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REVIEWING THE PROPERTIES OF RARE EARTH ELEMENT-BEARING MINERALS, RARE EARTH ELEMENTS AND CERIUM OXIDE COMPOUND

PENGKAJIAN PROPERTI MINERAL PEMBAWA LOGAM TANAH JARANG, LOGAM TANAH JARANG DAN SENYAWA SERIUM OKSIDA

TATANG WAHYUDI
Research and Development Centre for Mineral and Coal Technology
Jalan Jenderal Sudirman 623 Bandung, 40211, Indonesia
Phone. +62.22.6030483, Fax. +62.22.6003373
e-mail: tatangw@tekmira.esdm.go.id

ABSTRACT

Of the 17 rare earth elements (REEs), 15 belong to the chemical group called lanthanides, plus yttrium and scandium. The lanthanides consist of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. Cerium is one of the most abundant REEs, comprises more of the earth's crust than copper or lead. At least, there are 29 potential REE-bearing minerals. Basnasite, monazite and xenotime are among them and serve as the most exploited minerals. The REEs are mostly applied for high technology application such as computer, telecommunication, nuclear and sophisticated instruments for exploring the outer space.

Keywords: REEs, lanthanides, cerium, bastnasite, monazite, xenotime, high technology

SARI

Logam tanah jarang atau LTJ terdiri atas 17 unsur; 15 di antaranya termasuk kedalam kelompok lantanida dan 2 sisanya adalah itrium dan skandium. Ketujuh-belas unsur yang termasuk lantanida adalah lantanum, serium, praseodimium, neodimium, prometium, samarium, europium, gadolinium, terbium, disprosium, holmium, erbium, tulium, iterbium dan lutetium. Di antara ke-17 unsur tersebut, serium merupakan salah satu unsur LTJ yang paling melimpah. Di alam, LTJ sering ditemukan sebagai senyawa kompleks fosfat atau karbonat. Sedikitnya ada 29 mineral pembawa LTJ yang secara ekonomi bersifat potensial. Dari ke-29 mineral tersebut, basnasit, monasit dan senotim merupakan mineral LTJ potensial yang banyak dieksploitasi. Aplikasi LTJ kebanyakan berkaitan dengan industri teknologi tinggi karena sifatnya yang mendukung untuk penggunaan teknologi tinggi tersebut seperti komputer, telekomunikasi, nuklir dan peralatan canggih untuk eksplorasi luar angkasa.

Kata kunci: LTJ, lantanida, serium, basnasit, monasit, senotim, teknologi tinggi

INTRODUCTION

Rare earth elements or known as REEs consist of seventeen chemical elements in the periodic table. Of the 17 elements, 15 of them belong to lanthanides and two of them are scandium and yttrium. The lanthanides include lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. Scandium and yttrium are considered REE as they are commonly found in the same ore deposits as

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the lanthanides and show similar chemical properties with lanthanides (Figure 1; http://geology.com/articles/rare-earth-elements/). Though its name contains the word “rare”, such elements are relatively abundance in nature (except radioactive promethium), for example cerium is being 25th most abundant element at 68 ppm (similar to copper). The reason that the elements belong to rare condition is their geochemical nature. REE tends to disperse and is rarely found to be concentrated as rare earth minerals in economically exploitable ore deposits. Its mineral scarcity leads to the term of “rare earth”. As an example is gadolinite; extracted from a mine in the village of ytterby - Sweden, gadolinite is the first discovered REE mineral. The mineral is named after Gadoli who successfully separated main minerals from its gangue in 1794. It contains a compound of cerium, yttrium, iron, silicon and other elements. Chemically, its formula is $(Ce,La,Nd,Y)_2FeBe_2Si_2O_{10}$. The mineral is also called ytterbite.

In nature, REE is found as a complex compound, normally in complex phosphate or carbonate compounds. Fast development in processing technology causes the need of REE is important. The REE application is mostly related to high technology industries such as computer, telecommunication, nuclear and outer space. Cerium is one of abundant REEs. The metal is a malleable, soft, ductile, iron-grey metal, slightly harder than lead. It is very reactive and tarnishes readily in the air. Cerium oxidizes slowly in cold water but rapidly in hot water. It dissolves in acids and can burn when heated or scratched with a knife. Its quantity within the earth crust is around 0.0046%. Cerium-bearing minerals include alanite or also known as orthite- $(Ca,Ce,La,Y)_2(Al,Fe)_3(SiO_4)_3(OH)$, monazite - $(Ca,Ce,La,Y)_2(Al,Fe)_3(SiO_4)_3(OH)$, bastnasite - $(Ce,La,Y)CO_3F$, hydroxyl-bastnasite - $(Ce,La,Nd)CO_3(OH,F)$, rabdophane - $(Ce,La,Nd)PO_4\text{-}H_2O$, zircon - $ZrSiO_4$ and synchysite - $Ca(Ce,La,Nd,Y)(CO_3)_2F$. Both monazite and bastnasite currently are the important cerium source. Those above minerals along with allanite - $\{CaCe\}\{Al_2Fe^{2+}\}(Si_2O_7)(SiO_4)O(OH)$ are cerium, thorium and other REE sources in the future. Figure 2 shows allanite and monazite as the cerium sources.

A compound of cerium and oxygen performs cerium(III)oxide or Ce_2O_3 and cerium(IV)oxide (CeO_2) or also known as ceric oxide, ceria, cerium oxide or cerium dioxide. Both belong to REE-oxides. Cerium(III)oxide performs gold-yellow in color and molecular weight of 328.24 $gmol^{-1}$. Its density and melting point are 6200 kgm^{-3} and 2450°K respectively. Figure 3a illustrates the crystal structure of Ce_2O_3 based on International Union of Pure and Applied Chemistry (IUPAC) that shows hexagonal structure. Compared to (CeO_2), Ce_2O_3 is more stable at standard temperature

