Compositional Variation and Performance Analysis of Wolframites at Dawei District

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Abstract

Wolframite samples were collected from near and around the mining area (Kanbauk, Pharchaung and Harminegyi) in Dawei District. Trace element compositions of ores were analyzed by Energy Dispersive X-rays Fluorescence (EDXRF) spectroscopy and the structural properties of these minerals were determined by X-rays Diffraction (XRD) and Scanning electron microscope (SEM). The magnetic properties of these samples were identified with Permagraph L apparatus. The DTA analysis highlights the endothermal and exothermal effects and temperature ranges, which are correlated with the removal of physically present in the wolframite. It was observed that the major elements of wolframites are uniform over distances in Harminegyi mine area than other areas.

Keywords: Tungsten, Wolframite, X-ray diffraction, SEM, Permagraph L, DTA, endothermal and exothermal

Introduction

There are some parallels between the schemes used to classify ore minerals and those used to classify ore deposits. Most tin and tungsten deposits are spatially associated with granitic rocks. Characterization of a mineral ore is a very important step to perform before any processing takes place whereby quantity, grade or quality, densities, shape, and physical characteristics are determined to allow for appropriate application of technical and economic parameters to support production planning and evaluation of the economic viability of deposits.

Scheelite and wolframite are the main ore minerals of tungsten deposits, which form due to either magmatic-hydrothermal processes associated with felsic magmas (i.e. granite, pegmatite) or metamorphic processes (i.e. orogenic veins), with the former being by far the dominant in past and current production globally. Tungsten, more specifically scheelite, is also known to occur, albeit rarely, in stratiform/stratabound and commonly tourmaline-rich horizons associated with submarine basic volcanic rocks and clastic and chemical (i.e. carbonate) rocks.

Mineral, Wolframite, is a principal ore of tungsten. It is an iron and manganese tungstate mineral. It has a hardness of 5 to 5.5 mhos, specific gravity of 7.1 to 7.5, is dark gray, reddish brown, brownish black, or iron black in color. Wolframite is commonly found in granite and pegmatite dikes, and is often associated with cassiterite; it also occurs in sulfide veins and placer deposits. Because heat causes tungsten to expand at about the same rate as glass, the metal is widely used to make glass-to-metal seals. Tungsten or its alloys are used for filaments for electric lamps, electron and television tubes, electrical contact points for automobile distributors, heating elements for electrical furnaces, and space, missile, and high-temperature applications. Other important tungsten compounds are calcium and magnesium tungstates, which are used in fluorescent lighting, and tungsten disulfide, which is used as a high-temperature lubricant at temperatures up to 500 deg C. It has been suggested that the name ferberite be limited to mixtures containing not more than 20 per cent of the hubnerite molecule and the name hubnerite to those containing not more than 20 per cent of the ferberite

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molecule. This would leave the name wolframite for mixtures containing more than 20 per cent of both $FeWO_4$ and $MnWO_4$.

When a material is heated its structural and chemical composition can undergo changes such as fusion, melting, crystallization, oxidation, decomposition, transition, expansion and sintering. Using Thermal Analysis such changes can be monitored in every atmosphere of interest. The obtained information is very useful in both quality control and problem solving.Thermal Analysis is the term applied to a group of methods and techniques in which chemical or physical properties of a substance, a mixture of substances or a reaction mixture are measured as function of temperature or time, while the substances are subjected to a controlled temperature programme.

The primary objective in this research was to provide comprehensive data on the characterization and chemical composition. These included mineral phase analysis and elemental composition with a view of finding out and understanding the best possible technique by which the ore could possibly be processed.

Figure (1). The photograph of raw minerals from Harmyingyi, Kanbauk and Pharchaung mine.

