

## Maternalmetallomics: Concept and Analytical Methodology

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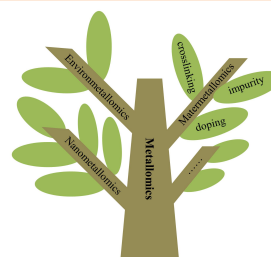
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*Received: January 30, 2021; Revised: February 19, 2021; Accepted: February 19, 2021; Available online: March 6, 2021.*

**DOI: 10.46770/AS.2021.101**

**ABSTRACT:** The emerging field of maternalmetallomics refers to all research activities aimed at the clarification of the role and function of metallic elements in materials. This paper discusses the concept of maternalmetallomics and the related analytical techniques used for probing the interactions between structure-activity relationships. The main object of maternalmetallomics research is metallic elements in materials, and includes the significance and contributions to materials science. This paper also introduces the analytical approaches used in maternalmetallomics, which includes the techniques of imaging, spectroscopic, X-ray-based, ion beam, MS-based and atomic spectrometry.



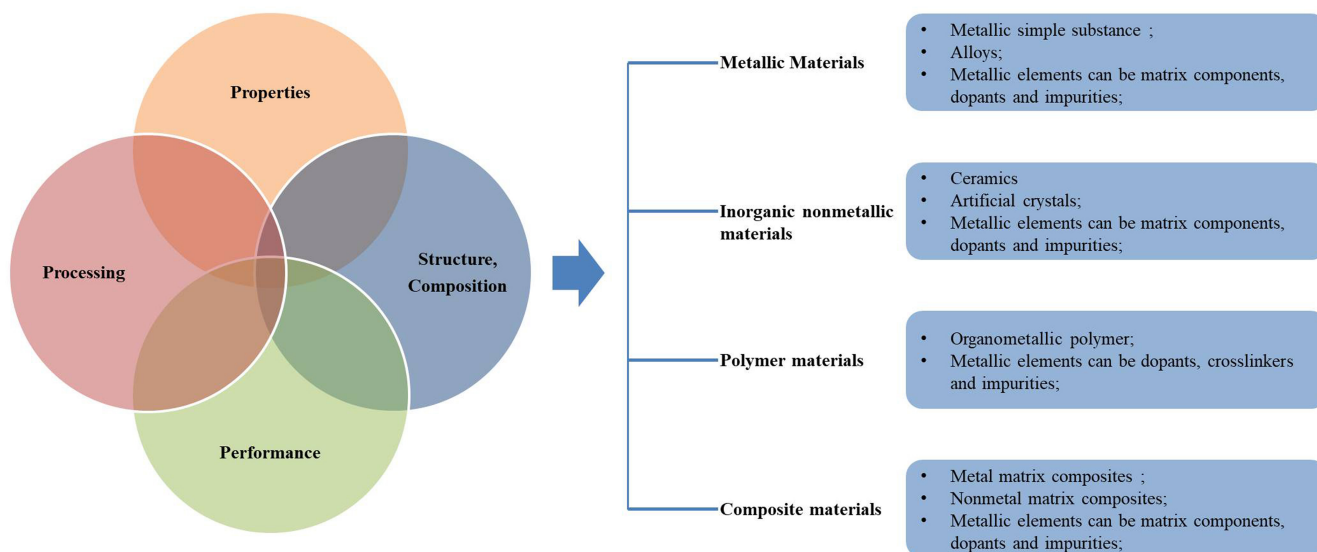
## INTRODUCTION

Materials and their use are a part of all aspects of people's lives, they are very important for the development of human economic society and the continuous innovations developed through science and technology. They have been successfully synthesized and contain mechanical, physical, chemical properties or machinabilities, and more new materials continue to be synthesized to meet additional applications scenarios. As is known, the "Materials Genome Initiative" was proposed 10 years ago with the aim to shorten the research and development cycle of new materials from discovery to application in industry and to support rapid economic development. It combines big data and high-throughput screening to achieve efficient materials discovery and parameter optimizations, and greatly reduces the developmental costs for new materials. Thus, the quantitative relationships between composition, structure, process, properties, and performance are of great significance for research and development of new materials, which is also an important content of materials genomics.<sup>1</sup>

Recently, this technology has been successfully applied to some novel materials, such as energy materials, gas separation materials, alloy materials, catalytic materials, polymer materials and others for specific applications.<sup>2-7</sup> Studies have shown that the composition as genes of materials is an important link in the chain

of processing, structure, properties, and performance, which is worthy of attention and discussion.