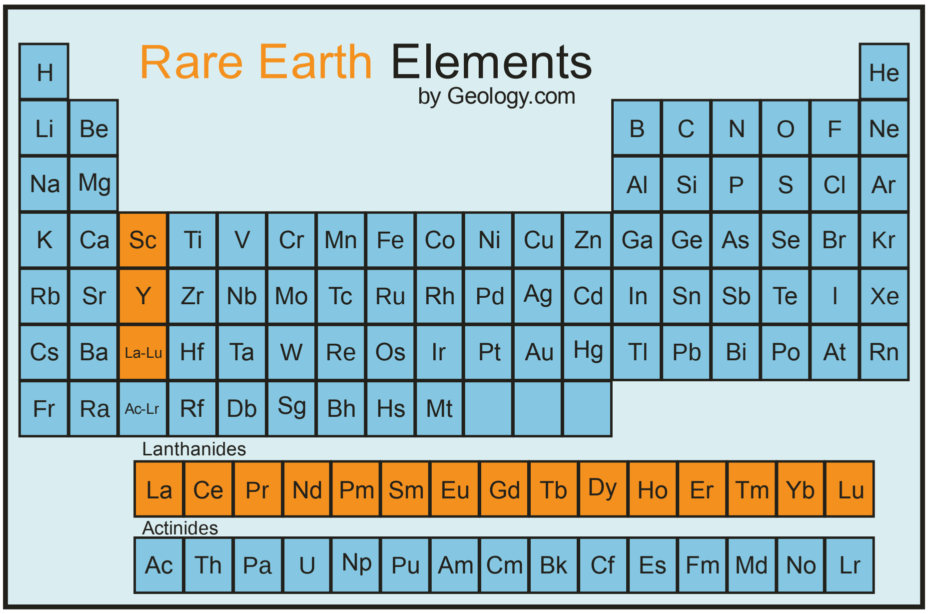
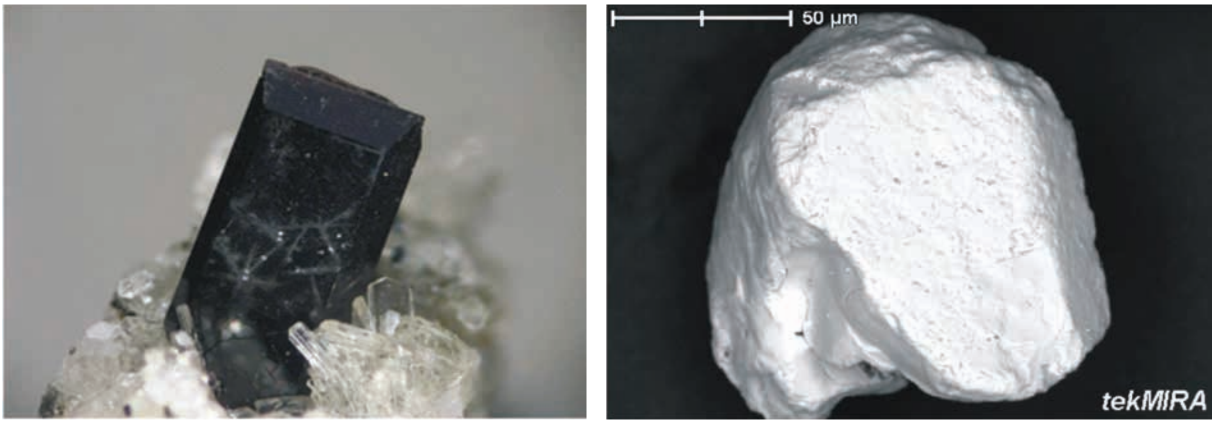


Figure1. Periodic table of the elements. The REE belongs to yellow column and row (http://geology.com/articles/rare-earth-elements/)



(a) (b)

Figure 2. Allanite (a; http://www.mindat.org/photo-95141.html) and monazite (b; Wahyudi et al., 2009) are REE-bearing minerals

and pressure (273,15°K and 100 kPa). Referring to such stability, discussion regarding cerium oxide belongs to CeO_2. Different from Ce_2O_3, CeO_2 retains fluorite structure or known as cubic one (Figure 3b). The oxide presents yellow-white powder. The powder is slightly hygroscopic and will absorb a small amount of CO_2 from the atmosphere. Cerium (IV) oxide is derived by calcining cerium oxalate or cerium hydroxide or precipitating cerium nitrate as raw material and ammonium acid carbonate as precipitation agent. Its density and molar mass are around 7.65 g/cm^3 and 172.12 g/mol respectively.

The objective of this study is reviewing the characteristics of rare earth element-bearing minerals, rare earth elements and cerium oxide compound based on their physical, chemical and mineralogical properties. Understanding the characteristics will help when processing the material such as determining the proper process, anticipating arisen problems during and after the process, etc.

METHODOLOGY

A literature survey was the main method used for this study. The studied literatures also included personal researches regarding REE-bearing minerals and REE extraction that had been already published. The former dealt with SEM and optical microscope tests on the samples while the later coped with processing monazite minerals to be extracted their REEs, Both studies employed sample materials from derived from the field

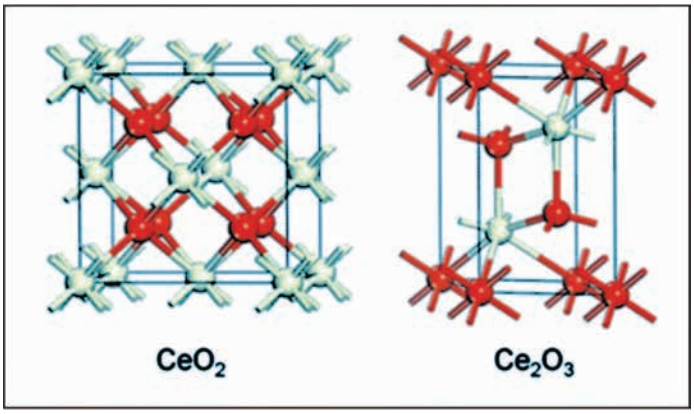


Figure 3. Crystal structure of CeO_2 and Ce_2O_3 (http://jgraciani.com/wp-content/uploads/2014/07/2011JCTC.jpg)

Bangka Island. Ye, experiments related to REE making were conducted from monazite mineral.

RESULTS AND DISCUSSION

Characteristics of REE-bearing Minerals

The fact that almost all of REE production comes from less than 10 minerals is quite incompatible with the quantity of REE-bearing minerals. At least there are 28 the commercially REE-bearing as shown in Table 1 (Castor and Hedrick, 2006), however, the most common REE-bearing minerals include bastnasite, monazite and xenotime. Reason that people select certain REE-bearing minerals to be processed includes deposit condition. The minerals that are easy to be concentrated are desirable due to its coarse grain size or other attributes. Carbonate bastnasite, for example, is desired due to its easily broken down property compared to silicate allanite that are difficult to dissociate. Similar case occurs to placer monazite. Though the deposits belong to the important source of REEs, such minerals are left behind due to its high thorium content. Recently, China as one of REE producers took the REEs from clay mineral within laterite deposit.

Table 1. Potentially economic deposits of REE-bearing minerals (Castor and Hedrick, 2006)

Mineral	Formula	REO wt. %
Aeschynite	$(Ln,Ca,Fe,Th)(Ti,Nb)_2(O,OH)_6$	36
Allanite (orthite)	$(Ca,Ln)_2(Al,Fe)_3(SiO_4)_3(OH)$	30
Anatase	TiO_2	3
Ancylite	$SrLn(CO_3)_2(OH).H_2O$	46
Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$	19
Bastnasite	$LnCO_3F$	76
Brannerite	$(U,Ca,Ln)(Ti,Fe)_2O_6$	6
Britholite	$(Ln,Ca)_5(SiO_4,PO_4)_3(OH,F)$	62
Cerianite	$(Ce,Th)O_2$	81
Cheralite	$(Ln,Ca,Th)(P,Si)O_4$	5
Churchite	$YPO_4.2H_2O$	44
Eudialyte	$Na_{15}Ca_6(Fe,Mn)_3Zr_3(Si,Nb)Si_{25}O_{73}(OH,Cl,H_2O)_5$	10
Euxenite	$(Ln,Ca,U,Th)(Nb,Ta,Ti)_2O_6$	<40
Fergusonite	$Ln(Nb,Ti)O_4$	47
Florencite	$LnAl_3(PO_4)_2(OH)_6$	32
Gadolinite	$LnFeBe_2Si_2O_{10}$	52
Huanghoite	$BaLn(CO_3)_2F$	38
Hydroxylbastnasite	$LnCO_3(OH,F)$	75
Kainosite	$Ca_2(Y,Ln)_2Si_4O_{12}CO_3.H_2O$	38
Loparite	$(Ln,Na,Ca)(Ti,Nb)O_3$	36
Monazite	$(Ln,Th)PO_4$	71
Mosandrite	$(Ca,Na,Ln)_{12}(Ti,Zr)_2Si_7O_{31}H_6F_4$	<65
Parisite	$CaLn_2(CO_3)_3F_2$	64
Samarskite	$(Ln,U,Fe)_3(Nb,Ta,Ti)_5O_{16}$	12
Synchisite	$CaLn(CO_3)_2F$	51
Thalenite	$Y_3S_3O_{10}(OH)$	63
Xenotime	YPO_4	61
Yttrotantalite	$(Y,U,Fe)(Ta,Nb)O_4$	<24

