

Application of phosphonium ionic liquids to separate Ga, Ge and In utilizing solvent extraction: A review

Soniya Dhiman ^{a,*}, Shubhangee Agarwal ^b, Himanshu Gupta ^b

^a Department of Biochemical Engineering and Biotechnology, Indian Institute of Technology Delhi, New Delhi, India

^b Department of Chemistry, School of Sciences, IITM University, Lodhipur Rajput, Moradabad 244102, Uttar Pradesh, India

ARTICLE INFO

Keywords:

Phosphonium ionic liquids
Solvent extraction
Recovery
Gallium
Germanium
Indium

ABSTRACT

Due to the sudden rise in demand, a shortfall in the supply of critical metals or high technology metals, especially gallium (Ga), germanium (Ge) and indium (In) is experienced throughout the globe. The different primary and secondary resources are being utilized to recover and recycle these metals through the widely accepted technique, solvent extraction (SX). The extraction of metals may be potentially achieved by compounds of negligible volatility, phosphonium ionic liquids (Phos ILs). Ionic liquids (ILs) are potential and useful compounds to separate and recover Ga, Ge and In from synthetic solutions and waste materials due to their tunable nature to achieve higher selectivity, superior physicochemical properties and diverse structural properties. Ion exchange mechanism was mainly found applicable for the extractive separation of such metals through Phos ILs. Based on the efficiency, extraction mechanism and diverse operating conditions of Phos ILs, the present review provides a comprehensive description of separation as well as recovery of Ga, Ge and In from the synthetic solutions as well as waste materials.

1. Introduction

Presently, global fossil fuel consumption has increased at an alarming rate, which poses one of the biggest challenges to environmentalists for the development of competent mitigating techniques to enhance energy efficiency. As per the European Union (EU) guidelines, in 2030, the consumption of renewable energy as well as energy efficiency must be enhanced to 27 %, whereas, greenhouse emissions must be reduced to 40 % of emissions in 1990 (European Commission 2014). The accomplishment of such targets necessitates the development of low carbon energy technologies such as solar cells, photovoltaic power generation etc., which are dependent on critical metals such as gallium (Ga), germanium (Ge) and indium (In) (Sun et al., 2017). These metals are utilized in solar photovoltaic cells and light emitting diodes (Lv et al., 2019; Kuroiwa et al., 2014a). The energy efficiency and device performance are enhanced by these metals. The production of Ga, Ge and In is adequate, but due to stockpiling at some countries, high growth in demand and export restrictions, the economically viable supply of these metals in future is at risk (Directorate General Enterprise and Industry 2015). Therefore, these metals are regarded as highly critical raw materials. Also, due to global digitalization, the demand for Ga, Ge and In

has been magnified (European Commission 2016). At present, in India, the large scale production of these metals is not available. Hence, these metals are required to be recovered from various resources. Presently, an extremely low amount of these metals is recycled and their recycling habits are required to be systematically changed for the accomplishment of future demands (Nassar et al., 2015). Huge possibilities are expected from metallurgy or hydrochemistry due to high possibility of secondary waste elimination, selectivity in the extraction of critical metals, flexibility and moderately high recovery rate (Gulliani et al., 2023; Khalil et al., 2014).

Different metallurgical operations are applied for recovery of various metals using sources of a secondary nature. Pyrometallurgy is one of them, which refers to a conventional technique for recovery of different metals from various wastes. The method of pyrometallurgy has certain limitations, such as the generation of poisonous substances and the consumption of higher energy to increase the high temperature (Wędrychowicz et al., 2022). Recently, based on hydrometallurgical processes, the recovery of important metals from wastes can be achieved. The hydrometallurgical process is a suitable alternative to treat electronic wastes due to their effectiveness, simple control of the procedure, operational selectivity, less poisonous gasses, dust formation,

* Corresponding author.

E-mail address: soniyadhiman.17.sd@gmail.com (S. Dhiman).

and cost-effectiveness (Chen et al., 2015). Compared to pyrometallurgy, the hydrometallurgical process uses lower temperatures and is highly controllable and predictable (Cui and Zhang, 2008). Currently, various hydrometallurgical methods are being employed to recover metals through primary or secondary industrial waste, including solvent extraction (SX) (Kumar et al., 2010; Ahmed et al., 2018), ion exchange (Parhi and Sarangi, 2008; Alyüz and Veli, 2009) and chemical precipitation (Huisman et al., 2006; Mirbagheri and Hosseini, 2005). Among these, SX has been extensively utilized for metal recovery and purification because it is simple, fast, cost-effective and selective (El-Nadi, 2017).

The SX strategies are flexible for variation in the composition of wastes compared to other processes. SX is one of the most flexible processes to remove, separate and concentrate metal ions from mixed metal aqueous solution. SX or liquid-liquid extraction depends on the differential distribution of components to be separated between two immiscible liquid phases, an organic solvent and aqueous phase. The substance is extracted from one liquid phase to another. It depends upon the mass exchange of the substance from the first liquid phase to the second liquid phase (Rydberg et al., 2004; De et al., 1970).

Several extractants such as organophosphorus compounds (Gupta et al., 2007; Iyer and Dhadke, 2001; Jha et al., 2013; Padhan and Sarangi, 2014), chelating agents (Lupi and Pilone, 2014; Nusen et al., 2015), carboxylic acids (Cheng, 2006; Cheng et al., 2010), high molecular weight amines (Nayl, 2010; Mishra et al., 2011) and bifunctional extractants (mixture of two extractants such as organophosphorus compound and high molecular weight amine) (Zhou et al., 2022) were examined to separate and recover different metals through various wastes and aqueous media. In the aqueous phase, the metal ion extraction using acidic extractants is dependent on concentration of H^+ ion. The extraction efficiency is adversely affected by the H^+ ion release in the aqueous medium. In order to avoid these conditions, there is a requirement for released acid neutralization and extractant saponification during the extraction process. In acidic media, Oximic extractants like LIX65 and LIX63 are hydrolyzed (Wilson et al., 2014). Amine extractants with high molecular weights mainly observe aggregation of colloids with organic diluents, which results in poor selectivity and emulsion formation (Moore, 1960). Poor extractant is reported with water soluble neutral organo phosphorous extractants (Kumari et al., 2016).