Materials can be divided into metallic materials, inorganic nonmetallic materials, polymer materials and composite materials depending on their chemical composition (Fig. 1). Metallic materials mainly include two types: metallic simple substances and alloys. In the periodic table, about 50 kinds of metallic elements are labelled as metallic simple substances, and almost all metallic elements and some non-metallic elements have been prepared into alloys. These are important materials used in the fields of aerospace, energy, mechatronics and automobile because of their good thermal conductivity, strength, hardness, and ductility. Studies also show that these properties are directly related to the type and proportion of metals. Besides, inorganic nonmetallic materials, polymer materials and composite materials involve metallic elements, such as rare earth doped laser crystals, metal organic frameworks (MOF), Mxenes, and so on. MOFs are organic-inorganic hybrid materials with intramolecular pores formed by self-assembly of organic ligands and metal ions or clusters through coordination bonds.<sup>8</sup> Mxenes, a large family of transition metal carbides, nitrides, and carbonitrides, received considerable attention in recent years because they showed enhanced optical, thermal, mechanical, and electrical properties compared to their bulk counterparts.<sup>9</sup> The different valence and coordination abilities of different metals results in a diversity of



**Fig. 1** Metallic elements play an important role in materials. Composition as genes of materials is an important link in the chain of processing, structure, properties, and performance. Metallic elements are used in all kinds of materials as matrix, dopants, impurities or crosslinkers.

hydrogen 1 H 1.0079																		helium 2 He 4.0026																	
lithium 3 Li 6.941		beryllium 4 Be 9.0122																		boron 5 B 10.811		carbon 6 C 12.011		nitrogen 7 N 14.007		oxygen 8 O 15.999		fluorine 9 F 18.998		neon 10 Ne 20.180					
sodium 11 Na 22.990		magnesium 12 Mg 24.305																		aluminum 13 Al 26.982		silicon 14 Si 28.086		phosphorus 15 P 30.974		sulfur 16 S 32.065		chlorine 17 Cl 35.453		argon 18 Ar 39.948					
potassium 19 K 39.098		calcium 20 Ca 40.078		scandium 21 Sc 44.956		titanium 22 Ti 47.867		vanadium 23 V 50.942		chromium 24 Cr 51.996		manganese 25 Mn 54.938		iron 26 Fe 55.845		cobalt 27 Co 58.933		nickel 28 Ni 58.693		copper 29 Cu 63.546		zinc 30 Zn 65.39		gallium 31 Ga 69.723		germanium 32 Ge 72.61		arsenic 33 As 74.922		selenium 34 Se 78.96		bromine 35 Br 79.904		krypton 36 Kr 83.80	
rubidium 37 Rb 85.468		strontium 38 Sr 87.62		yttrium 39 Y 88.906		zirconium 40 Zr 91.224		niobium 41 Nb 92.906		molybdenum 42 Mo 95.94		technetium 43 Tc [98]		ruthenium 44 Ru 101.07		rhodium 45 Rh 102.91		palladium 46 Pd 106.42		silver 47 Ag 107.87		cadmium 48 Cd 112.41		indium 49 In 114.82		tin 50 Sn 118.71		antimony 51 Sb 121.76		tellurium 52 Te 127.60		iodine 53 I 126.90		xenon 54 Xe 131.29	
cesium 55 Cs 132.91		barium 56 Ba 137.33		lanthanum 57-70 *<																															

**Fig. 2** Elements have been used for doping. Almost all metallic and semi-metallic elements have been used for doping in the periodic table.

structures and functions. In summary, metallic elements are essential elements of materials composition. They can be used as matrix, dopant, crosslinkers and impurities in the preparation process, which covers almost all the metallic elements in the

periodic table. In this paper, metallic elements as matrix are not discussed in detail, such as metallic simple substances, alloys, etc., since it is obvious that metals play an important role in such materials.

## METALLIC ELEMENTS AS DOPANTS

Doping is the purposeful incorporation of a small number of other elements or compounds into the material to change its composition, and making materials possess specific electrical, magnetic, and optical properties. At present, almost all the discovered metallic elements have been used in doped materials, such as crystals, ceramics, organic compounds, and other substances, which adds up to more than the non-metal elements. Table 1 lists the doping metallic elements in typical materials and related properties.

