Complex nanomineral formation utilizing kinetic control by PLAL

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ABSTRACT

We used pulsed-laser ablation in liquids (PLAL) of Cu or Zn foil targets in water or in aqueous Cu or Zn salt solutions. PLAL in neat water generated mixtures of metal and (thermodynamically preferred) metal oxide nanomaterials, whereas the availability of select dissolved anions predictably led to the fabrication of more complex phase-pure nanominerals. PLAL of Cu foil in aqueous CuCl₂ solution produced nano-paratacamite, Cu₂Cl(OH)₃, whereas nanorouaite, Cu₂(NO₃)(OH)₃, was formed in aqueous Cu(NO₃)₂ and NH₄OH solution. Likewise, we synthesized simonkolleite, Zn₅(OH)₈Cl₂ · H₂O, or layered zinc hydroxide nitrate, Zn₅(OH)₈(NO₃)₂ · 2H₂O, nanoparticles by PLAL of Zn targets in aqueous ablation liquids with added ZnCl₂ and NH₄OH or Zn(NO₃)₂, respectively. Bimetallic zincian paratacamite resulted from PLAL of Cu foil in aqueous Cu and Zn chloride solution. Our results show that kinetic control exceeded thermodynamic product formation during nanosecond ultraviolet PLAL.

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1. Introduction

Pulsed laser ablation in liquids (PLAL) has emerged as an innovative technique for the fabrication of nanomaterials with tailored properties. Henglein and Fojtik pioneered the method when they prepared Au, Ni, and C colloids in the early 1990s [1]. Since then, PLAL has been successfully applied to the controlled generation of numerous metal, alloy, oxide, semiconductor, ceramics, and carbon nanoparticles [2–66]. Specifically, PLAL of Cu targets in water yielded crystalline particles of Cu and/or CuO with diameters ranging from 2 to 100 nm [67–70]. Other phases, such as Cu₂O, were accessible at high pulse energies [71]. Similarly, PLAL of Zn targets in water has been shown to produce crystalline Zn or ZnO particles with diameters ranging from 5 to 100 nm [72–76].

PLAL offers many tunable experimental parameters and is capable of producing nanomaterials with unique electronic and catalytic properties. Very high temperatures, pressures, and atom densities exist in the liquid-confined plasma formed from precursors during PLAL, thus permitting exploration of extreme regions of materials' phase diagrams. Control of nanoparticle size, polydispersity, and composition is achieved by choice of laser pulse energy and the chemical nature of the solid target or liquid medium. Nanoparticle catalysts exhibit maximum surface area and introduce additional benefits through the modulation of electronic properties as a result of quantum confinement [13]. Another advantage of PLAL is the ease of handling and collecting the resulting nanoparticles, as they are suspended in the liquid upon synthesis.

Analogous to the creation of geological minerals, the PLAL process involves high temperatures and pressures. Rapid cooling and injection of nanoparticles into the liquid that surrounds the plasma quench kinetic products. In nature, the entire periodic system is the toolkit for material formation [77]. Therefore, natural minerals often have complex compositions. We show here that addition of select anions to the ablation solutions led to the fabrication of more complex phase-pure nanominerals (*ergo* the kinetic products) compared to PLAL of metals in water, which generated mixtures of metallic and (thermodynamically most stable) metal oxide nanomaterials.

2. Experimental Section

2.1. Materials and Methods

Pulsed laser ablation in liquids was performed in the Beckman Institute Laser Resource Center at California Institute of Technology, X-ray photoelectron spectroscopy in the Molecular Materials Research Center (Beckman Institute at California Institute of Technology), and energy-dispersive X-ray spectroscopy in the California Institute of Technology GPS Division Analytical Facility. Data analysis and graphing were performed with Igor Pro 6.37 (WaveMetrics).

All chemicals were used as received. Deionized water was obtained from a Barnstead Diamond Nanopure system and had a resistivity of ≥ 16 M $\Omega \cdot$ cm.