Due to their immeasurably low vapor pressure, ionic liquids (ILs) have attracted the attention of chemists as alternatives to conventional organic solvents from the past two decades. Therefore, these are referred to as 'green' solvents in contrast to traditional volatile organic compounds (Ghandi, 2014). The present review consists of discussion about various kinds of ILs and phosphonium ionic liquids (Phos ILs) advantages compared to other ILs. The importance of metals such as Ga, Ge and In and their recovery through SX are described. The purity, recovery, extraction mechanism, important results based on percentage extraction and variable operating parameters were also discussed as the flow sheet for the developed process.

2. Ionic liquids

The ILs are the organic salts that are composed of organic cations (such as 1-alkyl-3-methylimidazolium, N-alkylpyridinium, tetraalkylammonium and tetraalkylphosphonium) and inorganic or organic anions (like hexafluorophosphate, tetrafluoroborate, trifluoromethylsulphonate, acetate, nitrate and halide) and have melting points below 100 °C. Some of these are liquid at room temperature with a high boiling point and are called room temperature ionic liquids (RTILs). Among ILs, often beneficial properties are observed such as nonflammability, high ionic conductivity and wide electrochemical potential window, thermal and chemical stability. One of the attractive properties of ILs is that these may be obtained as water-immiscible salts by incorporating hydrophobic anions and extending the alkyl chain

length of the cation. These hydrophobic ILs are potential extractants for liquid-liquid extraction systems (Rout et al., 2014; Pandey, 2006).

Lately, nitrogen-based as well as phosphonium-based ILs have been explored as extractants for the separation of metal ions. Among the nitrogen-based ILs, imidazolium and ammonium types have been explored majorly (Wei et al., 2003; de los Rios et al., 2010; Heitzman et al., 2006; Li et al., 2007). ILs are better than conventional extractants because they do not release H^+ in raffinate thus neutralization of the released acid is not required (Rout and Binnemans, 2016). One of the disadvantages of imidazolium ILs is that during the extraction process, the imidazolium cation is released into an aqueous medium. This makes ILs based on imidazole unsuitable for eco-friendly perspectives. Hydrophobic ILs can be obtained by replacement of the imidazolium cation by quaternary phosphonium or ammonium cations having long alkyl chains (Ferreira et al., 2012). Phosphonium-based ILs is less viscous and more thermally stable than analogous ammonium-based ILs (Shirota et al., 2019). The phosphonium-based ILs are less expensive than their equivalent imidazolium and ammonium-based ILs (Fraser and MacFarlane, 2009).

A literature survey reveals that lately, phosphonium-based ILs have been widely investigated to extract and recover metal ions. Large quantities of phosphonium-based ILs are easily available commercially. The phosphonium-based ILs have high thermal stability and low toxicity (Fraser and MacFarlane, 2009).

3. Solvent extraction of Ga, Ge and In using Phos ILs

3.1. Gallium

Gallium is presently significant due to its growing uses in novel thin-film photovoltaics, solar cells and thermometers to measure high temperature. Gallium is used to make brilliant mirrors because of its capacity to frame metal alloys and silvery color (Lv et al., 2019; Chou et al., 2008) and is also important for clean energy technologies (Okabe, 2010). Microelectronic components present in various products contain gallium nitride (GaN) or gallium arsenide (GaAs). GaAs can convert electricity directly into laser light and are utilized in the production of optoelectronic gadgets such as solar cells, photodetectors, light-emitting diodes, and laser diodes, which are significant for aerospace, media communication applications, medical and industrial equipment (Frenzel et al., 2016). GaAs is also used to produce highly specific integrated circuits, transistors and semiconductors. GaN is mainly utilized in assembling radio-frequency (RF) electronics and power gadgets, laser diodes, and light emitting diodes (LEDs). Due to the higher efficiency of GaN power transistors than GaAs devices, the use of GaN-based items is expected to enhance in the future (Global LED Lighting Market Size, and Share Worth \$54.28 Billion by 2022 Zion Market Research 2017).

Gallium is presently recovered as a byproduct in the mining of other mineral products, mostly aluminum (Al), copper (Cu), and zinc (Zn). Nearly 70 % of Ga is used in media communications, high-performance PCs, and integrated circuits (both digital and analog). The remaining 30 % of Ga consumption is in medical equipment, industrial equipment, consumer goods, broadcast communication and aerospace applications (Moskalyk, 2003; De Almeida et al., 2014). Several studies have been reported to recover Ga using SX using Phos ILs.

Sumitra and Niharbala (Nayak and Devi, 2017b) reported extraction and recovery of Ga from synthetic solution and photodiodes using trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101). Job's method was applied to propose the extraction species at 2 mol L⁻¹ HCl. The results suggest that Ga extraction with Cyphos IL 101 occurs through an anion exchange mechanism. Separation of Ga from Al/Zn/Fe/Cu/Ni was studied. Stripping of Ga from photodiode leach liquor was 99.5 % using HCl (0.1 mol L⁻¹). The same research group (Nayak and Devi, 2017a) also studied Ga extraction with trihexyl(tetradecyl)phosphonium bis(2,4,4- trimethylpentyl)phosphinate (Cyphos IL 104). The effect of different experimental parameters on Ga extraction was investigated

and an ion-exchange mechanism was proposed. They reported stripping of 98 % Ga from photodiode leach solution and stripping of 96.4 % Ga along with 21.4 % V from red mud leach solution using 1 mol L⁻¹ H₂SO₄.

Bossche et al. (Bossche et al., 2019) recovered Ga, In and As from semiconductors (GaAs, GaN and InAs) using tributyldecyldiphosphonium tri bromide ionic liquid [P₄₄₄₁₀][Br₃]. They concluded that [P₄₄₄₁₀][Br₃] was effective in preventing the formation of high toxic arsenic (AsH₃). Selective stripping solutions were used to recover As and Ga. Results showed that 95 % As and 96 % Ga were recovered using 4 mol L⁻¹ NaBr and ultrapure water as stripping solution, respectively. 99 % In was precipitated and recovered as In(OH)₃ using NaOH solution. After stripping of all the metals, no damage was observed for both tribromide anion and phosphonium cation. Therefore, the IL can be reused. Upon molecular bromine addition, the regeneration of reacted tribromide anion was reported. Fig. 1 shows the flow sheet for the separation of As, Ga and In from GaAs and InAs semiconductors.

