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Spectral features of laser induced plasma from $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ high T_c superconductors

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Abstract. Laser induced plasma emission spectra from high T_c superconducting samples of $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ obtained with $1{\cdot}06\,\mu m$ radiation from a Q switched Nd:YAG laser beam has been analysed. The results clearly show the presence of diatomic oxides in addition to ionized species of the constituent metals in the plasma thus produced.

Keywords. Laser induced plasma; high T_c superconductor; superconducting thin films.

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Deposition of high T_c superconducting materials in the thin film form on suitable substrates is a crucial step in the process of fabrication of useful devices and circuits using these new class of materials. Recently it has been demonstrated that laser ablation is a viable technique to produce thin films of high T_c ceramic materials like $YBa_2Cu_3O_7$ (Dijkkamp *et al* 1987; Moorjani *et al* 1987; Neifeld *et al* 1988; Lynds *et al* 1988; Fogarassy *et al* 1988).

Ablation of sample using Nd:YAG or excimer lasers produces brilliant elongated plasma extending outwards from the target. As the sample kept in a vacuum chamber is irradiated, the material is vapourised and ejected from the surface towards the substrate positioned away from the target. The gaseous species condense on relatively cooler substrate to form thin film.

Thin films thus grown by laser ablation become superconducting only after annealing even though the "as grown" films have their elemental content identical to that of bulk superconductors. The post deposition annealing is necessary because the thin film thus formed usually do not retain the correct stoichiometry because of oxygen deficiency (Fogarassy *et al* 1988).

In the context of manufacturing of active devices, it is highly desirable to form superconducting thin films without the annealing step which may be harmful to the interconnections etc. Evaporation techniques using thermal sources produce mainly neutral metals in the gas phase and results in the deposition of oxygen deficient films (Naito *et al* 1987). The production of metal ions during laser ablation is therefore important in achieving "as grown" superconducting thin films. Consequently, it is necessary to control the deposition parameters like laser power, substrate temperature, deposition chamber pressure etc. to prepare superconducting thin films. Spectroscopic study of plasma emission during laser ablation is a very convenient method to control the growth parameters by identifying characteristic lines of various ionized and neutral species. Studies on laser induced plasma emission (Weimer 1988), provide information about various species ejected from the target and the same could be used as a signal source for process monitoring or for studying the mechanisms involved in the formations of thin films. In this communication we present the result of our spectroscopic studies on the plasma from high T_c superconducting samples of $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ produced by 1·06 μm laser radiation from a Q switched Nd:YAG laser. In particular we report the observation of the presence of diatomic oxides in the plasma produced by laser ablation with 1·06 μm radiation.

A schematic diagram of the experimental technique is shown in figure 1. The sample in the form of a pellet of 3 mm diameter and 2 mm thickness was kept at the centre of a vacuum chamber (200 mTorr pressure) made of stainless steel provided with quartz windows. Laser pulses (150 mJ) from Nd:YAG laser (1·06 μm, 10 ns duration) was focussed on to the sample by means of a quartz lens. Using the laser spot size, (10 μm) the photon flux at the target was estimated to be $1{\cdot}5 \times 10^{12}$ W/cm^2. Bright plasma emission was observed through a window at 90° with respect to the laser beam axis. Emission spectra were recorded photographically using a Carl-Zeiss three prism glass spectrograph alongwith mercury spectrum. Plasma spectra for $YBa_2Cu_3O_7$ ($T_c = 90$ K) and $GdBa_2Cu_3O_7$ ($T_c = 93$ K) in the region $\lambda = 400$ nm to 600 nm are given in figures 2 and 3 respectively. Emission wavelengths observed were compared with literature values and they are given in table 1.

Spectra show prominent lines due to Y^+, Ba^+, Cu and Gd^+, Ba^+, Cu in the case of $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ targets respectively. The emission spectra thus reveal the presence of rare earth ions and Ba^+ in the plasma. Lines due to Cu^+ do exist in the spectra though they are comparatively weak due to the higher ionization