2.2. Synthesis

Nanomaterials were synthesized by PLAL. A 30 mm diameter metal disk was sonicated for 10 min in 10% aqueous HCl to remove surface oxides

and thoroughly washed with water. The clean disk was placed horizontally on a glass flange in a 30 mL glass beaker, which was filled with 10 mL liquid. All glassware was thoroughly cleaned with aqua regia before use. The disk moved between laser pulses (Section 3). The metal disks consisted of Cu (0.15 mm thick, A.J. Oster) or Zn (0.25 mm thick, Alfa); all metal sheets had purities of $>99.9\%$. For preparation of monometallic materials, the liquid was water or aqueous solutions of 3.4 M CuCl₂ · 2H₂O, 3.4 M Cu(NO₃)₂ · 3H₂O, 3.3 M Zn(NO₃)₂ · 6H₂O (all Sigma-Aldrich), or saturated solutions of Cu(NO₃)₂ · 3H₂O or ZnCl₂ (EM Science) in 1.0 M aqueous NH₄OH (JT Baker). Cu or Zn foils were used in aqueous Cu or Zn solutions, respectively. Bimetallic nanoparticles were made from Cu foil in an aqueous solution of 2.1 M CuCl₂ · 2H₂O and 0.7 M ZnCl₂. Each sample was irradiated for 60 min by 150 mJ, 355 nm, 8 ns pulses, which were provided by a frequency-tripled 10 Hz Q-switched Nd:YAG laser (Spectra-Physics Quanta-Ray PRO-Series). The laser beam was focused with a 100 mm focal length plano-convex quartz lens 1.0 mm below the surface of the liquid, at the metal disk. The nanoparticle suspensions were transferred into glass vials after synthesis. Dry materials were obtained by centrifugation and washing with water until the supernatant did no longer show any salt absorption. The nanoparticles were dried under vacuum after washing twice with 3 mL acetone (EMD, Omni-Solv®).

2.3. Characterization

X-ray photoelectron spectroscopy (XPS) data were taken with a Surface Science Instruments M-probe surface spectrometer, using monochromatic Al K α radiation (1486.6 eV) and a vacuum chamber pressure of $<5 \times 10^{-9}$ Torr. Nanomineral samples were drop-cast from aqueous suspensions on clean Ti foil and dried in ambient air at room temperature. Survey scans were collected to identify the elements present in the materials. Depending on the elemental composition of the nanoparticles, high-resolution spectra were taken in the Cu 2p, Zn 2p, Cl 2s, N 1s, or O 1s regions. Binding energies and peak area quantifications were obtained from Gaussian-Lorentzian peak fits after Shirley background subtraction [78], using relative sensitivity factors, and were referenced to the C 1s peak arising from adventitious carbon, taken to have a binding energy of 284.8 eV [79]. XPS data analysis was performed with CasaXPS (Version 2.3.16 PR 1.6).

Powder X-ray diffraction (XRD) data were obtained with a Bruker D2 PHASER diffractometer, using monochromatic Cu K α radiation (1.5418 Å; tube power 30 kV, 10 mA). The instrument resolution was 0.050° in 2 θ , and the counting time was 3.0 seconds per step. Solid samples were mounted with Vaseline (X-Alliance GmbH) on a zero-diffraction silicon plate (MTI Corporation). Background subtraction and XRD pattern matching was performed with the Bruker DIFFRAC.SUITE software. Powder XRD peak assignment was carried out using the International Centre for Diffraction Data (ICDD, 2012) database; powder diffraction file (PDF) numbers are referenced throughout the Results and Discussion section.

Energy-dispersive X-ray spectroscopy (EDX) data were collected to determine the metal ratio in the PLAL-made bimetallic material. We used an Oxford X-Max SDD X-ray Energy Dispersive Spectrometer, which allowed quantitative elemental analysis with a relative accuracy of better than 5% and detection limit of better than 0.5%. A working distance of 8 mm was used to maximize X-ray counts, and analysis was performed with the AZtec software package.

