STRUCTURAL, ELECTRICAL AND MAGNETIC PROPERTIES OF WOLFRAMITE ($FeMnWO_4$) FROM PHARCHAUNG MINE IN TANINTHARYI REGION

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Abstract

The sintering process of ore mineral which is important for designing scientific and economic sintering schedule. The sintering behavior of electrical conductivity and a structural tile were investigated using thermal analysis techniques. In this paper, the conductivity of $FeMnWO_4$ sample was determined by annealing method and the activation energy was observed 0.4147 eV. And also the thermal loop was observed in the temperature range between 303K-623K-303K. The weight loss was observed 4.599% from TGA curve and the oxidation process occurred from the exothermic peak at 464.56 °C. The crystal structure and the morphology of $FeMnWO_4$ powder were observed by XRD and scanning electron microscope. The magnetic properties of wolframite was also observed by PERMAGRAPH L.

Keywords: Sintering process, TGA curve, Wolframite, electrical conductivity

Introduction

Materials science uses the laws of physics (e.g. thermodynamics, heat and mass transfer, fluid dynamics) to understand how various physical phenomena influence materials behavior. 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

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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 molecule. This would leave the name wolframite for mixtures containing more than 20 per cent of both $FeWO_4$ and $MnWO_4$. Scintillators for dark matter search, semiconducting photoelectrodes for photoelectrolysis or humidity sensors for meteorology are some of the direct applications that wolframite-type compounds with chemical formula *A*WO4 present. On top of that, an especially interesting case is the one with the divalent magnetic ion *A*=Mn2+, which shows three different antiferromagnetic phases below 13.7 K, with the intermediate one presenting an in commensurate magnetic structure able to lift the center of inversion in MnWO4 originating a polar moment . The high-pressure (HP) behavior of these materials has attracted a lot of attention in recent years , with the search of new structures with enhanced scintillating properties being the major cause. At ambient pressure, wolframites crystallize in a monoclinic structure with $Z = 2$ and space group *P*2/*c***.** A theoretical work has shown that the monoclinic (*P*2/*c*) wolframite structure is energetically competitive with a triclinic (*P*1_) one of CuWO4-type.

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. For specific application, the magnetic properties are important. Non-magnetic materials have to be used whenever the magnetic fields can be perturbed in radiation equipment or when shielding is positioned near electrical sensors.

Experimental

Characterization Techniques

Electrical Conductivities with Temperatures: To measure the variation of electrical conductivity with temperature, a simple home-made apparatus was developed in the laboratory. The apparatus consists of a sample holder attached with the 300 W heater and the steel chamber. The desired temperature of the samples was maintained with the help of a temperature controller. The sample was sandwiched between two copper plates that are in contact with two copper rods. These two copper rods serve as two electrodes. To ensure better electrical contact, silver paste was applied evenly on both surfaces of the sample. The sample in the sample holder was placed on the copper cylinder that was heated by 300 W heater. Thermal conducting mica shield is used between the sample holder and the copper cylinder to protect from electrical conduction. The apparatus was immersed in a heating steel chamber surrounded by asbestos to reduce the thermal flow from the environment. The resistances were measured using FLUKE 45 digital resistance-meter. The capacitances were measured using FUKE DM6013A CAPACITANCE METER. The K-type thermocouple was inserted near the sample to record its temperature.

X-ray diffraction (XRD): In this work, X-ray diffraction were carried out using a Rigaku x-ray powder diffractometer which employs Cu-K_α x-radiation of wavelength λ = 1.54056 Å between a 2θ angle of 5° to 70°. X-ray diffraction was carried out to determine the crystalline structure of the materials

Scanning Electron Microscopy (SEM): The SEM provides useful analysis of surface structures and morphology. SEM was carried out using the JSM-5610 scanning electron microscope at the Research Center, Yangon University. Scanning electron microscopy was performed in order to understand further the results obtained from other techniques such as XRD.

