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Ultra-fast dehydration and reduction of iron oxides by infrared pulsed radiation

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Abstract

Laser irradiation of iron oxides (goethite and hematite) is studied in order to understand their interaction with short duration pulses. Results have shown that Nd:YAG laser provides enough energy to induce fast chemical transformation of goethite and hematite.

Keywords: Nd:YAG laser; Iron oxide; Amorphous materials; X-ray diffraction

1. Introduction

The understanding of laser interaction with many compounds used as pigments (in most cases oxides) is of central importance to the laser cleaning of artworks and artifacts having cultural and historical relevance [1–7]. A Q-switched laser equipment can deliver pulses of high energy that can promote a great variety of structural and state changes. These changes are related to the great amount of energy transferred to materials as thermal and mechanical energy (shock waves). The purpose of this work is to present and discuss results issued from laser-induced changes in previous structures of two iron oxides extensively used as pigments: goethite and hematite. Experiments were performed with a Nd:YAG laser operating in its fundamental mode (1064 nm). We have studied the irradiation of iron oxides (goethite and hematite) under specific laser treatment conditions (fluence, frequency, etc.) in order to understand their interaction with short duration laser pulses (4 ns). Very fast dehydration and reduction processes were observed simultaneously to amorphous compounds formation.

After laser irradiation, samples were analysed by XRD (X-ray diffractometry) in order to verify structural changes. Visual and optical microscopical observations revealed changes in color, specifically a darkening of the original powder particles.

Analysis of XRD patterns taken before and after irradiation confirm the reduction of goethite into hematite and of the hematite into magnetite. The darkening of the particles is due to this chemical modification.

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2. Experimental details

During the last few years many research groups have employed lasers to solve cleaning problems carrying out experiments to test supports, different soiling layers and to deal with several related challenges, i.e., darkening of treated surfaces [1–7]. Observed chromatic variations are associated with eventual changes due to laser interaction with pigments. This discoloration phenomenon was well investigated by Sansonetti and Realini [1] for six different pigments often employed in the art field.

In our work, powders of goethite (FeOOH) and hematite (Fe_2O_3) were prepared by mechanical milling accordingly to conventional laboratory procedures. Samples were then submitted to irradiation under confined pulses of Nd:YAG laser at 1064 nm, 10 Hz and 4 ns pulse duration. The energy of each pulse was around 300 mJ. Adequate confinement of laser pulses produces high pressure front waves that, depending on the values attained,