The doped elements cover almost all the metallic elements in the periodic table of elements and semi-metallic elements, such as B, Si, As, Se, Te *etc.*, as shown in Fig. 2. The introduction of different metals into the same material can improve the performance of different aspects and broaden the application direction. Metallic element doping can effectively change the photoluminescence (PL) characteristics of the metal halide perovskite (the general structure is  $ABX_3$ ).<sup>10</sup> Intriguingly, Mn-doping and lanthanide-doping both demonstrate multi-peak emission with PL peaks related to transitions from energy levels of the dopant ions.<sup>11,12</sup> Spinel ferrite materials containing dopants have good electrical and magnetic properties and are used in various fields. It has been reported that  $CoFe_2O_4$  nanoparticles have been doped with more than 20 kinds of metal elements to achieve applications in different fields.<sup>13</sup> According to UV-Vis analysis, a blue shift was shown with Ni doping,<sup>14</sup> while Zn doping produced particles with a similar shape, size (5 nm), and structure while possessing various magnetic anisotropies.<sup>15</sup> The Aurivillius

phase of  $Bi_2VO_{5.5}$  is an interesting oxide ion conductor.<sup>16</sup> The electrolyte ceramic membrane doped with  $Cu^{2+}$  and  $Sb^{5+}$  has the highest oxygen ion conductivity, reaching the  $10^{-3}$ - $10^{-1}$  s/cm level in the working temperature range of 300-600 °C. When doped with  $Sb^{5+}$ ,  $Nb^{5+}$ , and  $Ta^{5+}$ , it has a stable structure and a low thermal expansion coefficient and does not easily undergo phase transition. GaN-based magnetic semiconductor materials incorporated with metallic elements have been extensively studied for their potential applications in opto-electronics and spintronics. It was found that different metallic elements changed different degrees of magnetic performance. The non-magnetic dopant Cu has a 0.70  $\mu B$ /atom, and the magnetic moment of Ag doped GaN was larger than that of Pd doped because the N sites contribute 0.42  $\mu B$ , which is much greater than any other 4d metal doped GaN. In addition, there was a unique observation reported as a colossal magnetic moment in Re doped GaN.<sup>17</sup> Atomically precise noble metal (mainly silver and gold) nanoclusters are an emerging category of promising functional materials. Without doping, the magnetic response of noble metal clusters is generally weak. Doping with ferromagnetic metals, such as Fe, Co, and Ni, is a promising pathway to introduce magnetic properties into such clusters.<sup>18</sup>

In addition to the type of doped metal elements, closely related to the properties of the materials, the content of the doped elements also greatly affects the properties of the materials. Shobana et al.<sup>19</sup> found that the increase in  $Y^{3+}$  content in yttrium doped cobalt ferrite prepared by sol-gel combustion can increase the crystallite size and decrease the conductivity of the nanoparticles. Yang<sup>20</sup> synthesized the  $Bi_2V_{1-x}Mn_xO_{5.5-\delta}$  electrolyte from  $MnO_2$ .

**Table 1 Doping and Properties of Some Representative Materials**

Material	Doping metal elements	Related performance
<b>Metal halide perovskites</b>	Sb, Bi, Sn, Pb, transition metals ( <i>e.g.</i> V, Ni, Cu, Zn), lanthanide metals ( <i>e.g.</i> Sm, Dy, Er, Yb), and alkali metals ( <i>e.g.</i> Li, Na, K, Rb)	Optoelectronic properties ( <i>e.g.</i> , absorption band gap, PL emission, and quantum yield (QY)) and stabilities Power conversion efficiency (PCE), the reproducibility and stability
<b>Ceramic-magnetic nanoparticles</b>	Mg, Al, In, 3d metals ( <i>e.g.</i> Ti, V, Cr, Mn), 4d metals ( <i>e.g.</i> Y, Ag, Cd), rare-earth metals ( <i>e.g.</i> La, Ce, Pr, Nd)	Electrical Structural Optical characteristics
<b>Nitride ceramic phosphor</b>	Rare-earth metals ( <i>e.g.</i> Eu, Ce, Tb, Er, Gd)	Optical characteristics
<b>Zinc oxide semiconductor</b>	Transition metals ( <i>e.g.</i> Mn, Cu, Fe) Noble metals ( <i>e.g.</i> Au, Ag, Pd, Pt)	Photocatalytic properties (energy levels mobility, conductivity, and optical and magnetic properties). Gas sensing properties
<b>Graphite carbon nitride</b>	Alkali metals ( <i>e.g.</i> Na, K), transition metals ( <i>e.g.</i> Fe, Cd, Co, Mo), rare-earth metals ( <i>e.g.</i> Ce, Eu, Se, Y)	Photocatalytic properties (band gap, interlayer resistance)
<b>Silicon Carbide Ceramics</b>	Transition metals ( <i>e.g.</i> Fe, Ti)	Band diagram Conduction Spin-related-features
<b>Electrolyte ceramics</b>	Cu, Sb, Nb, Ta, Mn	Oxygen ion conductivity
<b>Noble metal nanoclusters</b>	Fe, Co, Ni	Ferromagnetic properties
<b>GaN based magnetic semiconductor materials</b>	3d metals ( <i>e.g.</i> Fe, Co, Ni, Cu), 4d metals ( <i>e.g.</i> Ag, Pd), rare-earth metals ( <i>e.g.</i> Eu, Gd, Ce)	Ferromagnetic properties
<b>Structural ceramics</b>	Rare-earth metals ( <i>e.g.</i> La, Y, Ce)	Compactness properties Thermal conductivity Mechanical properties
<b>Conductive polymer</b>	Transition metals ( <i>e.g.</i> Fe, Co, Ni)	Electrical properties Electrochemical activity