Results and discussion

X – ray Powder Diffraction (XRD)

Analysis of X-ray diffraction was performed on the wolframite raw material. The samples were placed in a lucite holder on the goinometer of the XRD-6100 powder diffractometer. The diffraction beam monochromator operated at 20 KVA with step size of 0.02° for 120 minutes to create x- ray patterns with enough intensity to produce lines to identify minerals at the 2θ angles (10° – 80°). Scanning rate was 0.75 degree per minute. Minerals were identified using the ICDD software of the Joint Committee on Powder Diffraction Standard (JCPDS).

It was found that the sample from Harmyingyi mine shown in figure (2) was in tetragonal structure having p42/m n m space group. The average lattice constants are calculated to be a = 4.737Å and c = 3.185 Å from the refinement of the XRD data. The prominent peaks in the plot are indexed to various (hkl) planes of Hubnerite (Fe, $MnWO_4$). The secondary peaks were observed in the form of Ferberite (Fe WO_4) and Dolomite (Ca, MgC_2O_6). The sample calcined at 500° C and 700º C are having stronger peak of (211) plane compared with other samples, but there have more other planes and impurities.

The XRD pattern of wolframite the mineralogical component of the crushed ore bearing cassiterite from Kanbauk mine was shown in figure (3). The main minerals found in this sample were cassiterite with JCPDS card numbers 41-14445, rutile with JCPDS card number 21-1276, manganocolumbite with JCPDS card number 45-1360, zircon (06-0266), quartz in the form of rodiocolite (50-1635), monazite, siderophyllite (JCPDS 25-1355). Each JCPDS card number has the phase information from the XRD patterns.

The structural analysis of the wolframite sample from Pharchaung by XRD was shown in figure (4). $FeMnWO_4$ compounds with orthorhombic structure were observed in this study. When these samples were heated between 400° C and 500° C, the structure phase was transformed to monoclinic. As-obtained $FeMnWO_4$ (70%) at room temperature was finally investigated by X-ray diffraction. The crystal structure was observed orthorhombic. The average lattice parameters were observed a = 4.7535 Å b = 5.6818 Å and c = 5.0120 Å.

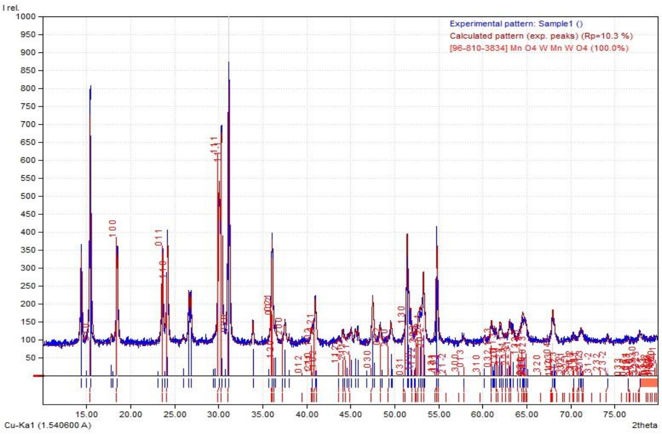

Figure (2). The XRD pattern of raw mineral from Harmyingyi mine.

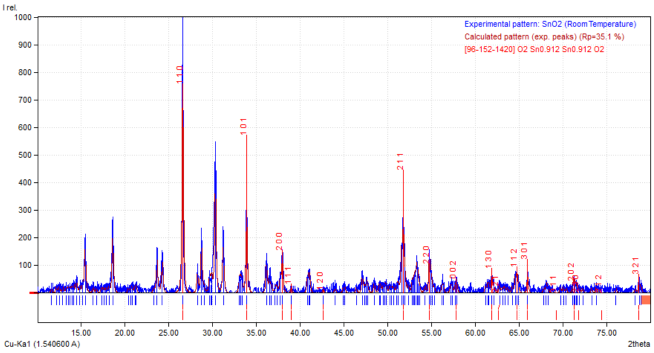

Figure (3). The XRD pattern of raw mineral from Kabauk mine.

