Synthesis and Characterisation of AWO₄ (A = Mg, Zn) Tungstate Ceramics

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Abstract. The AWO₄ (A = Mg, Zn) tungstate ceramics have been prepared using conventional solid-state route and characterised. Samples were analysed X-ray diffraction (XRD), scanning electron microscopy (SEM) and impedance spectroscopy (IS). Phase-pure ZnWO₄ and MgWO₄ were successfully obtained at temperatures 1000°C for 24 and 12 hours, respectively, where both compounds had a wolframite-like structure monoclinic, space group P2/c (13). Preliminary results of electrical properties of ZnWO₄ indicated that ZnWO₄ is a dielectric insulator with permittivity, εᵣ ~ 20 at room temperature. The inhomogeneous electrical properties of ZnWO₄ is observed where the grain boundary and bulk contributions effects were seen at temperature excess of 100°C.

1. Introduction
In the past decade, microwave dielectric resonators and antennas have been developed for applications in communication systems such as cellular phone, broadcasting satellite and global positioning systems. Today, dielectric ceramic components need to be miniaturized, multilayered devices and packaged with conducting layers of minimal dielectric losses, in order to be reliable and competitive to meet the telecommunication and broadband industries’ demand [1]. Therefore, three important properties such as high permittivity, εᵣ, high quality factor, Qᵣ and near zero temperature coefficient of resonant frequency, TCᵣ are essential and should be precisely controlled in order for a material to be potentially used as dielectric resonator.

A relatively high dielectric constant enables the dielectric resonator to be smaller due to the physical size of the microwave device whereas the TCᵣ value should be less than 10 ppm/°C and temperature dependent, so that the signal would not drift in and out of resonance in any weather conditions. Qᵣ value which also associate with tan δ, should be high enough i.e. Q > 30,000 at 1 GHz so as to reduce the risk of cross-talk within a certain range of frequency [1,2].

Alkaline earth metal tungstates, AWO₄ compounds of scheelite and wolframite structures have drawn much interest in microwave applications due to their low permittivities (<12) but high Qᵣ values (> 50 000 GHz). For example, mineral scheelite, CaWO₄ is used for its optical properties (scintillation counters, lasers, optical fibres) and wolframite (Fe/Mn) WO₄ are commonly used as raw material for tungsten metal production [2]. Synthesis and the preparation of the materials are important and may

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contribute to the factors in accomplishing the desired properties of the samples. Pullar et al. reported that there was a small amount of unidentified second phase in MgWO₄ whilst for ZnWO₄, phase-pure sample has been achieved at 900°C. Santucci et al. [3] also reported that high purity of ZnWO₄ was achieved at 1000°C, 24 hours. The synthesis, phase analysis and structure of AWO₄ (A = Mg, Zn) ceramics was reported in this paper, and the sample was compared with literatures. However, limited studies on the electrical properties of both compounds were reported; in this paper only ZnWO₄ sample is available to be reported in the electrical properties section. In this work, all samples were prepared using conventional solid-state technique using high purity oxides.

2. Methodology

WO₃ (dried at 100°C), ZnO and MgO (dried at 800°C) with 99.99, 99.9 and 99.95% purity respectively, were used as reagents. Appropriate amount of each reagent was mixed in an agate mortar and pestle with acetone to form a slurry and grind until dry. Pellets were prepared by uniaxially pressing powders using stainless steel die, placed on a bed of sacrificial powder of the same composition in an alumina crucible and reacted at temperatures in the range 850 – 1100°C for 3 hours in an ambient air with heating rate of 5°C/min. The processes of regrinding and reacting were repeated until samples were phase pure by XRD.

The crystalline phases of the sintered ceramics powders were analysed using X-ray powder diffraction, XRD (D8 Advanced) with Cu Kα₁ radiation at CRIM, UKM and the patterns were analysed using DIFFRAC EVA Software. The micrographs of the samples were obtained using ultra high-resolution scanning electron microscope, FESEM (FEI NOVA NANOSEM 230) with an energy dispersive X-Ray, EDX, at ITMA, UPM.

For electrical properties measurements, sintered pellets were polished and silver electrode was pasted onto the opposite surfaces before dried them for overnight. Impedance measurements were performed using Agilent 4294A Impedance Analyzer, UPM at various temperatures and the data were corrected for overall geometry.

