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Luminescence and ESCA analysis of laser-ablated materials

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An investigation on laser-induced luminescence of simple solid oxides, their mixtures and other compounds is reported. Both a pulsed TEA CO_2 and a frequency-doubled Nd:YAG laser have been used. The luminous plume produced under the laser action by these compounds has been analyzed by an optical multichannel analyzer. The emission spectra show the presence of atomic, diatomic and more complex species. The ablated material was deposited on gold and $SrTiO_3$ substrates and analyzed by the ESCA technique.

1. Introduction

Large efforts have been made in the last few years to produce thin films of ceramic oxides and carbides for technological applications, ranging from optics and microelectronics to superconductivity [1]. Laser ablation of solid materials is quite a new method in the preparation of films and is considered a very promising technique [2]. The study of the evaporation process and of the chemical reactivity of the ablated species, ions and neutrals, is important in understanding fundamental aspects of the chemistry and physics of deposition [3]. This work presents the irradiation effects and the analysis of composite solid targets made from mixtures of simple oxides and carbides. The results will be discussed in relation to previous studies on laser cluster ion formation of these materials and on their chemical reactivity.

2. Experimental

The ablative photodecomposition of SiC, $BaCO_3$, CuO and Y_2O_3 powders, either pure or mixed with graphite, and of YBCO has been performed both with a pulsed TEA CO_2 laser operating on the 10P20 line, and with a frequency-doubled Nd:YAG laser. The experimental procedures and apparatus have been described in detail before [4]. The samples pressed into pellets are mounted on a blind flange in a stainless steel vacuum chamber equipped with three optical windows, so that the laser ablation occurs at about normal incidence. The visible irradiation is accomplished using a beam energy of about 10 mJ and a laser pulse with a duration of 14 ns, with the laser focussed down to a 1 mm diameter spot. The irradiation by CO_2 laser has been performed using a laser pulse with an energy of 300 mJ focussed to

a 2 mm diameter spot. The peak pulse duration is $\tau \simeq 90$ ns followed by a tail of $\simeq 1$ μs. Both lasers were operated at 1 Hz repetition rate.

The ablated material originates a luminous plume of $\simeq 1$ cm height whose emission has been collected at right angles, focussed by a glass lens on the entrance slit of a 32 cm monochromator placed in front of an optical multichannel analyser detector (OMA III EG&G). The OMA system was operated either with 12 ms exposure time, called CW, or gated by a pulse generator with typical gate widths of 1 μs. At zero delay ($\tau = 0$), the luminescence is collected in the last 200 ns of the gate. A delay of 1 μs monitors the next 1 μs for the luminescence. The ablated material emerging from the target at large angles with respect to the target normal (about 45° and 90°) was intercepted by gold or $SrTiO_3$ substrates at a distance of 1 and 2 cm, respectively.

The XPS spectra of the deposited films were collected by a commercial Leybold LHX1 spectrometer and excited by Al Kα radiation operated at 13 kV and 20 mA. The FRR mode was used for wide scans ($R = 10$) while the FAT mode was always used for detailed spectra with a pass energy of 50 eV and 0.1 eV channel width. Data acquisition and analysis was performed by using an in-house program [5]. All the XPS figures are not corrected for eventual surface charging.

3. Results and discussion

3.1. Silicon carbide

Two different SiC pellets have been examined, one formed by ultrafine powders produced by an LCVD process in a mixture of SiH_4/C_2H_2 [6] and another one prepared by an industrial method by ENI Ricerche (pelletization of a mixture of silicon and carbon suspended in methanol).