Dynamic light scattering (DLS) data were acquired at room temperature with a Brookhaven ZetaPals instrument. Mean values and size distribution widths (σ) were calculated from the measured intensity histograms by the built-in software; they were obtained by averaging five 1 min sweeps and had an estimated relative error of $\pm 4\%$. An aqueous solution of 0.027 M cetyltrimethylammonium bromide (CTAB) and 0.010 M sodium chloride was passed through a 0.45 μm Millipore syringe filter three times into a freshly cleaned glass scintillation vial to remove all dust. Nanomaterials were suspended in this solution ($5\text{ }\mu\text{g mL}^{-1}$) and sonicated for 30 min.

3. Foil Target Setup

Large amounts of thermal energy are generated during PLAL. Efficient heat dissipation in the liquid is crucial to achieve reproducibility since bubble formation and thermal distortions of the laser beam interfere with the ablation process [12]. Flow cell and magnetic stirring methods have been successfully employed in the synthesis of silver colloids from stationary solid targets at pulse energies below 13 mJ [2, 12]. We previously reported PLAL preparations of transition metal oxide and hydroxide nanoparticles with 355 nm nanosecond pulses with energies ranging from 30 to 210 mJ [13, 15]. The higher pulse energies necessitated moving the metal target. The simplest (oft-used) solution is target powder swirling in magnetically stirred ablation liquid.

We found that the target powder size mattered. Powder particles had to be small enough that gravity did not interfere with individual particles floating in the stirred liquid through the laser focus, which was located just below the liquid surface. Yet particles needed to be large enough that their surface appeared flat with respect to the focal beam waist, so that the main propagation vector of the shock wave was opposite to the incident light direction. A shock wave originating from a convex surface is less powerful than one from a flat surface, thereby leading to less rapid nanoparticle formation. Hence, the optimal powder particle size depends on the density of the solid target, the viscosity of the ablation liquid, the stirring velocity, and the focal beam waist. While some metals can easily be obtained commercially as powders in the desired size range, PLAL nanomaterial synthesis becomes more versatile if widely available metal foils can be used.

Both the foil target and ablation liquid must move at higher pulse energies, which were employed in the syntheses of metal oxide and hydroxide nanomaterials with 355 nm light. When we placed stationary Cu or Zn foil targets with thicknesses of $\geq 0.1\text{ mm}$ in magnetically stirred liquids we observed the appearance of holes within minutes after irradiation with focused 90 mJ, 355 nm, 8 ns, 10 Hz repetition rate laser pulses. Therefore, we designed and built a PLAL setup that allowed us to move the target foil within its plane between each laser pulse and to simultaneously agitate the liquid.

Moving the target instead of the laser focus is technologically easier. We placed a metal foil disk on a glass flange in a 30 mL beaker (Fig. 1a), which spun at 50 rpm and simultaneously moved back and forth horizontally; the travel distance was 23 mm so that the convergent vertical laser beam hit only the target and not the beaker walls. Two low-cost electrical motors powered both motions. The glass flange had an outside diameter of 30 mm at the bottom, 20 mm at the top, and its height was 10 mm. The disk was cut from commercially available metal foil such that it just fit horizontally into the beaker. A 4 mm diameter hole in the center of the disk facilitated convection of the liquid above and below the target disk.

Two disposable, 4 mm diameter glass balls were placed under the metal foil disk to further agitate the liquid. We note that thin Cu foil (0.05 mm thickness) did not withstand the heat generated during PLAL and crumpled after a few minutes under our conditions. Therefore, we used foil targets of at least 0.1 mm thickness. We found that we succeeded in evenly ablating the metal target with our setup (Fig. 1b).

Fig. 1 - (a) Schematic of PLAL setup (the arrows indicate motions); (b) Photos of foil targets after PLAL.

