



# A Review on Recycling of End-of-Life Light-Emitting Diodes for Metal Recovery

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The generation of end-of-life light-emitting diodes (LEDs) requires efforts to minimize waste and recycle critical raw elements (gallium, indium, and rare earths). This review critically analyzes recycling processes such as physical, hydrometallurgical, and pyrometallurgical treatments. An insight into gallium compounds (GaN, GaAs) and their influence on recycling strategies is provided. Pre-treatment plays a critical role in dissociating the rigid structure of GaN. The major gaps in recycling are identification, segregation, selective recovery, and limited studies on the elemental flow of toxic arsenic. It is calculated that the processing of 1 ton of LEDs is equivalent to 7.8 tons, 3.2 tons, and 42 tons of primary Ga ore, In ore, and Au ore in metallurgical value, respectively. The market value calculations revealed significant economic values of Au, Ag, and REEs. A recycling flowsheet based on the literature for the holistic recovery of Ga, In, Au, and REEs is proposed.

## INTRODUCTION

Because of enhanced energy-efficiency standards, economic benefits, and lower environmental impact, a shift from conventional to green lighting has spurred the product demand for light-emitting diodes (LEDs).<sup>1–3</sup> The growth of LEDs is caused by their low energy consumption (10 W/800 lumens), low heat emissions, long life, diversity of colors, and mercury absence.<sup>4–6</sup> The application of LEDs worldwide is promoted by actions such as marketing, replacement campaigns, and legislation.<sup>1,7,8</sup> LEDs are extensively used in displays, screens, backlights for liquid crystal displays, televisions, cellular phones, signage, lightings in homes, cars, and instrument panels.<sup>5,8,9</sup> The diverse applications of LEDs lead to an increased flow of waste LEDs; their recycling and associated challenges may become environmentally relevant in the future.<sup>4,10,11</sup>

LEDs were expected to cover 46% of the lighting market in 2019 and reach 87% by 2030.<sup>1,3,12</sup> The global LED lighting market is expected to grow at a compound annual growth rate of 13% onwards from

2021, thus increasing revenue from \$50.91 billion in 2020 to \$54.28 billion in 2022.<sup>4,13</sup> The adoption of LEDs will reduce the global carbon emissions by more than a factor of 7 from 2010 to 2050, with annual savings expected to reach 260–400 TWh by 2030.<sup>14</sup> Since 2015, India's LED (lamps) growth has grown ten-fold from 63 million units to 669 units in 2018.<sup>15</sup> In India, the replacement target is 770 million with an expected energy savings of 100 billion kWh and an estimated GHG emission reduction of 79 million tons of CO<sub>2</sub>.<sup>7,16</sup>

LEDs contain elements such as indium (In), gallium (Ga), rare earth elements (REEs: Y, Eu, Ce) classified as critical raw metals (CRMs) because of high supply uncertainties, higher economic value, and national priority.<sup>5,17</sup> The demand for Ga increases at 7.4% and can be met by producing ten times the currently produced Ga. The demand is expected to exceed 5% and 4% for In and REEs, respectively.<sup>4</sup> The major consumption of Ga is confined to GaAs and GaN electronic components used in various integrated circuits and optoelectronic devices (LEDs, solar cells, laser diodes, etc.).<sup>18</sup> By 2020, 48% of the global GaAs produced could be used in LED applications.<sup>19</sup> Hence, under current trends, recycling LEDs may aid in

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mitigating the rising demands for CRMs, will contribute to the safety of supply, and lead to a circular economy.<sup>9,10,20</sup> It is possible to recycle 98% of LED devices if proper economic and environmental measures such as separating critical element-rich components before metallurgical operations are adopted.<sup>21,22</sup>

The degradation of LEDs can originate from the semiconductor die, interconnect, or packaging material because of the operating temperature, voltage, mechanical stresses, and failure of heat sinks. The lifespan of the LED bulb is deduced at a point when it reaches 30% lumen depreciation, with indicators of end-of-life LEDs being: color shift, chromaticity, phosphor degradation, and discoloration of epoxy resins (after repeated exposures to high temperature).<sup>23,24</sup>

Even though the LED market has recently expanded, limited studies targeting a few specific metal/elements for recycling are published. A recent review presented the aspect of recycling Ga and REEs from LEDs.<sup>3</sup> However, the variability, composition difference, and distribution of critical elements in LEDs are not presented. This review analyzes the effect of Ga phases on recycling operations. Evaluation of LEDs' detailed compositional and toxicity characteristics, review of current recycling processes, and recycling challenges are carried out. Comparison based on material recovery from primary ore and LED waste is made, and a suitable recycling flowsheet and guidelines are proposed for the holistic recovery of Ga, In, Au, and As. Economic potential for recovery of various possible elements in mixed feed stream of LED is evaluated through market value calculations.

### Primary Source of Ga

Ga is a common trace element that does not form its own minerals. Ga occurs in small concentrations (~ 50 ppm average) in ores (or minerals) of other metals where it can substitute the elements of similar charge and size such as Fe, Zn, and Al.<sup>19,25,26</sup> Ga and In are produced as a by-product of alumina production from bauxite and primary zinc production.<sup>27,28</sup> Nearly 90% of Ga is produced from bauxite (~ 20 ppm–100 ppm),<sup>15,29</sup> while other sources include coal fly ash (100 ppm)<sup>28,30</sup> and sphalerite (10 ppm–1000 ppm).<sup>4,31</sup> Approximately 70–80% of Ga is extracted, while 20–30% remains in red mud (bauxite residue) during Bayer's processing.<sup>31</sup> Ga is extracted at elevated pressure and temperature (1100°C, 3.5 MPa) under highly alkaline conditions (NaOH), making Ga recovery complex.<sup>15,32</sup> Furthermore, selective Ga recovery (separation from Al) is carried out using fractional precipitation (carbonation and lime addition), electrochemical deposition (mercury cathode electrolysis), solvent extraction (Kelex 100), and ion exchange (Duolite ES-346 and DHG586 resins).<sup>29</sup> In the case of zinc refinery residue, two-stage

leaching (H<sub>2</sub>SO<sub>4</sub>, oxalic acid) followed by solvent extraction using amine extractant (N235 + TBP, A/O::3:1) led to the sequential separation of Ga (99%) from Zn, Cu, Fe, and Ge.<sup>33</sup> Selective extraction of (98.5%) gallium from sulfate leach solution of zinc refinery using phosphate ester (H<sub>2</sub>R) (two-stage counter current, A/O::1:1) followed by H<sub>2</sub>SO<sub>4</sub> scrubbing was also reported.<sup>34</sup> These extraction methods can also be extended to recover (Ga) from leach solution of end-of-life LEDs because similar impurities (Al, Cu, As, Fe) are present. However, influencing parameters such as acid/reagent concentration, regeneration of solutions, process steps, environmental impact, and economic benefit need to be ascertained.