Thermogravimetry (TG) and Differential Thermal Analysis (TDA) : The instrument used in thermogravimetry (TG) is called a thermobalance. Under controlled and reproducible conditions, quantitative data can be extracted from the relevant TG curves. Most commonly, the mass change is related to sample purity or composition. TGA also provides information about the temperature range over which a particular sample appears to be stable or unstable. The heat changes within a material are monitored by measuring the difference in temperature (*T*) between the sample and the inert reference. This differential temperature is then plotted against temperature or time to get DTA curve.TG and DTA was carried out using the DTG-60H thermal analyser at the Research Center, Yangon University.

Magnetic Measuring Techniques: The measurement was carried out on the simple at room temperature. The magnetization (hysteresis graph) of FeMnWO4 was also identified by computer controlled PERMAGRAPH L system.

Results and Discussions

The investigation of the relationship among processing, structure, properties, and performance of materials. The phase transition between two allotropic forms can be exploited in a smart way to obtain sensors or actuators (especially to obtain thermal or strain sensors) . As an illustration, our team has focused for many years on the CuMoO4 and CoMoO4 phase transitions for thermochromic or piezochromic properties. More extensively, the ABX4 compounds exhibit numerous crystalline forms and the phase transitions between some of them were shown to be of great interest . In this paper, we concentrate on the $FeMnWO_4$ compounds; respectively, with orthorhombic structure. In the literature, it is known that $FeMnWO_4$ monoclinic structure crystallize in the wolframite structure when synthesized between 400°C and 500°C. As-obtained $FeMnWO_4$ (70%) at room temperature was finally investigated by X-ray diffraction. Characterization of the sample are structural analysis by XRD as shown in Figure.1. 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. SEM investigations on $FeMnWO_4$ (70%) at room temperature as-synthesized with orthorhombic form in Figure 2. SEM investigations are not adequate to confirm or otherwise the presence of deleterious phase. The temperature induced phase transition exhibited by a single compound make it suitable as a shock detector and a thermal sensor.

Thermal properties are related to transmission of heat and heat capacity. To measure the variation of electrical conductivity with temperature, a simple home-made apparatus was developed in the laboratory. Thermal analysis by TG-DTA as shown in Figure.3, 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. Figure.4 shows the $\ln\sigma$ versus 1000/T curve of the $FeMnWO_4$ in the temperature range 303 K–623 K -303K.

Differential thermal analysis is well established as a technique for the characterization and control of materials which undergo characteristic changes on heating. It is less well established as a method for investigating the products obtained when such a material is heated, since equilibrium is an inherent impossibility of the method. However, the latter is not an obstacle when thermodynamic considerations control the design of the apparatus and when good recording equipment is employed. With the addition of dynamic atmosphere control much useful information about the products of heating can be assembled in a short time. Because differential thermal analysis is most useful when the apparatus is designed so that several different techniques can be employed.

The most important class of magnetic materials is the ferromagnets: iron, nickel, cobalt and manganese, or their compounds. The magnetization curve looks very different to that of a diamagnetic or paramagnetic material. Ferromagnetism is distinguished from paramagnetism by more than just permeability because it also has the important properties of remnance and coercivity. Although susceptibility is seldom directly important to the designer of wound components which explain the theory of magnetism. The non-ferromagnetic substances the permeability is so close to μ_0 that characterizing them by μ is inconvenient. Instead use the magnetic susceptibility, χ - via the permeability. The paramagnetic substances have positive susceptibilities and the diamagnetic substances have negative susceptibilities. The susceptibility of a vacuum is then zero.

The magnetic properties of a material is likely to include the type of graph known as a magnetization or B-H curve. The magnetic field strength as the horizontal axis and the magnetic flux density as the vertical axis. The magnetization curve of $FeMnWO_4$ is shown in Figure.5. The linear dependence between applied field H and magnetic induction B proves that at room temperature is paramagnetic. The measurement of the magnetic properties could be a method for on line testing or estimating the properties of produced heavy alloys which is routinely done in the case of cemented carbides. In that work saturation coercivity as well as several composites were determined.