Our method offers a number of advantages: It is amenable to all target metals that are available as foils of at least 0.1 mm thickness. The glassware is low-cost and commercially available or easily made. All chemicals, including the resulting nanomaterials, come only into contact with thoroughly cleaned glass, preventing inadvertent contaminations. The method's simplicity allows for operation with any laser system of choice, as the target is moved with respect to the laser focus, eliminating the need for a laser scanner. Finally, the compactness of the setup permits its placement in inert gas atmosphere if desired.

4. Results and Discussion

In PLAL, the generated plasma consists of chemical elements from the solid and the liquid. Our work on mixed metal hydroxide nanoparticles has shown that the relative proportion of metals in the generated materials was a function of the concentration of the metal ions that were dissolved in the ablation liquid. At high dissolved ion concentrations the metal composition of the resulting nanomaterials was predominantly governed by the ion species. For example, ferrous and ferric oxides were obtained from metallic Ni powder in aqueous $\text{Fe}(\text{NO}_3)_3$ solutions, whereas PLAL of Fe target powder in 3.0 M aqueous $\text{Ni}(\text{NO}_3)_2$ solution resulted in $[\text{Ni}_{0.78}\text{Fe}_{0.22}]$ -layered double hydroxide nanosheets [15].

We also found that nanomaterial yields were higher when metal ions were present in the ablation liquid, while all other experimental conditions were kept virtually identical. This was also true when the metal target and ion species were comprised of the same element. Syntheses with added metal ions typically yielded about 100 mg per batch, whereas we collected only $< 10\text{ mg}$ per batch from PLAL in pure water. Select anions of the dissolved salts were incorporated into the prepared nanoparticles, thus forming more complex nanominerals utilizing kinetic control. Syntheses in neat water yielded simple metals or (thermodynamically preferred) metal (hydr)oxides.

For a direct comparison of nanomaterial syntheses by PLAL, we used Cu or Zn foil in pure water or with added Cu or Zn salts, respectively. All materials were prepared at virtually the same physical conditions. We identified crystal phases of the PLAL-made nanomaterials by XRD. The bulk Cu/Zn ratio of the bimetallic material was determined by EDX. Surface compositions were probed by XPS. Note that the interrogation depths

of XRD and EDX range from a few to a few hundred micrometers, whereas X-ray photoelectrons escape only from the top few nanometers of solid surfaces. We also assessed nanoparticle size distributions by DLS. Characterization data in tabular form are available in the Supporting Information. Our approach allowed us to investigate if kinetic control transcended the generation of thermodynamic products. The synthesized nanomaterials are summarized in Table 1 and described in more detail below.

Table 1 - Nanomaterials synthesized by PLAL of metal foils in water or aqueous solutions.

Foil target	Added salt	Obtained material ^a
Cu	None	Cu, CuO
Cu	CuCl ₂ · 2H ₂ O	Cu ₂ Cl(OH) ₃ (Paratacamite)
Cu	Cu(NO ₃) ₂ · 3H ₂ O, NH ₄ OH	Cu ₂ (NO ₃)(OH) ₃ (Rouaite)
Zn	None	Zn, ZnO (Wurtzite)
Zn	ZnCl ₂ , NH ₄ OH	Zn ₅ (OH) ₈ Cl ₂ · H ₂ O (Simonkolleite)
Zn	Zn(NO ₃) ₂ · 6H ₂ O	Zn ₅ (OH) ₈ (NO ₃) ₂ · 2H ₂ O
Cu	CuCl ₂ · 2H ₂ O, ZnCl ₂	Cu ₃ (Cu, Zn)Cl ₂ (OH) ₆ (Zincian paratacamite)

^aDetermined by XRD.

4.1. Copper Materials

We used PLAL to synthesize Cu-containing nanomaterials from Cu foil targets in pure water, or equimolar aqueous solutions of copper chloride or nitrate. Because of its limited solubility in water, we could not use Cu(OH)₂ as a dissolved precursor. Depending on the ablation liquid, we obtained different materials.