The emission spectra of the plume obtained by irradiation of both pellets at 532 nm are identical within the reproducibility limits of our apparatus. The CW emission spectrum in the range 400–500 nm is reported in fig. 1. Emission lines corresponding to excited Si^+ and C^+ are present together with H_β, and H_γ. It can be seen that the

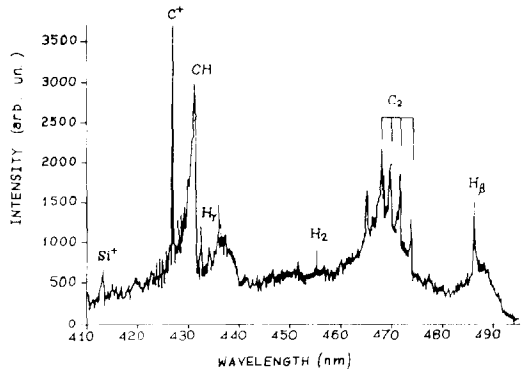


Fig. 1. CW emission spectrum in the range 400–500 nm of the plume formed irradiating at 532 nm an industrial SiC sample.

C^+ ion intensity is predominant and several molecular species are present as well (C_2, CH, H_2). The most intense are the C_2 Swan Band and the CH $A^2\Delta$–$X^2\Pi$ system. Time and space resolved measurements (fig. 2) indicate that the excited ions after 1 μs are not present anymore in the plume. The same happens after a flight of 5

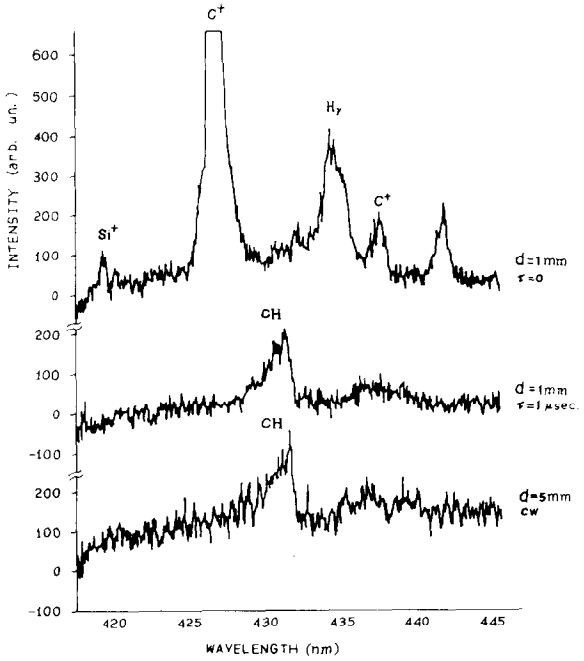


Fig. 2. Time (b) and space (c) resolved emission spectra of SiC plume.

mm. Excited molecules and clusters like C_2, CH, H_2 and C_3 [6] are formed.

3.2. YBCO and oxide mixtures

In order to verify the presence of reacting charged species, time-resolved luminescence experiments on YBCO and oxide mixtures were performed. The emission was detected in the wavelength range from 350 to 700 nm. The CW emission in the range 420–500 nm is reported in fig. 3 together with time resolved data. At $\tau = 0$, Y^+ and Ba^+ excited ions predominate, while Cu^+ intensity is quite low. At $\tau = 2$ μs only excited neutral species are present. It should be noted that in the wavelength region ranging from 500 to 700 nm also Cu and YO emission lines are detected. The lack of charged species at times of the order of a few microseconds, might be explained by the higher reactivity of ions which can produce ionized