3.2. Germanium

Germanium is referred to as a critical element because of its numerous applications in optics and electronics industries. Germanium is primarily utilized in transistors because of its semiconductor properties (Kuroiwa et al., 2014b). Germanium is also used in polymerization catalysis, chemotherapy, metallurgy, fiber optics and solar cells (Nguyen and Lee; Chen et al., 2017). The major sources of Ge are sulfide minerals of Cu, Pb and Zn, coal deposits, residues and byproducts from coal processing (smelting flue dust and coal fly ashes). In fact, 30 % of worldwide Ge consumption is met by its recycling (Cruz et al., 2018). Germanium has low chromatic dispersion, high refractive index and capacity to prepare expanded 3-D networks of Ge-O tetrahedral similar to Si-O. Such physical characteristics decide the higher economic significance of Ge and its compounds in industries. Germanium finds applications in manufacturing lenses and window sheets for IR detectors in view of its transparency to IR radiations. Germanium is used as an alloying constituent (0.35 %) for Au or Al-Mg alloys for toughness enhancement (Moskalyk, 2004; Arroyo and Fernandez-pereira, 2008).

In the case of Ge, not many studies have reported on the extraction, separation and recovery of Ge using Phos ILs. Only one study has been reported by Gupta and Dhiman (Dhiman and Gupta, 2020b). Authors developed a sensitive, fast and simple technique for Ge separation and recovery from Zener diodes. Detailed partition behavior of Ge

employing toluene diluted Cyphos IL 104 was examined. The significance of various parameters like temperature, Cyphos IL 104 concentration, shaking time, nature of diluents, nature and concentration of acid on the partition of Ge were investigated. Loading capacity as well as recyclability of Cyphos IL 104 was reported. The partition behavior of correlated metal ions, namely Cu, Hg, Fe and Al with Cyphos IL 104 was investigated. The optimum parameters were evaluated for the successful recovery of Ge from Zener diodes. McCabe-Thiele extraction diagram was plotted and the theoretical stages of counter-current extraction were calculated. They recovered 99.9 % pure Ge from Zener diodes leach liquor using readily available and cost-effective stripping solution i.e., deionized water. Mercury (Hg), a toxicant present in the leach liquor, was removed before its disposal (Fig. 2).

3.3. Indium

Indium is one of the essential metals for communication development and sustainable economy. The abundance of In is around 0.05 ppm in the continental crust (Redlinger et al., 2015). Indium has no primary sources. Indium tin oxide (ITO), accounting for around 85 % of In consumption, prepares transparent conductive coating for displays like touch panels and flat panel liquid crystal plasma displays (Bleiwas, 2010). It is used in flat screen television and computer monitors as flat-panel liquid crystal displays. It consumes >50 % of primary In across the globe. ITO thin films were employed in solar cells and organic LEDs. Around 8 % of In is consumed in solders and alloys (Buchert et al., 2009). The copper indium gallium selenide semiconductor applied in preparing thin-film solar cells is synthesized using In (Ramanujam and Singh, 2017). The wind turbines and photovoltaic cells future development as well as deployment are majorly dependent on the presence of various elements including In (Öhrlund, 2011). In Li-ion batteries, anode material is proposed as nanocomposite, which is prepared from a facile solvothermal method based on graphene nanosheet and tin indium oxide (SnO₂-In₂O₃) (Yang et al., 2013). According to European Commission, In is estimated to be among the most critical metals in coming years due to the increasing demand and supply gap (European Commission 2010). The application of Phos ILs in SX has been initiated for In recovery in various research.

Deferm et al. (Deferm et al., 2016) reported a sustainable SX process to purify In using Cyphos IL 101. The percentage of In extraction was >95 % in a wide range of HCl concentrations. Upon stripping with NaOH

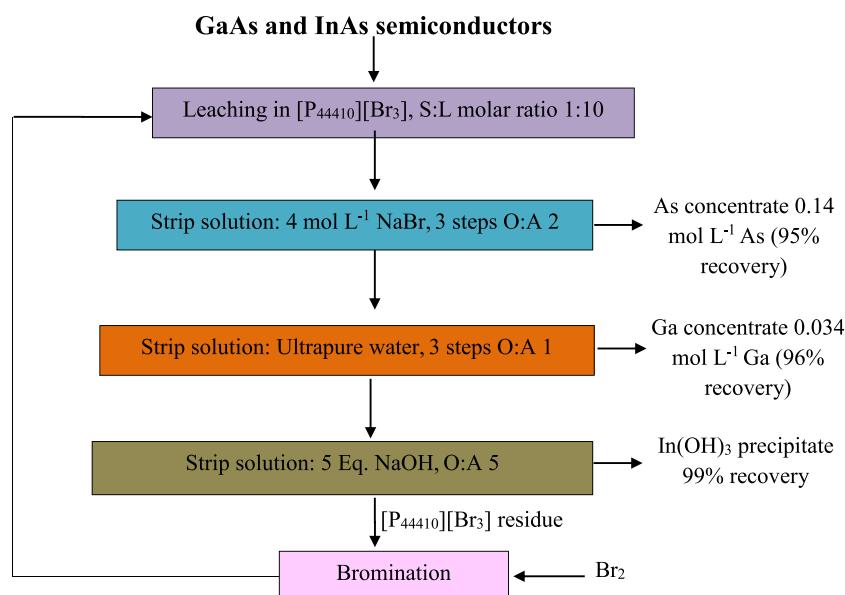


Fig. 1. Flow sheet for the leaching and separation of As, Ga and In from GaAs and InAs semiconductors (Bossche et al., 2019) (Reprinted with permission from {Bossche et al., 2019}) Copyright {2019} American Chemical Society.