PLAL of Cu in water generated a mixture of CuO and metallic Cu nanoparticles. Interestingly, we obtained a more complex nanomineral from PLAL of Cu foil in copper chloride solution: Cu₂Cl(OH)₃ in the paratacamite phase. In contrast, PLAL of Cu foil in an aqueous solution of copper nitrate and ammonium hydroxide led to the formation of rouaite nanoparticles. PLAL of Cu foil in Cu(NO₃)₂ solution without NH₄OH did not yield particles, presumably because a relatively high concentration of hydroxide ions was needed for solid-state material formation.

Paratacamite and rouaite are not the thermodynamically most stable phases or compositions of oxidized copper [80, 81]. The preparation of Cu₂Cl(OH)₃ and Cu₂(NO₃)(OH)₃ shows that our PLAL synthesis favored the formation of kinetic products if appropriate anions were present.

A reddish-black solid was obtained by PLAL of Cu in water (Fig. 2). XRD data showed two phases consisting of metallic Cu (PDF 01-070-3038) and CuO (PDF 01-078-0428); no other crystal phases were detected. The XP spectra in the Cu 2p region exhibited a doublet with the expected branching ratio of 2:1 and corresponding satellite features. Central binding energies of Cu 2p_{3/2} peaks were 932.7 and 933.8 eV, consistent with assignment to metallic Cu [82] and divalent Cu–O [83], respectively. Relative peak quantitation revealed that the surface ratio of Cu^{0/2+} was 4.0:1. We observed a single O 1s peak at 530.7 eV, attributable to CuO [84]. The nanoparticles had a monomodal size distribution and a hydrodynamic diameter of (225 ± 40) nm.

Fig. 2 - (a) XRD data (blue), reported fixed-slit intensities of Cu (PDF 01-070-3038, red) and CuO (PDF 01-078-0428, black), inset: photo of the PLAL-made material; (b) XPS data in the Cu 2p and O 1s regions (open circles, data; lines, fits); (c) DLS particle size distribution.

Addition of CuCl₂ to the aqueous ablation liquid led to the formation of a green solid (Fig. 3). XRD data confirmed that it consisted of basic copper chloride, Cu₂Cl(OH)₃, in the paratacamite phase (PDF 01-070-0821). The obtained diffraction pattern matched literature data very well [85] and showed no other crystal phases. XPS data in the Cu 2p region exhibited a doublet with a branching ratio of 2:1 and corresponding satellite features. The peaks with central binding energies of 933.4 and 935.4 eV were assigned to Cu–O and Cu–Cl 2p_{3/2} components, in accordance with reported data [84, 86]. We detected single Cl 2s and O 1s core level peaks with binding energies of 270.0 and 531.5 eV, which we attributed to Cu–Cl and Cu–OH, respectively [84]. The nanoparticles exhibited a monomodal size distribution and a hydrodynamic diameter of (258 ± 43) nm.

Fig. 3 - (a) XRD data (blue), reported fixed-slit intensities of paratacamite (PDF 01-070-0821, black), inset: photo of the PLAL-made material; (b) XPS data in the Cu 2p, Cl 2s, and O 1s regions (open circles, data; lines, fits); (c) DLS particle size distribution.

Paratacamite is thermodynamically the most stable polymorph of Cu₂Cl(OH)₃ [87]. The mineral crystallizes in the rhombohedral $R\bar{3}$ space group [88]. It occurs naturally as an oxidation product of other copper minerals under arid, saline conditions [89]. Paratacamite is well studied in

the context of archaeological objects and art, since it is a corrosion product of Cu-containing alloys; it is often called "bronze-disease" [90, 91].