### Primary Production of LEDs

Approximately 75% of the global production of gallium (574 tons in 2013) is used to produce semiconductor materials.<sup>35</sup> Ga is widely used in the electric and electronic industry as compounds (GaN, GaAs, GaInAs, etc.) to provide better electric conductance, high power density, and voltage breakdown limits. Refined Ga (high purity) is applied in wafer and chip production in LEDs (semiconductors), and a significant Ga (93%) is lost in the process of cutting, etching, and polishing of single crystal (GaN, GaAs, etc.).<sup>3</sup> The major losses during semiconductor manufacturing include stages of (1) primary production (33%), (2) refining (16%), (3) wafer production (19%), (4) recycling from wafer (6%), and (5) chip production (28%).<sup>31</sup> The metal oxide chemical vapor deposition technique is used to manufacture epitaxial wafers (GaN, GaInN) and often results in the generation of Ga-(In)-rich dust. However, only 5% of these losses are recovered/recycled.<sup>36</sup> Given resource conservation, it becomes imperative to also recycle the high amounts of critical elements lost in the production stage of LEDs.

### CHARACTERISTICS OF LEDS

LEDs are solid-state devices composed of inorganic semiconductors (0.25 mm<sup>2</sup>) emitting light by electroluminescence (Fig. 1a) where no energy is lost because of the transfer of electrons between the conduction and valence band.<sup>3,21</sup> The structure of LED, as shown in Fig. 1b, constitutes the transparent encapsulating material made of epoxy resin containing the LED chip, silver line, and surface support made of white PPA plastic (polyphthalamide) and metal heat sink joined by adhesives (epoxy resin and additives).<sup>6–8</sup> The transparent casing contains organic compounds (brominated flame retardants) (1.5 mm–3 mm), which are considered persistent organic pollutants and are harmful to the environment.<sup>8,37</sup>

The LED chip consists of elements such as Ga, In, Au, As, and RE (phosphor),<sup>3,9</sup> tightly packed with resins, plastics, electrodes, and other metals.<sup>11</sup> The

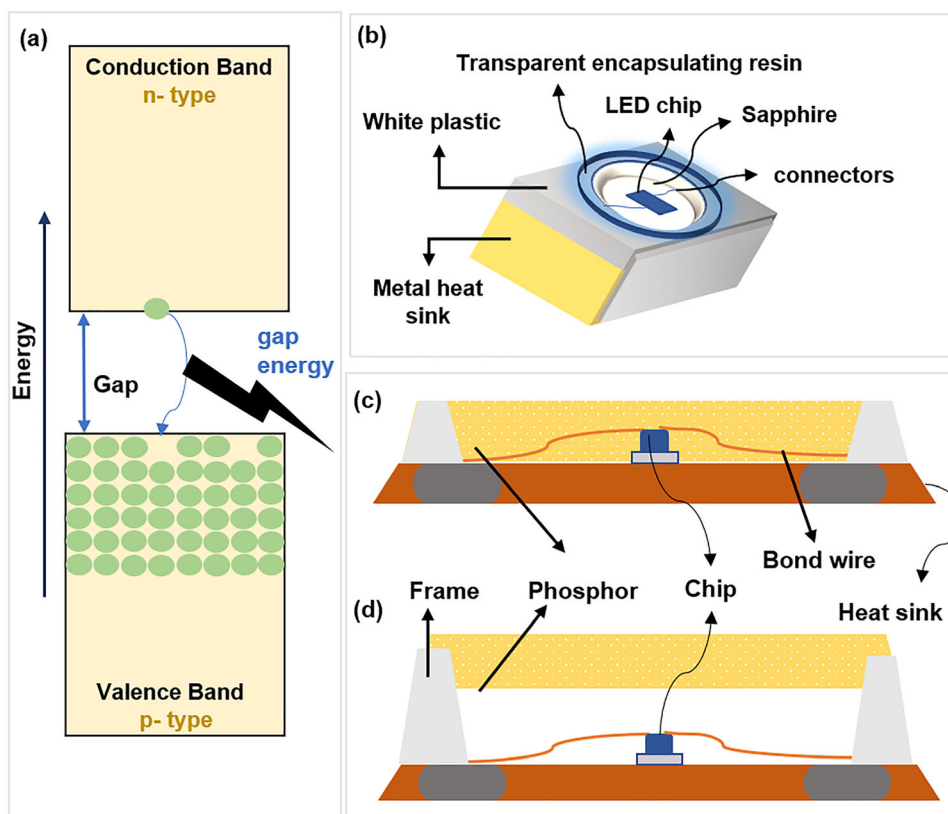


Fig. 1. Schematic of (a) emission in a semiconductor (chip) of LED, (b) SMD LED, schematic of (c) direct and (d) remote phosphor contact<sup>38–40</sup>

chip is mainly made of group III–V compounds, such as gallium arsenide (GaAs), gallium nitride (GaN), indium gallium (InGaAs), indium gallium nitride (InGaN), and other semiconductors<sup>6,36</sup> in a deposition layer of a few micron thicknesses.<sup>3</sup> The various chemical combinations of Ga in the p-n junction semiconductor chips (Al, As, P, In, and N as dopants) determine the color of the LED light and their emission wavelength.<sup>4,21,23</sup> However, such LEDs cover a limited wavelength range; hence, down-converting phosphors and quantum dots were introduced. Phosphor-based LEDs containing REEs (Y, Eu, Tb, Gd, Ce, Tm, Sm) are present in display backlighting [plasma display panels (PDP) and liquid crystal displays (LCD)]<sup>22,41</sup> owing to optical properties such as fluorescence, high refractive index, and low power consumption.<sup>23,42</sup> Au, Ag, and Pb are employed in electrical contacts and solders, while metals such as Cu, Sn, and Al are used for mechanical, thermal, and electrical purposes.<sup>1</sup>

The chip, the main functional part of the LED, emits blue light in the electric field,<sup>1</sup> which is converted into a visible spectrum by a phosphor converter. The phosphor is coated on encapsulant walls or LED chips (Fig. 1c and d) and is doped with  $\text{Ce}^{3+}/\text{Eu}^{2+}$  ( $\text{CaAlSiN}_3:\text{Eu}^{2+}/\text{Ce}$ ;  $\text{Y}_3\text{Al}_5\text{O}_{12}/\text{Tb}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ ) to emit longer wavelength light.<sup>23,42,43</sup> The white LEDs consist of GaN/InGaN chips, which produce highly efficient white lighting as it emits a

wide range of wavelengths for suitable commercial applications.<sup>1,2,11</sup> White LEDs are widely used as backlighting in devices such as notebooks (50 in no.), PC monitors (100 in no.), and TFT TVs (150 in no.).<sup>31</sup> In LEDs with low In and Ga concentration due to less height,  $\text{In}_x\text{Ga}_{1-x}\text{N}$  is utilized with 45% of In (0.029 mg/LED), 41% of Ga (0.0325 mg/LED), and 14% of N<sup>44</sup> with variable die areas between 0.22 mm<sup>2</sup> (mobile phones) and 77 mm<sup>2</sup> (direct-lit televisions).<sup>42</sup> For a 1-mm<sup>2</sup> die area of white LED, 0.007 mg and 0.009 mg of Ga and In are required, respectively.<sup>45</sup>

