7th Asia-Pacific Conference on Plasma Physics, 12-17 Nov, 2023 at Port Messe Nagoya

Laser-induced breakdown spectroscopy based on thermodynamic equilibrium and corona equilibrium for estimating atomic composition in powdered milk

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In this work, we adopted thermodynamic equilibrium and corona equilibrium to the optical emission spectra of a plasma produced by laser ablation of a powdered milk target. The quantitative analysis of the atomic composition is an issue of laser-induced breakdown spectroscopy (LIBS). A standard method in the LIBS field is to apply the local thermodynamic equilibrium (LTE) to the laser-induced plasma with the electron density exceeding the McWhirter criterion. However, according to the framework of plasma spectroscopy developed by Fujimoto [1], the electron density exceeding the McWhirter criterion (it is called the Griem boundary in plasma spectroscopy) is a necessary condition but it is not sufficient for LTE. In the case of an ionizing plasma, the Boltzmann distribution is realized among the energy levels with principal quantum numbers lower than the Byron boundary. On the other hand, the corona equilibrium is expected for the optical emission spectrum from an ionizing plasma with an electron density below the Griem boundary. In this work, we compared the applicability of LTE and the corona equilibrium to the LIBS spectra observed by the laser ablation of a powdered milk target [2].

We observed the optical emission spectra at various delay times after the irradiation of an Nd:YAG laser pulse, and we evaluated the relative excited-state densities of Mg, Ca, Na, and K. The Stark broadening widths of the Balmer-α and β lines of atomic hydrogen indicated that the electron density of the plasma at a short delay time was higher than the Griem boundary. In addition, the optical emission spectrum was dominated by the line emissions of light elements, suggesting a high electron temperature. Although the electron density was higher than the Griem boundary, the relative excited-state densities of Mg, Ca, Na, and K at a short delay time ($t_d \leq 1$ μs) were not explained by assuming LTE for the plasma, suggesting that the Byron boundary corresponding to the high electron temperature was lower than the effective principal quantum numbers of the first excited states. This means the difficulty in the estimation of the atomic composition by applying LTE.

The optical emission spectrum changed with the delay time, and it was dominated by Mg, Ca, Na, and K when the delay time was longer than $t_d \geq 10$ μs. The domination by the alkali and alkaline earth metals suggests the decrease in the electron temperature with the delay time. In addition, we can expect an electron density below the Griem boundary at the long delay time. We calculated the rate coefficients of electron impact excitation for Mg, Ca, Na, and K, and we estimated the ground-state density ratios of [Ca]/[Mg], [Na]/[Mg], and [K]/[Mg] that result in the ratios of the optical emission intensities observed experimentally. Figure 1 shows the density ratios that result in the experimental ratios of the optical emission intensities as a function of the electron temperature. The dotted lines show the true density ratios, which were confirmed by inductively coupled plasma mass spectrometry. As shown in the figure, the density ratios close to the true values are obtainable by assuming $T_e \approx 1.5$, 1.2, and 0.8 eV at t_d=25, 30, and 35 μs, respectively. This means the corona equilibrium works well for the optical emission spectrum observed at the long delay times. Accordingly, the present work indicates that applying the corona equilibrium to the low-density plasma which is observed at a long delay time can work as an alternative method for quantitative LIBS.

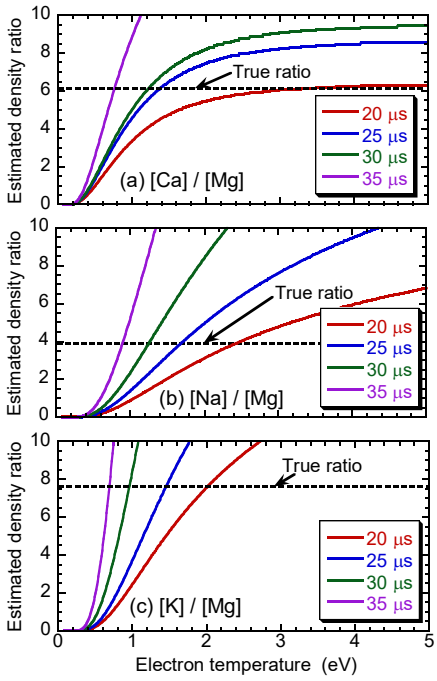

Figure 1 Ground-state density ratios of [Ca]/[Mg], [Na]/[Mg], and [K]/[Mg] that result in the ratios of the optical emission intensities observed at t_d=20, 25, 30, and 35 μs.

References
[1] T. Fujimoto, *Plasma Spectroscopy* (Clarendon Press, Oxford, 2004).
[2] K. Sasaki and K. Maruyama, Appl. Phys. A **128**, 736 (2022).