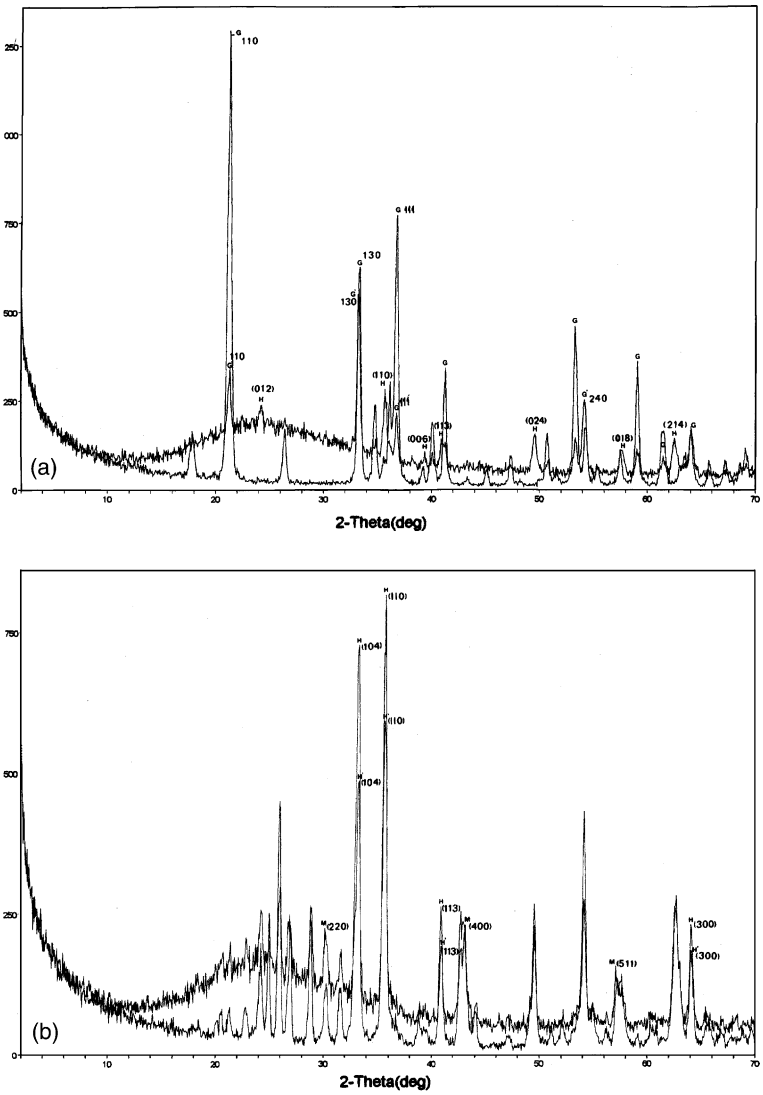

Fig. 1. XRD spectra of non-irradiated and irradiated samples: (a) goethite; (b) hematite.

promote particle milling, modify the surface microstructure and improve mechanical properties [8–11]. According to Peyre et al. [8] confinement can allow pressure levels up to 6 GPa in the 0–10 GW/cm^2 power density range. Such pressure levels are capable of promoting structural and particle size changes in a very short time interval, by compressive stress fields. Depending on the experimental conditions, the changes correspond to a long-range scale deformation, causing the formation of amorphous phases [9,10]. To obtain greater shock-wave intensities, an overlay transparent to 1064 nm is used, to confine the plasma volume expansion to the target material and overlay. The spot size touching the sample was 6.8 ± 0.3 mm in diameter and implies an energy density of 8.3 ± 0.7 mJ/mm^2. The spot diameter being greater than the target thickness guarantees a planar shock-wave propagation. Irradiation was done in air, at room temperature and 65% relative humidity. XRD patterns of powders were taken with a Rigaku diffractometer operating at 40 kV, delivering CuK$\alpha = 1.544$ Å.

3. Results and discussion

XRD patterns, Fig. 1(a) and (b) show that chemical modifications were induced by laser treatment. Under such conditions and taking into account that laser pulses transfer heat into the powder, dehydration seems possible.

Before laser irradiation, the peaks of hydrated iron oxide ($Fe_2O_3 \cdot H_2O$) or FeOOH, goethite, are dominant in the spectrum. In contrast, after laser irradiation, although the goethite peaks remain in the XRD patterns, they are less pronounced. At the same time the formation of new peaks, due to the mineral hematite, becomes evident. These facts strongly suggest that the powder composition changes from FeOOH to Fe_2O_3 by releasing one molecule of water (dehydration). The mechanism of this reaction involves breaking of chemical bonds. Instantaneous browning of particles is evidence of the dehydration of goethite transforming it to hematite.

Table 1 gives the main crystallographic parameters obtained from the XRD experiments. These experiments also show the presence of amorphous materials—see the spectra at Fig. 1(a) and (b). The modulation of the post-irradiated spectra indicates the loss of long-range ordering of the previous crystalline structures. Non-crystallised material was obtained as a result of the interaction of laser pulses with previous crystals of goethite and hematite. This phenomenon suggests fast quenching of non-organised material generated during

Table 1
Main XRD parameters of identified phases in iron oxides before and after (italic) laser irradiation

