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Ultraviolet laser irradiation induced chemical reactions of some metal oxides

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The interaction of ultraviolet laser light of wavelength 308 nm and a pulse length of 28 ns with 24 inorganic oxides was studied. The laser fluence was varied between 0.009 and 4 J cm^{-2}. The visible result of the laser impulse could be divided into three categories. A number of oxides, CeO_2, TiO_2, Nb_2O_5, MoO_3 and WO_3, gave intense blue-black marks under irradiation. The oxides V_2O_5, Cr_2O_3, Fe_2O_3, NiO, CuO, CdO and Tl_2O_3 gave dark silver-metallic marks. The third group, consisting of MgO, ZrO_2, Ta_2O_5, ZnO, Al_2O_3, Ga_2O_3, Sb_2O_4, In_2O_3, SnO_2, Y_2O_3, Eu_2O_3 and Sm_2O_3, did not mark or showed a brownish discoloration. The reactions that occurred, especially any darkening, could be correlated with the non-stoichiometric nature of the oxides.

Introduction

Although there has been extensive literature concerning the interaction of laser light with solids from the point of view of ablation or other aspects of physical removal and damage (see *e.g.* refs. 1–3), much less attention has been given to the chemical effects of such irradiation. This is understandable, as ablation is of considerable significance to a wide field of endeavour ranging from opto-electronics to micro-machining and laser surgery. However chemical effects are also important and are an interesting area of study.

A significant survey of attempts to synthesise chemical compounds using CO_2 laser irradiation was given by Möhr and Müller-Buschbaum.[4] This radiation lies in the infrared, and chemical changes were inherently brought about by heating. There is much less information about the use of ultraviolet radiation, although this has the advantage of exciting electrons from the valence band to the conduction band and thus creating chemically active entities without the necessity of using high temperatures. One of the earliest reports to describe chemical aspects of ultraviolet laser irradiation of oxides concerns irradiation of zinc oxide varistors with 248 nm wavelength radiation from a KrF excimer laser.[5] The results suggested that surface reduction of the varistor material was occurring. The darkening of TiO_2, Nb_2O_5 and WO_3 that occurs on ultraviolet irradiation is also attributed to oxygen loss.[6–8] In both of these cases it is believed that reduction of the oxide has occurred, resulting in the production of lower valence cations. The darkening is then the result of charge transfer between Ti^{4+} and Ti^{3+} in TiO_{2-x}, Nb^{5+} and Nb^{4+} or Nb^{2+} in Nb_2O_5 and W^{6+} and W^{5+} or W^{4+} in WO_{3-x}. This charge transfer leads to changes in the absorption spectra, endowing the irradiated materials with a blue-black coloration. More recently there have been reports of the effects of ultraviolet laser irradiation of CeO_2, leading to the formation of members of the homologous series of intermediate oxides and Ce_2O_3.[9,10] The darkening of stabilised ZrO_2 on ultraviolet irradiation has been attributed to the formation of oxygen vacancies in the surface regions.[11] The interaction of ultraviolet laser pulses with indium tin oxide films has been reported to produce colour changes due to defects formed by displaced oxygen atoms in the structure.[12,13] The onset of modification by ultraviolet laser irradiation has been correlated with enthalpy of formation for the small group of oxides TiO_2, V_2O_5, Nb_2O_5 and Ta_2O_5.[14]

However, the reports concerning ultraviolet laser irradiation of oxides are sporadic and refer to a variety of sample preparation conditions and lasers. In this paper, which extends an earlier report,[15] the results of laser irradiation of a number binary oxides is reported. This has allowed a correlation of the more chemical aspects of the irradiation process to be made.

Experimental

Oxides used in these studies were high purity chemicals of "Specpure" quality supplied by Johnson Matthey or Analar quality supplied by BDH.