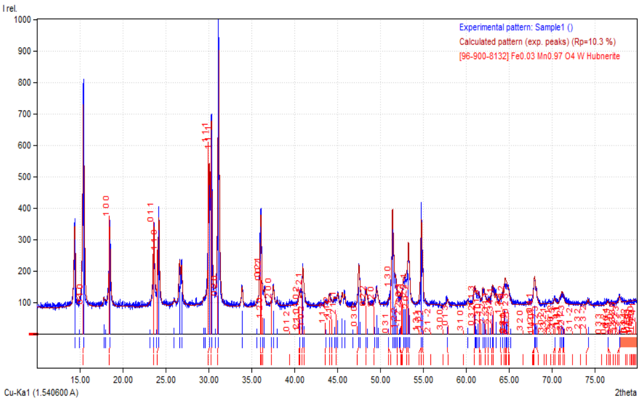

Figure (4). The XRD pattern of raw mineral from Pharchaung mine.

Scanning Electron Microscopy (SEM)

The morphology of the wolframite ore was analyzed in a JEOL JSM-6400 scanning electron microscope at accelerating voltage of 20KVA, real time of 21-36 and live time of 60 seconds. SEM investigations on wolframite raw samples at room temperature were shown in figure (5). It was investigated that they are not adequate to confirm or otherwise the presence of deleterious phase. The gray patches represent the tungsten ore, which shows that it is opaque, non-fluorescent and sub metallic. It also shows that the darker patches between the tungsten ore represent iron. There were two different types of morphological feathers along with voids are visible. The unreacted $MnWO_4$ grains which exhibit flowery feathers depict breaking up morphology, evenly distributed on the whole pellet surface. The increase in the furnace temperature enhances the rate of reaction and the images were formed faceted particles and agglomerated rods.

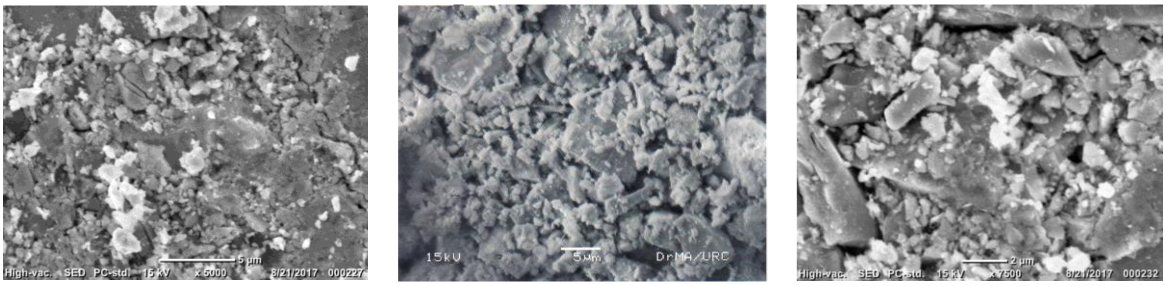

Figure (5). The SEM image of raw mineral from Harmyingyi, Kanbauk and Pharchaung mine.

Energy Dispersive X-ray Fluorescence Analysis (EDXRF)

The EDXRF result of the raw mineral from Harmyingyi mine was shown in table 1. From these results, the main concentration was observed 64.313 % as tungsten (W) and Manganese (Mn), tin (Sn), iron (Fe) were as the major concentrations. The other S, Bi, Pb, Se, Cu, Ca, Nb and Mo were found as the minor elements. Their concentrations were being slightly changed in the range of calcinations temperature 150°C and 300°C. For the calcinations temperature up to 700°C, the percentage of tungsten (W) was increased and minor concentrations were decreased.

From the elemental analysis of raw mineral from Kanbauk mine samples, Tin (Sn), Tungsten (W), Iron (Fe), Manganese (Mn) were observed as major elements. When increasing of the treatment of annealing temperature, the concentration of Tin (Sn) element was decreased and the concentration of Tungsten (W) and Iron (Fe) were increased. The elemental concentrations of these samples with heat treatment were shown in Table 2. The other Mg, Al, Si, P, S, Pb, Bi, Cu, Y, Ta and Zn were found as the minor elements.

