–300°C. This effect was weaker relative to that exhibited by the non-irradiated sample.

With CeO₂ powder calcined at 1000°C as reference, the DTA curves more clearly revealed the exothermic effect at 290–300°C. Thus, no matter what the irradiation power, the exothermic effect at 290–300°C exhibits a lower intensity

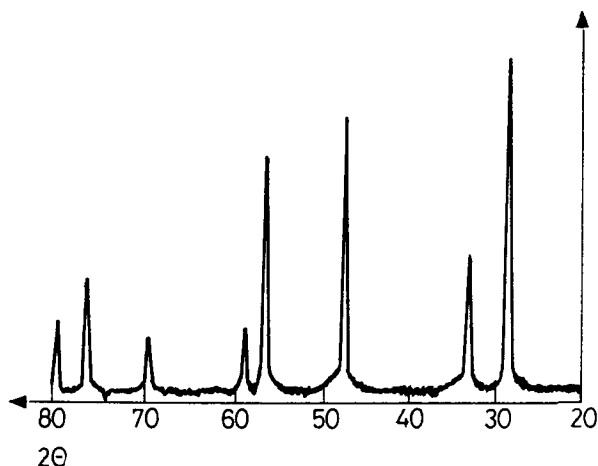


Fig. 19 The diffractogram of a CeO₂ powder heated irradiated with 1.39 kW/cm² and then heated for 2 min at 560°C

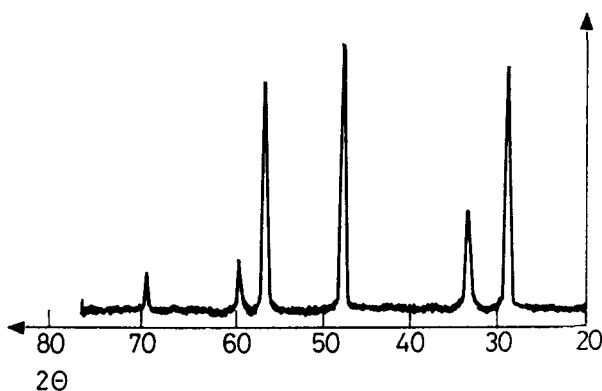


Fig. 20 The diffractogram of a CeO₂ powder heated irradiated with 0.83 kW/cm² and then heated for 2 min at 1000°C

with respect to that for the non-irradiated sample. Increase of the irradiation power resulted in an intensification of this effect.

These findings suggest that the crystallinity of powdered CeO_2 samples decreases with increase of the irradiation power. The differences between the DTA curves with references calcined at 400 or 1000°C are quite insignificant, showing that crystallization is accomplished at round 300°C.

It may be assumed that irradiation is accompanied by the generation of a metastable form, whose content increases with increase of the irradiation power. The X-ray diffractograms confirm this. As shown for samples that were irradiated and then calcined for 2 min, the crystallinity was lower than for samples that were irradiated or calcined at 1000°C. A period of 2 min is high enough only to destroy the metastable form, but not to form the lattice of CeO_2 . The decrease in crystallinity is more significant at higher calcination temperatures.

The only effects induced by irradiation are those at 110 and 550°C, which were obtained only at low irradiation powers. The decrease in their intensity at irradiation powers higher than 0.69 kW/cm² is probably due to the generation of metastable phases.

Conclusions

1. The laser irradiation of CeO_2 samples with powers lower than 0.69 kW/cm² results in structural changes, as shown by weak exothermic effects at 110 and 550°C.

2. Increase of the irradiation power leads to the appearance of an exothermic effect in the temperature range 290–300°C. At higher irradiation powers, a metastable phase is probably generated. This phase is destroyed at high temperatures.

3. Even at low powers, laser irradiation induces a loss in mass similar to that induced by calcination at 325°C.

References

- 1 A. G. Rubalin and K. Bergman, *Ann. Rev. Phys. Chem.*, 41 (1990) 735.
- 2 R. Teghil, A. Giardini-Guidoni and S. Piccirillo, A. Mele and F. Polla-Mattiot, *Appl. Surface Sci.*, 46 (1990) 220.
- 3 M. Shimizu, T. Katayama, Y. Tanako, T. Shiosaki and A. Kawabata, *J. Crystal Growth*, 101 (1990) 177.

Zusammenfassung — Es werden die TG- und DTA-Kurven sowie die Diffraktogramme von CeO_2 -Pulverproben beschrieben, die mittels einem CO_2 -Laser zuvor mit einer Leistung zwischen 0.41 und 1.39 kW/cm² bestrahlt wurden. Diese Laserbehandlung verursachte strukturelle Veränderungen und wahrscheinlich die Bildung einer metastabilen Phase. Zur Ermittlung der strukturellen Veränderung in den bestrahlten Proben wurde nach dem Erhitzen eine Kombination von Röntgendiffraktion und Thermoanalyse eingesetzt.