Samples were prepared by several methods. The standard technique used for most experiments was to grind the powders together in Perspex (polymethyl methacrylate) attrition vials using Perspex ball pestles in a Glen Creston Spex mill for approximately five minutes. The resulting powders were mixed into a slurry with Analar quality butan-1-ol and allowed to flow over a microscope cover slip 2 cm on edge, to form a uniform layer of about 1 mm thickness. To aid the retention of the powder on the glass surface the cover slip was coated with an adhesive prepared as a 2% mass/volume solution of neoprene in toluene. Some additional samples of TiO_2, NiO, Cr_2O_3 and Fe_2O_3 were ground by hand in an agate mortar rather than milled and some powders were formed into pellets before irradiation.

The samples were irradiated with a Lambda Physik LPX 205 xenon chloride excimer laser at a wavelength of 308 nm (equivalent to 4.04 eV) with a pulse length of 28 ns and a variety of fluence values lying between 0.009 J cm^{-2} and 4 J cm^{-2}.

After irradiation specimens were examined optically using Meiji, Vickers Photoplan and Reichert Polyvar microscopes. Surface morphology and texture were studied using a Hitachi S580 scanning electron microscope operated at 30 kV. Additional EDAX analysis was carried out using a JEOL 35CF scanning electron microscope operated at 30 kV. Diffuse reflectance spectra were obtained with a Perkin-Elmer Model 330 spectrophotometer. Reflectance was

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recorded as a percentage of the incident radiation. X-Ray powder diffraction was carried out using a Guinier-Hägg focussing camera and strictly monochromatic CuKα_1 radiation. Transmission electron microscopy was carried out using a JEOL 200CX electron microscope fitted with a double tilt stage and operated at 200 kV with an LaB_6 filament. Samples were dispersed in high purity butan-1-ol and a drop of the resultant suspension was deposited on a conventional grid covered with a holey carbon film.

Some samples were reoxidised by heating in air at temperatures up to 550 °C using Carbolite temperature controlled furnaces.

Results

Although materials were irradiated with fluences up to 4 J cm^{-2}, the results of interest here refer to lower fluence values, which did not cause ablation of the surface. In general, at fluences below 0.08 J cm^{-2} a thin layer of product, or nothing, was seen. In the fluence range 0.5–1 J cm^{-2} sintering of particles, fusion and ablation effects began to be noticed, shown in Fig. 1. Additional increase in the fluence led to increasing ablation of the irradiated area. The exact threshold for these effects depended upon the oxide tested (and probably upon particle size and compaction, although these were not investigated). The periphery of the ablated region resembled the irradiated region at lower fluences. The main effects of the irradiation recorded were the colour of the irradiated area and morphological changes such as melting or sintering. These are summarised in Table 1.

The colour changes observed on irradiation were sometimes rather difficult to describe, as the observations tend to be influenced by the illumination and observation technique used. Nevertheless they provide a useful broad comparison of the materials. A group of oxides gave dark well-defined sharp-edged marks which could be described as blue-grey, blue-black or black, as a function of laser fluence. These were CeO_2, TiO_2, Nb_2O_5, MoO_3 and WO_3. Examples of these marks on CeO_2 and TiO_2 are shown in Fig. 2(a, b). The intensely coloured dark blue-black marks were not coherent or fused at lower fluences and gave the impression that individual grains had coloured without any melting or significant degrees of sintering. At higher fluences, melting and sintering had occurred, allowing the dark mark to be lifted from the surface with a fine probe as can be seen in the case of Nb_2O_5, illustrated in Fig. 2(c).

A second group, illustrated in Fig. 3, gave marks that showed a silver or dark metallic appearance. These oxides were V_2O_5, Cr_2O_3, Fe_2O_3, NiO, CuO, CdO and Tl_2O_3, although the latter three oxides were difficult to characterise because of the colour of the parent oxide. The mark on CdO appeared a brown-orange colour to the eye. However, microscopic examination suggested that the mark was silver metallic but the orange underlayer gave the overall impression of brown-orange. CuO gave silver-metallic looking marks with the addition of a peripheral ring of reddish-brown.