The electrolyte was the  $\gamma$  phase in the range of  $0.1 \leq x \leq 0.25$ . The doped  $\text{Mn}^{4+}$  was reduced to  $\text{Mn}^{3+}$ , and when the temperature was higher than 650 °C, it was reduced to  $\text{Mn}^{2+}$ , which was due to the release of  $\text{O}_2$ . Alga<sup>21</sup> believed that the solute was the  $\gamma$  phase in the range of  $0.075 \leq x \leq 0.25$ ,  $\text{Mn}^{3+}$  in the range of  $0.075 \leq x \leq 0.10$ , and  $\text{Mn}^{3+}/\text{Mn}^{4+}$  in the range of  $0.15 \leq x \leq 0.25$ .  $\text{Mn}^{4+}$  increased with an increase in  $\text{MnO}_2$ , and the highest oxygen ion conductivity was obtained when the doping amount of  $\text{MnO}_2$  was  $x = 0.1$ .

The dopants are mainly in the form of species (ion, atom, isotope) nanoparticles and compounds. For example, when adding metal halide salts (e.g.  $\text{SbCl}_3$ ,  $\text{BiCl}_3$ ,  $\text{VCl}_3$ ,  $\text{NiCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{SnCl}_2$ ,  $\text{SnCl}_4$ ,  $\text{PbCl}_2$  and  $\text{CuCl}_2$ ) as dopants to  $\text{CsPbCl}_3$  nanocrystals, the difference in the photoluminescence quantum yield (PLQY) enhancements was not due to the doping of these different doping metallic ions, but because of the varied ability of these metal compounds to release active chloride ions for surface passivation.<sup>22,23</sup> Recently, single-atom electrocatalysts (SACs), which comprise singly isolated metal atoms immobilized onto a heterogeneous support, have attracted attention as a robust analogue of organometallics.<sup>24</sup> SACs are the ultimate form of size reduction of metal electrodes and maximize the efficiency of metal atom use. Different from Pt nanoparticle ( $\text{Pt}_{\text{nano}}$ ) doping, single Pt atom doping can reduce Pt atom usage on the one hand, and selectively catalyze the hydrogen oxidation reaction (HOR)/hydrogen evolution reaction (HER) over oxygen reduction reaction (ORR) on the other hand. The temperature-frequency behavior of the dielectric permittivity (9–300 K; 100 Hz–1 MHz, and at 100 GHz) of  $\text{K}_{0.984}\text{Li}_{0.016}\text{TaO}_3$ , containing the natural ratio of the Li isotopes (7.56% of  $^6\text{Li}$  and 92.44% of  $^7\text{Li}$ , KLT-7) and only the  $^6\text{Li}$  isotope (KLT-6), was studied.<sup>25</sup> The results revealed that the activation energy for  $^6\text{Li}^+$  relaxation appeared to be smaller and the relaxation time pre-exponent was larger than for the  $^7\text{Li}^+$  centers. The optical and photocatalytic properties of materials were usually related to the valence states of the elements, which should be paid attention to when doping. For ferric chloride doped polyvinyl alcohol (Fe: PVA) polymer films, the decrease of the refractive index in the visible range induced by UV exposure was related to the reduced oxidation state of the doping metal ( $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ ).<sup>26</sup> Structural ceramics are widely used in daily life, and have been extended to aerospace, integrated circuit, energy, and the environmental protection fields, such as alumina, silicon nitride, silicon carbide, and so on. In order to improve the compactness, thermal conduction and reduced sintering temperature, rare earth oxides are often doping, such as  $\text{La/Y-Al}_2\text{O}_3$ .<sup>27,28</sup>