The surface-mounted device (SMD) LEDs (Fig. 1b) are easily available in different sizes and shapes and have a relatively simple structure and are favorable for recycling.<sup>11,36</sup> SMD-type LED chip consists of different layers of Ga (compounds) with gold electrodes on its surface. The chip is present on synthetic sapphire ( $\text{Al}_2\text{O}_3$ ) and packaged in an epoxy resin dome. Various applications of SMD LEDs are in indicators, car lamps, LCD backlights, and indoor lighting. Presently, electronics employ Ga in GaAs or GaN form, and in particular, OLEDs and LCDs use GaAs.<sup>3</sup> Due to the low solubility of nitrogen in Ga and the high vapor pressure of N on GaN, the native substrate of GaN is not available in large quantities.<sup>11</sup> GaN is used as the single crystal in electronic components<sup>5,28</sup> and is refractory because of high bond energy crystal (7.72 eV/molecule), mechanical stability, high heat capacity, and

thermal conductivity.<sup>5,10</sup> The hexagonal wurtzite type of crystal structure (Fig. 2a) in which both Ga and N atoms are coordinated tetrahedrally via strong covalent bonds makes the dissolution of locked Ga difficult.<sup>27,46,47</sup> However, GaAs consist of a zinc-blend crystal structure wherein the central atoms are occupied by the Ga atoms (Fig. 2b). The structure consists of two FCC lattices made entirely of Ga atoms and the other by As atoms. The surface properties (such as etch rates or attack of lixivants) are governed by its orientation.<sup>48</sup> Moreover, due to higher cohesive energy for GaN (~9.05 eV), dissociation is difficult compared to GaAs (1.63 eV).<sup>27,49,50</sup>

### Hazardous Elements

Unlike fluorescent lamps, LEDs do not contain Hg; however, they contain As (9–1350 ppm) and Pb (16–900 ppm) as hazardous metals,<sup>6</sup> and LEDs are listed as hazardous wastes in certain regions such as the EU, US, and Canada.<sup>8,53</sup> The widely adopted disposal practice of landfilling and incineration for waste LEDs threatens the environment with simultaneous loss of valuable resources.<sup>3,54</sup> In general, the acute lethal dose of inorganic arsenic to humans was estimated to be ~ 0.6 mg/kg/day.<sup>55</sup> The toxicity characteristics (generally for e-waste and particularly for LEDs) are determined using Toxicity Characteristics Leaching Procedure (TCLP) and Total Threshold Limiting Concentrations (TTCL) regulations. Generally, the TCLP method classifies a substance as hazardous based on the leached concentrations (mg/L) of specific chemicals that would leach in landfill facilities. On the other hand, TTCL determines whether a discarded or end-of-life product can be considered hazardous (mg/kg).<sup>41</sup> TCLP test determines the As limit as 5 mg/L, recently reduced to 1 mg/L.<sup>56</sup> The summarized

results of various toxicity characteristics are shown in Table I. Lim et al. studied the As toxicity in various types of LEDs (color/lumen) and reported the values as 5–111 mg/kg, which is under the regulatory limits (500 mg/kg).<sup>37</sup> In an overall mixture of linear LEDs, using TCLP, and KET (Korean extraction test) hazardous elements (Cu, Pb, As) were determined to be within the regulatory limits. Components such as LEDs (As, Pb) and drivers (Pb and Cu) were classified as hazardous.<sup>55</sup> The higher leaching concentrations observed in TCLP were due to the lower pH of the solvent (2.8) than KET (5.8–6.3). The parameters in all the toxicity tests were TCLP: particle size < 9.5 mm; pH 2.88–4.93; 18 h TTCL: < 2 mm; pH < 1; 0.5 h KET: < 5 mm; 5.8–6.3; 6 h.

Arsenic is toxic and carcinogenic, and in humans, it may cause skin, respiratory cancer, perforation of the nasal septum, and leach into the soil, posing a threat to the environment.<sup>4,58</sup> Ga and In components affect human health (dermatitis, skin rash, decreased blood cells, joint pains, pneumonia).<sup>6,11,18,28</sup> Moreover, the arsine gas [AsH<sub>3</sub>] is the most toxic form of arsenic, generated in aqueous solutions during hydrometallurgical treatment of LEDs (Eq. 1). Considering LED waste consists of GaAs with an average composition of ~ 710 g/ton, 1 ton of LED yields ~ 382 ppm of arsine on leaching. The inhalation of > 25 ppm of arsine gas is reported to be lethal within an hour of exposure, while > 250 ppm is instantaneously lethal.<sup>59</sup> Hence, extensive studies regarding the release mechanism of arsine, the effect of acidic concentrations, temperatures, and quantification of values are needed for hydrometallurgical treatment of LEDs.

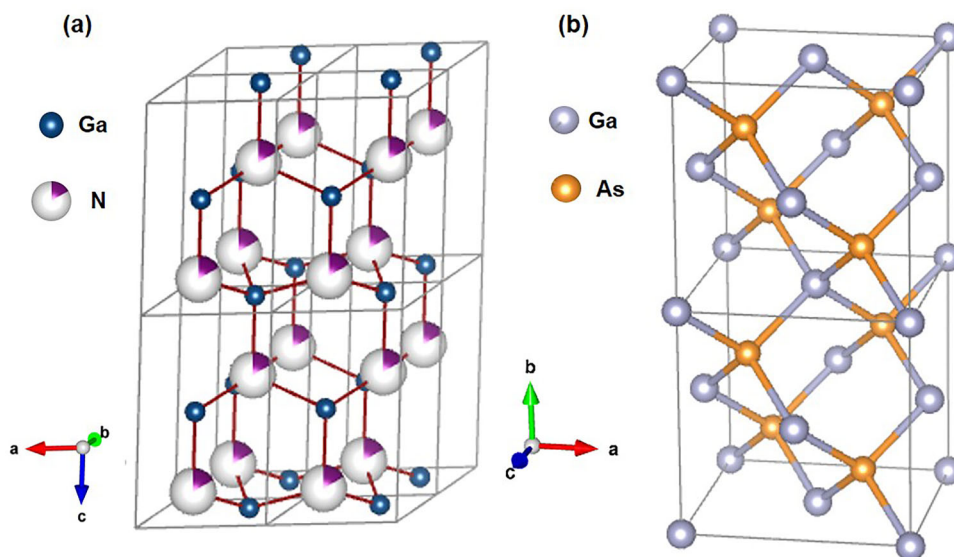
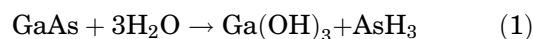


Fig. 2. Crystal structure of (a) GaN<sup>46,51</sup> and (b) GaAs<sup>48,52</sup> (drawn using Vesta software)

**Table I. Toxicity characteristics of LEDs**

Metals	TTLC (mg/kg)		TCLP (mg/L)			KET (mg/L)		
	Limit	LED <sup>a,b,c</sup>	Limit	LED <sup>a,b,d</sup>	LED <sup>d,*</sup>	Limit	LED <sup>d</sup>	LED <sup>d,*</sup>
Arsenic	500	5.4–111	3–5	N/D	<b>8.01</b>	1.5	N/D	<b>3.16</b>
Copper	2500	<b>31.8–33892</b>	N/A	1–3.1	0.037	3	0.48	0.004
Lead	1000	<b>7.7–8103</b>	5	<b>1.4–186</b>	<b>5.83</b>	3	0.8	<b>3.3</b>
Nickel	2000	<b>290–4797</b>	N/A	17	–	–	–	–
Silver	500	<b>30–721</b>	5	N/D	–	–	–	–
Mercury	20	N.D; 0.4	0.2	N/D	N/D	0.005	N/D	N/D
Antimony	500	1.3–150	N/A	N/D	–	–	–	–

Bold values signify that the concentration of these elements are above the threshold toxicity value/limit as determined by various toxicity tests (TTLC, TCLP, KET)

<sup>a</sup>Ref. 37 (pin-type LEDs), <sup>b</sup>Ref. 57 (LED bulbs), <sup>c</sup>Ref. 53 (LED lamps), <sup>d</sup>Ref. 55 (linear LED lamps)