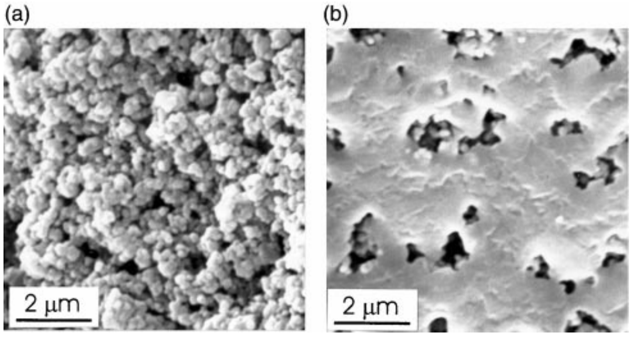

Fig. 1 Scanning electron micrographs of Cr_2O_3 powder (a) before and (b) after irradiation with a fluence of 0.5 J cm^{-2}, showing that extensive sintering and melting has occurred.

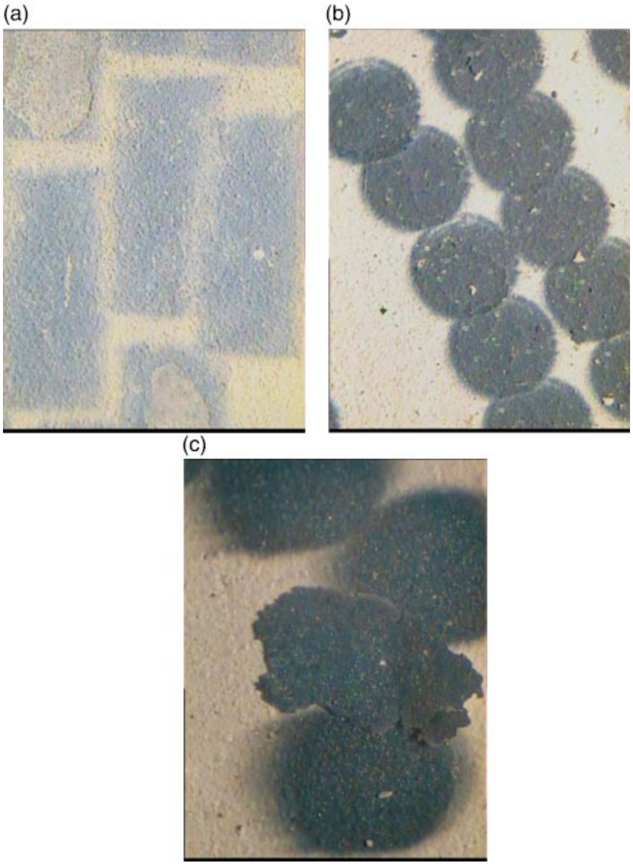

Fig. 2 Optical micrographs of irradiated oxides. (a) CeO_2, fluence 0.5 J cm^{-2}. The marks are approximately 3 mm wide and 6.5 mm high. (b) TiO_2, fluence 1 J cm^{-2}. The marks have a diameter of approximately 1 mm. (c) Nb_2O_5, fluence 1 J cm^{-2}. The central area shows a fused mark that has been lifted away from the substrate powder. The marks have a diameter of approximately 1 mm.

Fig. 3 Optical micrograph of irradiated Cr_2O_3 powder, fluence 0.5 J cm^{-2}, showing a silver-metallic rectangular mark. The mark is approximately 3 mm wide and 7.5 mm high.