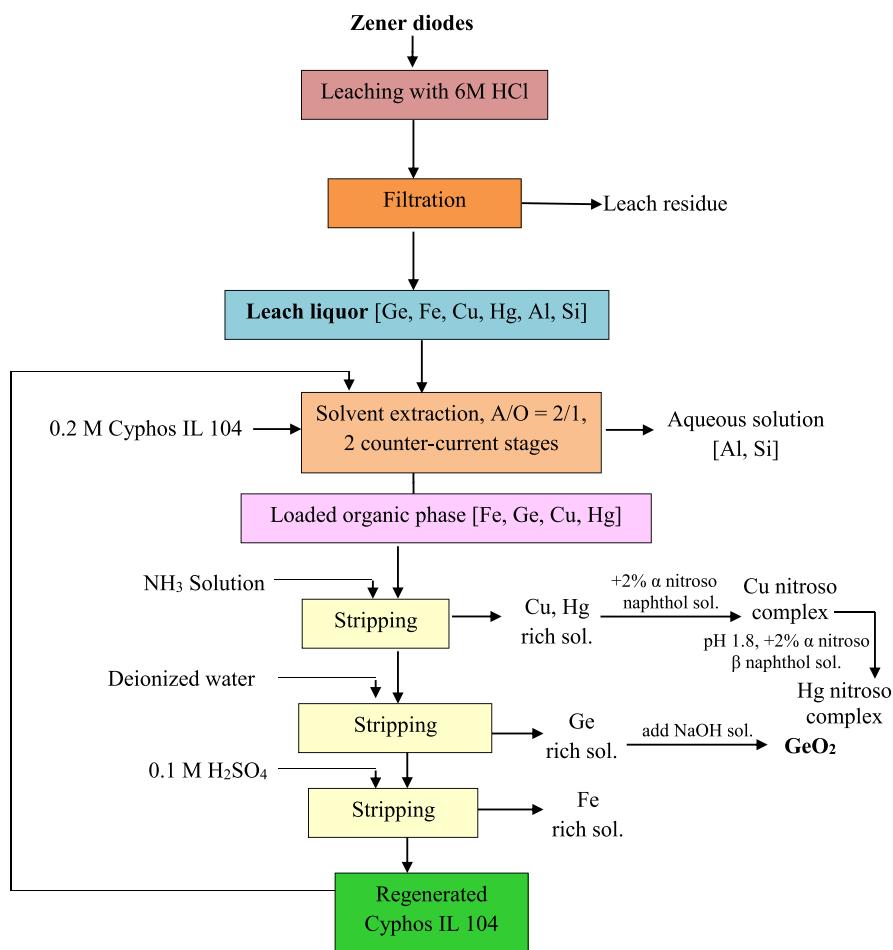


Fig. 2. Flow sheet for Ge recovery from Zener diodes (Dhiman and Gupta, 2020b) (Reprinted with permission from {Dhiman and Gupta (Dhiman and Gupta, 2020b)} Copyright {2020} Elsevier).

solution, In has been recovered as In(OH)_3 . Cyphos IL 101 was regenerated in the stripping step itself.

Deferm et al. (Deferm et al., 2017) also studied the speciation of chloro complexes of In during the extraction of In from HCl medium using Cyphos IL 101. In an aqueous HCl phase ($0\text{--}12 \text{ mol L}^{-1}$), In exists as octahedral mixed complexes, $[\text{In}(\text{H}_2\text{O})_{6-n}\text{Cl}_n]^{3-n}$ ($n = 0\text{--}6$). These species were characterized by Extended X-ray absorption fine structure (EXAFS) and ^{115}In Nuclear Magnetic Resonance (NMR).

A hydrometallurgical solvent extraction process was developed by Nayak and Devi (Nayak and Devi, 2020) for In recovery from waste liquid crystal display (LCD) using Cyphos IL 101. The authors have optimized various extraction factors like equilibration period, chloride ion and acid concentration to extract In. Quantitative extraction was observed at 0.005 mol L^{-1} Cyphos IL 101 and 2.0 mol L^{-1} HCl, and quantitative stripping was found with 1.0 mol L^{-1} H_2SO_4 .

Dhiman and Gupta (Dhiman and Gupta, 2020a) demonstrated the environmental and economic advantage of using waste LCD screens to separate and recover In, Zn and Sn using Cyphos IL 104. In the organic phase, extraction of In was in the form of $[\text{InCl}_3\text{R}_3\text{R}'\text{P}^+\text{A}^-]$. The evaluated thermodynamic parameters propose the endothermic and spontaneous nature of the process. The metals were selectively recovered from waste LCD screens by application of optimized conditions. Using Cyphos IL 104, Sn, Zn and In were extracted over Mn, Sr, Ca, Al and Fe. Applying 0.1 mol L^{-1} Cyphos IL 104 at $\text{A}/\text{O} = 3/2$, in two counter-current stages, at 3 mol L^{-1} HCl, quantitative extraction of Sn, Zn and In was achieved. In two counter-current stages, at $\text{O}/\text{A} = 3/2$, the stripping solutions, conc. HCl, 4 mol L^{-1} HNO_3 and 0.001 mol L^{-1} HNO_3 were used to strip Sn, Zn and In from the loaded organic phase. The

experiment based on Mc-Cabe Thiele diagrams achieved a recovery of $>98\%$ with $>99\%$ purity. Through the strip solutions, SnS , ZnO and In_2O_3 nanoparticles were recovered with a particle size of 68.8, 41.1 and 42.4 nm, respectively. The theoretical stoichiometric composition was matched with an atomic percentage of constituent atoms using the outcome of EDX analysis for SnS , ZnO and In_2O_3 . The flow sheet of this study has been presented in Fig. 3.

Kumar et al. (Kumar et al., 2022) studied In extraction employing Cyphos IL 104 from nitrate medium and its mathematical modeling to predict the transport of In ions through a flat-sheet-supported liquid membrane (FSSLM). The results indicated a good agreement for the In extraction and modeling outputs at different extractant concentrations.

The extraction study for Ga, Ge and In has been reported in the literature and is summarized in Table 1. It suggests that Phos ILs such as Cyphos IL 104, Cyphos IL 101 and $[\text{P}44410]\text{[Br}_3]$, were the most applied extractants for separating and recovering Ga, Ge and In from various other metal ions.

4. Conclusion

The present review describes the recovery of critical metals such as Ga, Ge and In. There is a gap between supply and demand of the studied metals due to less abundance of these metals in their natural resources and enhancement of applications at various levels. Heavy metals may cause health risks as these reach living beings through the food chain, accumulate in water and soils, and are non-biodegradable. In order to reuse the waste metals, technologists and scientists have applied continuous efforts due to their economic, environmental and health