The element concentrations of raw mineral sample from Pharchaung mine was shown in table 3 and there have four major elements Tin (Sn), Tungsten (W), Iron (Fe), Manganese (Mn) was observed. From EDXRF results, the largest amount of the tungsten (W) element was found in mineral from Harmyingyi mine.

TGA-DTA Analysis of wolframite raw samples

Thermal properties are related to transmission of heat and heat capacity. The DTA analysis highlights the endothermal and exothermal effects and temperature ranges, which are correlated with the removal of physically present in the wolframite. Thermal analysis by TG-DTA as shown in Figure (6), the weight loss was observed 4.599% from TGA curve and the oxidation process occurred from the exothermic peak at 464.56° C from DTA result .

Table (1). The elemental concentrations of raw mineral from harmyingyi mine.

Elements	Concentration (%)				
	room temperature	Calcinations for 1 hour			
		150°C	300°C	500°C	700°C
Tungsten (W)	64.313	64.674	65.001	68.112	72.021
Manganese (Mn)	11.387	11.552	11.984	10.486	9.662
Tin (Sn)	9.217	8.350	8.205	7.221	5.534
Iron (Fe)	7.514	7.226	6.711	6.414	5.013

Table (2). The elemental concentration of raw mineral from Kanbauk mine.

Elements	Concentration (%)				
	room temperature	Calcinations for 1 hour			
		150°C	300°C	500°C	700°C
Tungsten (W)	26.949	26.390	26.730	26.897	28.353
Manganese (Mn)	7.053	7.102	7.189	7.298	7.530
Tin (Sn)	34.251	44.331	31.878	26.737	25.965
Iron (Fe)	30.210	31.644	32.290	36.015	36.082

Table (3). The elemental concentration of raw mineral from Pharchaung mine.

Elements	Concentration (%)				
	room temperature	Calcinations for 1 hour			
		150°C	300°C	500°C	700°C
Tungsten (W)	1.36	2.05	2.35	2.98	3.12
Manganese (Mn)	1.91	1.98	1.99	2.00	2.10
Tin (Sn)	87.7	89.12	81.52	67.23	41.58
Iron (Fe)	0.759	0.82	0.88	0.91	0.94

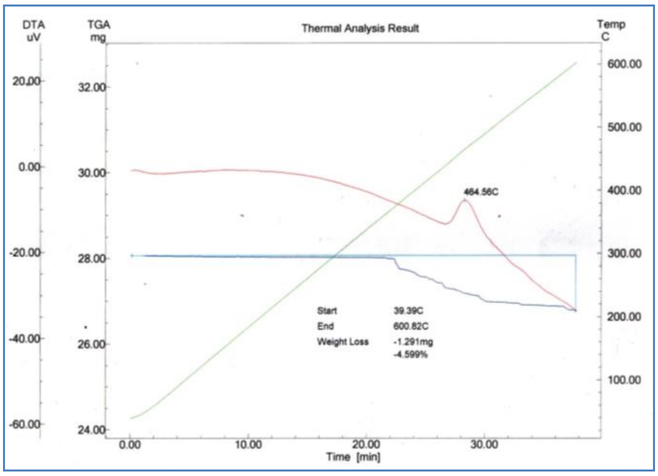

Figure (6). The TGA-DTA curve of wolframite raw mineral.