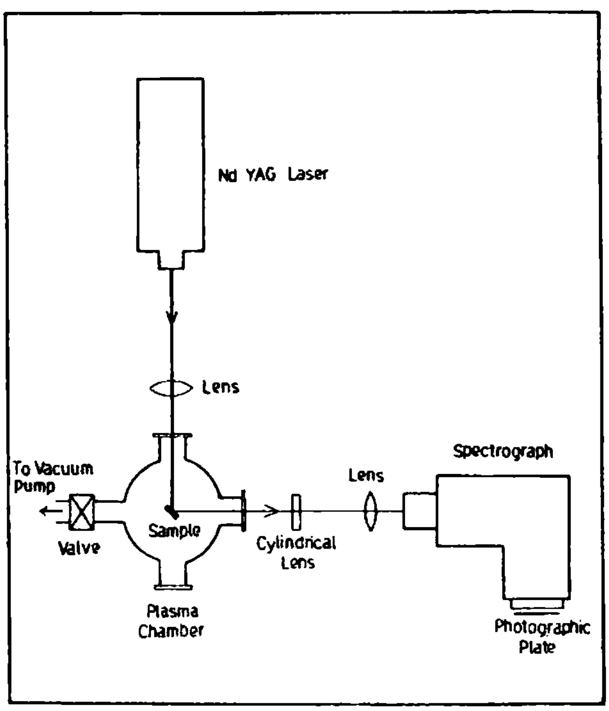

Figure 1. Schematic diagram of the experimental set-up.

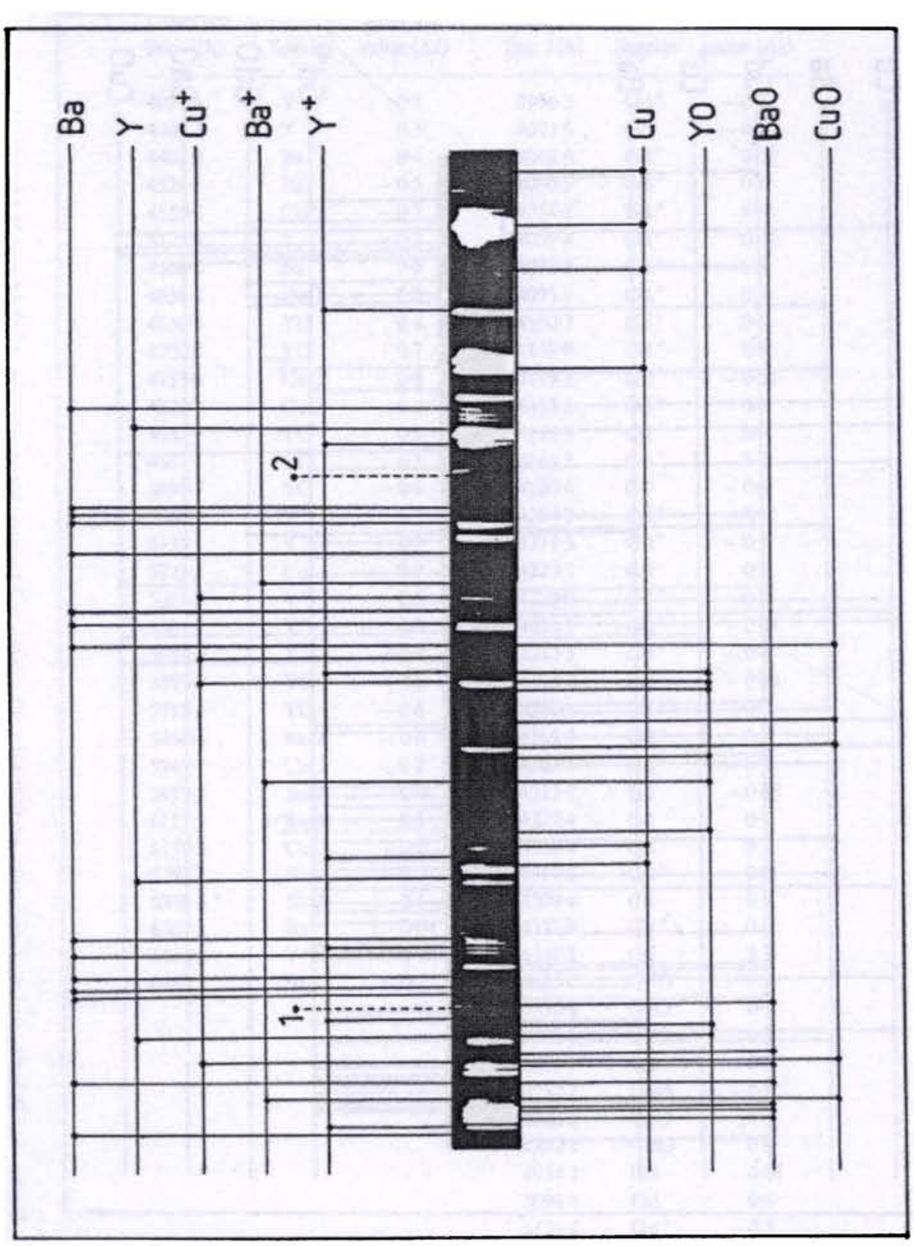

Figure 2. Plasma emission spectrum of $YBa_2Cu_3O_7$ sample. Mercury standards are, (1) 576·9 nm (2) 435·8 nm.