We collected a green solid upon PLAL of Cu foil in an aqueous solution of $\text{Cu}(\text{NO}_3)_2$ and NH_4OH (Fig. 4). We deliberately chose NH_4OH as the hydroxide source, as to not introduce additional chemical elements to the ablation liquid. We identified the material as rouaite, $\text{Cu}_2(\text{NO}_3)(\text{OH})_3$, by XRD; no other crystal phases were present. The XPS Cu 2p core level region exhibited a doublet with a branching ratio of 2:1 and corresponding satellite features, indicative of Cu^{2+} species. The peak with a central binding energy of 935.3 eV is consistent with Cu-OH and Cu-NO_3 2p_{3/2} components [84]. We detected an N 1s core level peak with a binding energy of 407.3, which we attributed to Cu-NO_3 [84]. A minor contribution of a component with a central binding energy of 403.6 eV was also present, consistent with a metal nitrite [92]. We assigned the two components in the O 1s region with binding energies of 531.5 eV and 532.5 eV to Cu-OH and Cu-NO_3 , respectively [93, 94]. The nanoparticles exhibited a monomodal size distribution and a hydrodynamic diameter of (156 ± 62) nm.

Fig. 4 - (a) XRD data (blue), reported fixed-slit intensities of rouaite (PDF 01-075-1779, black), inset: photo of PLAL-made material; (b) XPS data in the Cu 2p, N 1s, and O 1s regions (open circles, data; lines, fits); (c) DLS particle size distribution.

Rouaite is a rare mineral that was only described in 2001 [95]; it was named after its locality of discovery at old Cu mines of Roua, Alpes-Maritimes, south-eastern France [96]. It is the thermodynamically least stable polymorph of $\text{Cu}_2(\text{NO}_3)(\text{OH})_3$ minerals; decomposition to CuO occurs upon heating [81]. Copper hydroxide nitrates are well investigated as artificial patinas to restore archaeological copper and bronze surfaces [97, 98].

4.2. Zinc Materials

Analogous to our Cu-based materials, we used PLAL to prepare Zn-containing nanomaterials from Zn foil targets in pure water or in zinc chloride or nitrate aqueous solutions. Addition of $\text{Zn}(\text{OH})_2$ as a precursor was not practical as its solubility in water is less than 0.01 g per 100 mL [99]. We obtained different materials from the three ablation liquids.

PLAL of Zn in water produced a mixture of wurtzite ZnO and metallic Zn nanoparticles, as evidenced by XRD data (Fig. 5). Again, similar to our Cu materials, we generated more complex, but phase-pure nanominerals from PLAL of Zn foil in Zn salt solutions. We predicted that PLAL of

ZnCl_2 in basic solution would produce the mineral simonkolleite. For maximum material yield, we prepared a saturated solution of ZnCl_2 in 1.0 M aqueous NH_4OH and indeed formed $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ in the simonkolleite crystal phase. In contrast, the anionic clay $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was the product of PLAL in aqueous $\text{Zn}(\text{NO}_3)_2$ solution. Both complex minerals exist in nature, but are not the thermodynamically most stable compositions or phases of oxidized Zn under standard conditions [100–103]. Hence, our results further substantiated that kinetic control exceeded thermodynamic product formation during PLAL under our conditions.

Fig. 5 - (a) XRD data (blue), reported fixed-slit intensities of Zn (PDF 00-004-0831, black) and wurtzite ZnO (PDF 01-075-6445, red), inset: photo of PLAL-made material; (b) XPS data in the Zn 2p and O 1s regions (open circles, data; lines, fits); (c) DLS particle size distribution.

The powder diffraction pattern of the material made by PLAL of Zn in water (Fig. 5) was well matched by two crystalline phases, metallic Zn (PDF 00-004-0831) and wurtzite ZnO (zincite, PDF 01-075-6445). The XP spectra in the Zn 2p region confirmed the presence of metallic Zn and ZnO species at the surface (Fig. 5). The Zn 2p core level region consisted of a doublet with an expected branching ratio of 2:1. The Zn 2p_{3/2} peaks exhibited binding energies of 1021.2 and 1022.4 eV, allowing assignment to metallic Zn and ZnO [104], with a surface $\text{Zn}^{0/2+}$ ratio of 1.1:1. The particles had a monomodal size distribution and a hydrodynamic diameter of (258 ± 40) nm.