\*Refers to the analysis of main LED chip within LED (as a component) and not an overall mixture of LED lamps

N/A not applicable, N/D not detected

## RECYCLING OF LEDs

Due to ascending resource scarcity and environmental burden, end-of-life LEDs need significant attention. Various studies adopted for the recycling of LEDs (Table II) reveal a significant difference in metallic content (Ga, In, As, Au) and semiconductor type (GaAs, GaN, InGaN). A comparative analysis of Ga concentration in LEDs of tubular and bulb lamps revealed higher Ga (0.38%) in bulb than tubular (0.084%) LEDs.<sup>60</sup> SMD has a higher concentration of Ga than other types due to the number of chips enclosed within the LEDs. Indium gallium zinc oxide (IGZO) targets used in organic LEDs (owing to better resolution, speed, and energy efficiency) is comparatively a concentrated source of ~ In (30–43%) and Ga (22–26%).<sup>61</sup>

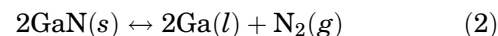
### Pre-treatment Methods

Physical, chemical, thermal pre-treatments are widely used to enrich valuable elements in LEDs. Milling is often required to physically separate various constituents due to the strong interlocked/merged structure.<sup>4,5,11,27</sup> The critical metals are concentrated in size fractions (< 1 mm) (Table II), which are subsequently processed through pyro- and hydrometallurgy. Electrostatic separation was done to separate the (non-conductive) LED chips from other metallic parts (Cu) before chemical treatment to reduce the acid consumption, which increased the Ga concentration by twofold.<sup>5</sup>

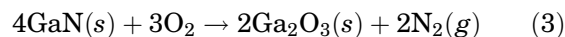
Sequential mechanical separation involving crushing, classification, electrostatic, magnetic, and gravity separation was conducted to segregate various components of LED bulbs.<sup>2</sup> Electrostatic separation of phosphor activated/GaN LED resulted in the segregation of conductive (Au, Ag, Cu, Pb) and non-conductive (Ga, Ce, Y) fractions.<sup>1</sup> However, losses of ~ 11% in fines (< 0.25 mm) [30% Sn, Y, 9% Au, 6% Ag] corresponding to process steps of

milling, particle size separation, and electrostatic separation may limit its applicability at an industrial scale.

Pyrolysis (500°C) and incineration were used to decompose the plastics and organics surrounding the LEDs, wherein pyrolysis reduced organics by 22–57%.<sup>11,28,36</sup> Moreover, thermal decomposition of the highly stable GaN phase is also observed under vacuum as per Eq. 2 due to the low vaporization coefficient ( $4 \times 10^{-10}$  at 727°C).<sup>36,47</sup> However, a proper explanation for Ga (l)/Ga(g) formation during pyrolysis and its subsequent influence on secondary treatments is required.



Various combinations of pre-treatments were investigated for converting GaN into soluble Ga<sub>2</sub>O<sub>3</sub> form. Mechano-chemical oxidation (Na<sub>2</sub>CO<sub>3</sub>) (with or without preliminary leaching) led to the formation of more stable ~ Ga<sub>2</sub>O<sub>3</sub> characterized by the growth of the Ga<sub>2</sub>O<sub>3</sub> layer on GaN. The possible reaction at 1200°C is shown in Eq. (3) with a negative change in free energy for oxidation [– 357 kcal/mol]. The pre-treatment improved Ga leaching from 4.91 wt.% to 73.6 wt.%; however, In is evaporated during the oxidation process.<sup>68,70</sup> The oxidation (1100°C) process before leaching (4 M HCl) was also adopted by Mareefvand et al.; however, it involved high temperature, grain growth (reduced surface area affecting leaching), and reduced Ga recovery due to diffusion in Al substrate.<sup>28</sup> Furthermore, In detected in the LED industry waste (due to decomposition of InN at room temperature) could be treated by oxidation as the free energy of In<sub>2</sub>O<sub>3</sub> in the range of 0°C to 1600°C and was negative (feasible).



**Table II. Summary of recycling processes used for recovery of metallic values from different types of LEDs**

<b>Feed type/phases/concentration</b>	<b>Pre-treatment process</b>	<b>Recovery (%)</b>	<b>References</b>
Pyrometallurgy <b>SMD GaAs</b>	Mixing (waste LEDs and GaAs chips 10:1), pyrolyzed (450°C, 30 min) Vacuum metallurgy separation (1000°C, 1 h, 20 Pa)	Ga, As-95	Ref. 62
<b>SMD GaN/InGaN</b> (ppm) Ga-2.07, In-1.06, Au-16.66 <i>Pure GaN (99.99%)</i>	Pyrolysis (500°C, 1 h); crushing (< 40 mesh) Vacuum metallurgy (1100°C, 1 h, 0.01–0.1 Pa) Mixing (GaN + NH <sub>4</sub> Cl, 1:6), palletizing (10 MPa) Chlorination (20 vol.% O <sub>2</sub> in N <sub>2</sub> , 500°C, 30 min)	Ga-93.5, In-95.7 Ga > 90	Ref. 11 Ref. 63
Hydrometallurgy <i>Edge type /SMD GaN</i> ; Ga-253 ppm	Crushing (106–1000 μm), electrostatic separation, MCA (1:1 Na <sub>2</sub> CO <sub>3</sub> , 2 h) Leaching (4M HCl, 2 h, S/L-20g/L, 80°C) Crushing (1–2 mm)	Ga-99	Ref. 5
<i>Automobile-red /SMD GaAs, GaN</i> (g/kg) Ga = As-1.35, Au-0.36, Cu-290	Two-stage leaching 40°C, S:L-1:46 [I-1.5 M HNO <sub>3</sub> , 90 min; II-1.5 M aqua regia, 6 h] UF/NF (pH-0.18–4)	<i>NF: rejection</i> Ga-85, Cu-74, As-52.7	Ref. 4
<b>GaAs, InAs, GaN</b> (LS) ppm As = Al-53; Ga-109; Au-142; Cu-63; Fe-238; Pb-73; Sn-28; Ni-40.	Crushing, classification [fine (< 710 μm), coarse (> 710 μm), electrodes] Leaching (IL-[P <sub>44410</sub> ][Br <sub>3</sub> ], S/L-1:10, 60°C); stripping of As (4M NaBr, O:A::2), Ga (ultrapure water, O:A::1); stripping-precipitation of In (5 eq. NaOH, O:A:: 0.5) Crushing < 2.5 μm	As-95, Ga-96, In(OH) <sub>3</sub> -99	Ref. 27
<b>IGZO (InGaZnO<sub>4</sub>, In<sub>2</sub>Ga<sub>2</sub>ZnO<sub>7</sub>)</b> (%) In- 0.045–48.7, Ga- 0.26–27.8, Zn-23.54	Leaching (3–9 M HNO <sub>3</sub> /HCl, 50–80°C, 1–2 h). For In and Ga: SX (0.015–0.02 M D2EHPHA/30% T-iso-BP, A/O:: 2:1–3:1), stripping (HCl, pH-2). In extraction: SX (15% D2EHPA; A/O::2:1); stripping (1M HCl). Cementation (Zn dust, pH:7–12) Crushing < 2.5 μm	Ga-94.6–96.2, In-97.8–98.6, Zn-98.3	Refs. 61, 64
<i>Industrial waste (1–2 μm) GaN</i> (%) Al <sub>2</sub> O <sub>3</sub> -89.9, Fe <sub>2</sub> O <sub>3</sub> 3.39, Ga-3.38, SiO <sub>2</sub> -1.91	PBM (isopropanol media, 24 h, zirconia, 150 rpm, 1–100 μm) Pressurized leaching (0.25M HCl, S/L: 30 g/mL, 200°C, 15 atm, 3 h)	Ga-98.5	Ref. 10
<i>Lamp /COB</i> LS (mg/g) Au-2.17, Ag > 1.96, Fe-12.8, Ca-6.77	Leaching (12M aqua regia, 80°C, 24 h), Adsorption: anion exchanger (Diaion WA21J O/A-1, 25°C, 24 h), elution (0.1 M thiourea). Precipitation-reduction (NaBH <sub>4</sub> , pH > 8)	Au-97.6	Ref. 65
<b>GaN</b> Ga-9.3μg/chip	Incineration, disassembly, oxidation (1100°C, 150 min) Leaching (4 M HCl, 93°C, S/L: 3g/L, 2 h)	Ga-91.4	Ref. 28
<b>SMD GaN</b> (ppm) Ga-22.65, Fe-657879, Cu-13930.7	Pyrolysis (500°C, 1 h); PBM (450 rpm, 15 min); size classification Leaching (0.7 M OxA, 10 g/L, 90°C, 48–75 μm, 1 h)	Ga-90.4	Ref. 36
(ppm) Ga-8, Fe-24, Ni-18, Al-10, Cu-2, Mn-1	Separation of Ga coated portion Leaching (2 M HCl, 100 g/L, 24 h), SX (0.5 M cyanex 272/Cyanex 923 A/O:1), stripping of Al (0.01M HCl), Ga (0.1M HCl)	Ga-91	Refs. 66, 67