In nature, the REE-bearing minerals are classified into carbonate, phosphate, oxide, silicate and fluoride minerals. Most of REEs in such minerals performs a complex compound. As a result, it needs to be separated from its complex compound when beneficiated. Bastnasite, monazite, xenotime and zircon are the most common minerals. The first three retains relatively high REE oxide content. Bastnasite or known as fluoro-carbonate cerium ($CeFCO_3$) contains 60-70% REE-oxides such as lanthanum and neodymium. Such a mineral gets its name from its type locality - Bastnäs mine, Sweden. It serves as the main source of REEs in the world and is normally available in carbonatites, dolomitic breccias, pegmatite and amphibole skarn (Yunxiang Ni et al., 1993). Bastnasite has been found in Hungary, Greece and Balkan region. It is also found at Fen, Norway; Bayan Obo, Mongolia; Kangankuunde, Malawi; Kizilcaoren, Turkey and the Mountain Pass, California. So far, no bastnasite was found in Indonesia until today. Physically, characteristics of bastnasite are shown in Table 2. Figure 4 shows basnasite minerals.

The REE content within monazite [(Ce, La, Y, Th)PO_3] ranges from 50-70%. Monazite is a light rare-earth element (LREE)-bearing accessory phase common in felsic granitic rocks and strongly influences LREE concentrations in granites and the chemistry of melts and residues formed during partial melting (Watt, 1995; Rafiudin et al., 2014). Indonesia maintains monazite along with xenotime and zircon. They come from tin-processing tailing. Figure 5 shows location of tin-processing at Marbuk-Central Bangka owned by PT Koba Tin-Indonesia (Wahyudi et al., 2009). The company is one of Indonesian tin entrepreneurs that produces tin metal. Its tin concentrates obtained from hydraulic mines, sluice boxes and dredges provide 20-40% Sn and leave some gangue minerals containing monazite, xenotime, zircon, ilmenite, pyrite, and quartz. An XRF test on Indonesian monazite sample is shown in Table 3 (Rodliyah et al., 2015). It is shown that of the various detected element, Ce provides the biggest content and as usual the sample also contain radioactive element, namely thorium (Th) as many as 6.47%.

Figure 4. Bastnasite as one of REE-bearing minerals (http://www.mineral-forum.com)

Optical microscope analyses of Sungai Liat, Bangka - PT Timah concession (Figure 6) showed that the sand consisted of cassiterite, the tailing sand from xenotime, zircon and

Table 2. Physical characteristics of bastnasite mineral (http://webmineral.com/data/Bastnasite-(Ce)

Mineral facts	Physical nature
Color	pale white, tan, gray, brown, yellow and pink
Luster	pearly, vitreous, greasy to dull
Transparency	translucent to opaque
Crystal system	hexagonal
Crystal habits	small hexagonal rounded flakes, short prismatic rosettes and spheres, massive and granular
Cleavage	distinct in one direction(basal), poor in three directions (prismatic)
Fracture	uneven
Hardness	4 to 4.5
Specific gravity	4.7 to 5.0
Streak	white


(a) (b)

Figure 5. Sluice box for concentrating tin-bearing minerals at PT Koba Tin-Indonesia (a) and tailing sand from tin processing that contains REE-bearing minerals (b). The REE-bearing minerals are commonly monazite, xenotime and zircon (Wahyudi et al. 2009)

Table 3. Detected element within monazite, analyzed by XRF instrument (Rodliyah et al., 2015)

Element name	Element	Oxide
	content (%)	
La	11.34	19.10
Ce	18.27	30.67
Nd	8.64	14.33
Pr	0.54	0.91
Th	6.47	10.00
Others (Si, Zr,Sn, Y, Gd, Dy, U)	-	24.99

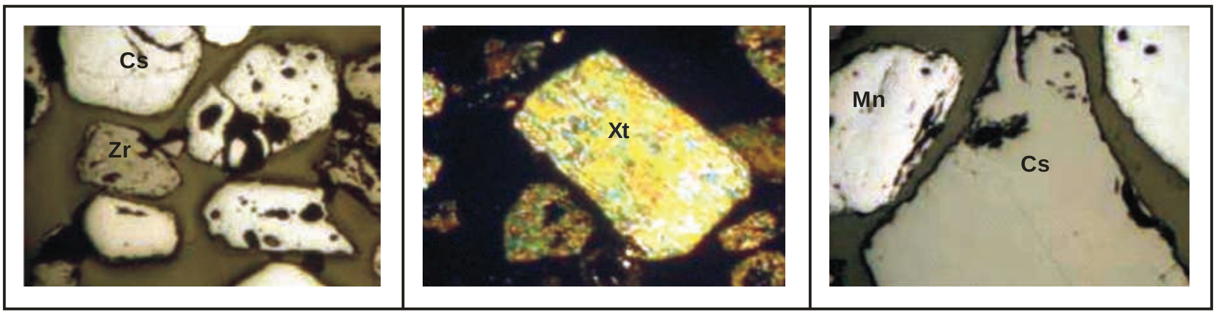


Figure 6. Mineral composition of tin-processing tailings from Sungai Liat, Bangka consists of cassiterite (Cs), zircon (Zr), xenotime (Xt) and monazite (Mn); (Wahyudi et al. 2009)

monazite Indonesian monazite performs high thorium content and radiates the α monazite. Indonesian monazite performs high thorium content and radiates the α ray with low radiation (Wahyudi et al. 2009; Suprapto, 2009). Scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) tests on lamprophyre dyke in Abu Rusheid area, Egypt by Ali (2012) showed that the chemistry of monazite-(Nd) and xenotime-(Y) were enriched by U and Th. The monazite-(Nd) associated with fluorapatite in the studied dyke was poor in Th (0.02 ≤Th≤0.81 t%), but usually rich in U (0.92 ≤U≤2.91 wt%), which indicates that monazite formed as a result of flourapatite metasomatism.

Similar to monazite, xenotime belongs to phosphate compound. The mineral that keeps YPO_4 formula contains 54-64% REEs including erbium, cerium dan thorium and found in heavy mineral sands, pegmatite and igneous rocks. Wahyudi et al. (2009), found at least six elements when SEM-EDS analysis using X-ray mapping method was conducted to Bangka xenotime (Figure 7). The elements included yttrium, iridium, thulium, cobalt, iron and silicon. However, another SEM-EDS method (spot analysis) also detected gadolinium, erbium and dysprosium.