The other oxides studied showed either no mark or a brownish discoloration. This group was comprised of MgO, ZrO_2, Ta_2O_5, ZnO, Al_2O_3, Ga_2O_3, Sb_2O_4, In_2O_3, SnO_2, Y_2O_3, Eu_2O_3 and Sm_2O_3. At lower and moderate fluences, ZnO samples showed a rather faint mark immediately after irradiation, but this faded rapidly to leave no obvious alteration in the surface colour. At higher fluences the oxide film was ablated leaving a crater in the powder. No conditions of irradiation led to the production of a metallic mark. The

Table 1 Changes accompanying irradiation at 308 nm, 28 ns pulse length

Oxide	Band gap/eV[a]	Fluence/J cm^{-2}	Colour change	Morphological change
MgO	7.8	0.5	nil	
		1.0	nil	
		2.0	nil	ablation
Y_2O_3	5.5	0.5	nil	
		0.7	nil	
		1.0	nil	ablation
CeO_2	3.4	0.5	blue-grey	some crystallisation; sintered surface
Eu_2O_3	4.5	0.4	nil	ablation
Sm_2O_3	5.0	0–1.0	nil	
TiO_2	3.1	0.08	nil	no sintering/melting
		0.5	blue-grey	sintering/melting
		1.0	dark blue-grey	melted/detached from surface
		2.0	blue-black	ablation
ZrO_2	4.5	0.5	faint grey-brown	some sintering
V_2O_5		0.5	dark silver-grey metallic, shining	melted/detached from surface
Nb_2O_5	3.3	0.5	dark blue-black	melting
		1.0	dark blue-black	melting
Ta_2O_5	3.9	0.07	faint grey-brown	
		0.5	brown	
		1.0	golden-brown	melting/detached from surface
Cr_2O_3	3.0	0.07	very faint silver metallic	no melting
		0.5	silver metallic	small particles have melted; larger particles are sintered
		1.0	silver metallic periphery	melting/ablation
MoO_3		0.5	blue-black	sintering/fusion
WO_3	2.4	0.5	blue-green	nil
		1.0	dark blue-black	sintering/melting
Fe_2O_3	2.2	0.08	faint darkening	some sintering and partial melting
		0.5	dark metallic	melting
		1.0	dark metallic periphery	melting/ablation
		2.0	dark metallic periphery	ablation
NiO	4.3	0.07	very faint brown-silver	melting
		0.5	silver metallic	no melting
		1.0	silver metallic	melting
CuO	1.4	0.08	silver metallic, reddish periphery	
		0.5	silver metallic, reddish periphery	melting
		1.0	silver metallic, reddish periphery	ablation/melting
		2.0	silver metallic, reddish periphery	ablation/melting
ZnO	3.2	0.009	nil	
		1.0	nil	ablation
CdO	2.5	0.5	silver-brown, faint orange periphery	melting
Al_2O_3	9.0	0.5	nil	
		1.0	nil	
		2.0	nil	ablation
Ga_2O_3	4.4	0.7	faint brown	ablation
In_2O_3	3.1	0.5	grey-brown	some sintering of small particles
Tl_2O_3		0.5	brown/golden flecks	
SnO_2	3.6	0.5	faint brown discoloration	
Sb_2O_4	1.6	0.5	nil	ablation

[a]Band gap values in the literature vary widely. The values given are representative. 1 eV = 1.60219×10^{-19} J.

lanthanide oxides Sm_2O_3 and Eu_2O_3, and Y_2O_3 were similar to ZnO.

Optical microscopic examination of several marks gave a value of approximately 20 μm for the mark depth.

Several simple chemical and physical tests were carried out on the marks to obtain further information. To determine if the silver metallic marks were actually metal, dissolution in mineral acids was studied. A filter paper was saturated with either hydrochloric or nitric acid and the marks lifted from the irradiated powder and placed on the paper. Subsequent reaction was observed in a binocular microscope. The only marks to show any reaction were those on CuO, CdO and V_2O_5. All other marks, including the very metallic-looking marks on Cr_2O_3, Fe_2O_3 and NiO, did not react. The silver marks were also checked for ferromagnetic behaviour with an $SmCo_6$ permanent magnet. Only those on Fe_2O_3 were strongly ferromagnetic, so much so that irradiated pellets could be picked up. The other two marks did not show this behaviour.