**Table II. continued**

<b>Feed type/phases/concentration</b>	<b>Pre-treatment process</b>	<b>Recovery (%)</b>	<b>References</b>
<i>Backlighting</i> <b>YAG:Ce, Ca<sub>0.985</sub>AlN<sub>3</sub>:Eu<sub>0.015</sub>, Al<sub>0.08</sub>Ga<sub>0.92</sub>N, In<sub>0.98</sub>Ga<sub>0.42</sub>N, GaN</b> (Ce, Eu, Y, Ga, In)	Leaching (HCl, 2 h, 70°C), precipitation of CeO <sub>2</sub> (ozone, pH 3, 90°C, 2 h), SX (10% HDEHP, 5 stages), stripping (4 M HCl, 25°C), zinc column exchange, precipitation of Eu (using H <sub>2</sub> SO <sub>4</sub> ), Y (using KOH). Calcination (OxA, 200°C, 2 h)	Ce-97, Eu-88, Y-78.9	Ref. 22
<i>MOCVD</i> <b>(0.1–100 μm) GaN/InGaN/Ga<sub>0.97</sub>N<sub>0.9</sub>O<sub>0.09</sub>/In</b> (wt.%) Ga-74.3–97.7, In-1.86–6, Al-0.59–0.84, Mg-0.16, Si-0.08, Fe-0.05	Leaching (4M HCl, 100 g/L, 100°C, 1 h), PBM (Na <sub>2</sub> CO <sub>3</sub> , 1:1, zirconia, 150 rpm, 24 h), and/or (direct) oxidative roasting (1100°C, 4 h) or of residue Leaching (2–4 M HCl, NaOH, KOH, HNO <sub>3</sub> , 100g/L, 80–100°C, 1 h) Leaching (4M HCl, 50 g/L, 100°C, 1 h)	Ga-64.6–73.7, In-95.8 Ga-4.91 (DL)	Refs. 68, 69
Supercritical and physical treatment <i>SMD GaAs, InGaAs</i> (ppm) Ga-40; In-20; As-9; Au-800	Chemical treatment (ethanol; 250°C, 7.5 MPa, 90 min) Subcritical water-ethanol mixture (300°C, 60% water, 4 h)	Ga, As-93, In-85.7, Ag-99.99	Ref. 6
<i>SMD GaAs</i> (ppm) As-42.5, Ga-37, Ag-805	sc. Water: 250°C, 500 rpm, 3% H <sub>2</sub> O <sub>2</sub> , 12 min 300°C, 300 rpm, 3% H <sub>2</sub> O <sub>2</sub> , 400 min	As-98.4, Ga-80.5	Ref. 8
<i>Bulbs/SMD/SiC type</i>	Crushing (25 mm sieve) < 25 mm ~ electrostatic separation (30 kV, 20 rpm), > 25 mm ~ magnetic separation (50 rpm, 3 stage), gravity separation (KI) on non-magnetic fraction	Components-98–100	Ref. 2
<i>Tubular GaN/Ce:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub></i> (%) Au-0.06, Ag-0.12, Cu-65.03, Sn-4.26, Ga-0.17, Ce-0.01, Y-0.36	Crushing (1 mm), Physical separation (size < 0.25 mm, 0.5–0.25 mm, > 0.5 mm) electrostatic separation (V-20–35 kV, roll speed-30–90 rpm)	Au-80.2, Ag-89.3, Cu, Ga-96, Pb-93.3, Ce-100, Y-95.2	Ref. 1

Bold values represent the phases present in LEDs and italics represent the feed type  
*SMD* surface mount device, *COB* chip on board, *MOCVD* metal organic chemical vapor deposition, *sc* supercritical, *SX* solvent extraction, *IL* ionic liquid, *DL* direct leaching, *OxA* oxalic acid, *PBM* planetary ball milling, *LS* leach solution, *MCA* mechanochemical activation

The solvothermal method was used for the separation of encapsulation (resin, chip, Ag line) and surface support (plastic, metal sink) of LEDs using ethanol (7.5 MPa) and water.<sup>6,8</sup> Above the critical temperature of ethanol (> 243°C), the solvent effect is exhibited, which softens, dissolves, and degrades the organic matter/adhesive.<sup>6</sup> Two-stage hydrothermal treatment, first for the degradation of PPA (surface support), promoted by H<sub>2</sub>O<sub>2</sub> oxidant followed by the removal of encapsulating material, was found successful.<sup>8</sup> Comparatively, the solvothermal method is environmentally friendly with minimal losses and allows for pre-separation of hard plastic-containing harmful flame retardants.