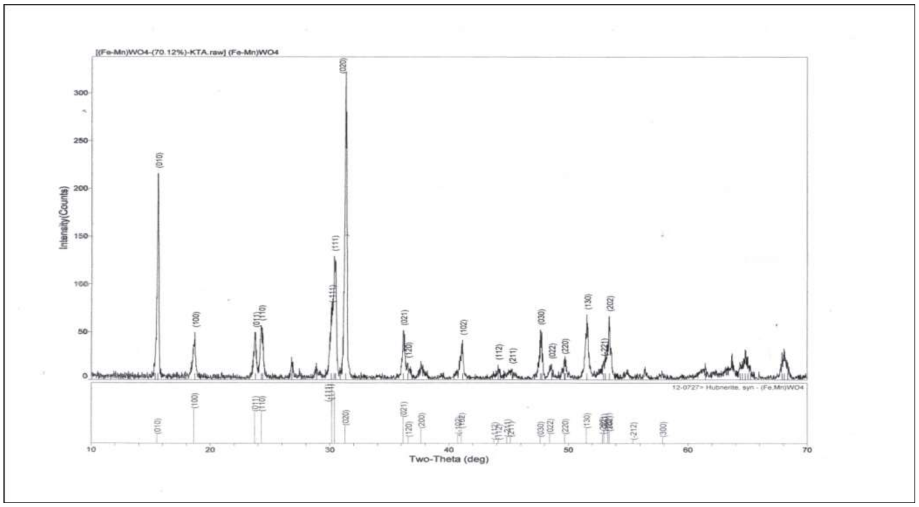

Figure 1. XRD pattern of wolframite ($FeMnWO_4$)

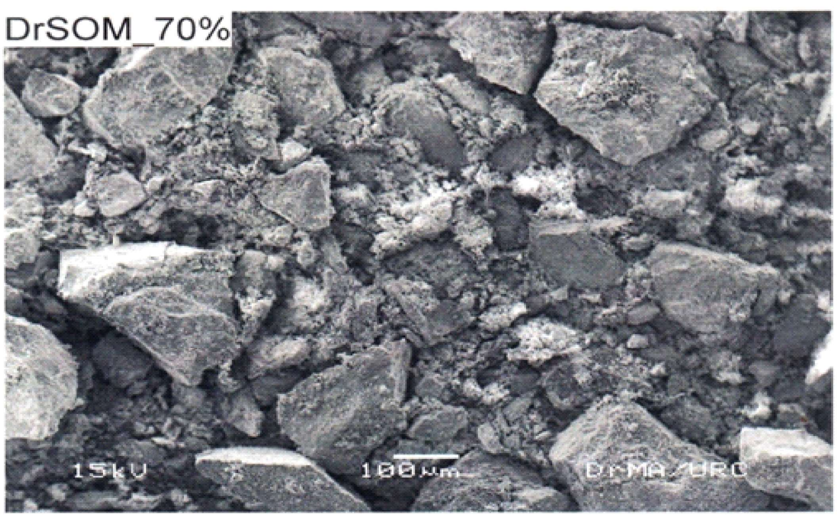

Figure 2. SEM micrograph of wolframite ($FeMnWO_4$)