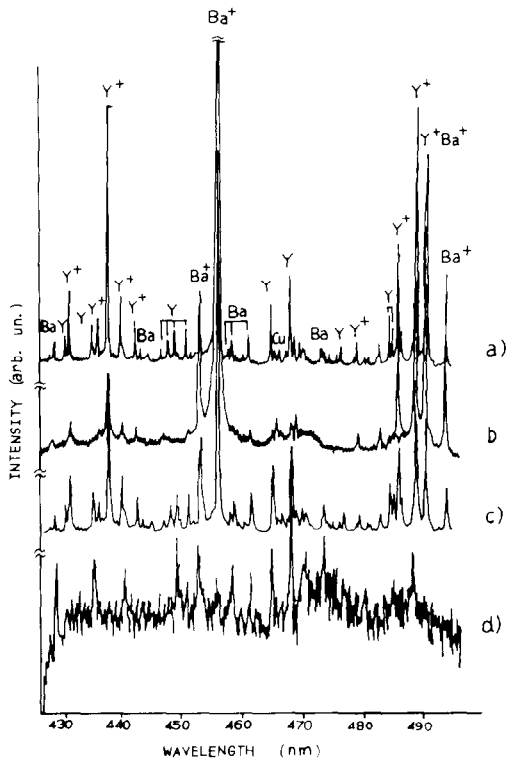


Fig. 3. CW and time resolved emission spectra of YBCO: (a) CW, (b) $\tau = 0$, (c) $\tau = 1$ μs, (d) $\tau = 2$ μs.

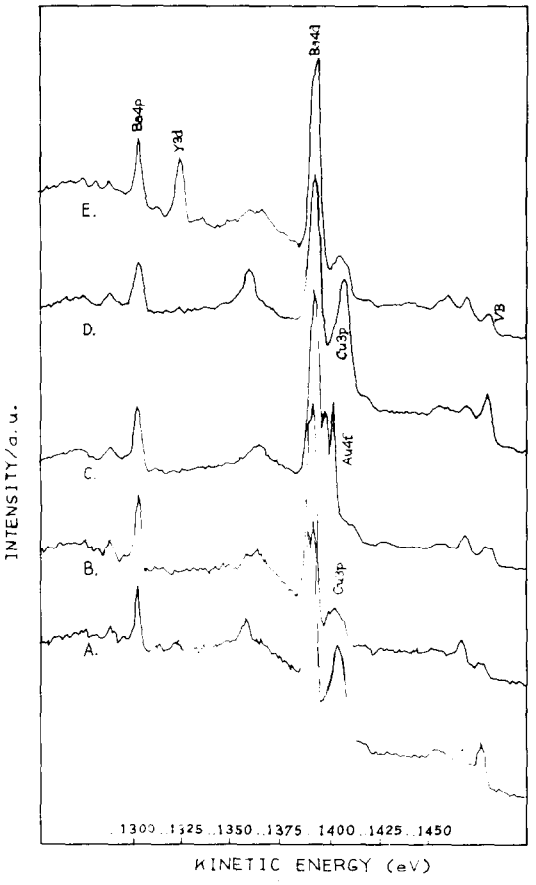
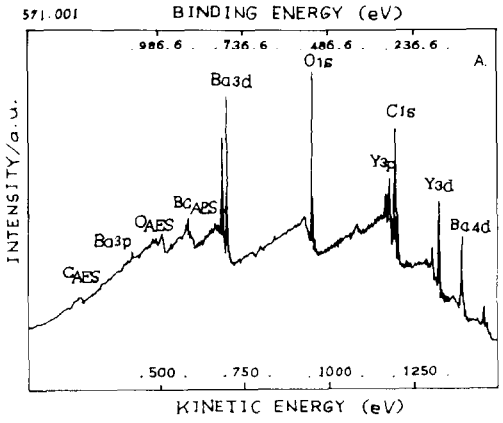


Fig. 4. XPS analysis of: (A) YBCO deposited at 90° on $SrTiO_3$, (B) YBCO deposited at 45° on $SrTiO_3$, (C) YBCO deposited at 90° on Au foil, (D) YBCO deposited on YBCO target at 90°, (E) standard YBCO.

clusters, as already observed in the Lamma experiments [6].