Bimetallic/polymetallic doping has been tried because single metal doping sometimes cannot achieve satisfactory results. The Ni and Mn co-doping influence on electrical, structural, and optical characteristics of  $\text{CoFe}_2\text{O}_4$  nanoparticles prepared via the co-precipitation route was reported.<sup>14</sup> Bimetallic doping caused shifts of the absorption and emission band maxima in the luminescence spectra and the appearance of optical properties

unattainable for mono-doped materials.<sup>29</sup> Moreover, such systems often demonstrate the sensitization effect which allows a considerable enhancement of the luminescence intensity and thus avoids the limitations imposed by the concentration quenching effect. Experimental and theoretical studies have proven that incorporation of co-dopants advances the photocatalytic properties of graphite gallium nitride ( $\text{g-C}_3\text{N}_4$ ) photocatalyst more efficiently.<sup>30</sup> Fan et al.<sup>31</sup> first obtained ZnO nanorods by the hydrothermal method and then fabricated Pt and Au co-doped ZnO nanorods with the response of this bimetallic semiconductor hydrogen sensor much higher than those made of pure ZnO or single noble metal doped ZnO.

In summary, doping improves the properties of materials by changing their composition or structure and is widely used in materials science. It was found that advanced materials with different properties of optical, magnetic, and electrical properties have been obtained by doping metallic elements. The doped elements include almost all metallic elements and semi-metallic elements, and the forms of doping involves ions, atoms, isotopes, valence states, nanoparticles, bimetallic/polymetallic doping. At the same time, the doping of non-metallic elements has been rarely reported.

## METALLIC ELEMENTS AS IMPURITIES

In addition to doping by introducing metal elements into the material, the impurities of the raw materials and the contamination accompanying the process (such as the diffusion from crucible material and matrix material) will also affect the final quality and performance of the materials. Appropriate impurity species and contents are very helpful for the improvement of material properties. Cobalt and copper oxides have shown more important contribution to the observed electroactivity, and their presence as impurities in carbon nanotubes (CNTs) should be considered in the evaluation of their electrochemical response.<sup>32</sup> It is considered that the ferromagnetism of some fullerene polymers and graphite, such as hard carbon phase samples, is not related to fullerene at all.<sup>33</sup> Most of the works published previously as evidence of ferromagnetism in fullerene polymers synthesized at high pressure high temperature (HPHT) conditions can be explained by contamination with magnetic impurities. Formation of iron carbide ( $\text{Fe}_3\text{C}$ ) due to the reaction of metallic iron with fullerene molecules explains the observed Curie temperature of close to 500 K and the levels of magnetization reported for "magnetic carbon."

However, the existence of some impurities with the content exceeding a certain limit often causes adverse effects and the impurity removal process usually should be carried out. Metallic impurities such as iron, chromium and titanium can reduce the carrier diffusion length in polysilicon. In polysilicon cells, copper affected not only the composition of the substrate, but also the composition of the emitter and, more importantly, it affected the



performance of the cell.<sup>34</sup> Pumera et al.<sup>35</sup> investigated the electrochemical response of carbon nanotubes containing different amounts of impurities towards the reduction of an important biomarker, hydrogen peroxide, and the oxidation of an important impurity marker. They found that the borderline between being redox active/inactive for iron-based impurities was in the middle-ppm range.

## METALLIC ELEMENTS AS CROSSLINKERS

Metal coordination is a special non-covalent interaction with both high bond energy and dynamic characteristics, for which metal ions are widely used as crosslinkers to assemble and regulate materials<sup>36</sup> and to broaden the properties and applications prospects of materials. For example, crosslinking can fix the structure of polymer micelles and improve the stability of polymer micelles, and the use of some chemicals can be avoided in the formation of non-covalent crosslinking with metal ions (*e.g.*  $\text{Eu}^{3+}$ ,  $\text{Ru}^{2+}$  and  $\text{Zn}^{2+}$ ), which has been applied in the fabrication of metal coordination crosslinked polymer micelles.<sup>37</sup> Alginate is known to form a hydrogel in the presence of divalent cations, such as calcium, which acts as crosslinker between the functional groups of alginate chains.<sup>38</sup> In recent years, various kinds of metal ions (*e.g.*  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Mg}^{2+}$ ) were utilized to crosslink the alginate to prepare the flame-retardant films and fibers.<sup>39</sup> In principle, metal–ligand interactions can be utilized for intrinsic self-healing, as the reformation of coordinative bonds does not require demanding conditions, such as high pressure or harsh chemical environment, but it can occur *in situ* for polymers in a suitable environment. It has been reported that the hexabrachial star copolymer system crosslinked by ferric (II) salt shows good self-healing performance at the medium temperature of 80–120 °C and the time interval of 6–8 h, which was better than for the linear polymer system.<sup>40</sup> Based on the unique advantages of metal ion crosslinking, such as forming a reversible network and simply tuning material properties, it has also been applied to polyethylene glycol (PEG)-based links, crosslinked with metal ions (*e.g.*  $\text{V}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$ ) as materials for 3D extrusion printing, thus facilitating the adaptation of the system to the requirements of the printing process broad range of the printing parameters and application with remarkable flexibility.<sup>41</sup> All in all, metal crosslinking is a good way to adjust and assemble materials, which has been successfully applied in many fields.