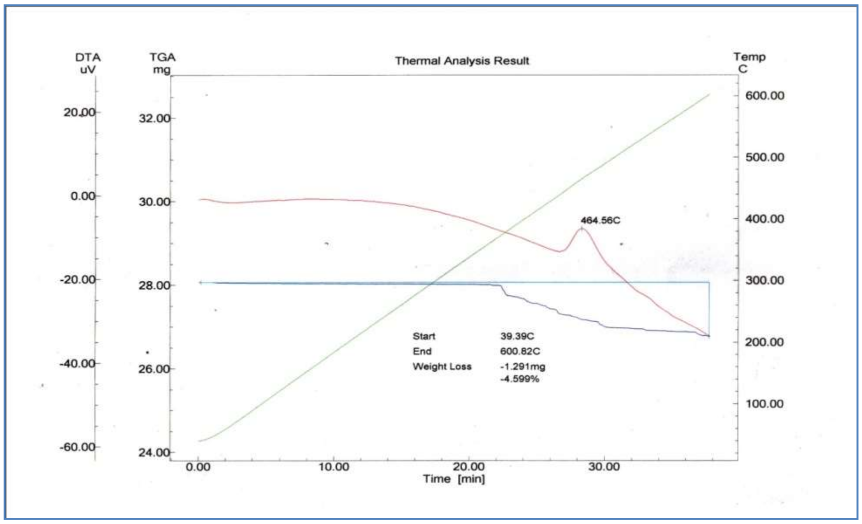

Figure 3. TGA and TDA curve of the $FeMnWO_4$

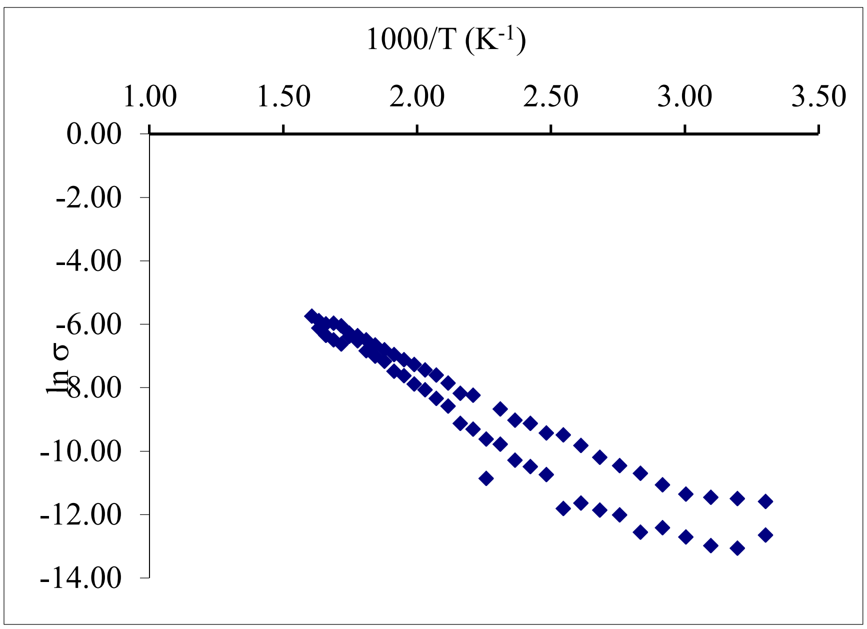

Figure 4. Plot of the lnσ versus 1000/T curve of the $FeMnWO_4$ in the temperature range 303 K – 623 K -303 K