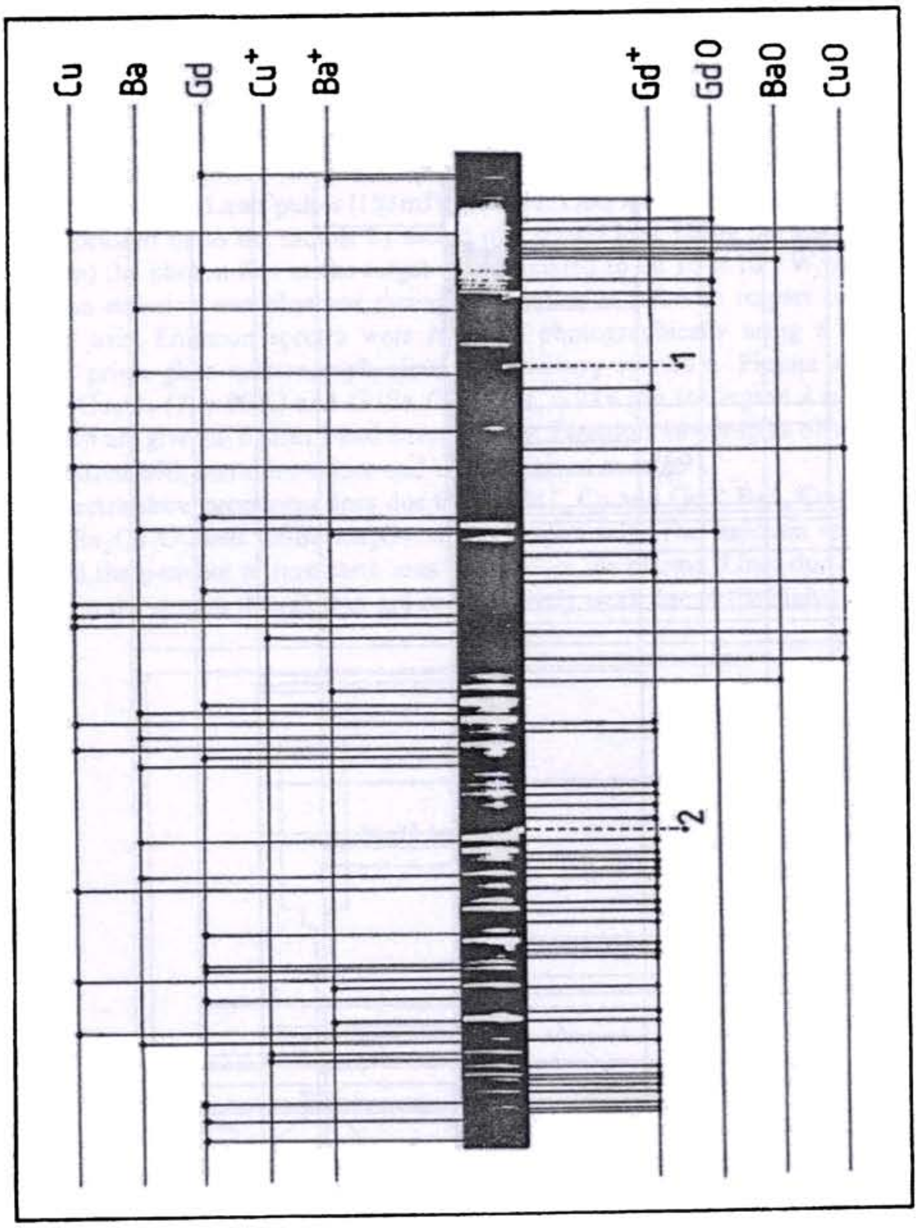

Figure 3. Plasma emission spectrum of $GdBa_2Cu_3O_7$ sample. Mercury standards are, (1) 435·8 nm (2) 546·1 m.

Table 1. Assignments of plasma spectra. Observed values have been compared with literature values (Zaidel *et al* 1961).