Zircon is a mineral that belongs to nesosilicate group. Retaining zirconium silicate ($ZrSiO_4$) as its chemical name, the mineral shows tetragonal crystal system. Forming in silicate melts with large proportions of high field strength incompatible elements, zircon has a common empirical formula for the range of substitution, namely $(Zr_{1-y}, REE_y)(SiO_4)_{1-x}(OH)_{4x-y}$. The common REEs associated in zircon are thorium, yttrium

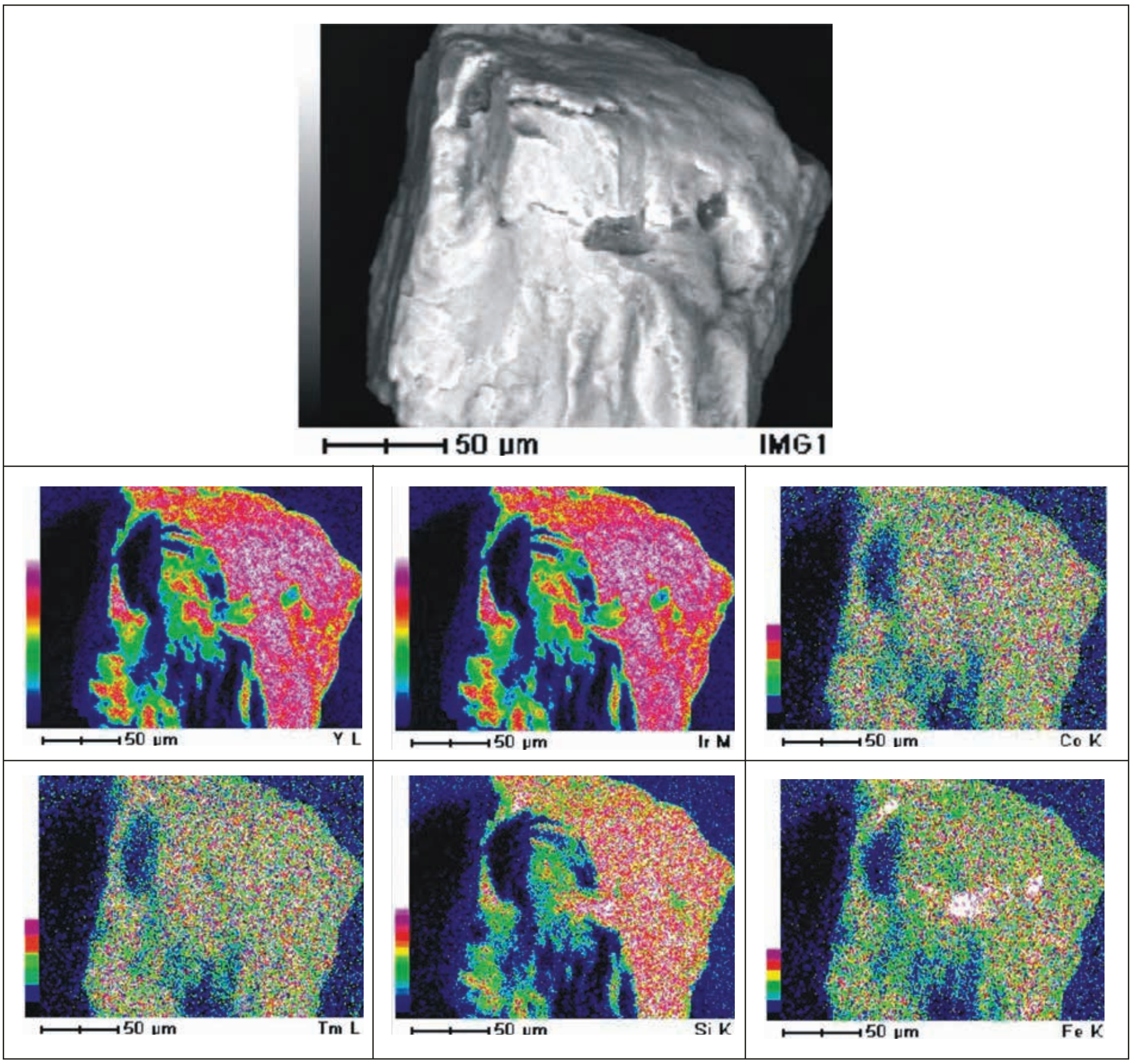


Figure 7. SEM-EDS analysis conducted to tin-processing tailing from PT Timah showing six detected elements; three of them belong to REEs (Wahyudi, et al., 2009)

and cerium. The mineral is mostly found within granite and felsic igneous rocks as a common accessory to trace mineral constituent. Hardness, durability and chemical inertness properties of this mineral results in the mineral, as a common constituent of most sands, retains endurance character in sedimentary deposit. Found rare in mafic rocks and very rare in ultramafic rocks except in sedimentary deposit. Found rare in mafic rocks and very rare in ultra-mafic rocks except in ultrapotassic intrusive rocks (kimberlites, carbonatites and lamprophyre), its existence is occasionally found as trace mineral that belongs to the unusual magma genesis of the rocks.

Economic concentrations of zircon normally occur within heavy mineral sands deposit, certain pegmatites and some rare volcanic rocks such as those hosted by Toongi trachyte of Dubbo at New South Wales, Australia. The Toongi trachyte is one of a number of alkaline bodies which form part of a relatively extensive alkaline volcanic complex in the Dubbo region, composed of both intrusive and extrusive trachytic rocks, which in turn are related to the major Eastern Australian alkaline igneous event. It intrudes into and overlies a flat lying sequence of interbedded sandstone and siltstone of the Triassic Napperby Formation. Australia leads the world in zircon mining, producing 37% of the world total and accounting for 40% of world EDR (economic demonstrated resources) for the mineral. Yttrium, the rare earth, is found within Toongi trachyte along with zirconium, niobium and zirconium.

Characteristics of Rare Earth Elements

The common properties of rare earths (both lanthanides and actinides) include: silver, silvery-white, or gray metals in color; high luster but tarnish readily in air; high electrical conductivity; difficult to separate or distinguish among them due to many common property; very small differences in solubility and complex formation between the REEs; in nature, mutually occurrences within minerals for example monazite is a mixed rare earth phosphate; found with non-metals. Of the 17 REEs, 15 elements belong to lanthanide series and the rest is additional elements that have similar chemical properties with the lanthanide series. The REEs commonly keep high reaction characters to water and oxygen and stable condition in their oxide form. Their melting point is relatively high (Suprapto, 2009). Consequently, the elements are used as high temperature conductor material. Based on ionic radius and electron structure, the REEs can be classified into:

- light REEs or cerium sub-group that includes lanthanum through europium;
- heavy REEs or Yttrium sub-group that consists of gadolinium through lutetium and yttrium.