All irradiated samples were heated in air to determine the stability of the mark produced by irradiation. It was found that heating at 500 °C for 2 hours was sufficient to remove any mark from TiO_2, ZrO_2, Nb_2O_5, Ta_2O_5, CeO_2, MoO_3, WO_3, In_2O_3 and CdO and to remove the reddish coloration from CuO, although the silver-metallic mark persisted at this temperature. Heating at 500 °C for 4 hours removed most of the mark from V_2O_5 but some blackish traces remained. After 5.5 hours at 500 °C the silver-metallic marks were obliterated from Fe_2O_3, CuO and NiO. The silver-metallic mark on Cr_2O_3 still persisted after 7.5 hours at 500 °C.

Powder X-ray diffraction of a number of samples, even using a Guinier-Hägg focussing camera which is particularly sensitive to small amounts of low symmetry material, gave no firm proof of the presence of new phases. In the case of Fe_2O_3, the darkened irradiated material could be separated magnetically and examined by X-ray diffraction. Only the pattern of hematite was recorded. Transmission electron microscopy was limited to the irradiated Fe_2O_3 material as this could be separated magnetically from the un-irradiated powder. None of the crystallites examined could be differentiated from un-irradiated Fe_2O_3 despite the colour change observed.

In order to quantify the colour changes noted, diffuse reflection spectra of all samples before and after irradiation were recorded. Broadly speaking the results fell into four

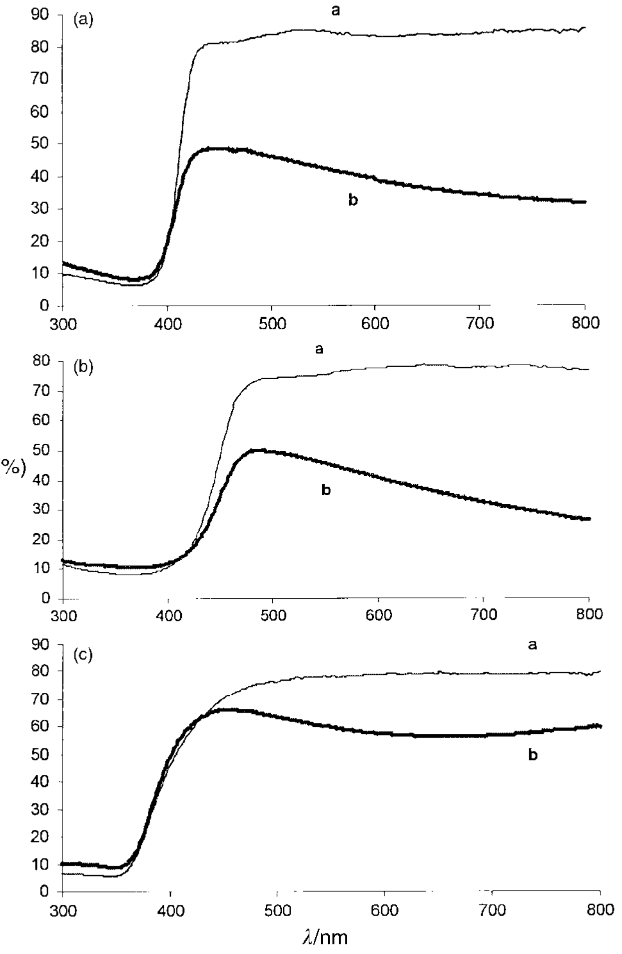

Fig. 4 Reflectance spectra of (a) TiO_2, (b) WO_3 and (c) CeO_2. On each graph, (a) refers to the powder before irradiation and (b) after irradiation. The ordinate of each graph shows the percentage of incident radiation reflected by the powder and the abscissa shows the wavelength of the incident radiation.