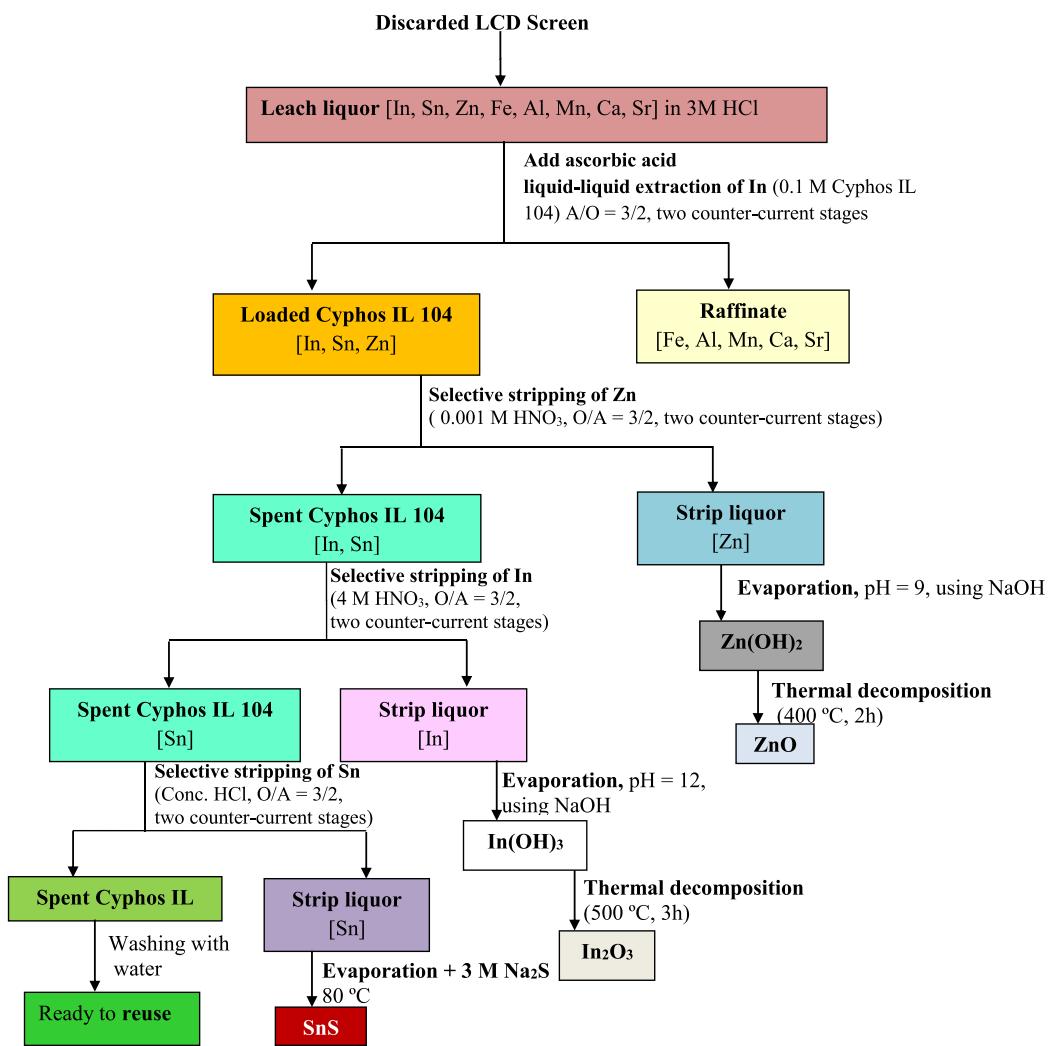


Fig. 3. Flow sheet for Sn, Zn and In recovery from discarded LCD screen (Dhiman and Gupta, 2020a).

Table 1

Summary sheet on the extraction of Ga, Ge and In using Phos ILs.

S. No.	Starting metals (mg L ⁻¹)	Extractant	Aqueous medium	Extraction mechanism	Extracted metals ions	Comments	References
1.	69.72 Ga	Cyphos IL 101	HCl	$\text{GaCl}_{(\text{aq})} + [\text{R}_3\text{R}'\text{P}^+\text{Cl}^-]_{(\text{org})} \leftrightarrow [\text{R}_3\text{R}'\text{P}^+\text{GaCl}_4^-]_{(\text{org})} + \text{Cl}_{(\text{aq})}$	Ga	Quantitative extraction and stripping were achieved at 2 mol L ⁻¹ HCl and 0.1 mol L ⁻¹ HCl, respectively	(Nayak and Devi, 2017b)
2.	16.03 Ga, 1.25 As, 0.02 Pb, 1.09 Al, 1.73 Ag, 1272 Cu, 2.4 Ni	Cyphos IL 104	HCl	$\text{GaCl}_{(\text{aq})} + \text{H}_3\text{O}^+ + [\text{R}_3\text{R}'\text{P}^+\text{A}^-]_{(\text{org})} \leftrightarrow [\text{R}_3\text{R}'\text{P}^+\text{GaCl}_4^-]_{(\text{org})} + \text{HA}_{(\text{org})}$	Ga, Fe, Zn, V, Pb, Cu	98 % recovery of Ga from photodiodes using Cyphos IL 104 (0.002 mol L ⁻¹)	(Nayak and Devi, 2017a)
3.	500 Ga, 500 As, 500 In	[P ₄₄₄₁₀] [Br ₃]	–	$[\text{M}]^{+3} + 3\text{Br}^- + [\text{P}_4\text{44410}][\text{Br}] \leftrightarrow [\text{P}_4\text{44410}][\text{MBr}_4]$	Ga, As, In	99.6 % As and 96.5 % Ga were recovered using NaBr and water, respectively	(Bossche et al., 2019)
4.	108 Ge, 1590 Cu, 16.1 Si, 1990 Fe, 100 Hg, 10.5 Al	Cyphos IL 104	HCl	$\text{Ge}^{+4}_{(\text{aq})} + 6\text{Cl}_{(\text{aq})} + 2\text{H}_3\text{O}^+ + 2[\text{R}_3\text{R}'\text{P}^+\text{A}^-]_{(\text{org})} \leftrightarrow [\text{R}_3\text{R}'\text{P}^+\text{GeCl}_6^{2-}]_{(\text{org})} + 2\text{HA}_{(\text{org})}$	Ge, Cu, Fe, Hg	94.6 % Ge with purity of 99.9 % was recovered using water as stripping solution	(Dhiman and Gupta, 2020b)
5.	5000 In	Cyphos IL 101	HCl	$\text{InCl}_{(\text{aq})} + [\text{R}_3\text{R}'\text{P}^+\text{Cl}^-]_{(\text{org})} \leftrightarrow [\text{R}_3\text{R}'\text{P}^+\text{InCl}_4^-]_{(\text{org})} + \text{Cl}_{(\text{aq})}$	In	In was recovered as In(OH) ₃ by precipitation stripping with a NaOH solution	(Deferm et al., 2016)
6.	91.5 In, 20.6 Sn, 78.4 Cu, 4.3 Al	Cyphos IL 101	HCl	$\text{In}^{3+}_{(\text{aq})} + 3\text{Cl}_{(\text{aq})} + [\text{R}_3\text{R}'\text{P}^+\text{Cl}^-]_{(\text{org})} \leftrightarrow [\text{R}_3\text{R}'\text{P}^+\text{InCl}_4^-]_{(\text{org})}$	In, Sn	99.1 % and 99.7 % of In and Sn were recovered by selective stripping	(Nayak and Devi, 2020)
7.	162 In, 507 Sn, 112 Zn, 2947 Fe, 1279 Al, 232 Mn, 3145 Ca, 320 Sr	Cyphos IL 104	HCl	$\text{In}^{3+}_{(\text{aq})} + 3\text{Cl}_{(\text{aq})} + 2[\text{R}_3\text{R}'\text{P}^+\text{A}^-]_{(\text{org})} \leftrightarrow [\text{InCl}_3\text{L}_2\text{R}_3\text{R}'\text{P}^+\text{A}^-]_{(\text{org})}$	Sn, Zn, In	99.6 % Sn, 100 % Zn and 98.9 % In, recovered with >99 % purity by selective stripping	(Dhiman and Gupta, 2020a)
8.	100 In	Cyphos IL 104	HNO ₃	$\text{In}^{3+}_{(\text{aq})} + 2\text{NO}_{(\text{aq})} + \text{E}_{(\text{org})} \leftrightarrow [\text{In}(\text{NO}_3)_3\text{E}]_{(\text{org})}$	In	>95 % In was extracted using HNO ₃ (0.001 mol L ⁻¹) with Cyphos IL 104 (0.01 mol L ⁻¹)	(Kumar et al., 2022)