Scandium is a soft, silvery-white transition element which occurs in rare minerals from Scandinavia. It develops a slightly yellowish or pinkish cast when exposed to air. Scandium tarnished in air and burn easily, once it has been ignited. It reacts with water to form hydrogen gas and will dissolve in many acids. Pure scandium is produced by heating scandium fluoride (ScF_3) with calcium metal. The metal is used in many popular consumer products such as television and fluorescent or energy-saving lamps. The primary use of scandium is to strengthen metal compound. Its availability in nature is rare due to it occurs in very small amounts. The only concentrated sources of scandium currently known are in rare minerals such as thortveitite, euxenite and gadolinite from Scandinavia and Madagascar (Lide, 2004; http://www.lenntech.com/periodic/elements/sc.htm#ixzz3I3nkNRgU). The use of scandium as an alloying element in aluminium has gained an increasing interest even though scandium is difficult to extract, which makes the metal very expensive. Its effect in aluminium alloys was studied by Röyset (2007) and showed some performances that included grain refinement during casting and welding, precipitation hardening and grain structure control.

Another non-lanthanide series REE, yttrium, is a highly crystalline iron-gray, rare-earth metal. Yttrium never occurs in nature as a free element but is available in almost all rare earth minerals and uranium ores. Xenotime is the common yttrium mineral performing 50% Y of the content. Around 2.5% of the element is also found in monazite and smaller quantities are presented in other minerals such as bastnasite, fergusonite and smarskite (Bau and Dulski, 1996). The formation of a stable oxide film on its surface makes yttrium is fairly stable in air; however, it oxidizes readily when heated. Yttrium decomposes when reacted with water and releases hydrogen. It also reacts with mineral acids. The output of yttrium is about 600 tons per year, measured as yttrium oxide, and world reserves are estimated to be around

9 million tons. Its usage is for superconductors, powerful pulsed lasers, cancer treatment drugs, rheumatoid arthritis medicines, and surgical supplies as well as color televisions and camera lenses.

Although lanthanum belongs to the REEs, it is not rare at all. The metal is available in relatively large quantities (32 ppm in Earth's crust). The term "rare" relates to the fact that its mining process is difficult, time consuming and expensive (http://www.reehandbook.com/lanthanum.html). Monazite and bastnasite are two common minerals containing lanthanum. Yet, there is more lanthanum in bastnasite than in monazite. Possessing soft, malleable, ductile, silver-white metal performance; lanthanum is the most reactive REEs. It rapidly oxidizes in the air. The metal also reacts with water to form the hydroxide. Lanthanum is easily ignited and its salts are often very insoluble. Its usage can be can be found in houses in equipment such as color televisions, fluorescent lamps, energy-saving lamps and glasses. Special optical glasses, made from lanthanum oxide (La_2O_2), are used for infrared adsorbing glass, camera and telescope lenses. Improving steel malleability and resistance can be conducted by adding small amounts of lanthanum. Lanthanum is also applied for core material within carbon arc electrodes while its salts are included in zeolite catalysts for refining petroleum (Gupta and Khrisnamurti, 2005).

The most abundance REE refers to cerium that makes up about 0.0046% of the earth's crust by weight. The metal is named after the Roman goddess of agriculture, Ceres. It is found in a number of minerals such as monazite [(Ce,La,Th,Nd,Y)PO4], bastnasite [(Ce,La,Y)CO_3F], hydroxylbastnasite [(Ce,La,Nd) CO_3(OH,F], rhabdophane [(Ce,La,Nd)PO_4•H_2O], zircon ($ZrSiO_4$), synchysite [Ca(Ce,La,Nd,Y) $(CO_3)_2$F] and allanite [$(Ca,Ce,La,Y)_2(Al,Fe)_3(SiO_4)_3(OH)$]. Of the various Ce-bearing minerals, monazite and bastnasite are presently the two most important cerium sources. This REE has malleable, soft, ductile and iron-grey characters and if compared to lead, it is slightly harder. Its reactivity is strong that performs tarnish when exposed to the air and rapidly oxidized in hot water but slowly in cold water. The metal can dissolve in acids and is burnt when heated or scratched by a knife (Lee et al., 2013). The use of cerium includes a core for carbon electrodes of arc lamps, incandescent mantles for gas lighting, aluminum and iron alloys, precipitation hardening agent in stainless steel and permanent magnets. Its oxide is used as a catalyst in catalytic converters for cleaning up exhaust vehicles and catalyzes NO_x reduction to nitrogen gas. Cerium is also used to replace cadmium in red pigments for containers, toys, household wares and crates due to the metal is environmental friendly compared to cadmium.

Rodliyah et al. (2015) studied REE-extraction from Bangka monazite. The study was to figure out the REE performances when extracted from such a mineral. It was shown that the highest REE-extraction (28.41%) was achieved at the 1:2-sulfuric acid to water (v/v) ratio, 220°C-leaching temperature, 150-minute leaching time and 5%-hydrogen peroxide as an oxidizer. Precipitating the pregnant solution and then calcining it at 900°C for 3 hours retained the REE-oxides that contained Ce (29.10%), Gd (1.54%), Y (1.53%), Nd (11.53%), La (14.02%), Dy (0.489%) and Sm (1.85%). In terms of increasing the grade of REE-oxide from 62.48 to more than 90%, Rodliyah et al. (2015) suggested using sulfuric acid in an autoclave pressure leaching.

Monazite and bastnasite are the major commercial ores for praseodymium (Pr). The metal retains soft, silvery, malleable and ductile characters. When exposed to the air, it forms green material that will go through to another oxidation form. Yet the material is more resistant in air than the other rare earth metals such as europium, lanthanum, cerium or neodymium. Praseodymium tarnishes slowly in air and readily burns at 150°C to form Pr (III, IV)-oxide. The metal is also quite electropositive and reacts slowly in cold water but quite fast in hot water to form Pr-hydroxide (Vovk et al., 2014). Its applications include coloring glasses and gemstones, rare earth magnets, high-strength metals in aircraft and flint for starting fires. As soft and silvery metal, neodymium along with praseodymium is used to create some of the strongest permanent magnets in most modern vehicles and aircraft as well as headphones, microphones and computer discs. It is found in nature as the free element but in minerals that include all lanthanide minerals such as monazite and bastnasite. Neodymium is very reactive and tarnishes quickly in the air. As a result, it must be stored away from contact with air as its coated formed does not protect the metal from further oxidation.

Promethium with symbol Pm has atomic number 61 (Lide, 2004). The element is very radioactive and rare and occurs within earth crust in tiny amounts of some uranium ores. Physical properties of this element are intermediate between neodymium and samarium such as its first three ionization degrees, melting point and hydration energy. Such properties are greater than those of neodymium but lower than those of samarium. Promethium is easy to decay into other elements. The element is currently produced artificially from the byproducts of uranium fission or bombarding 146Nd with neutron to be 147Nd. The 147Nd then decays into 147Pm through beta decay with a half-life of 11 days. Most promethium is used only for scientific research purposes. Some applications include beta radiation source in luminous paint, watches, pacemakers, nuclear batteries for guided missiles and a light source for signals.

Performing yellowish metal with a melting point of 1,072°C, samarium is a fairly reactive metal and can be combined with many other substances under relatively mild conditions (Danford, 2014). It is found in monazite and bastnasite as well as in samarskite, cerite, orthite, ytterbite and fluorspar. Samarium releases hydrogen gas when combined with water and causes fire with oxygen. As the hardest and most brittle REE, the metal is applied for making very powerful magnets in many transportation, defense and commercial technologies; nuclear reactors as well as medicinal treatment for cancer diseases (Gupta et al., 2014).