The specific mechanisms of the relationship between doping, crosslinking or impurity elements and properties are still unclear and worthy of further study, especially regarding the Materials Genome Initiative. The composition and microstructure, just like "genes" which determine the properties of materials, of the metallic elements are essential components of various gene sequences. Thus, it is important to materials science that the

distribution, species, and content of doping, crosslinking or impurity elements, and the effects on the resulting properties of the materials. Therefore, the "concept of matermetallomics" is defined as a structure-activity relationship of materials between their components and their properties and performance. Furthermore, the techniques for characterizing the distribution, species, and content of metallic elements in materials are discussed detailed in section "Analytical approaches for matermetallomics". Although many related studies have been published recently, only representative work is cited here.

## METARMETALLOMIC AND RELATED TERMS

In the study of metallomics, it refers to the study of a metallome, interactions and functional connections of metal ions and their species with genes, proteins, metabolites and other biomolecules within organisms and ecosystems. The most important research target of metallomics is to elucidate the physiological roles and functions of the biomolecules binding with metallic ions in the biological systems.<sup>42</sup> Similarly, metallomics of materials should clarify the role and function of metallic elements in materials, named as Matermetallomics. It is therefore important to specify that a metallomics study implies:

- (i) A focus on metallic or semi-metallic elements (*e.g.* As, Se, Sb) in the context of materials science. It is not recommended to extend the term extended to non-metals, such as sulfur or phosphorous.
- (ii) A correlation of the element concentration mapping or element speciation with materials. This correlation may be statistical (the distribution, content and species of elements coincides with the presence of a particular property or character), structural (the interaction between the elements and microstructure) or functional (the presence of elements is the result of process adjustment).
- (iii) A systematic, comprehensive, or global approach. If a metal species does not explain its significance and contribution to materials science, it is not matermetallomics!

Matermetallome is defined as the distribution, species, and concentration of metal elements in micro and macro structures. From the above consideration, a matermetallome refers to the metallic matrix, dopants, impurities or crosslinkers in inorganic nonmetal materials, polymer materials and composite materials.

## ANALYTICAL APPROACHES FOR MATERMETALLOMICS

In the study on the subjects in matermetallomics, many existing analytical techniques have been widely used, more advanced