Summit peak location (2θ)	Int. (%)	Phase	*hkl*
21,292	100	Goethite	110
21,338	*38.4*	*Goethite*	*110*
24,294	*11.1*	*Hematite*	*012*
33,291	*100*	*Goethite*	*130*
33,322	47.7	Goethite	130
35,704	*39.1*	*Hematite*	*110*
36,152	21.0	Goethite	040
36,754	59.4	Goethite	111
36,789	*26.2*	*Goethite*	*111*
39,394	*9.4*	*Hematite*	*006*
40,914	*16.6*	*Hematite*	*113*
41,269	26.1	Goethite	140
49,596	*23.4*	*Hematite*	*024*
53,342	35.1	Goethite	221
54,199	*39.7*	*Goethite*	*240*
57,648	*14.6*	*Hematite*	*018*
59,109	27.4	Goethite	151
61,495	11.8	Goethite	002
62,542	*18.3*	*Hematite*	*214*
64,038	11.8	Goethite	061
64,053	*27.3*	*Hematite*	*300*
24,227	18.2	Hematite	012
30,159	*27.5*	*Magnetite*	220
33,205	90.2	Hematite	104
33,292	*76.9*	*Hematite*	104
35,653	*100.0*	*Hematite*	110
35,667	100.0	Hematite	110
40,912	31.3	Hematite	113
40,951	*25.5*	*Hematite*	113
43,143	*32.9*	*Magnetite*	400
49,540	32.2	Hematite	024
54,151	49.5	Hematite	116
57,105	*19.9*	*Magnetite*	511
57,252	14.0	Hematite	122
57,603	15.7	Hematite	018
62,604	*40.4*	*Magnetite*	440
64,060	*25.5*	*Hematite*	300
64,089	27.3	Hematite	300

irradiation. The characteristic modulation observed in the post-irradiation spectra—an amorphous signature—is typically of non-crystallised material. Remaining peaks of crystallised powder is evidence of partial transformation.

As said before, in the case of the transformation of goethite to hematite, one can suppose a thermal process involving release of molecules of water from the previous structure. On the other hand, in the case of hematite to magnetite, structural changes point to a reduction of the previous species (Fe_2O_3) instead of the oxidation conditions surrounding the particles powder (air). If reduction was confirmed, we have to admit that during interaction, a localised reducing environment was created around the particles. This seems possible if we consider that the interaction zone, due to plasma formation, prevented the powder–air interaction. In other words this corresponds to admit that laser pulses can act as localised explosions that expand the air creating a free oxygen localised environment. Shock waves generated from this plasma volume expansion, coupled with high temperatures, alter the microstructure of the irradiated sample.

This phenomenon, supports the formation of a dense plasma above the interaction region, which causes a local shortage of oxygen and prevents oxidation. Under such intense heating-pressure levels, and with no oxygen diffusion to the powder particles, decomposition of Fe_2O_3 converting it to Fe_3O_4 is acceptable if oxygen–iron bonds are broken by photolysis.

In both cases, darkening of the powder has been observed simultaneously with pulses interaction: browning in the case of goethite dehydration and blackening for hematite reduction.

4. Conclusions

Ultra-fast dehydration of goethite is possible if large amounts of energy are delivered into powder particles in a very short period of time. Nd:YAG Q-switched laser, operating in its fundamental mode, provides these conditions. Goethite is converted to hematite as a consequence of dehydration.

Nd:YAG Q-switched laser also provides enough energy in a very short time, creating conditions for ultra-fast chemical decomposition of hematite. In this case the previous oxide is reduced to magnetite. This phenomenon only depends on breaking of chemical bonds releasing oxygen atoms.

A short duration reduction environment is created above iron oxide particles submitted to a dense plasma generated by laser pulses allowing the hematite to be reduced rapidly, in air.

In both cases—dehydration of goethite and reduction of hematite—amorphous material was detected by XRD. The loss of long-range ordering of iron oxides resulting in amorphous material could be attributed to the role played by shock waves coupled with high temperatures due to laser pulses.

Nd:YAG infra-red laser pulses cannot be recommended as a cleaning tool of artworks if iron oxides are present as pigments because of the irreversible transformations they can promote.

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