### Pyrometallurgy

The vacuum metallurgy process facilitates the decomposition of GaN, GaAs, and InGaN by lowering decomposition temperature and results in non-entrainment of impurities (sealed system) with

enrichment of critical elements. The vacuum metallurgy process involved 0.01–0.1 Pa pressure and 1100°C temperature (above the boiling point of In and Ga) under which In and Ga elements are condensed together (324–802°C) while Au and Cu are condensed in another zone (802–1012°C), thus leading to separation. However, Au losses (~ 69%) from the electrode are evident because of limited evaporation of Au (as covered by bond wires) and the formation of Cu-Au alloy.<sup>11</sup> Vacuum separation of pyrolyzed GaAs chips led to their decomposition into As and Ga vapors, which can be separated and recovered (1000°C, 20 Pa) in different zones because of different condensation properties and vapor pressures.<sup>62,71</sup> However, due to limited temperature gradient, overlapping of Ga and As was also observed. For improvements in purity, further refining/purification using solvent extraction is required. Chlorination of GaN powder using NH<sub>4</sub>Cl resulted in the formation of soluble GaCl<sub>3</sub>, and the process was successful in spatial separation of Ga

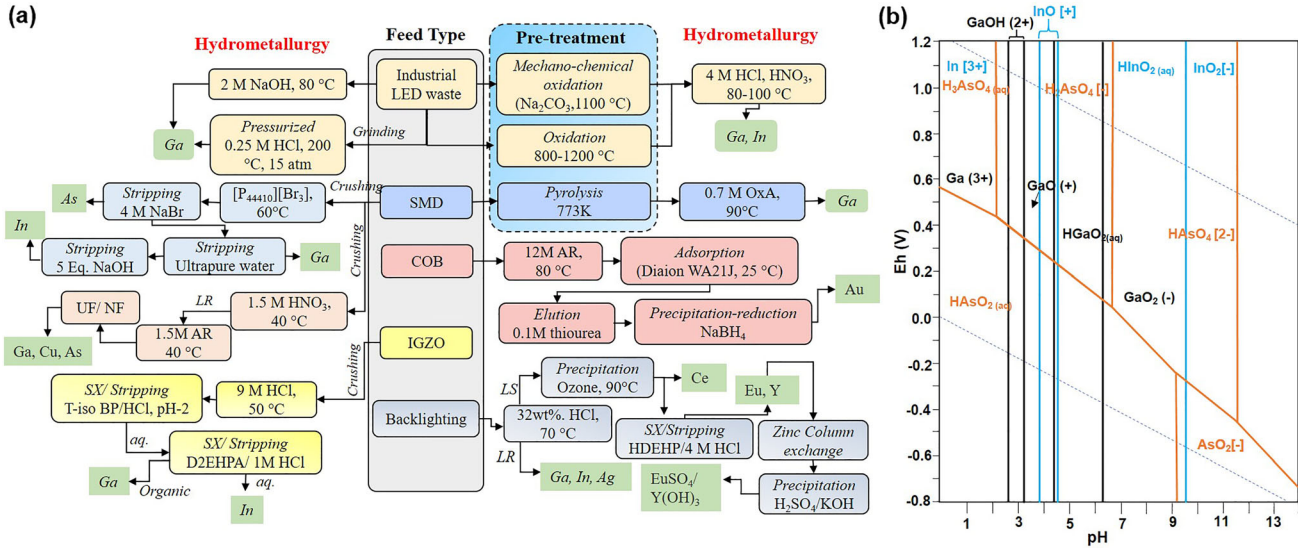


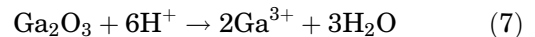
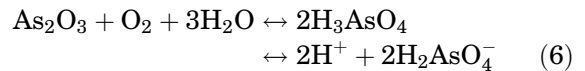
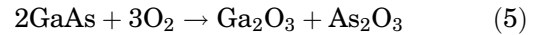
Fig. 3. (a) A summarized flowsheet of various hydrometallurgical processes and (b) Eh-pH diagram for solubility of Ga, In, and As.<sup>8,69,70</sup> UF ultrafiltration, NF nanofiltration, AR aqua regia, aq. aqueous, SMD surface mount device, COP chip on board, IGZO indium gallium zinc oxide, OxA oxalic acid

(III) and In (III) because of considerable differences in their (chloride) vapor pressures.<sup>63</sup> Apart from that, two-stage heating—sulfurization (180°C) and evaporation (800°C) under N<sub>2</sub> flow to form arsenic sulfides (low toxicity)—was studied for As recovery.<sup>72</sup> LED recycling via conventional pyrometallurgical operations (copper and gold recycling process) is limited because of preferential transfer of Ga to copper or precious metal slags, low-grade waste, and the presence of arsenic.<sup>3</sup>

### Hydrometallurgy

Most LED recycling studies employing hydrometallurgy are based on Ga recovery, while limited studies exist on the recovery of Ga and In and other associated REEs and precious metals (Fig. 3a). Inorganic (HCl, HNO<sub>3</sub>, aqua regia) and organic acids (oxalic acid) are studied for the dissolution of metallic values.<sup>5,36,60,64</sup> Swain et al. revealed the efficiency order of lixivants as HCl > HNO<sub>3</sub> > H<sub>2</sub>SO<sub>4</sub>,<sup>68</sup> and the reactions involved in HCl leaching of oxidized (pre-treated) Ga are shown in (Eq. 4). However, the process is complicated because of multiple steps, and further separation of Ga and In is required. For refractory GaN, pressurized leaching method (15 atm, 0.25M HCl) or one-step alkaline leaching (2M, 80°C) was investigated, which improved the leaching efficiency of Ga to 98% and 89%, respectively.<sup>10,69</sup> On the other hand, leaching of Ga from pyrolyzed residue revealed the extraction order as oxalic acid (83.42%) > HCl (79.9%) > DL-malic acid (71.7%) > citric acid (70.62%). Better leaching efficiency of oxalic acid was due to higher dissociation constant (among inorganic acids) and iron impurity (ferrous oxalate) removal. However, the effect of preliminary phases

on leaching was not discussed.<sup>36</sup> For GaAs type LEDs, oxidative hydrothermal degradation led to the separation of Ga and As in the leach solution, while Ag line and metal pin chip residues were recovered in the residue. The possible reactions are represented in (Eqs. 5–7).<sup>8</sup> Hydrophobic ionic liquid tributyl-decyl phosphonium tribromide [P<sub>44410</sub>][Br<sub>3</sub>] was effective for leaching GaAs and InAs with an advantage of non-formation of arsine (AsH<sub>3</sub>). However, GaN was not leached (due to high cohesive energy), and contaminants' effect in strip solutions needs further investigation.<sup>27</sup>



As per the combined Eh-pH diagram (Fig. 3b), Ga, In, and As are expected to dissolve under acidic and alkaline conditions. Therefore, all elements are expected to be present in the leach solution under any particular leaching condition, requiring individual elemental extraction (high purity) using precipitation, solvent extraction, and ion exchange. Selective Ga extraction from the leach solution of LEDs (Cl<sup>-</sup>) was studied using extractants Cyanex 272 and Cyanex 923 involving step-wise separation of impurities (Al, Fe, Zn, Ni Mn). However, drawbacks are low recovery, complex process, and high cost due to multiple steps.<sup>66,67</sup> From highly valued



IGZO targets, sequential solvent extraction (T-isobutylamine, and D2EHPA) resulted in > 96% Ga and In recovery.<sup>60</sup> The method of nano/ultra-filtration employed for Ga recovery revealed that the membrane integrity depended on the pH, and nanofiltration was more suitable at low pH. The retention of Ga by the ultrafiltration membrane is dependent on the Ga precipitation, and pH adjustment adds cost to the process, thus restricting the acid recovery.<sup>4</sup>

Although most studies are carried out for Ga recovery, recovery of Au from LEDs using the leaching-adsorption method was also seldom reported.<sup>65</sup> The demerits of the study include high acidic concentrations and high dilution of aqua regia for adsorption. Moreover, Rebello et al. also determined Au (350 mg/kg) and REEs (Y-20.8 mg/kg, Ce-16.2 mg/kg) in lamp LEDs; however, Ga was not detected, which could be due to variation in model or manufacturing.<sup>54</sup> Ruiz Mercado et al. discussed the recovery of REEs via leaching (HCl) of Eu, Y, Ce, and impurities (Al, Ni, Ca, and W), while Al, In, and Ga nitrides separated in the residue. Furthermore, REEs were extracted by SX, precipitation, and calcination in the form of rare earth oxides.<sup>22</sup>