Dielectric behaviour and ac conductivity of wolframite raw samples

The dielectric behaviour and ac conductivity σ_{ac} of these raw samples were calculated from the values of capacitance and resistance. These data were collected by Instek GW 821 LCR meter. According to the results, the dielectric constant was decreased with increasing frequency. Electrical conductivity σ_{ac} gives rise to energy dissipation in the material due to eddy currents that produce an out-of-phase secondary field. This field adds to the primary field, thus distorting its shape. As a result, the field magnitude decays fast through the material. Electrical conduction through the ground takes three different forms: electronic (ohmic), electrolytic (ionic), and dielectric (due to polarization). Dry rocks exhibit very low conductivity, but porous rocks can absorb large quantities of mineralized water. Igneous rock tends to have the lowest conductivity, whereas sedimentary rocks have the highest, but conductivity varies with the age of the rock, location and local conditions. However, the conductivity of most underground materials is sufficiently low, such that eddy currents can be ignored at very low frequencies. By contrast, high frequency radio waves experience extreme attenuation through the conductive ground, as well as distortion due to reflections. The dielectric effect and ac conductivity of these raw samples was shown in figure (7) and (8).

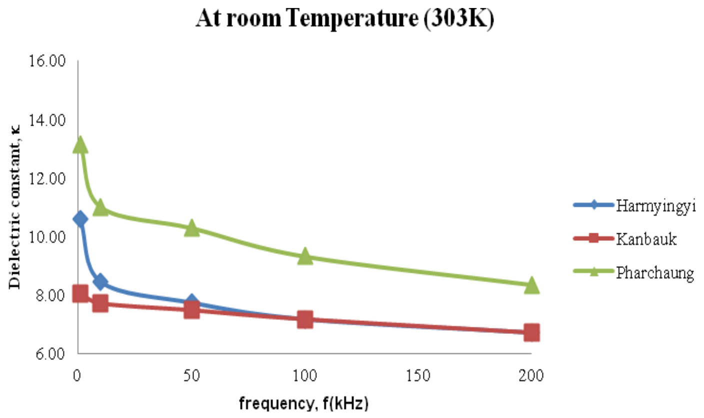

Figure (7). The capacitive effects of wolframite raw minerals

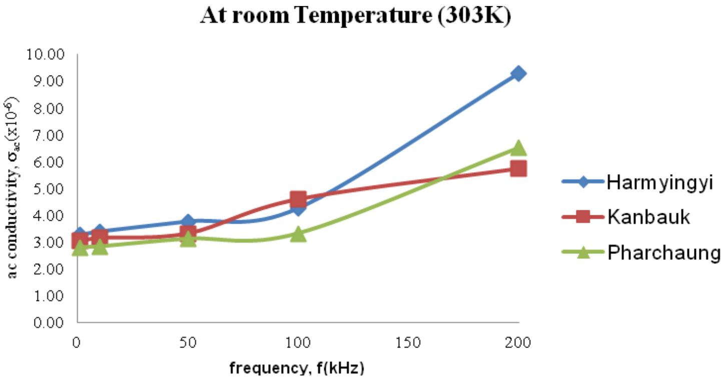

Figure (8). The frequency dependence ac conductivity of raw minerals.

Magnetic Properties (Permagraph L Apparatus)

The effect of different underground materials on low frequency magnetic fields was analysised and the process of magnetization consists of the movement of domain walls so that favorably oriented domains grow fast and the unfavorably oriented ones shrink. If the resistance to the movement of the domain walls is small, the coercive force is small and it is easy to demagnetize the material. Such materials are called soft materials. If the resistance to the movement of the domain walls is large, the coercive force is large and the material is called a hard material. The magnetization and demagnetization properties of wolframite mineral were shown in figure (9). The remanent value and maximum energy product of these samples were increased with increasing temperature. Table (4) shows the value of magnetic parameter of wolframite samples at room temperature. The magnitude and phase of magnetic fields is affected by two key material properties: magnetic permeability, μ and electrical conductivity, σ. These may undermine the validity of the dipole model underground. The magnetic permeability μ quantifies the extent of magnetization that a material obtains in the presence of an external magnetic field. It is denoted by $\mu = \mu_0 \mu_r$, where μ_0 is the permeability of free space, and μ_r is the relative permeability, which varies depending on the type of material.

