TIME - RESOLVED EMISSION SPECTRA OF PLASMA PRODUCED BY EXCIMER LASER ABLATION OF Pb-Bi-Sr-Ca-Cu-O

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1. Introduction

Time-resolved emission spectroscopy was employed to detect excited species formed at the laser ablation of superconductor Pb-Bi-Sr-Ca-Cu-O by the excimer laser at various pressures of background gases.

A simple model has been created to explain chemical kinetics of reaction in the plasma plume by its expansion. We are able to explain the time dependence of plasma emission on the wavelengths of lead, strontium and their oxides. For purpose of this paper we assessed reaction rates of lead deexcitation and the rate of recombination of Pb^+ ion.

2. Experimental

The experimental arrangement was described in [1, 2]. The radiation from the Lambda Physik excimer laser (ArF, $\lambda = 193nm$, 30ns pulse duration, pulse energy $\approx$ 100 mJ) was focused on the target surface at an angle 45° (spot size on the target was about 0.5 mm^2). The target was placed in a vacuum chamber permitting measurement of the emission spectra in an atmosphere of helium, argon, oxygen and nitrogen oxide in a flow-through arrangement at pressures in the range 1 Pa–100 kPa.

The radiation of the emitted particles leaving the target in the range 0.1-10 cm from the target surface was recorded in the direction parallel with the target surface. After separation using a grid monochromator (resolution better than 0.5 nm) it was detected by a photomultiplier (Hammamatsu R928).

Target with nominal composition of $(Bi_{0.85}Pb_{0.15})Sr_{1.6}Ca_2Cu_{2.8}O_y$ was prepared from components $PbCO_3$, Bi_2O_3, CuO, $CaCO_3$. The powder sample was pressed to form tablets and annealed repeatedly.

3. Results

3.1. Analytical model of reaction kinetics

To create analytical model of processes in plasma plume is very difficult especially on high pressure of a background gas. The time dependence of the concentration of specie X^i, (a metal atom M^i, ion M^+, or oxide $(MO)^i$) can be often described by:

$$-\frac{d[X^i]}{dt} = \sum_p k_p[X^i] - \sum_r k_r[A] - \sum_s k_s[B][C], \tag{1}$$

The first term denotes monomolecular reactions when $[X^i]$ decrease (deexcitation, etc.). The second term describes processes when $[X^i]$ increase (deexcitation of the specie at the state X^k, ...). The third term denotes collision processes (oxidation, recombination, ...). If we assume the reactions to be at least effectively monomolecular, we obtain for the time dependence of concentration $[X^i]$:

$$[X^i] = \sum_{m=1}^{n} a_m exp(-b_m t) \tag{2}$$

where a_m are preexponential factors, whose depend on the initial reactant concentrations and the rate constants, b_m are rate constants or their linear combinations.

Occurrence of the specie X deexcitation (between states X^i a X^j) is proportional to concentration of the specie $[X^i]$. From the time dependence of emission at the wavelength corresponding to the transition $X^i \rightarrow X^j$ we can assess rate constants. We consider the emission of plasma $f(t)$ as the Laplace transformation of the function $g(\tau)$:

$$f(t) = \int_0^\infty g(\tau) e^{-\tau t} d\tau \tag{3}$$

where $g(\tau)$ is described:

$$\forall m \in \langle 1, n \rangle : \; g(a_m) = b_m; \; \text{otherwise } g(\tau) = 0. \tag{4}$$

If we calculate the inverse Laplace transformation of the function $f(t)$ (by the means of the maximum likelihood method [3]), we obtain rate constants (b_m in the equation (2)).

3.2. Time resolved plasma emission

The model of processes was verified on the time dependence of the plasma emission at the wavelength of lead (402.0 nm, $^3F_3 \rightarrow {}^1D_2$) Figure 2a. shows the experimental data and their approximation by the means of model reaction kinetics listed above.

Figure 2b. shows the calculated function $g(\tau)$. The function $g(\tau)$ determines two constants b'_m (b_m in the equation (2)): $b'_1 = 2.10^4 s^{-1}$ and $b'_2 = 3.10^6 s^{-1}$.

The pressure dependence of constants b'_m is shown on the Fig. 3,4. To assign the constants b'_m to actual chemical reactions was assigned a system consisting of lead atoms (excited states Pb^i, Pb^j), iont Pb^+ and lead oxide (PbO^i, PbO^j). Further there were considered the following processes in the plume:

$$
\begin{array}{rcll}
Pb^+ + A & \xrightarrow[k_1]{} & Pb^i + A^+ & \text{recombination,} \\
Pb^i & \xrightarrow[k_2]{} & Pb^j + h\nu & \text{deexcitation,} \\
Pb^+ + O\ + A & \xrightarrow[k_3]{} & PbO^i + A^+ & \text{oxidation ion–neutral,} \\
Pb + O + & \xrightarrow[k_4]{} & PbO^i & \text{oxidation,} \\
PbO^i & \xrightarrow[k_5]{} & PbO^j + h\nu & \text{deexcitation.}
\end{array}
$$

Having solved the set of differential equations (1) for the b_m constants of the relations (2) we obtain these values: $b_1 = k_2$; $b_2 = k_1 + k_3$.