**Table 2 Representative Analysis Methods in Material Analysis**

Analyte	Analysis Method	Comments	Ref.
Cr, Co, Ni, and Cu	LA-ICP-MS	Quantitative analysis of Cr, Co, Ni and Cu in metallic materials without complex processing.	43
ratio of Fe (II)/Fe (III)	XPS	Analyze the ratio of Fe (II)/Fe (III) in 1045 steel and J55 steel.	44
Cr, Fe, Ni	SIMS	Depth-profiling analysis of Cr, Fe, Ni in oxidized steel samples.	45
Th and U	ICP-MS	Detect ultra-trace Th and U in copper	46
Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th	Glow discharge mass spectrometry (GD-MS)	Qualitative analysis of 72 impurity elements in high-purity copper powder.	47
Cd, Cr, Mn, Mo, Pb, V, and Zn	Electrothermal vaporization (ETV)-ICP-AES	Determination of Cd, Cr, Mn, Mo, Pb, V and Zn in 2.0–2.5 mg aliquots of nickel foam samples without pretreatment.	48
Cr, Mn, Fe, Co, Ni, Cu, Zn, As and Pb at trace level	Total reflection-XRF	Quantify trace elements in light and middle distillates (gasoline, racing and jet fuel).	49
sulfur and iron valence state	Wavelength dispersion (WD)-XRF	Determine the content of ferrous iron and to estimate sulfur valence state in coal concentrates and ashes from the pressed pellet without additional sample preparation.	50
lithium isotopic	MC-ICP-MS	Determination of lithium isotopes in coal to help to track atmospheric haze and polluted water in the environment.	51
C, H, Ni, S and V	LIBS&LA-ICP-AES	LIBS and LA-ICP-AES were used simultaneously for the elemental analysis of asphaltene samples using minimum sample pretreatment.	52
Cr, Hg and Pb	LIBS	Quantitative analysis of plastics by LIBS was used to measure Cr, Hg and Pb.	53
the <sup>137</sup> Cs and <sup>40</sup> K radio isotopes	High purity germanium gamma spectrometry (HPGe)	The HPGe method was used to detect the concentration of <sup>137</sup> Cs and <sup>40</sup> K isotope in edible salt.	54
Pd, Pt and Rh	High resolution continuum source graphite furnace (HR-CS)-GFAAS	HR-CS-GFAAS detected the Pd, Pt and Rh (PGMs) in spent automobile catalysts without chemical separation.	55
gas concentrations below a tungsten surface	LIBS-LAMS	LIBS-LAMS was used to measure the depth-dependent concentration of gaseous substances under the surface of tungsten.	56
<sup>235</sup> U/ <sup>238</sup> U ratio	NanoSIMS	The micro-scale isotopic heterogeneity of nuclear fuel pellets was characterization by nano-scale secondary ion mass spectrometry (NanoSIMS).	57
two Cm isotopic ratios	AMS	Two Cm isotopic ratios ( <sup>244</sup> Cm/ <sup>246</sup> Cm and <sup>245</sup> Cm/ <sup>246</sup> Cm) was determined to date irradiated in nuclear fuels.	58
Cu, Zr, Ag, W	FIB-TOF-SIMS	High spatial resolution of elemental distribution was determined.	59
Cu, Se, In, Ga	GD-OES	GD-OES was used for quantitative depth-profiling of copper indium gallium sulfur selenide (CIGS) thin films.	60
Mn, Cu, Fe	Electron probe micro analyzer (EPMA)	EPMA was used to measure the partial substitution of iron in the TiFe-system.	61
Al, Si, K, Ca, Ti, Mn, Fe, Cu, Zn and Sr	PIXE	Multi-elements and non-destructive analysis on the young leaves of Neem.	62
Na, Mg, Al	PIGE	In-situ quantitative analysis of four main elements (silicon, sodium, magnesium, and aluminum) in the soda lime glass sample.	63
Sc	NMR	Solid-state NMR ( <sup>45</sup> Sc MAS NMR) was used to measure the intramolecular charge transfers, which confirmed clearly the increase of electron density around the Sc <sup>3+</sup> species after Sc-EBTC interacted with the analytes.	64
Complexation of terpolymer and Ga ions	HPLC	HPLC was used to characterize the complexation of the terpolymer and Ga ions.	65
Na	MALDI-TOF-MS	MALDI-TOF MS spectra showed the ionization with H <sup>+</sup> and Na <sup>+</sup> were almost the same to the theoretical calculated values, confirmed chemical structure of octa carboxyl polyhedral oligomeric silsesquioxane.	66
Microstructure of La <sub>2</sub> CaB <sub>10</sub> O <sub>19</sub> crystal	Raman spectrometer	In situ Raman spectroscopy was applied to obtain the microstructure information on La <sub>2</sub> CaB <sub>10</sub> O <sub>19</sub> crystal and its growth solution.	67
Titanate	FTIR	FTIR measured the typical stretching vibrations band of Ti–O, explained the molecular structure of titanate nanofibers.	68

analytical techniques are also needed to explore the new research fields. Some representative analysis methods in materials analysis

are listed in Table 2. The analytical techniques were split into five main sections based on the research subject.

