様　式　Ｃ－１９、Ｆ－１９、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

平成 ２７ 年　 ６ 月　 ９ 日現在

機関番号：３２６４４
研究種目：基盤研究(C)
研究期間：2012～2014
課題番号：２４５６０８８２

研究課題名（和文）常圧から超臨界圧における液中レーザー誘起プラズマナノ構造物質合成

研究課題名（英文）Preparation of nanostructured materials via plasma induced by laser in liquid under pressures from atmospheric to over-critical

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交付決定額（研究期間全体）：（直接経費）　　4,200,000円

研究成果の概要（和文）：液相レーザーアブレーションによるナノ粒子作製おいて、液相の圧力および組成がナノ 粒子の形状や特性に与える影響を調査した。特に、高圧の水-エタノール混合溶液中でのZnOナノ粒子の作製と高圧のCO2中での錫のアブレー ションに取り組んだ。ZnOナノ粒子の作製では、フォトルミネッセンス測定を通し、粒子中の欠陥に対する溶媒の化学的性質と圧力による影響を 明らかにした。シャドウグラフィにより、錫のアブレーションが起こる領域の経時変化を調査し、発生したバブル構造の寿命が圧力に依存している ことを見出した。得られた結果から、液相の圧力と組成変化によりナノ粒子の構造と特性が効果的に変調されることを明らかにした

研究成果の概要（英文）：The effect of high pressure and medium composition on the properties and morphologies of nanoparticles (NPs) prepared via the laser ablation in liquid (LAL) technique was studied. We mainly focused on ZnO NPs (prepared in water-ethanol mixtures at different pressures) and on ablation of Sn target in pressurized CO2.In the first system, photoluminescence was measured and analyzed to reveal how different defects in ZnO NPs are governed by both medium chemistry and pressure. In the second system, in-situ shadowgraphy was used to study the behavior of the ablated zone over time, as it first emerged, then developed as a bubble-like structure (BLS), and finally collapsed. The BLS lifetime was shown to be pressure-dependent, being the longest near the density fluctuation ridge of the medium. The obtained results clearly indicate that both medium chemistry and pressure can be efficiently used to tune the morphology and properties of nanostructures produced via the LAL technique.

研究分野：Material science, Applied physics

キーワード：Laser ablation　Pressurized liquid　Nanomaterials　ZnO　Photoluminescence　Supercritical water　In-situ shadowgraphy　Sn

１．研究開始当初の背景

Laser Ablation in Liquid. Tremendous interest in various nanostructures is stimulated by the multifunctional characteristics of such materials and various options to tune their properties by controlling size, morphology, phase composition and surface states. Laser ablation in liquid (LAL) has recently attracted a lot of attention as one of synthetic techniques to prepare new attractive nanomaterials, with the ability to control both product chemistry and morphology in many systems [1-4]. Overall, the technique is easy to use, fast, uses minimum chemicals and permits to prepare nanostructures with diverse chemistries and morphologies [2-4].

Laser Ablation at High Pressure. While the material preparation via LAL has gained in popularity, reports on the synthesis of nanosturctures via LAL in pressurized liquids were very scarce [5-7], being limited to Si or Au nanoparticles [5,6] and carbon materials [7]. Though the effect of pressure on the chemical reactions and physical states of liquid-phase laser-ablation plasma has been postulated [8], no reports were found on metal oxide, hydroxide, sulfide, carbide and other nanostructures prepared by ablating metal targets in pressurized or supercritical media. Meanwhile, such nanomaterials are highly desirable for numerous applications, and thus new efficient preparation techniques providing high-quality materials with well-tuned properties are welcome.

２．研究の目的

In this project we studied in more detail the effect of pressure on the synthesis of certain (mainly ZnO) nanomaterials prepared via LAL. We applied the LAL to the preparation of ZnO nanostructures in different liquids (H_2O, ethanol and their mixtures) at high pressures up to subcritical and/or supercritical. We also ablated Sn targets in pressurized liquid CO_2, which was used as a model system to study the behavior of the cavitation bubble (generated by the laser beam hitting the target) over time.

The principal goals of this project were: (1) to study the effect of pressure on the LAL technique, by ablating metal targets in different media pressurized up to subcritical (or even supercritical) conditions; (2) to study the process at different pressures; (3) to compare the products prepared in different liquid media and at different pressures.

３．研究の方法

By taking advantage of both the LAL (two YAG lasers were used: of millisecond and nanosecond pulsed types) and high-pressure solvothermal synthesis, we prepared a series of nanomaterials through ablating Zn targets in liquid media (water, ethanol or their mixtures) at pressures from one atmosphere to 30 MPa. The obtained products were then thoroughly studied by means of scanning and transmission electron microscopies (SEM and TEM), X-ray diffractometry (XRD), and X-ray photoelectron spectrometry (XPS). Special attention was paid to photoluminescence (PL) measurements, as PL permits to analyze defects in obtained ZnO nanoparticles.

While ablating Sn targets in pressurized CO_2, we used shadowgraphy [9] to observe the behavior of the ablated zone (so-called “cavitation bubble”), whose lifetime and size are directly related to the properties and morphology of prepared nanostructures. The lifetime of the cavitation bubble (or bubble-like structure, BLS) was carefully investigated as a function of pressure, and a model was proposed.