XPS experiments performed on superconducting YBCO ablated by a CO_2 laser, and deposited at different angles on different substrates, are reported in fig. 4 and compared with standard material. Preliminary analysis of the data indicates that the film stoichiometry appears to depend on the angle of deposition. In particular the copper intensity, as deduced from the Cu 3p signal of fig. 4A, is higher than in fig. 4B, indicating that 90° is a better angle for copper deposition. Also in the standard YBCO pellet the Cu 3p signal is less intense than in the 90° deposit on gold. The yttrium deposition behaves differently; the Y 3d

peak is clearly present only in the standard YBCO pellet, being at the limit of detectability only in the 90° deposition on $SrTiO_3$. This behaviour is quite in agreement with a Lamma analysis of the deposited film [8] and with previous results [9]. For a better understanding of the details of YBCO deposition, laser ablation and subsequent deposition of two-component oxide mixtures were studied. In fig. 5 XPS wide scans of two equimolar mixtures of $Y_2O_3/BaCO_3$ and Y_2O_3/CuO, deposited at 45° on $SrTiO_3$, are reported. It can be seen that, at variance with the YBCO deposition, Y, Ba and Cu signals are well evident. As measured by quantifying the relevant signals in the corresponding detail scans (not reported here),



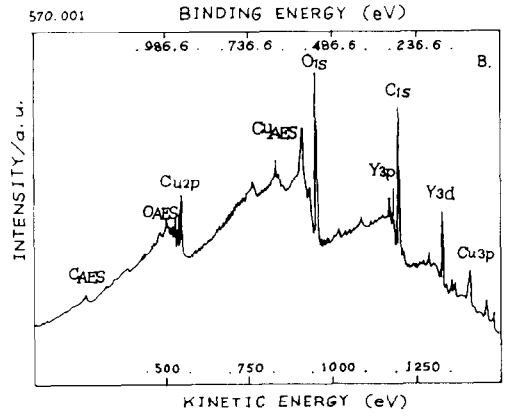


Fig. 5. XPS analysis in fixed relative resolution mode [7] of: (a) an equimolar mixture of Y_2O_3 and $BaCO_3$, (b) an equimolar mixture of Y_2O_3 and CuO.

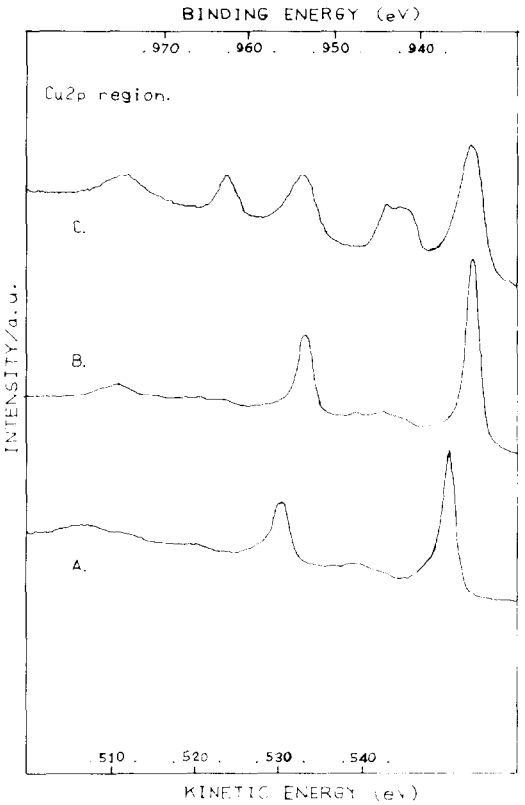


Fig. 6. Detail scans of the Cu2p region: (A) CuO deposited on Au at 30°; (B) CuO standard after 5 min sputtering at 3 kV, (C) CuO standard (as received).

while in the spectra of the $Y_2O_3/BaCO_3$ mixture the relative intensity of the Y and Ba signal is almost stoichiometric (0.6 ± 0.2), in the mixture Y_2O_3/CuO the Cu signal is higher than expected by a factor of 4. It should be noted that the XPS spectrum of the deposit on gold at 90°, reported in fig. 6 together with a CuO standard XPS spectrum and a CuO spectrum measured after ionic sputtering, is quite peculiar. From the modified Auger parameter ($\alpha' = 1849.2$ eV see ref. [10]) the oxidation status of copper is likely to be one, as shown also from the absence of the satellite structure characteristic of the CuO spectrum. This confirms that the copper valence is reduced by laser ablation processes as already found in Lamma experiments [7].

Acknowledgements

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