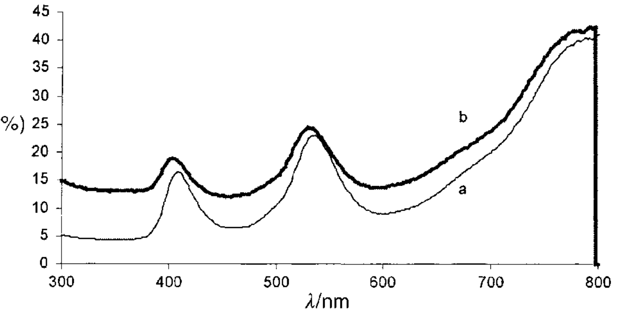

Fig. 5 Reflectance spectra of Cr_2O_3 powder before, (a), and after, (b), irradiation. The reflectance is higher after irradiation. The axes are the same as in Fig. 4.

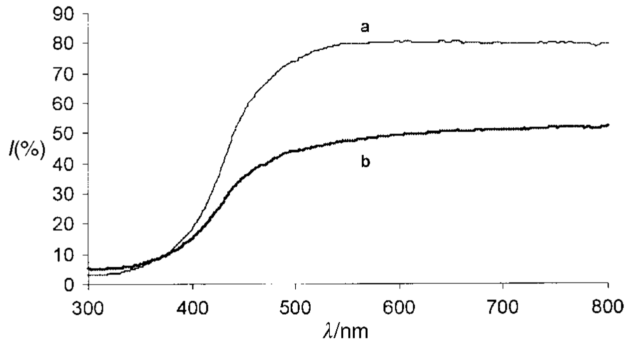

Fig. 6 Reflectance spectra of In_2O_3 powder before, (a), and after, (b), irradiation. The reflectance is lower after irradiation and blue light is reflected slightly less than red light, to give the mark a brownish appearance. The axes are the same as in Fig. 4.

groups. The oxides that showed an intense blue-black mark, CeO_2, TiO_2, Nb_2O_5, MoO_3 and WO_3, gave a much lower reflectivity after irradiation with a peak in the blue region of the visible spectrum. This peak was least noticeable in the cases of CeO_2 and Nb_2O_5. To illustrate this, spectra of TiO_2, WO_3 and CeO_2 before and after irradiation are shown in Fig. 4. These are in agreement with previously published spectra of CeO_2,[10] TiO_2,[7] and WO_3.[8,16,17] The spectra of the oxides NiO, Cr_2O_3, CuO and CdO after irradiation showed little change from the spectra recorded before irradiation, although the reflectance after irradiation was higher than that of the un-irradiated material, as can be seen from Fig. 5, the reflectance spectra of Cr_2O_3 before and after irradiation. This agrees with the silver-metallic visual appearance of the marks. For the oxides Ta_2O_5, SnO_2, ZrO_2 and In_2O_3 there was a drop in the reflectance after irradiation. This was not even across all of the visible spectrum, leading to the brownish coloration observed, as illustrated by the spectra of In_2O_3 in Fig. 6. Finally, the two oxides V_2O_5 and Fe_2O_3, which showed a high reflectance in the red region of the spectrum before irradiation, lost this high reflectance, as seen in Fig. 7, which accounts for the dark appearance of the irradiated areas.

Discussion

Although it is important to remember that the creation of chemically important electrons and holes is probably the initial reaction following ultraviolet pulse absorption it is generally presumed that the most important effects taking place in irradiated materials are thermal in origin. The picture presented by the results is in agreement with this suggestion and shows a coherent pattern. At higher fluences, sometimes as low as 500 mJ cm^{-2} and always at fluences of 2 or 4 J cm^{-2}, surface damage is obvious and the centre of the irradiated region had been ablated. This aspect of the results will not be taken further here. At lower fluences, some oxides showed noticeable dark marks and some a paler brownish discoloration. However, the majority of the materials seemed to be largely unchanged.