$YBa_2Cu_3O_7$			$GdBa_2Cu_3O_7$		
Observed line λ(A)	Species	Variation (A) from litt. value (Δλ)	Observed line λ(A)	Species	Variation (A) from litt. value (Δλ)
4021·8	Y^+	0·5	3996·2	Gd^+	−0·2
4306·3	Y	0·3	4023·5	Gd	−0·1
4402·9	Ba	0·4	4048·6	Gd^+	0·03
4524·4	Ba^+	−0·5	4050·5	Gd^+	0·1
4555·2	Cu^+	−0·7	4054·2	Gd^+	0·9
4575·9	Y	−0·3	4059·4	Gd^+	0·02
4580·6	Ba	0·9	4077·8	Gd^+	−0·3
4636·8	CuO	0·8	4095·1	Gd^+	0·5
4650·4	YO	0·4	4100·7	Gd^+	0·5
4700·8	YO	0·7	4108·9	Gd^+	0·5
4753·8	CuO	0·8	4119·3	Gd^+	−0·04
4820·2	CuO	0·2	4132·8	Gd^+	0·5
4841·9	YO	0·9	4141·9	Gd^+	0·9
4867·1	YO	0·1	4149·2	Gd^+	−0·3
4896·7	YO	−0·8	4190·6	Gd	−0·6
5067·5	Y^+	0·3	4204·2	Gd^+	−0·6
5135·1	Y^+	0·9	4211·3	Gd^+	−0·7
5221·1	Cu	0·9	4224·7	Gd	0·5
5281·2	Y^+	0·6	4229·9	Gd^+	0·2
5301·7	Y^+	0·8	4235·1	Gd^+	−0·04
5650·5	Y^+	−0·7	4243·5	Gd^+	−0·4
5699·2	YO	−0·8	4273·2	Gd	−0·05
5718·5	YO	−0·6	4282·1	Gd^+	−0·7
5868·4	BaO	−0·6	4289·9	Gd^+	0·1
5945·7	CuO	−0·2	4307·6	Gd^+	−0·2
5979·1	BaO	−0·9	4313·7	Gd	−0·08
6111·3	BaO	0·3	4327·4	Gd	0·3
6139·2	CuO	−0·8	4338·9	Gd^+	0·5
6297·2	BaO	0·2	4357·1	Gd^+	0·01
6330·4	BaO	−0·6	4509·4	Cu	0·3
6367·3	Ba^+	−0·04	4521·8	Gd^+	0·5
6462·6	Y^+	0·5	4548·1	Gd	0·5
6482·2	Ba	−0·7	4615·0	GdO	0·3
			4636·8	CuO	0·9
			4685·2	CuO	0·3
			4695·1	Gd	−0·5
			4752·2	CuO	−0·8
			4820·6	CuO	0·7
			4892·9	GdO	0·9
			4934·2	Gd	0·04
			5098·8	Gd^+	0·5
			5135·6	Gd^+	−0·5
			5217·3	Gd	−0·2
			5664·3	GdO	0·12
			5680·1	GdO	−0·8
			5771·5	GdO	0·3
			5868·2	BaO	0·8

(*Continued*)

Table 1. (*Continued*)

$YBa_2Cu_3O_7$			$GdBa_2Cu_3O_7$		
Observed line λ(A)	Species	Variation (A) from litt. value ($\Delta\lambda$)	Observed line λ(A)	Species	Variation (A) from litt. value ($\Delta\lambda$)
			5940·9	GdO	−0·1
			6006·6	CuO	0·7
			6036·7	CuO	0·8
			6127·7	Cu	0·2
			6163·7	CuO	0·3
			6241·9	GdO	0·3
			6646·7	Ba	−0·1

energy in copper (Cu = 7·726 eV; Ba = 5·211 eV; Y = 6·378 eV; Gd = 6·16 eV). It must be mentioned that the present spectra clearly show the bands due to the diatomic oxides YO and GdO in addition to the bands of BaO and CuO. These bands can be easily identified due to the better resolution possible with the prism spectrograph in comparison with a multichannel analyzer (Weimer 1988). The existence of gas phase oxides is encouraging since it reduces the possibility of deposition of oxygen-deficient thin films.

Presence of ions in the plasma is very significant since it will enhance the possibility of the formation of metal oxides within the plasma. Spectra also show intense lines due to the presence of excited neutral atoms produced by unionized species showing that the plasma is not fully ionized. As seen from the spectra, lines due to Gd and Y species can be easily identified by looking for lines which are not common to Gd and Y based samples.

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