The recycling of plastics (70 wt.%) by chemical dissolution of white plastic (polystyrene) using regenerative organic acids (S/L-1:5, 150 rpm, 60 min) was also studied. The effectiveness of solvents follows the order: dimethylacetamide (DMA) > dimethylformamide (DMF) > dimethylsulfoxide (DMSO), with major contributing factors being molecular structure, chemical properties, and temperature.<sup>73</sup> Leaching (HNO<sub>3</sub>), the addition of complexing agents, and gel formation were adopted for the reutilization of waste Ce doped YAG from industrial waste (of spent lamps) as a starting material in phosphor activators of LEDs.<sup>74</sup>

Bio-leaching was also adopted in a few studies to dissolve the metal compounds by naturally producing reagents (Fe<sup>3+</sup> or/and protons). Cu (84%), Ni (96%), and Ga (60%) recovery from pin-type LEDs was facilitated by *Acidithiobacillus ferrooxidans*. The optimal concentration of heavy metal (Cu, Ni, Zn) media is essential for bacterial growth.<sup>75</sup> *Arthrobacter creatinolyticus* was also studied for Ga recovery from GaN (< 38 μm)<sup>76</sup>; however, long reaction times and low recoveries are some of the limitations.

### Recycling Challenges

The recycling of LEDs consists of broad challenges linked to product (composition and design), recycling, and economics (see Fig. 4). The intrinsic structure of LEDs consisting of Ga compounds is difficult to recycle because of structural strength and low concentrations. A significant constraint in recycling is posed by a lack of motivation in scientific collection, sustainable disposal, or

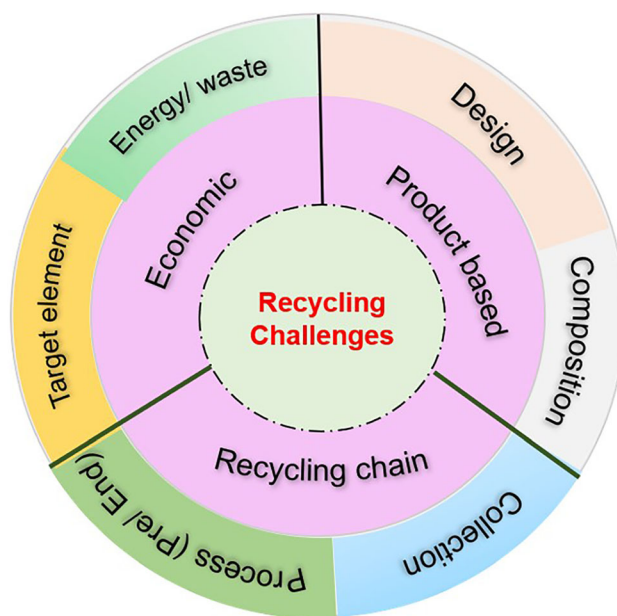


Fig. 4. Various challenges involved in the recycling of LEDs

industrial recycling. The low gallium concentration (~40–400 ppm), high energy requirements for recycling, and heterogeneous feed result in a low recycling rate (< 1%) of Ga from secondary sources such as LEDs.<sup>35</sup>

The current studies of recycling critical metals from LEDs are not holistic and suffer from drawbacks such as (1) recoveries of few specific elements, (2) little attention toward As (loss) and its process flow, (3) low recycling rates, a mixture of products, and (4) secondary emissions. Ideally, the recycling process should target all essential and valuable metals/resources with high purities. At present, the compositional characteristics reveal non-uniformity, which needs further understanding to ease classification, segregation, and recycling strategies. Furthermore, different substrate materials (SiC, sapphire, nanoscale patterned sapphire, various dopants), packaging materials (metallic/plastic materials, thermal sinks), phosphors (activators), and encapsulating materials result in a complex and heterogeneous feed stream, which causes dilution of low concentrated elements, decreased selectivity, and multiple-pre-processing steps.

Environmentally suitable LEDs (product) by adopting green design and manufacturing processes are important future requirements. Substitution of toxic metals by safer alternatives and reduction in losses of Ga during manufacturing needs significant attention. Prior knowledge about the distribution of valuable elements in LED components is important to facilitate targeted recovery with minimal losses. An assessment to address the release/treatment of hazardous constituents needs to be conducted to help formulate environmentally suitable recycling strategies.<sup>9,57</sup> The possible formation of volatile and hazardous AsH<sub>3</sub> gas during LEDs'