It is convenient to divide the oxides studied into three groups. The first of these, which showed no change in appearance after irradiation or else discoloured slightly, includes MgO, (ZrO_2), (Ta_2O_5), ZnO, Al_2O_3, (Ga_2O_3), Sb_2O_4, (In_2O_3), (SnO_2), Y_2O_3, Eu_2O_3 and Sm_2O_3. The oxides which became discoloured, adopting mainly a grey-yellow-brown tint, are enclosed in parentheses. The second group of oxides, (V_2O_5), Cr_2O_3, (Fe_2O_3), NiO, (CuO), (CdO) and

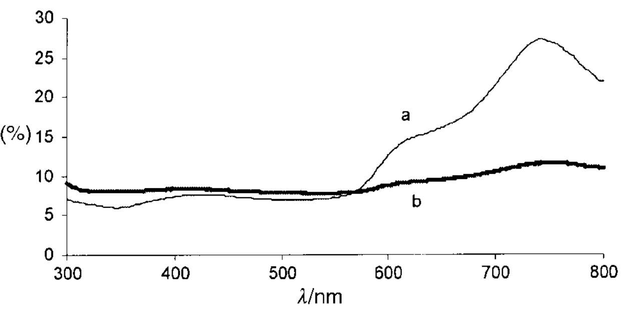

Fig. 7 Reflectance spectrum of Fe_2O_3 powder before, (a), and after, (b), irradiation. The reflectance is much lower in the red region after irradiation and somewhat higher in the blue region after irradiation, which contributes to the silver-dark colour of the marks. The axes are the same as in Fig. 4.

(Tl_2O_3) yielded a silver-grey metallic surface mark, although the oxides in parentheses were difficult to characterise because of the colour of the parent oxide. The third group of oxides become dark blue-black. The oxides in this group are CeO_2, TiO_2, Nb_2O_5, MoO_3 and WO_3.

All of the observations can be rationalised by assuming that the laser irradiation results in the formation of oxygen vacancies and relating the chemical aspects of this process to the non-stoichiometric behaviour of the parent oxide. The simplest group to consider are those oxides similar to TiO_2 that go dark on irradiation. These are all well known for having complex lower "non-stoichiometric" oxides very close in composition to the parent oxide and all of a dark blue-black colour. Even very small amounts of oxygen loss are well able to colour these materials blue-black. For example, single crystals of reduced rutile with compositions of the order of $TiO_{1.99}$ and reduced WO_3 of composition of $WO_{2.9999}$ are quite black and shiny in appearance.[18,19] The blackening occurs even when the crystals do not melt and it appears that the radiation has induced the formation of sub-stoichiometric crystallographic-shear phases.[20]

The actual degree of reduction in this group of oxides is difficult to estimate without surface and depth profile analytical techniques. However we note that the crystals do not lose their habit at low fluences and reduction of both MoO_3 and WO_3 to compositions of the order of $MO_{2.85}$ (M represents Mo or W) results in the formation of needles or whiskers. It is true that reduced crystals may remain pseudomorphic, but careful examination, both optically and *via* scanning electron microscopy, did not reveal any needle or whisker formation and thus composition changes are assumed to be relatively slight.

The largest group of oxides showed no significant reaction. This is in accord with the fact that none of these oxides displays any significant degree of non-stoichiometry. The brownish discoloration noted for many of these oxides is believed to be due to the formation of small numbers of defects on the oxygen sublattice. These introduce new localised energy levels into the band gap of these wide band-gap materials, capable of absorption of radiation usually towards the blue end of the spectrum, resulting in a yellowish-brown cast to the sample. For example, Al_2O_3 irradiated at high fluences can take on a colour varying from yellow to dark tan.[21] This coloration has been attributed to the formation of F-centres.[2] Similarly the slight brownish coloration of ZrO_2 has been attributed to the presence of oxygen vacancies formed by irradiation.[11,22] The coloration induced in indium tin oxide has similarly been attributed to oxygen defects.[12,13] These results suggest that the coloration in the other oxides in this group of wide band-gap materials is also due to the formation of similar defects.