In [4] there is stated the relation describing the pressure and temperature dependence of the deexcitation rate k_2:

$$k_2(p,T) = \sum_k (A_{ij} + p\sigma_{ij}\sqrt{\frac{8kT(p)}{\pi\mu}}) \qquad (5)$$

where T(p) is average temperature and it depends on pressure p of a background gas, A_{ij} is the Einstein coefficient, σ_{ij} is a collision cross section for an inelastic collision, which induces transition $X^i \rightarrow X^j$, μ is a reduced mass.

The measured pressure dependence of b'_m constants allows the supposition, that $b'_1 = b_1 = k_2$ a $b'_2 = b_2 = k_1 + k_3$. It's caused by the linear increase of $b'_1(p)$ (with a small influence of the type of the background gas) as supposes the equation (5).

4. Conclusion

The plume reactions created model proved to be useful. The results obtained have to be further tested by another independent method. The obtained dependencies of the reaction rate constants can be used in the future for optimizing conditions for the laser ablation of superconducting thin films.

Acknowledgements

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References

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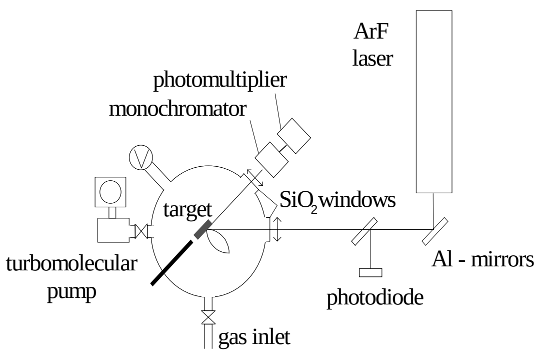

Figure 1. Schematic of the experimental setup.

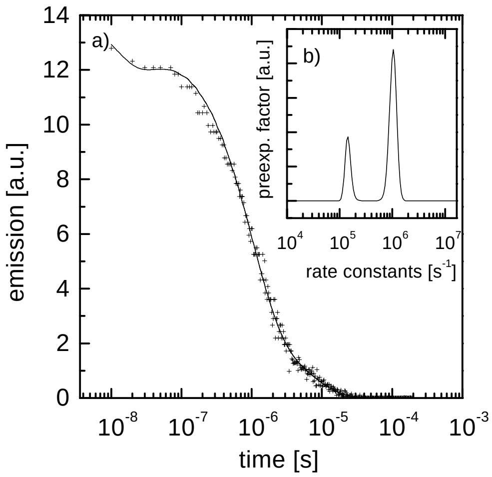

Figure 2. Plasma emission at wavelength 402 nm (Pb, $^3F_3 \rightarrow {}^1D_2$); helium, pressure 100 Pa).

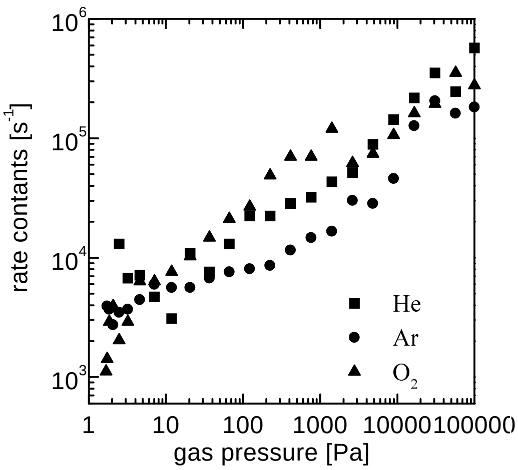

Figure 3. Pressure dependence of the constant b_1'.

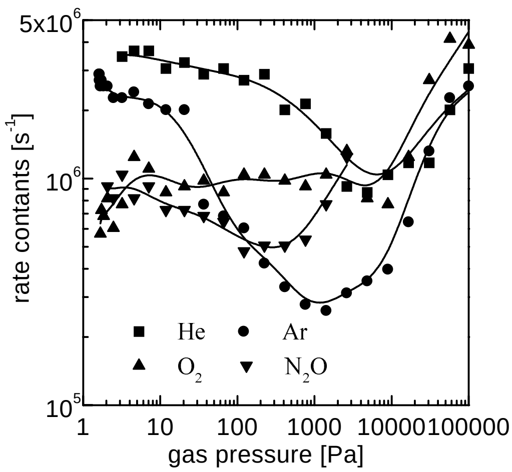

Figure 4. Pressure dependence of the constant b_2'.