The most reactive element of the lanthanide group is europium (Eu). Its atomic number is 63. The element performs ductile character with hardness similar to lead that tarnishes quickly and reacts quickly with water to give off hydrogen. It also reacts strongly with oxygen in the air, catching fire spontaneously (Tezuka et al., 2013). As neutron absorber, europium is used in nuclear reactors control rods. Its compound with phosphor help makes a bright red color in television tube and as an activator for yttrium-based phosphors (Gupta and Khrisnamurti, 2005). As a special phosphor compound, Eu is used to prevent counterfeiting by marking the Euro notes.

Possessing symbol Gd and atomic number 64, gadolinium is a silvery-white, ductile and malleable REE. It is actually not rare but difficult to separate. As one of the most abundant REEs, is never found as free element in nature, but it is contained in many rare minerals. The metal is associated with monazite, bastnasite, samarskite, gadolinite and xenotime. It performs hexagonal crystal structure, close-packed α- form at room temperature but it transform to β- form when heated to temperatures above 1235°C. Structure of the β- form is body-centered cubic. Gadolinium is not especially reactive. It dissolves in acids and reacts slowly with cold water as well as responds to oxygen at high temperatures. At room temperature, the metal belongs to strongly magnetic character and turns into superconductive below 1083o K. It does not tarnish in dry air but develops an oxide film in moist air (Gupta and Khrisnamurti, 2005). Its applications include control rods within nuclear reactors and nuclear power plants, microwave, color TV tubes, super magnet and electric component as well as compact disk and computer memory. For health treatment purposes, the metal can target tumors in neuron therapy and can enhance magnetic resonance imaging. X-rays and bone density tests can also use gadolinium, making this rare earth element a major contributor to modern health care solutions.

Performing symbol Tb and atomic number 65, terbium keeps silvery-white as well as soft that can be cut by a knife. The metal is never found in nature as a free element and normally included in cerite, gadolinite, monazite, xenotime, euxenite and other minerals (Gupta and Khrisnamurti, 2005). Due to its rare and expensive characters, terbium has few commercial uses such as in lasers, semiconductor devices and phosphorous in color television tubes. In solid-state devices, the metal is used as stabilizer of fuel cells which operate at high temperature and as alloy form, terbium has the highest magnetostriction of any such substance which means that due to its magnetization property, the metal changes its shape more than any other alloy. This property makes terbium a vital component of Terfenol-D, which has many important uses in defense and commercial technologies (Paradis et al., 2007).

Dysprosium, a moderately toxic element, retains atomic number 66 and has soft, silver metal and the highest magnetic strengths properties (Gupta and Khrisnamurti, 2005). The metal is used as a magnet component due to its tenacity at high temperature. As a result, such a magnet retains more efficient property. Good performance in absorbing neutrons results in such a metal is used as a component of dysprosium-oxide-nickel cement for control rod making in nuclear reactors (Hsiang and Lai, 2005). As one of more abundant lanthanide elements, dysprosium is never encountered as free element. It is found in many minerals such as monazite and bastnasite.

Holmium is a relatively soft and malleable element that is fairly corrosion-resistant and stable in dry air at standard temperature and pressure. The metal tarnishes slowly in air and burns readily to form holmium (III) oxide. Holmium is not naturally found as a free element (Gupta and Khrisnamurti, 2005). It occurs combined with other elements. In this case, holmium-bearing minerals include gadolinite, monazite and other rare-earth minerals. China, United States, Brazil, India, Sri Lanka and Australia serve as holmium-production countries with total estimated reserves as 400,000 tons. As the metal that has the highest magnetic strength, the metal is used to create the strongest artificially generated magnetic fields when placed within a magnetic flux concentrator (Tarnavich et al., 2014). Its character to absorb nuclear fission-bred neutrons makes such a metal is also used as a burnable poison to regulate nuclear reactors.

Erbium with atomic number 68 is another rare earth element that commonly serves for nuclear applications. Natural erbium is always found in chemical combination with other elements on Earth. It is mostly found in monazite and bastnasite (Gupta and Khrisnamurti, 2005). The metal retains silvery-white and metallic luster characters. Similar to other rare earth metals, its properties depend to a certain extent of impurities present. As a natural metal, erbium is fairly stable in air. Its oxidation rate is slower than that of the other rare-earth metal. Erbium addition to the alloys with metals such vanadium results in lowering the alloy hardness. The alloys are then more workable. Another erbium property is its capability to absorb the infrared light hence the metal can be used as a mixture of glass for special safety spectacles in welder and glass-blower industries (Corn, 2010). It is also applied for a photographic filter as well as doping optical fibers at regular intervals to amplify signals. Erbium is sometimes used as a glass and porcelain enamel glaze colorant due its pink color. Medical purposes benefit erbium characters to create lasers.

A silvery-gray metal with atomic number 69, thulium is the least abundant rare earths (Gupta and Khrisnamurti, 2005). It is found in gadolinite, monazite, xenotime and xenotime minerals. Principally, the metal is extracted from thulium-containing monazite through ion exchange process. The metal can be cut with a knife as it has a Moh's hardness of 2 to 3; it is malleable and ductile. Its magneticity belongs to ferromagnetic below 32 K, antiferromagnetic between 32 and 56 K, and paramagnetic above 56 K. Liquid thulium is very volatile (Misiak et al., 2013). Thulium is used for an active laser medium material with high efficiency, X-ray source in a nuclear reactor, high-temperature superconductors and ferrites - ceramic magnetic materials that are used in microwave equipment. The metal tarnishes slowly in air and burns readily at 150 °C to form thulium (III) oxide (Harbison et al., 1998).

Ytterbium, atomic number 70, is found in monazite. Other minerals that contain ytterbium are euxenite and xenotime. The metal is a bright, soft, silvery-white metal that is both ductile and malleable and is considered to be moderately toxic (Neikov et al., 2009; Gupta and Khrisnamurty, 2005). It tarnishes quickly in air and reacts slowly with water but dissolves rapidly in mineral acids. Ytterbium has few uses. The metal is used in alloys and is added to stainless steel to improve grain refinement and strength. Ytterbium fiber laser amplifiers are used in marking and engraving. Its compound is also used as catalysts in the organic chemical industry.

Lutetium is the last of the rare earth elements and also one of the least abundant lanthanides; however, it is still more abundant on earth than silver or gold. Its atomic number is 71 and retains several uses such as radiometric dating, petroleum refining and positron emission tomography (Settouti et al., 2015; Gupta and Khrisnamurty, 2005). This silvery white metal is found in monazite mineral with China, United States, Brazil, India, Sri Lanka and Australia as producer countries for this mineral. Lutetium resists to corrosion in dry but not moist air. It is the densest and hardest of the lanthanides. When present in compounds, lutetium exists usually in the trivalent state (Lu^{3+}). Most of its salts are colorless.