where A = bis-(2,4,4-trimethylpentyl)phosphinate; R₃R'⁺ = tetradecyl-(triethyl)phosphonium; E = Cyphos IL 104.

issues. The present review primarily focuses on applying Phos ILs through SX to recover Ga, Ge and In. By employing suitable cations or anions, Phos IL properties may be changed and these are designable. Upon application of a specific cation or anion, Phos ILs may show specific characteristics like good selectivity, high thermal stability and low volatility. In the separation and extraction mechanism, cation or anion nature significantly affects the ability to solubilize for stationary phase. In aqueous phases, to remove different solutes, Phos ILs are useful as extracting solvents due to the hydrophobicity of long alkyl chain. The present review demonstrates that during the metal ion extraction, anion exchange mechanism was adopted by the Phos ILs. The study also suggests that the leach solution of spent materials containing multiple elements can be used to recover valuable metals at a higher rate utilizing Phos ILs, promising extractants.

CRediT authorship contribution statement

Soniya Dhiman: Conceptualization, Methodology, Supervision, Writing – original draft, Writing – review & editing. **Shubhangee Agarwal:** Methodology, Writing – original draft, Writing – review & editing. **Himanshu Gupta:** Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

The authors would like to disclose that there is no conflict of interest with respect to the manuscript “Application of phosphonium ionic liquids to separate Ga, Ge and In utilizing solvent extraction: A review” submitted to the journal ‘Journal of Ionic Liquids’.

Data availability

Data will be made available on request.

Acknowledgements

The authors would like to thank IIT Delhi and IFTM University administration for providing necessary facilities for the completion of present review.

References

Ahmed, I.M., Ismail, Z.H., Hamed, M.M., 2018. Extraction and separation of Ga(III) from hydrochloric acid solution by Cyanex-921 in sulfonated kerosene. *J. Radioanal. Nucl. Chem.* 317, 969–976.

Alyüz, B., Veli, S., 2009. Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins. *J. Hazard Mater.* 167, 482–488.

Arroyo, F., Fernandez-pereira, C., 2008. Hydrometallurgical Recovery of Germanium from Coal Gasification Fly Ash. *Ind. Eng. Chem. Res.* 3186–3191.

Bleiwais, D.I., 2010. Byproduct Mineral Commodities Used For the Production of Photovoltaic Cells. Circular 1365. U.S. Department of the Interior, U.S. Geological Survey, Reston, Virginia.

Bossche, A.V.D., Vereycken, W., V.Hoogerstraete, T., Dehaen, W., Binnemans, K., 2019. Recovery of Gallium, Indium, and Arsenic from Semiconductors Using Tribromide Ionic Liquids. *ACS Sustainable Chem. Eng.* 7, 14451–14459.

Buchert, M., Schüller, D., Bleher, D., 2009. Critical Metals For Future Sustainable Technologies and Their Recycling Potential. United Nations Environment Programme & United Nations University. <http://www.foresightfordevelopment.org/sobipro/55/1312-critical-metals-for-future-sustainable-technologies-and-their-recycling-potential>.

Chen, W.S., Chang, B.C., Chiu, K.L., 2017. Recovery of germanium from waste optical fibers by hydrometallurgical method. *J. Environ. Chem. Eng.* 5, 5215–5221.

Chen, X., Chen, Y., Zhou, T., Liu, D., Hu, H., Fan, S., 2015. Hydrometallurgical recovery of metal values from sulfuric acid leaching liquor of spent lithium-ion batteries. *Waste Manage* 38, 349–356.

Cheng, C.Y., 2006. Solvent extraction of nickel and cobalt with synergistic systems consisting of carboxylic acid and aliphatic hydroxoxime. *Hydrometallurgy* 84, 109–117.

Cheng, C.Y., Zhang, W., Pranolo, Y., 2010. Separation of cobalt and zinc from manganese, magnesium, and calcium using a synergistic solvent extraction system consisting of versatic 10 and LIX 63. *Solvent Extr. Ion Exch.* 28, 608–624.

Chou, W.L., Wang, C.T., Yang, K.C., Huang, Y.H., 2008. Removal of gallium (III) ions from acidic aqueous solution by supercritical carbon dioxide extraction in the green separation process. *J. Hazard. Mater.* 160, 6–12.

Cruz, C.A., Marie, S., Arrachart, G., Pellet-rostaing, S., 2018. Selective extraction and separation of germanium by catechol based resins. *Sep. Purif. Technol.* 193, 214–219.

Cui, J., Zhang, L., 2008. Metallurgical recovery of metals from electronic waste: a review. *J. Hazard. Mater.* 158, 228–256.

De, A.K., Khopkar, S.M., Chalmers, R.A., 1970. *Solvent Extraction of Metals*. Van Nostrand Reinhold Co., London.

De Almeida, A., Santos, B., Paolo, B., Quicheron, M., 2014. Solid state lighting review-potential and challenges in Europe. *Renew. Sustain. Energy Rev.* 34, 30–48.