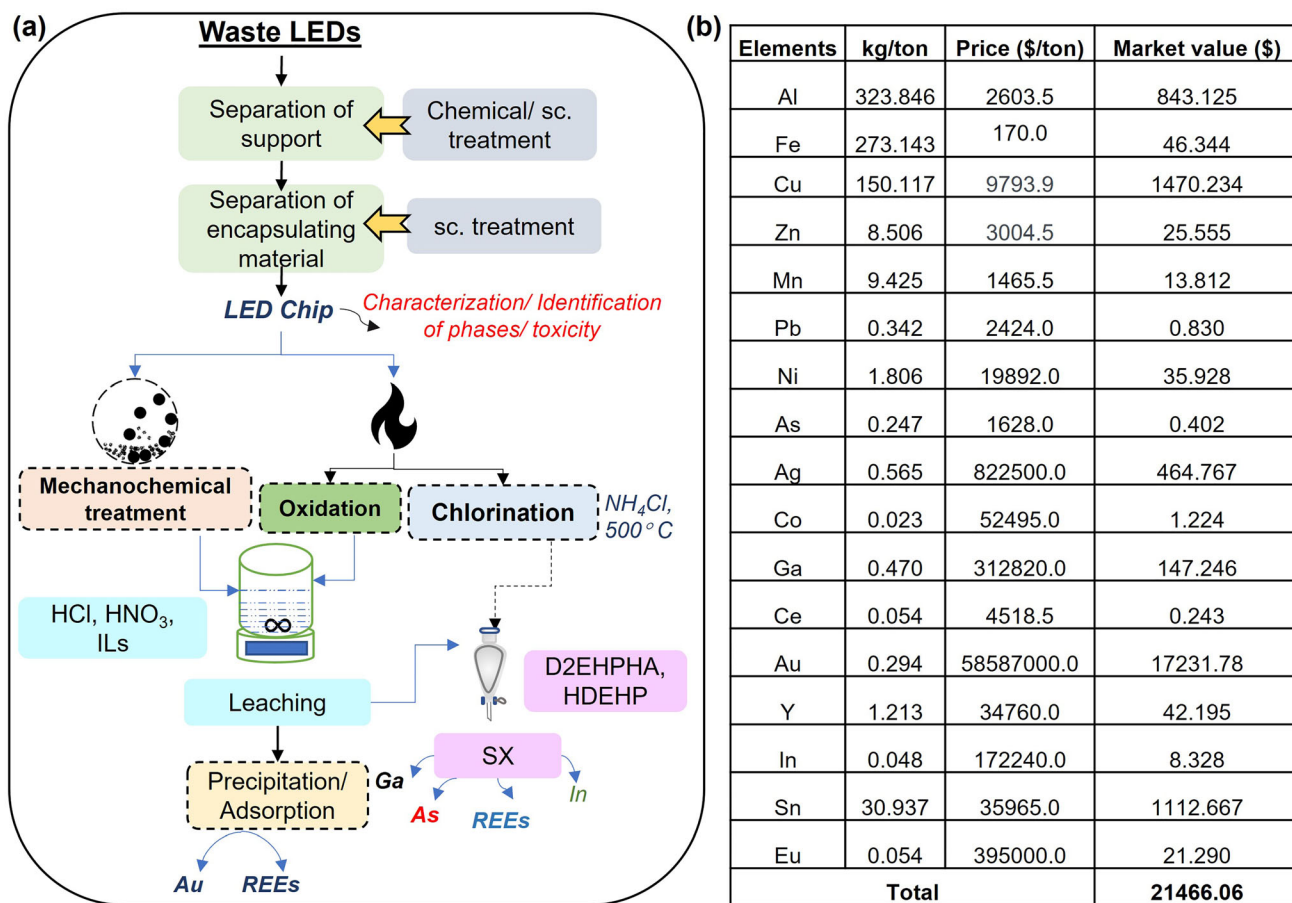


Fig. 5. (a) Conceptual flowsheet for recycling of valuable elements and (b) market value calculation of LEDs<sup>77,78</sup>

hydrometallurgical operations needs detailed investigation to ascertain the feasibility of leaching using aqueous solutions.

Furthermore, exploring non-aqueous solutions for efficient and selective leaching is required. It is essential that end recycling products meet the standard of re-utilization in semiconductors, LED manufacturing, or other raw material syntheses. Moreover, a special focus on analyzing the recycling potential of LEDs and economic incentives and environmental sustainability of recycling is required. In this direction, Fang et al. evaluated the recycling potential of various LEDs from the economic and technological perspective, using tools of criticality and recyclability, respectively. Recyclability refers to the difficulty of resource (metal, glass, plastic) recycling, and it is strongly dependent on the type, concentration, and grading of the valuable materials within the LED. The recyclability for white LEDs is determined as  $\sim 40$ – $43$ /bit, which is greater than the middle value ( $\sim 41$ ) and hence signifies comparatively simpler physical and chemical processes that can attain resource recovery.<sup>9</sup> There has been limited research on recycling LEDs from backlighting units of LCDs (displays, screens) due to a lack of an effective collection system. The recycling of discarded LCD screens for

In values present as an indium-rich conductive layer ( $\sim 125$  nm thick; 100–400 ppm In) is economically unfeasible. It is estimated that an indium price of about 400 USD/kg can cover the recycling cost, whereas the current price is only 172 USD/kg.<sup>35</sup>

Moreover, REEs (in small quantities  $\sim 0.005\%$ ) in such LEDs make recycling more complicated. Furthermore, electric vehicle/hybrid electric vehicles (EVs/HEVs) are expected to adopt GaN-based power devices with a market of \$600 million for GaN by 2020<sup>61</sup>; therefore, recycling methods should be in line with such growing diverse applications.

### OVERALL FLOWSHEET AND MARKET VALUE CALCULATION

Based on the average composition of LEDs, processing of 1 ton of LED waste yields approximately 470 g of Ga, 48.3 of In, and 528.6 g of Au, which is equivalent to the processing of 7.8 tons of primary Ga ore (60 ppm), 3.2 tons of primary In (15 ppm) ore, and 42 tons of Au (7 ppm) ore. A recycling flowsheet is proposed for LEDs in Fig. 5a. Before leaching, the suitable process route removes plastic support and epoxy resin encapsulation from critical element-rich LED chips. Critical elements are

concentrated in specific fractions of LEDs; thus, good recovery rates of these elements are not attained on milling. The support and encapsulation can be removed by supercritical treatment by avoiding the milling step, which otherwise would result in inevitable losses of valuable metals (such as Ga, In, and REEs) present in small fractions.

Furthermore, for an efficient recycling process, it is strongly recommended to characterize the separated LED chips for determining the concentration, phases, and toxicity characteristics of the semiconductor present in them. In the case of GaN-type LEDs that show resistance toward leaching, oxidation/mechanicochemical methods such as pre-treatments should be adopted to convert Ga into soluble forms. However, if the feed material consists of GaAs LEDs, direct leaching for solubilizing Ga can be employed. Hydrometallurgy is advantageous for recovering critical elements present in low concentrations; however, the hazardous release of effluents needs due consideration. Chlorination ( $\text{Ga} \rightarrow \text{GaCl}_3$ ) can be employed as it offers lower processing temperature and spatial separation of Ga/In compared to pyrometallurgical processing of LEDs. After leaching/chlorination, solvent extraction can be adapted to selectively separate the element of interest and increase the product purity. Novel environmentally friendly reagents for extraction need to be developed to favor the process economics.

The recycling process strongly depends on the metallic content present in end-of-life LEDs; therefore, it is essential to determine its market value. The potential market value ( $M_v$ ) was calculated for various elements present in LEDs using Eq. 8, where  $C_i$  and  $P_i$  are the metal content (grade) and market price or value of recoverable metal ( $x$ ), respectively.<sup>79</sup> Market value results depict the potential economic benefit of waste LEDs, assuming all the elements are recovered in pure form. The composition of LEDs is considered a mixed type with an average concentration adopted from published literature. The overall potential market value is \$21,466 per ton of LEDs, as shown in Fig. 5b. Market value reveals that the critical element recovery would be justified if precious elements (Ag/Au) and REEs (Y/Eu/Ce) are also recovered. The market value is importantly based on metal content; therefore, a homogeneous feed is necessary for metallic recoveries for efficient process economics.

$$M_v = \sum_i C_i P_i \quad (8)$$

## SUMMARY AND CONCLUSION

The emerging technology and vast lighting applications of LEDs would subsequently lead to the generation of incredibly large amounts of end-of-life LEDs. The LEDs consist of critical metals (Ga, In) higher than that of natural ores, thus making it an

attractive secondary source. It was observed that LEDs consist of heterogeneous composition, with significant variations in metallic concentration, phase associations, and design. Hence, the identification and characterization of valuable metals are a prerequisite for selecting a recovery process. Importantly, LEDs contain high supply risk critical elements (Ga, In, REEs) associated with toxic elements such as As, Pb, and Cu. Proper toxicity analysis before recycling should be conducted for LEDs as some of them are hazardous.

Dismantling from complex configurations of LEDs is a challenge but is essential for a good recycling yield. The recycling techniques should focus on the liberation of the LED chip (critical element rich) from other metallic and plastic associations. The small amounts of critical elements are a concern that gets diluted under various physical processing steps. Mostly, end-of-life LEDs are treated for the recovery of Ga through pyro- and hydro-metallurgical treatments. In GaN LEDs, appropriate pre-treatment methods are required to release Ga from a strongly bonded GaN wurtzite structure.

Furthermore, hydrometallurgical processing leads to the dissolution of multiple elements (Ga, In, As, REEs) in the leach solution, which requires selective separation by precipitation or solvent extraction. The market value calculations reveal the importance of recycling other valuable elements such as Au, Ag, and REEs also for an overall economic benefit. Considerable research efforts are needed for holistic, high-purity recycling of LEDs. Moreover, a research gap is observed in analyzing developed processes from the economic and technological perspectives. Reutilization of recycled end-products has not been explored, which is expected to increase demand/consumption, promoting greener lighting sources, resource scarcity, and geo-political supply risks.

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## CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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