We obtained a white solid upon addition of ZnCl_2 and NH_4OH to the aqueous ablation liquid (Fig. 6). XRD data revealed that the mineral simonkolleite, $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ (PDF 00-07-0155), was formed, as we had predicted. No other phases were detected. The XPS Zn 2p region showed a doublet with an expected branching ratio of 2:1; the Zn 2p_{3/2} component had a binding energy of 1022.8 eV, allowing assignment to Zn-OH [104]. The O 1s core level peak consisted of two components at 530.5 and 531.9 eV, assignable to ZnO (presumably from surface oxidation) and Zn-OH , respectively [104]. We detected a single Cl 2s core level peak with a binding energy of 271.0 eV, consistent with Zn-Cl [84]. We measured a narrow monomodal size distribution and a hydrodynamic diameter of (318 ± 14) nm.

Simonkolleite is a layered hydroxide salt [105], which occurs naturally as a weathering product of zinc-bearing slags [103]. It decomposes to ZnO upon heating [102, 106]. The mineral has recently attracted interest for hydrogen gas sensing [107], supercapacitor [108], catalyst support [109], and photocatalysis applications [102]. It has also found use as a corrosion inhibitor for automotive coatings [110], and as a nutritional feed additive with high bioavailability and antimicrobial activity to supplement zinc in livestock [111–114].

Fig. 6 - (a) XRD data (blue), reported fixed-slit intensities of simonkolleite (PDF 00-07-0155, black), inset: photo of PLAL-made material; **(b)** XPS data in the Zn 2p, Cl 2s, and O 1s regions (open circles, data; lines, fits); **(c)** DLS particle size distribution.

A white solid formed by PLAL of Zn foil in aqueous $\text{Zn}(\text{NO}_3)_2$ solution (Fig. 7). XRD data revealed that the material consisted of the layered anionic clay zinc hydroxide nitrate, $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (PDF 01-072-0627); no other phase was detected. The XRD pattern exhibited a strong reflection at $2\theta = 9.09^\circ$, attributable to the (200) diffraction of monoclinic $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ [115]. The intensities of the basal (00l) reflections decreased as l increased, which is characteristic for layered structures. Minor contributions from SiO_2 stemming from the silicon substrate were also present.

Fig. 7 - (a) XRD data (blue), reported fixed-slit intensities of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (PDF 01-072-0627, black), inset: photo of PLAL-made material; **(b)** XPS data in the Zn 2p, N 1s, and O 1s regions (open circles, data; lines, fits); **(c)** DLS particle size distribution.

High-resolution XP spectra in the Zn 2p region showed a doublet with an expected branching ratio of 2:1. We observed two Zn $2p_{3/2}$ components with binding energies of 1021.4 and 1023.7 eV, consistent with Zn–OH in tetrahedral and octahedral coordination, respectively [116]. Monoclinic $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ has a hydrotalcite-like structure, which consists of slabs of edge-shared $\text{Zn}(\text{OH})_6$ octahedra and $\text{Zn}(\text{OH})_4$ tetrahedra that are located above and below the plane of the octahedrally coordinated Zn ions. The bulk ratio of octahedral to tetrahedral sites is 3:2 [117]. We detected a surface ratio of 2.9:2. The O 1s region exhibited two peaks with binding energies of 531.8 and 533.0 eV, attributable to Zn–OH and Zn– NO_3 , respectively [104]. We detected two components in the N 1s core level region, with binding energies of 404.9 and 407.4 eV. We tentatively assigned the lower binding energy peak to N-bound Zn– NO_2 [118]; the higher binding energy peak is consistent with a transition metal nitrate [84]. We obtained a very narrow monomodal size distribution and a hydrodynamic diameter of (178 ± 0.5) nm.

Zinc hydroxide nitrate is a layered anionic clay mineral [119], and consists of Zn^{2+} containing layers, whose net positive charge, stemming from the incorporation of tetrahedrally coordinated Zn^{2+} ions into the crystal structure of otherwise octahedrally coordinated metal ions, is balanced by intercalated nitrate anions [115]. Zinc hydroxide nitrate is an effective heterogeneous catalyst for the esterification of free fatty acids and the transesterification of vegetable oils [120].