Deferm, C., Ongena, B., Hoogerstraete, T.V., Banerjee, D., Luyten, J., Oosterhof, H., Fransaer, J., Binnemans, K., 2017. Speciation of indium(III) chloro complexes in the solvent extraction process from chloride aqueous solutions to ionic liquids. *Dalt. Trans.* 46, 4412–4421.

Deferm, C., Van de Voorde, M., Luyten, J., Oosterhof, H., Fransaer, J., Binnemans, K., 2016. Purification of indium by solvent extraction with undiluted ionic liquids. *Green Chem.* 18, 4116–4127.

de los Rios, A.P., Hernandez-Fernandez, F.J., Lozano, L.J., Sanchez, S., Moreno, J.I., Godinez, C., 2010. Removal of metal ions from aqueous solutions by extraction with ionic liquids. *J. Chem. Eng. Data* 55, 605–608.

Dhiman, S., Gupta, B., 2020a. Cyphos IL 104 assisted extraction of Indium and recycling of Indium, Zinc and Tin from discarded LCD screen. *Sep. Purif. Technol.* 237, 1–12.

Dhiman, S., Gupta, B., 2020b. Recovery of pure germanium oxide from Zener diodes using a recyclable ionic liquid Cyphos IL 104. *J. Environ. Manage.* 276, 111218.

Directorate General Enterprise and Industry, 2015. EU Critical Raw Materials Profiles, p. 77e85. Ref. Ares(2015)1819595 - 29/04/2015.

El-Nadi, Y.A., 2017. Solvent extraction and its applications on ore processing and recovery of metals: classical approach. *Sep. Purif. Rev.* 46, 195–215.

European Commission, 2010. Critical raw materials for the EU, Report of the Ad-hoc Working Group on defining critical raw materials.

European Commission, 2014. In: Conclusions Adopted by the European Council at the Meeting in Brussels, 24 October 2014, EUCO 169/14.

European Commission, 2016. Priorities For Critical Materials For a Circular Economy. DVZ-Daten-Service GmbH, Halle/Saale, Germany. ISBN: 9783804728974.

Ferreira, A.F., Simoes, P.N., Ferreira, A.G.M., 2012. Quaternary phosphonium-based ionic liquids: thermal stability and heat capacity of the liquid phase. *J. Chem. Thermodyn.* 45, 16–27.

Fraser, K.J., MacFarlane, D.R., 2009. Phosphonium-based ionic liquids: an overview. *Aust. J. Chem.* 62, 309–321.

Frenzel, M., Ketris, M.P., Seifert, T., Gutzmer, J., 2016. On the current and future availability of gallium. *Res. Policy* 47, 38–50.

Ghandi, K., 2014. A review of ionic liquids, their limits and applications. *Green. Sustainable Chem.* 4, 44–53.

Global LED Lighting Market Size & Share Worth \$54.28 Billion by 2022 Zion Market Research, 2017.

Gulliani, S., Volpe, M., Messineo, A., Volpe, R., 2023. Recovery of metals and valuable chemicals from waste electric and electronic materials: a critical review of existing technologies. *RSC Sustain.* 1, 1085–1108.

Gupta, B., Mudhar, N., Singh, I., 2007. Separations and recovery of indium and gallium using bis(2,4,4-trimethylpentyl) phosphonic acid (Cyanex 272). *Sep. Purif. Technol.* 57, 294–303.

Heitzman, H., Young, B.A., Rausch, D.J., Rickert, P., Stepinski, D.C., Dietz, M.L., 2006. Fluorous ionic liquids as solvents for the liquid–liquid extraction of metal ions by macrocyclic polyethers. *Talanta* 69, 527–531.

Huisman, J.L., Schouten, G., Schultz, C., 2006. Biologically produced sulphide for purification of process streams, effluent treatment and recovery of metals in the metal and mining Industry. *Hydrometallurgy* 83, 106–113.

Iyer, J.N., Dhadke, P.M., 2001. Liquid–liquid extraction and separation of gallium(III), Indium(III), and thallium(III) by Cyanex 925. *Sep. Sci. Technol.* 36, 2773–2784.

Jha, A.K., Jha, M.K., Kumari, A., Sahu, S.K., Kumar, V., Pandey, B.D., 2013. Selective separation and recovery of cobalt from leach liquor of discarded Li-ion batteries using thiophosphinic extractant. *Sep. Purif. Technol.* 104, 160–166.

Khaliq, A., Rhamdhani, M.A., Brooks, Geoffrey, Masood, Syed, 2014. Metal extraction processes for electronic waste and existing industrial routes: a review and australian perspective. *Resources* 3, 152–179.

Kumar, R., Dhiman, S., Gupta, H., 2022. Indium extraction from nitrate medium using Cyphos ionic liquid 104 and its mathematical modeling. *Environ. Sci. Pollut. Res.* <https://doi.org/10.1007/s11356-022-24936-z>.

Kumar, V., Sahu, S.K., Pandey, B.D., 2010. Prospects for solvent extraction processes in the Indian context for the recovery of base metals. A review. *Hydrometallurgy* 103, 45–53.

Kumari, A., Sinha, M.K., Sahu, S.K., Dhar, B., 2016. Solvent extraction and separation of trivalent lanthanides using Cyphos IL 104, a novel phosphonium ionic liquid as extractant solvent extraction and separation of trivalent lanthanides using. *Solv. Extr. Ion Exch.* 34, 469–484.

Kuroiwa, K., Ohura, S., Morisada, S., Ohto, K., Kawakita, H., Matsuo, Y., Fukuda, D., 2014a. Recovery of germanium from waste solar panels using ion-exchange membrane and solvent extraction. *Miner. Eng.* 55, 181–185.

Kuroiwa, K., Ohura, S.I., Morisada, S., Ohto, K., Kawakita, H., Matsuo, Y., Fukuda, D., 2014b. Recovery of germanium from waste solar panels using ion-exchange membrane and solvent extraction. *Miner. Eng.* 55, 181–185.

Li, Z., Wei, Q., Yuan, R., Zhou, X., Liu, H., Shan, H., Song, Q., 2007. A new room temperature ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate

as a solvent for extraction and preconcentration of mercury with determination by cold vapor atomic absorption spectrometry. *Talanta* 71, 68–72.

Lupi, C., Pilone, D., 2014. In(III) hydrometallurgical recovery from secondary materials by solvent extraction. *J. Environ. Chem. Eng.* 2, 100–104.