４．研究成果

Effect of High Pressure on ZnO Nanoparticles. XRD analysis (not shown here) demonstrated that all products of Zn ablation in water were ZnO nanostructures. Their PL properties depended much on medium pressure during preparation: (i) UV emission shifted implying smaller nanoparticles prepared at higher pressures; (ii) visible emission was significantly improved with pressure. TEM observations confirmed the smaller sizes and more uniform size distribution for ZnO nanoparticles prepared at higher pressures (see Fig.1). Interestingly, this finding agrees well with the independent results recently reported by others [10], who also observed smaller-sized ZnO prepared via LAL at

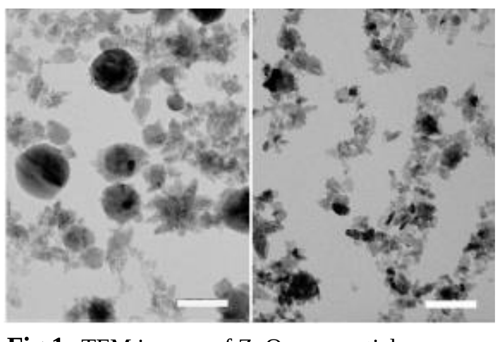

Fig.1: TEM images of ZnO nanoparticles prepared in water at 1 atm. (left) and 15 MPa (right). Scale bars indicate 100nm.

high pressures. Thus, applying pressure during LAL experiments is shown to be an additional means to tune the product’s morphology, size distribution and optical properties. This shows promise for preparation of novel promising nanomaterials with unique properties in the future.

Effect of Medium Composition and Laser Pulse on ZnO Product. The effect of liquid medium composition on the morphology, phase and chemical composition of ZnO nanosturctures prepared via LAL was studied first at atmospheric pressure. Based on XRD results, it was found that metallic zinc phase merged as a second phase in nanoparticles ablated in ethanol-rich liquids.

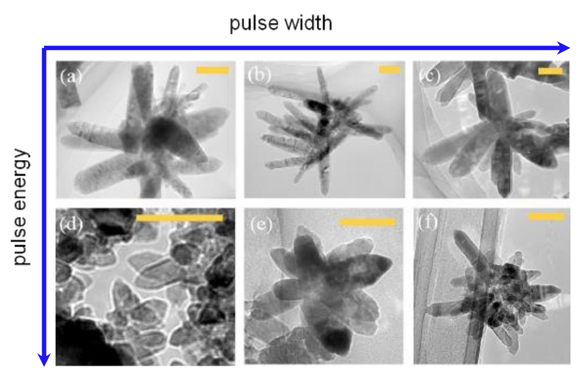

Fig.2: Morphology of ZnO nanostructures prepared via ablating Zn by millisecond laser in water as a function of pulse width and pulse energy used. Scale bars indicate 100 nm.

While all the products of laser ablation by means of nanosecond pulsed laser were appeared as spherical nanoparticles (not shown here), the use of millisecond laser (at varied pulse width and pulse energy) allowed for a better control over the product morphology. As seen in Fig.2, ZnO nanorods with different sizes and dimentional ratios could be prepared.

Effect of Medium Composition and Pressure on PL of ZnO Product. Both medium composition and medium pressure during LAL processing were demonstrated to influence the PL properties of prepared ZnO nanostructures. Fig.3 shows how PL spectra of ZnO products prepared at atmospheric pressure changed as a function of medium composition (liquids from pure water to pure ethanol were used). The presented results imply that the liquid media used for ablation significantly affects the behavior of various surface and bulk defects available in the prepared ZnO nanostructures (the latter defects are well-known to be sources of PL emission [10,11].

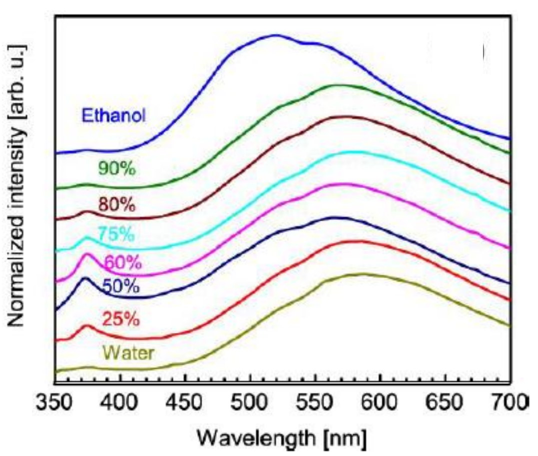

Fig.3: PL spectra of ZnO prepared via ablation of Zn in water-ethanol mixtures at 1 atm.