The third group of oxides gave a dark mark that showed a silver metallic appearance. The metal oxides Cr_2O_3, NiO and CdO are not considered to accommodate significant levels of oxygen non-stoichiometry and so any oxygen loss would be considered to give rise to a metallic surface film of Cd, Cr or Ni. However, we consider this to be unlikely. The films did not behave as metals when treated with mineral acids and in the case of NiO no magnetic effects were detected although Ni is one of the few ferromagnetic metals. Moreover, in investigations of ZnO varistors, a similar silvery mark was shown to be a metal-rich ZnO layer and not the metal itself.[5] [Note that in the present study, high purity ZnO never showed a similar metallic film and dopants in the varistors may be involved in the formation of the silvery layer.] The failure of these metal-like marks to dissolve in acids supports the view that they were metal-rich films.

It is believed that Fe_2O_3, Tl_2O_3 and CuO follow similar patterns. All systems contain lower oxides, but the stability of these is limited. In the case of iron, Fe_3O_4 is black and crystals can show a metallic lustre. The fact that the product of irradiation is strongly ferromagnetic lends support to the possible formation of a surface layer of Fe_3O_4. However, neither X-ray diffraction, diffuse reflection spectroscopy or transmission electron microscopy showed evidence for the formation of this spinel phase. It is possible that a slightly reduced form of hematite has been produced which is strongly ferromagnetic. It should be mentioned that there are several records of the production of unexpected metastable phases in the literature. These have been found even by irradiation of the extremely stable α-Al_2O_3. Both γ-Al_2O_3[23] and amorphous material[24] have been identified, and a number of other unidentified phases have been recorded. Surface structural analysis is needed to take this further.

If it is assumed that oxygen vacancies are the primary product of irradiation it is possible to make an estimate of the thickness of the reduced layer. The steps in the analysis are these. All incident radiation is assumed to be converted into electrons and holes, which are in turn converted into oxygen vacancies. A knowledge of the incident energy then allows the number of oxygen vacancies to be calculated and hence the mark thickness to be found. An example is given in the Appendix. Values of the order of 30–40 μm are found for mark thickness. Considering the many approximations made, these values are in good accord with the experimental measurements and provide support for the suspicion that the formation of oxygen vacancies is an important part of the irradiation process.

The present study correlates the visual appearance of an oxide after irradiation with ultraviolet radiation with the degree of non-stoichiometry supported by the parent phase. It seems that the actual degree of reduction is very small. It is clear that more precise study of the surface phases formed after irradiation would be of considerable interest.

Acknowledgements

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Appendix

Estimation of mark thickness

Consider WO_3 as typical. The absorption spectrum, Fig. 4(b), indicates that almost all incident radiation at the laser emission of wavelength 308 nm (3.75 eV) is absorbed. Assume that this initially produces holes and electrons and to allow for any losses suppose that the production of one electron–hole pair requires 4.0 eV. Converting this to joules, $4 \times 1.60219 \times 10^{-19}$ J per electron–hole pair are required. At a typical fluence of 1 J cm^{-2}, 1.56×10^{20} electron–hole pairs are created per cm^2 of surface. Each oxygen ion requires two holes to convert it to an atom that is able to leave the crystal and leave behind an oxygen vacancy. (The two corresponding electrons will localise upon W^{6+} ions to form an equal number of W^{4+} ions in the structure.) Thus a total of $(1.56 \times 10^{20})/2$, that is, 7.8×10^{19}, oxygen vacancies can form.

Each unit cell of WO_3 contains 1 oxygen ion. Thus the number of unit cells that become reduced is 7.8×10^{19}. The area irradiated, 1 cm^2, contains approximately 6.9×10^{14} unit cells (taking the unit cell of WO_3 as cubic with a lattice parameter of 0.38 nm). Thus the volume of reduced material is given by $6.9 \times 10^{14} \times d$ where d is the depth of the reduced volume in unit cells. Equating these two values, $6.9 \times 10^{14} \times d = 7.8 \times 10^{19}$ and d is given by 1×10^5 unit cells. As the unit cell edge is approximately 0.38 nm, the depth of the marked region is approximately $1.5 \times 10^5 \times 0.38$ nm, that is, 43 μm.

Similar values are found for other oxides.

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