4.3. Bimetallic Mineral Nanoparticles

Finally, based on the insights we gained in our PLAL syntheses of monometallic materials, we aimed to prepare a mixed-metal nanomineral. We targeted a basic copper-zinc chloride material. Since we had synthesized paratacamite by PLAL of Cu foil in aqueous CuCl_2 solution, we anticipated the formation of a similar mineral upon addition of ZnCl_2 to the CuCl_2 -containing aqueous ablation liquid. A likely candidate was the Zn-substituted basic copper chloride zincian paratacamite, also called herbertsmithite.

We collected a blue-green solid from PLAL of Cu foil in an aqueous solution of CuCl_2 and ZnCl_2 in a 3:1 molar ratio (Fig. 8). PLAL of Zn foil in the same ablation liquid was unsuccessful, as the Zn target dissolved during synthesis. XRD data confirmed that we synthesized zincian paratacamite (PDF 00-050-1558), as we had predicted. The material is a naturally occurring mineral with the formula $\text{Cu}_3(\text{Cu}, \text{Zn})\text{Cl}_2(\text{OH})_6$ [121], which forms rhombohedral, blue-green crystals [122]. Zincian paratacamite has recently gained attention for its quantum spin liquid properties due to its kagomé lattice structure [123–125]. We note that monometallic and zincian paratacamite crystals exhibit similar powder diffraction patterns, albeit with different reflection intensities. Differences are particularly pronounced in the region of $56^\circ < 2\theta < 58^\circ$ (inset in Fig. 8a). For a fair comparison of reflection intensities, we normalized measured XRD data of our mono- and bimetallic paratacamites to the strongest reflections. Clearly, the nanomaterial we synthesized by PLAL of Cu foil in an aqueous solution of CuCl_2 and ZnCl_2 was better matched by zincian paratacamite.

Fig. 8 - (a) XRD data (blue), reported fixed-slit intensities of zincian paratacamite (PDF 00-050-1558, black), insets: left, expanded region in which reflections of mono- and bimetallic paratacamites differ most (blue, zincian paratacamite, PDF 00-050-1558; gray, monometallic paratacamite, PDF 01-070-0821); right, photo of the PLAL-made material; **(b)** XPS data in the Cu 2p, Cl 2s, and O 1s regions (open circles, data; lines, fits); **(c)** DLS particle size distribution.

As with monometallic paratacamite, we observed in the XP spectra a doublet with a 2:1 branching ratio and corresponding satellite features in the Cu 2p region of XPS data. The Cu $2p_{3/2}$ peak consisted of two components with central binding energies of 933.3 and 935.4 eV, attributable to CuO and Cu-Cl , respectively [84, 86]. We could not detect any peaks in the Zn 2p region, indicating a Cu-rich surface. EDX measurements showed that the bulk contained 0.1 atomic % Zn. We detected single Cl 2s and O 1s peaks at 270.1 and 531.6 eV, consistent with Cu-Cl and Cu-OH , respectively [84]. DLS data showed that our PLAL-made zincian paratacamite had a monomodal size distribution and a hydrodynamic diameter of (208 ± 35) nm.

5. Conclusions

We synthesized mono- and bimetallic Cu and Zn nanomaterials by pulsed laser ablation in aqueous liquids, using 150 mJ, 355 nm, nanosecond pulses and a novel foil target setup. PLAL of Cu or Zn foil in pure water or with added Cu or Zn salts predictably produced different materials, depending on the chemical composition of the ablation liquid. Addition of select anions to the ablation solutions led to the fabrication of more complex phase-pure nanominerals. In contrast, PLAL of metals in neat water generated mixtures of metal and metal oxide nanomaterials. Our results demonstrate that kinetic control transcended thermodynamic product formation during nanosecond ultraviolet PLAL nanomaterials synthesis.

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