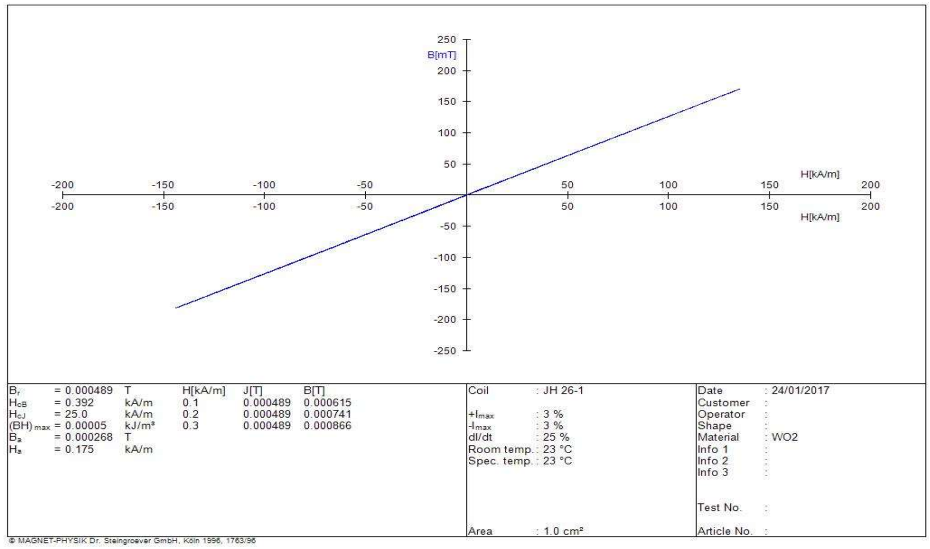

Figure 5. Magnetization curve of $FeMnWO_4$

Conclusion

Based on the analysis of electrical and magnetic properties, it may be safely suggested that the wolframite can be efficiently used as natural materials for production of pellets and sinters. In the present work, the crystal structure of $FeMnWO_4$ was observed orthorhombic from XRD analysis. SEM investigations on $FeMnWO_4$ (70%) at room temperature as-synthesized with orthorhombic form. SEM investigations are not adequate to confirm or otherwise the presence of deleterious phase. The conductivity of $FeMnWO_4$ sample was determined by annealing method and the activation energy was observed 0.4147 eV . And also the thermal loop was observed in the temperature range between 303K-623K-303K. A thermoanalys is test aids in understanding the behaviour of the wolframite when subjected to raised temperatures. 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 further highlights the occurrence of phase transformations. The values of weight loss during heating of the $FeMnWO_4$ sample was observed 4.599% from TGA curve and the oxidation process occurred from the exothermic peak at 464.56 °C DTA curve. The phase transition of 70% wolframite ($FeMnWO_4$) can be changed orthorhombic to monoclinic structure, it should be analysed the temperature between 400°C and 500°C. The humidity sensors for meteorology is the direct applications that wolframite-type compounds with chemical formula $FeMnWO_4$. The phase transformation is associated with a drastic thermochromic behavior and the marked temperature can be tuned with the tungsten concentration. Hence, the study opens up the window for the use and the optimization of a new generation of shock sensors and thermal sensors. In the magnetic properties of $FeMnWO_4$ was examined no hysteresis loop was registered. The dependency between magnetic field and magnetization was linear. B_r (remanent flux density) and H_c (coercive field) were observed 0.000489 T and 0.392×10^3A/m from B-H graph. The results obtained for this grade confirmed that the material in the examined was in a paramagnetic state. The relative permeability (μ_r) was obtained 1.2193, so the susceptibility value was 0.2193. The results obtained for this grade confirmed that the material in the examined was in a paramagnetic state.

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References

1. Braham J.B. Muwanguzi et al.,(2012), "Characterisation of the Physical and Metallurgical Properties of Natural Iron Ore for Iron Production", Department of Material Science and Engineering, KTH Royal Institute of Technology, Brinellvägen 23, 100 44 Stockholm: Sweden.

2. Grega Klančnik, (2009), "Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) as a method of material investigation", University of Ljubljana, Faculty of natural science and engineering, Department of materials and metallurgy, Aškerčeva 12, SI-1000 Ljubljana, Slovenia.

3. Janusz J. Bucki, (2011), " Magnetic Properties of Tungsten Composites", Department of Material Science and Engineering, Warsaw University of Technology, Poland.

4. Ruiz-Fuertes J. "Room-temperature vibrational properties of multiferroic MnWO4 under quasi-hydrostatic compression up to 39 GPa" Abteilung Kristallographie, Geowissenschaften, Goethe-Universität, 60438 Frankfurtam Main, Germany.

5. Veronica Blanco-Gutierrez, Alain Demourgues, Eric Lebreau, and Manuel Gaudon*, (2016), "Phase transitions in Mn(Mo1_xWx)O4 oxides under the effect of high pressure and temperature", Universite de Bordeaux, France.

www.Wolframite_mineral_info.htm