Characteristics of REE-oxides

Cerium oxide or also known as cerium (IV) oxide, ceric oxide, ceria or cerium dioxide is one of REE-oxide families that has fluorite structure

(Badwal et al., 2013). The CeO_2 presents pale yellow-white powder and at high temperatures, it can be reduced to a non-stoichiometric, anion deficient form that retains the fluorite lattice. The non stoichiometric form has a blue to black color, and exhibits both ionic and electronic conduction with ionic being the most significant at temperatures > 500 °C). Cerium(IV)oxide is used for several applications such as ceramics, sensitizing photosensitive glass, catalyst and catalyst support, polishing glass and rocks and an alternative to jeweler's rouge in lapidary. A good cerium oxide for polishing the glass should have a size between 0.25 -0.30 microns. The oxide is also applied in the walls of self-cleaning ovens as a hydrocarbon catalyst during the high temperature cleaning process (Gray, 2010). Its transparency characters can absorb ultraviolet radiation. As a result, the material is prospective to replace zinc- and titanium dioxide in sunscreens due to it has lower photo-catalytic activity (Zholobak et al., 2011). In infrared filters, the oxide is used as oxidizing species in catalytic converters and thorium oxide replacement in incandescent mantles.

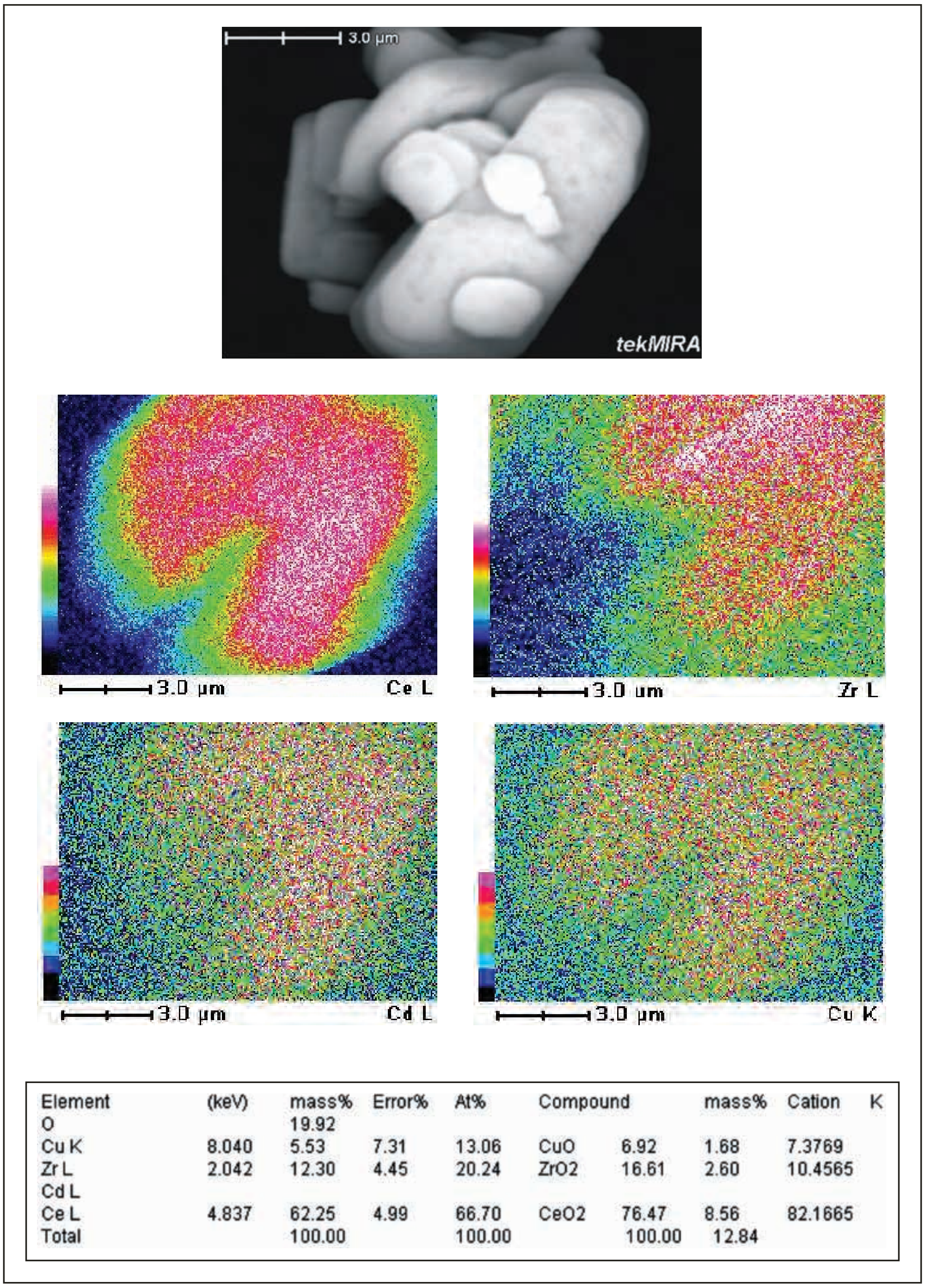
One of the charcteristics REE-oxide was examined by Lee et al. (2013. The researchers enhanced natural antioxidant properties of cerium oxide nanocrystals to make it useful for medical applications. The result showed that serium oxide nanocrystals have the ability to absorb and release oxygen ions — a chemical reaction known as reduction oxidation or known as redox. When the particles were injected into the bloodstream as organ protection from oxidation, they worked immediately to absorb reactive oxygen species (ROS) free radicals and continue to work over time as the particles revert to their initial state.

Experiments on REE-oxide making from monazite had been conducted (Rodliyah et al., 2015). Materials used for the experiments came from PT Mutiara Prima Sejahtera (MPS) and the employed method was high pressure acid leaching within autoclave at 200 - 220 °C. Such experiments that yielded total REE-oxide from 26.55 to 62.97% employed experiment condition as follows: ratio sulfuric acid to water as the main reagent was 1:2 (v/v), 150-minute leaching time and 5-% hydrogen peroxide as an oxidizer. Table 4 illustrates the available REEs within REE-OH and REE-oxide derived from the experiment. Of the 12 elements, cerium performs the highest percentage within the oxide. It is almost similar to uranium quantity while the impurities comprise silicon, aluminum, iron, copper, etc.

Table 4. A series detected REEs within REE-oxide from extracted Bangka monazite (Rodliyah et al., 2015)

Element name	Symbol	Quantity of	
		REE within REE-OH (%)	REE within REE-O (%)
Cerium	Ce	12.22	29.10
Gadolinium	Gd	0.57	1.54
Yttrium	Y	0.559	1.53
Neodymium	Nd	4.93	11.53
Terbium	Tb	0.0558	0.124
Lanthanum	La	6.04	14.02
Dysprosium	Dy	0.201	0.489
Europium	Eu	0.0327	0.095
Samarium	Sm	0.771	1.85
Praseodymium	Pr	1.17	2.69
Thorium	Th	0.0762	0.165
Uranium	U	0.04	29.10
Total REEs		26.55	62.97
Total impurities		73.45	37.03

SEM-EDS analyses on one of REE-oxide products also help determine the element content within monazite samples (Wahyudi, et al., 2009). The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays is a characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted; this allows the elemental composition of the specimen to be measured. The SEM-EDS analyses of the REE-oxide products mapped four detected elements within samples (Figure 8). Those are cerium, zircon, cadmium and copper. The oxide contains material that presents flake characters. Cerium dominates the specimen as



Element	(keV)	mass%	Error%	At%	Compound		mass%	Cation	K
O		19.92							
Cu K	8.040	5.53	7.31	13.06	CuO	6.92	1.68	7.3769	
Zr L	2.042	12.30	4.45	20.24	ZrO2	16.61	2.60	10.4565	
Cd L									
Ce L	4.837	62.25	4.99	66.70	CeO2	76.47	8.56	82.1665	
Total		100.00		100.00		100.00	12.84		

Figure 8. SEM-EDS analysis conducted to REE- showing four detected elements, namely Ce, Zr, Cd and Cu

shown by intense mapping noted by red color. The element performs the contents of 66.70%. The next dominant element belongs to zircon as many as 20.24%. Its mapping performance is also powerful while copper and cadmium may serve as impurities. The quantity of cadmium was not detected. The metal is supposed to be in ppb unit. The detected elements within REE-oxide can also be known from EDS spectra (Figure 9). Its peaks are labeled with the corresponding element, namely Ce, Zr, Cu and Cd.