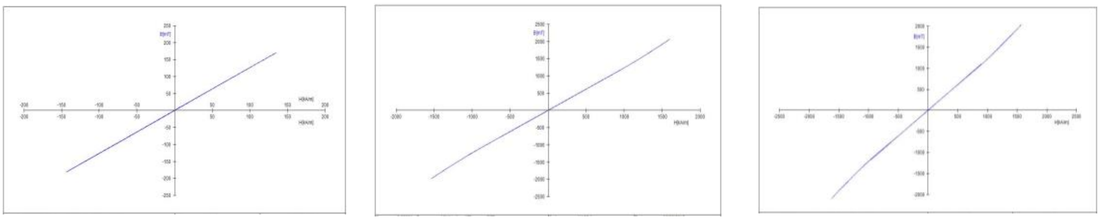

Figure (9). The Magnetization and demagnetization properties of wolframite raw mineral from Harmyingyi mine, Kanbauk mine, and Pharchaung mine.

Table (4) The magnetic parameter of wolframite raw mineral.

Raw samples	Remanence (B_r) (T)	Normal coercivity (H_{CB}) (kAm^{-1})	Intrinsic coercivity (H_{CJ}) (kAm^{-1})	Maximum energy product $(BH)_{max}$ (kJm^{-3})
Harmyingyi mine	0.00441	3.82	2.5	0.00055
Kanbauk mine	0.00391	1.16	3.2	0.00032
Pharchaung mine	0.00489	3.92	2.8	0.00052

Conclusion

The primary objective of this work was the characterization of an ore bearing wolframite mineral from Harmyingyi, Kanbauk and Pharchaung mines, at Dawei distrist, Tanintharyi region. The XRD analysis also revealed the presence of chrysotile, hematite, nacrite, riebeckit, quartz, establishing that it is an iron manganese tungstate that is intermediate between Ferberite (Fe^{2+} rich) and Hubnerite (Mn^{2+}). XRD phase patterns could also confirmed the availability of minerals such as Hubnerite, Ferberite, Dolomite, cassiterite, manganocolumbite, and quartz. The mineralogical studies carried out with SEM point imaging showed the presence of different aggregates of minerals. The chemical elemental composition determined by EDXRF was W, Mn, Sn, Fe, S, Bi, Pb, Se, Cu, Ca, Nb and Mo. The underground magnetic transmission medium consists mostly of inorganic materials (rock, soil, minerals, water and gases, etc.), and rarely, organic materials. The vast majority of natural underground materials have relative magnetic permeability close to the free-space value, and therefore permeability does not play a crucial role in the field characterization. However, electrical conductivity and permittivity of underground materials depend heavily on water content, chemical composition and constitution, as well as environmental factors such as temperature, pressure, etc. The Permagraph L apparatus conforms that the high values of (B-H), coercivity and remanence can be achieved in these materials and show that the vast majority of rocks were non-magnetic, and that magnetically important minerals were surprisingly few in number. They also point out that ferromagnetic materials do not exist in nature, and that, practically, all minerals are ferrimagnetic. Most common minerals such as coal, rock salt, graphite, quartz, gypsum, calcite, clay, etc. have magnetic susceptibility close to zero (in general, below 10^{-3}), hence, the magnetic susceptibility is too small to change the relative permeability appreciably from unity. The same can be said about the most common types of sedimentary rocks such as dolomite, limestone, sandstone, etc., metamorphic rocks such as amphibolite, schist, phyllite, quartzite, etc., and igneous rocks such as granite, rhiolyte, dolorite, basalts, andesite, etc. Conductivity of the materials gives rise to eddy currents that produce an out-of-phase secondary field. This secondary field superimposes with the primary field, thus distorting the dipole field shape. High conductivity also leads to higher attenuation of the field magnitude that passes through. In conclusion, since most soils in nature do not contain massive amounts of magnetic minerals in high concentrations, it can be safely assumed that the relative magnetic permeability of most underground environments is close to one.

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