Lv, Y., Xing, P., Ma, B., Liu, B., Wang, C., Zhang, Y., Zhang, W., 2019. Separation and recovery of valuable elements from spent CIGS materials. *ACS Sustainable Chem. Eng.* 7, 19816–19823.

Mirbagheri, S.A., Hosseini, S.N., 2005. Pilot plant investigation on petrochemical wastewater treatment for the removal of copper and chromium with the objective of reuse. *Desalination* 171, 85–93.

Mishra, R.K., Rout, P.C., Sarangi, K., Nathsarma, K.C., 2011. Solvent extraction of Fe(III) from the chloride leach liquor of low grade iron ore tailings using Aliquat 336. *Hydrometallurgy* 108, 93–99.

Moore, F.L., 1960. Liquid-liquid Extraction with High-Molecular-Weight Amines. Oak Ridge National Laboratory (ORNL), Oak Ridge.

Moskalyk, R.R., 2003. Gallium: the backbone of the electronics industry. *Miner. Eng.* 16, 921–929.

Moskalyk, R.R., 2004. Review of germanium processing worldwide. *Miner. Eng.* 17, 394–402.

Nassar, N.T., Graedel, T.E., Harper, E.M., 2015. By-product metals are technologically essential but have problematic supply. *Sci. Adv.* 1.

Nayak, S., Devi, N., 2017a. Studies on extraction of gallium (III) from chloride solution using Cyphos IL 104 and its removal from photodiodes and red mud. *Hydrometallurgy* 171, 191–197.

Nayak, S., Devi, N., 2017b. Separation and recovery of gallium(III) ions from aqueous phase by liquid-liquid extraction using a novel extractant, Cyphos IL 101. *Turk. J. Chem.* 41, 892–903.

Nayak, S., Devi, N., 2020. Development of hydrometallurgical process for indium recovery from waste liquid crystal display using Cyphos IL 101. *Trans. Nonferrous Met. Soc. China* 30, 2556–2567.

Nayl, A.A., 2010. Extraction and separation of Co(II) and Ni(II) from acidic sulfate solutions using Aliquat 336. *J. Hazard. Mater.* 173, 223–230.

Nguyen, T.H., Lee, M.S., 2020. A review on germanium resources and its extraction by hydrometallurgical method. *Miner. Process. Extr. Metall. Rev.* <https://doi.org/10.1080/08827508.2020.1756795>.

Nusen, S., Zhu, Z., Chairuangsr, T., Cheng, C.Y., 2015. Recovery of germanium from synthetic leach solution of zinc refinery residues by synergistic solvent extraction using LIX 63 and Ionquest 801. *Hydrometallurgy* 151, 122–132.

Öhrlund, I., 2011. Future Metal Demand from Photovoltaic Cells and Wind Turbines - Investigating the Potential Risk of Disabling a Shift to Renewable Energy Systems. *Science and Technology Options Assessment (STOA)*, European Parliament.

Okabe, T., 2010. The current status and prospect on precious & rare metals. *Chem. Eng. Jpn* 74, 102–108.

Padhan, E., Sarangi, K., 2014. Separation of molybdenum and cobalt from spent catalyst using Cyanex 272 and Cyanex 301. *Int. J. Miner. Process.* 127, 52–61.

Pandey, S., 2006. Analytical applications of room temperature ionic liquids: a review of recent efforts. *Anal. Chim. Acta* 556, 38–45.

Parhi, P.K., Sarangi, K., 2008. Separation of copper, zinc, cobalt and nickel ions by supported liquid membrane technique using LIX 84I, TOPS-99 and Cyanex 272. *Sep. Purif. Technol.* 59, 169–174.

Ramanujam, J., Singh, U.P., 2017. Copper indium gallium selenide based solar cells - a review. *Energy Environ. Sci.* 10, 1306.

Redlinger, M., Eggert, R., Woodhouse, M., 2015. Evaluating the availability of gallium, indium, and tellurium from recycled photovoltaic modules. *Sol. Energy Mater. Sol. Cells* 138, 58–71.

Rout, A., Binnemans, K., 2016. Efficient separation of transition metals from rare earths by an undiluted phosphonium thiocyanate ionic liquid. *Phys. Chem. Chem. Phys.* 18, 16039.

Rout, A., Wellens, S., Binnemans, K., 2014. Separation of Rare Earths and Nickel by Solvent Extraction with Two Mutually Immiscible Ionic Liquids. *RSC Adv.* 4, 5753.

Rydberg, J., Cox, M., Musikas, C., Choplin, G.R., 2004. Solvent Extraction Principles and Practice, 2nd ed. Marcel Dekker Inc.

Shirota, H., Takahashi, K., Ando, M., Kakinuma, S., 2019. Liquid properties of ionic liquids based on phosphonium cations with (alkylthio)alkyl groups. *J. Chem. Eng. Data* 64, 4701–4707.

Sun, Z., Cao, H., Xiao, Y., Sietsma, J., Jin, W., Agterhuis, H., Yang, Y., 2017. Toward sustainability for recovery of critical metals from electronic waste: the hydrochemistry processes. *ACS Sustain. Chem. Eng.* 5, 21–40.

Wędrychowicz, M., Piotrowicz, A., Skrzekut, T., Noga, P., Bydalek, A., 2022. Recovery of non-ferrous metals from PCBs scrap by liqation from lead. *Materials* 15, 2089.

Wei, G.T., Yang, Z., Chen, C.J., 2003. Room temperature ionic liquid as a novel medium for liquid/liquid extraction of metal ions. *Anal. Chim. Acta* 48, 183–192.

Wilson, A.M., Bailey, P.J., Tasker, P.A., Turkington, J.R., Grant, R.A., Love, J.B., 2014. Solvent extraction: the coordination chemistry behind extractive metallurgy. *Chem. Soc. Rev.* 123–134.

Yang, H., Song, T., Lee, S., Han, H., Xia, F., Devadoss, A., Sigmund, W., Paika, U., 2013. Tin indium oxide/graphene nanosheet nanocomposite as an anode material for lithium ion batteries with enhanced lithium storage capacity and rate capability. *Electrochim. Acta* 91, 275–281.

Zhou, H., Ye, Y., Tan, Y., Zhu, K., Liu, X., Tian, H., Guo, Q., Wang, L., Zhao, S., Liu, Y., 2022. Supported liquid membranes based on bifunctional ionic liquids for selective recovery of gallium. *Membranes* 12, 376.