1. Imaging techniques mainly refer to element imaging, includes microscope and traditional spectroscopic techniques. Electron microscopes combined with energy dispersion X-ray analysis (EM-EDS) are the instruments specifically developed to acquire images of target materials at high magnification and analyze the elements on surface or cross-sections of materials, but its disadvantage is that it cannot analyze elements with an atomic number less than 5, in addition, the elemental sensitivity is poor. The new methods based on laser plasma technology are also gradually used in the imaging of elements in materials, such as laser-induced breakdown spectroscopy (LIBS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). LIBS is an imaging technology developed in recent years. Its advantages are that it can realize micro-area and fast elemental analysis without complicated preparation. Its disadvantages are poor stability, high sensitivity (up to  $\mu\text{g/g}$  level). In addition, the LIBS method can be applied to qualitative and quantitative analysis of elements, as well as in situ and remote real-time analysis such as iron and steel smelting.
2. Spectroscopic techniques, such as infrared, Raman spectroscopies and nuclear magnetic resonance (NMR), are frequently used to characterize the molecular structure in inorganic and organic compounds. The FTIR method is a non-destructive analysis and free from the restriction of the sample's physical state, but it is suitable for qualitative analysis, rarely for quantitative analysis. Raman spectroscopy can obtain the microstructure information of materials, such as bond length, coordination number information, cluster information with different coordination numbers, and quantitatively obtain the corresponding content of the microstructure types. What's more, it can be used for in situ detection at high temperature. High temperature in situ analysis technology also includes XRD, NMR. NMR is the most frequently used method for molecular structure characterization, which can obtain sample structure, composition, and kinetic information under non-destructive conditions with highly specific and good repeatability, but its low sensitivity limits its application in low doped materials.
3. X-ray-based technologies have a wide range of applications. X-ray fluorescence (XRF) is one of the most frequently used techniques for elemental analysis because of the advantages of fast analysis speed and no complex preprocessing. Its disadvantages are that the sensitivity to low atomic number elements is lower and it is easily affected by mutual element interference and overlapping peaks. X-ray diffraction (XRD) is often used for phase structure analysis, but it can also be used for component analysis of materials. X-ray photoelectron spectroscopy (XPS) is applied to quantify the valence and electronic levels of specific elements at the micro-area surface, which can analyze all elements, except H and He, and the qualitative identification of elements is strong. But elemental sensitivity is low, 0.1 % of detection limit, and data acquisition is slower.
4. Ion beam techniques can quantify trace elements with high sensitivity. Particle-induced X-ray emission (PIXE) and proton-induced gamma-ray emission (PIGE) have the advantages of high sensitivity, micro loss, and micro area analysis, but elements can be analyzed  $Z > 12$ .
5. MS-based techniques are most widely used for identification of unknown species, content determination and distribution imaging. Gas/liquid chromatography-MS is mainly applied to identify unknown organic substances containing metallic elements, but the analysis time is generally longer than with other MS-based techniques. Secondary ion mass spectroscopy (SIMS) is a very sensitive method for surface composition analysis, which can analyze all elements or isotopes including hydrogen, and depth analysis can be performed on samples with a depth resolution of less than 1 nanometer. However, it is very difficult to quantitative analysis because of the great difference between the secondary ion difference values of various elements. The secondary ion transmission efficiency of the mass analyzer is low and the measurement accuracy is insufficient. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) is a mass spectrometry technique developed in the late 1980s, which is widely used in protein sequencing and microbial identification. It has the advantages of fast analysis speed, high resolution ( $\mu\text{m}$ ), high sensitivity (f mol), high flux and high precision. It cannot analyze non-covalent bond interactions because of the soft ionization mode. ICP-MS is also a sensitive element analysis technology, which can realize micro area analysis of solid samples combined with laser ablation.
6. Atomic spectrometry technology includes atomic absorption spectrometry (AAS), atomic emission spectrometry (AES) and atomic fluorescence spectrometry (AFS), and so on, which are common elemental quantitative techniques in materials analysis. So far, many techniques, such as XRF, ICP-AES, ICP-MS as mature techniques, have been developed as the analytical methods for chemical speciation of trace metals in materials.

## CONCLUSIONS

To meet the needs of human beings for materials, systematic and in-depth research of the quantitative relationship among composition, structure, process, properties, and performance is the most possible solution to solve the problem. In this context, matermetallomics is proposed to study the relationship between metallic components and materials. This includes the systematic study of the distribution, content and species of the metallic elements, and the interaction between the metallic elements and

structure, process, properties, and performance. Further, it includes analytical approaches to matermetallomics and can be divided into six main categories: the imaging techniques, spectroscopic techniques, X-ray based techniques, ion beam techniques, MS-based techniques, and atomic spectrometry techniques. The emerging field of matermetallomics as an interdisciplinary field addresses the systematic view of the analytical methodology, role, and function of metallic elements in materials, across several disciplines including science and engineering of metallic materials, inorganic nonmetallic materials, polymer materials and composite materials, and materials characterization.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the National Consortium for Excellence in Metallomics and the Shanghai Platform for Metallomics, Science and Technology Innovation Project of Shanghai Institute of Ceramics, and Shanghai Technical Platform for Testing and Characterization on Inorganic Materials (19DZ2290700).

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