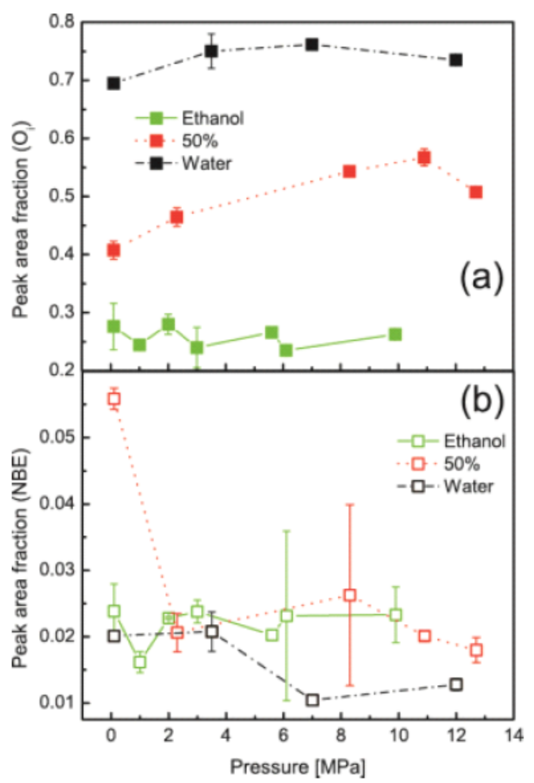

Fig.4: Influence of medium chemistry and pressure on defects in produced ZnO nanomaterials. Behavior of (a) interstitial oxygen related defects and (b) near-band-edge defects. Trends for pure water (black), pure ethanol (green) and their mixture (1:1, red color) are shown.

The pressure applied to liquid media during ZnO nanoparticle preparation also affected the PL of the product [12]. Fig.4 shows how the fraction of two defects (interstitial oxygen and near-band-edge related defects) varied over pressure (dependencies are presented for three liquids: pure water, pure ethanol and water-ethanol mixture with the ratio of 1:1). It is well seen that pressure affected the two defects in both water or water-ethanol mixtures, while no obvious effect was observed in pure ethanol media. These findings can be used in the future for better tuning properties of diverse compound nanostructures prepared via LAL in different systems.

Effect of High Pressure on Cavitation Bubble Lifetime. The behavior of the caviation bubble (or so-called "bubble-like structure", BLS) was studied by ablating Sn targets in pressurized CO_2, as this medium permits to conduct experiments at relatively lower pressures. The knowledge obtained in such a system (where metallic Sn nanoparticles were produced) will be then of use during detailed studies in more complex systems in which chemical reactions with the media occur during LAL experiments.

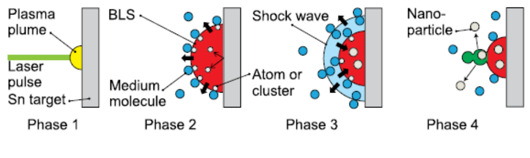

Fig.5: Four phases of the ablated zone evolution observed during Sn ablation in pressurized CO_2 in shadowgraphy images.

Fig.5 presents schematically four distinct stages observed in the system during experiments by means of shadowgraphy. Phase 1 consisted in the interaction between the laser pulse and the metal target. In the second phase, the BLS was expanding, while phase 3 was associated with its shrinkage (implying that the BLS reached its maximum between stages 2 and 3). Finally, during phase 4, the BLS disintegrated from its tip, releasing Sn species from the ablated zone.

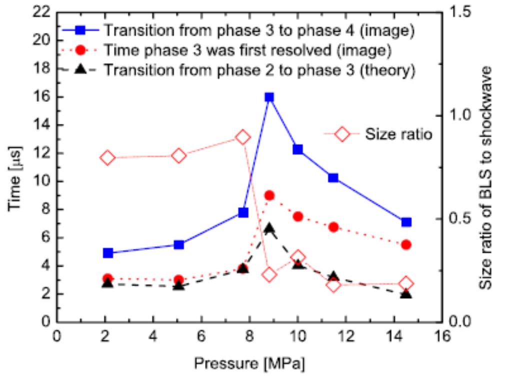

Fig.6: Evolution of phases 2-4 over time as function of medium pressure at 40 °C (solid symbols) and size ratio of BLS to shockwave front at the moment phase 3 was first observed in shadographs (open diamonds).

Fig.6 presents the evolution of the above phases 2-4 over time as a function of medium pressure. Also shown is the size ratio of the BLS to its separated shockwave at the time when phase 3 was first observed in shadowgraph images. It is clearly seen that at ~8.8 MPa the BLS demonstrates the slowest dynamics (both expansion and shrinkage). This pressure corresponds to the pressure with the largest density fluctuation at 40 °C [13,14].

It is thus demonstrated that by adjusting the medium conditions, it is possible to use the lifetime of the BLS (or ablated zone) as another parameter: since the lifetime of the zone is directly related to nanoparticles forming during BLS formation, expansion and shrinkage, this should permit to control the product's properties more. The BLS lifetime has an impact on the product nanoparticles (their size distribution, size, surface defects and states), and this can be used for better and more precise tuning of the product properties.

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〔図書〕（計 0 件）

〔産業財産権〕
○出願状況（計 0 件）

○取得状況（計 0 件）

〔その他〕
ホームページ等

http://www.pr.tokai.ac.jp/tuiist/tt/announcement_kulinich.html
http://www.dma.jim.osaka-u.ac.jp/view?l=ja&u=897
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