It is clear that as the dominant elements, both Ce and Zr retain high spectra compared to Cu and Cd. Moreover, the Ce and Zr are also characterized by lower spectra that suggest that the two elements are dominant. The fact that raw material for REE-oxide comes from monazite suggests that the presence of copper and cadmium may be due to the remnants of precursor monazite impurity. Both elements perform some spectra but their peaks are low. It implies that the elements occur as trace ones.

CONCLUSIONS

In nature, most of REEs in REE-bearing minerals performs a complex compound. It needs to be separated from its complex compound when beneficiated. Bastnasite, monazite, xenotime and zircon are the most common minerals. Of the 17 REEs, cerium is one of the abundant ones. The metal is a malleable and slightly harder than lead.

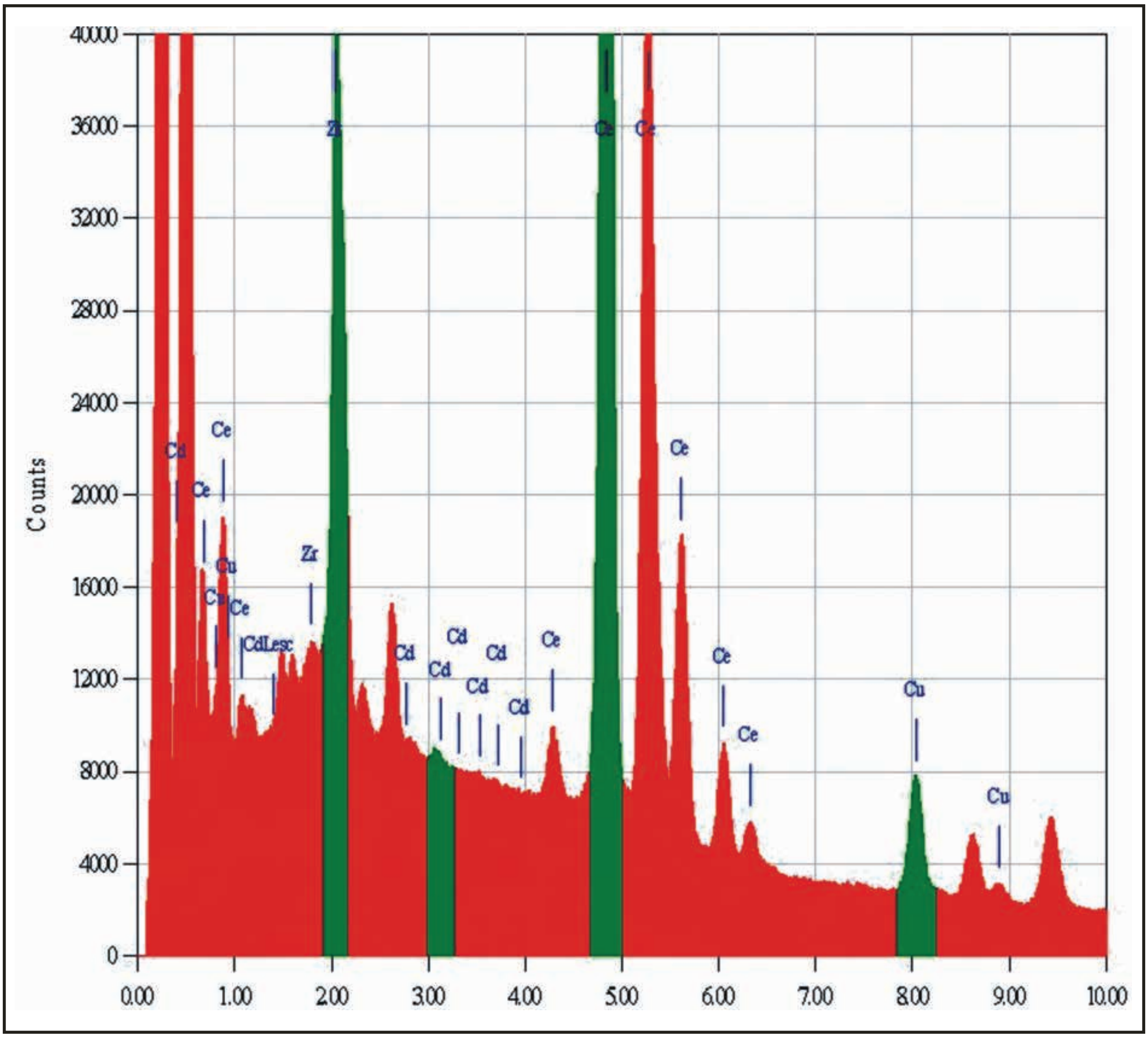


Figure 9. EDS spectra of the REE- showing high and low peaks of four detected elements

Of the 17 REEs, 15 elements belong to lanthanide series and the rest is additional elements that have similar chemical properties with the lanthanide series. The common properties of rare earths (both lanthanides and actinides) include: silver, silvery-white, or gray metals in color; high luster but tarnish readily in air. The REEs also retain high electrical conductivity and difficult to separate or distinguish among them due to many common property. Due to its high melting point character, the metals are commonly used for high temperature conductor material and are also mostly applied in nuclear reactors.

REE- bearing minerals in Indonesia are characterized by monazite, xenotime and zircon. Chemical formula of zircon is $ZrSiO_4$. Referring to such a formula, it seems that no REE within the mineral but zircon has empirical formula of $(Zr_{1-y'}REEy)SiO_4)_{1-x}(OH)_{4x-y''''}$. Indonesian REE-bearing minerals come mostly from Bangka Island as by-products of tin ore processing. The experiment results from extracting Bangka monazite suggest that cerium is the main component within such a mineral along with gadolinium, yttrium, neodymium, terbium, lanthanum, dysprosium, europium, samarium, praseodymium, thorium and uranium. Yet, no bastnasite was found in Indonesia.

Based on their characteristics, the REEs are mostly beneficiated for advanced materials such as active laser medium material with high efficiency, X-ray source in a nuclear reactor, high-temperature superconductors and ferrites - ceramic magnetic materials that are used in microwave equipment. As a research center, experiments on REEs at the Research Development Centre for Mineral and Coal Technology or known as tekMIRA related to REE-oxide making from monazite. Calcination process of REE-OH into REE-oxide increased the REEs from 26.55 to 62.97%. Cerium was the highest yielded element that was similar to uranium. The impurities included silicon, aluminum, iron and copper.

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