3. Results and Analysis

3.1. Phase Analysis

Powder diffraction data for ZnWO₄ and MgWO₄ are shown in Figures 1 and 2, respectively. Peak positions of ZnWO₄ and MgWO₄ samples were indexed on a monoclinic unit cell, space group P2₁/c (13). Lattice parameters for ZnWO₄: a = 4.6935 Å, b = 5.7211 Å and c = 4.9300 Å and for MgWO₄: a = 4.6906 Å, b = 5.6782 Å and c = 4.9315 Å. These lattice parameters are comparable with the ICDD cards 01-078-4464 and 01-073-0562, respectively.

Both compounds, ZnWO₄ and MgWO₄ were initially calcined at 850°C and several impurities were identified. For ZnWO₄, un-reacted WO₃ was seen at ~ 26°, 27° and 28° whilst the un-reacted ZnO was detected at 31°, 47° and 48°. As the temperature gradually increased to 1000°C, the impurities were steadily disappeared therefore, single-phase ZnWO₄ is attained after firing at 1000°C, 24 h. As for MgWO₄, at temperature of 850°C, un-reacted peaks of WO₃ were identified at ~ 27°, 33° and 35°, but as the temperature gradually increased to 1000°C, the un-reacted peaks gradually decreased and a phase-pure MgWO₄ was achieved at 1000°C, 12 hours. However, according to literature [2], Pullar et. al reported a small trace of unidentified second phase at ~ 37.5° and therefore failed to achieve single-phase MgWO₄. Peak intensities for both compositions corresponded well with the ICDD cards, except for 010 and 020. Both peaks were relatively higher than that of the standard cards’ intensity, which may be due to higher degree of crystallinity and increase in the crystallite size [5].

Energy dispersive X-ray analysis, EDX has been carried out for all samples. Figure 3 shows the presence of Zn, W and O elements in ZnWO₄ whilst in MgWO₄, the existence of Mg, W and O elements were observed, Figure 4 indicating the purity of the compounds. The analysis shows that the calculated ratio of Zn:W and Mg:W are both 50:50 (within the experimental accuracy) parallel in comparing to 50% and 50% of Zn, Mg and W in stoichiometric ZnWO₄ and MgWO₄. Subsection
Figure 1: X-ray diffraction patterns for ZnWO$_4$ ceramic at 1000°C for 24 hours.

Figure 2: X-ray diffraction patterns of MgWO$_4$ ceramic at 1000°C for 12 hours.
Figure 3: (a) EDX spectrum for (a) ZnWO₄ sintered at 1000°C/24h and (b) MgWO₄ sintered at 1000°C/12h.

3.2. Scanning Electron Microscopy Analysis

Figure 4 shows the scanning electron micrographs of phase-pure ZnWO₄ and MgWO₄ samples, respectively. Sintering temperature effect of 1000°C, 24 hours on crystallite size of ZnWO₄ contributed to well crystallization of uniform rock-like structure depicted in Figure 4(a). For MgWO₄ sample, it shows well sintered at 1000°C, 12 hours despite its low density which can be observed from the microstructure shown in Figure 4(b). Literature reported that with further increment in firing time and temperature, a non-uniform of grain growth will be observed resulting to the existence of extremely large grain due to the discontinuous grain growth (DGG) [2]. The DGG phenomenon will resulted to a very poor $Q$-value where it may decline sharply even if the density and the permittivity, $\varepsilon_r$ continue to rise. Therefore, synthesis of microwave materials should be carried out in care so that the materials’ quality i.e. $Q_f$ and $TC_f$ will not be diminished by any parameters during the synthesis.

Figure 4: FESEM micrograph of (a) ZnWO₄ sintered at 1000°C for 24 hours and (b) MgWO₄ sintered at 1000°C for 12 hours.
3.3. Electrical properties of ZnWO₄
Preliminary results of electrical properties of ZnWO₄ sample were carried out using impedance spectroscopy (IS), at different temperatures, in air. The electrical data were recorded over the frequency range 10 Hz to 1 MHz and analysed in conventional impedance format as a function of frequency at fixed temperature. The pellet density measured using Archimedes technique was ~ 91% and data were corrected for overall pellet geometry.

Figure 5(a) shows temperature-dependence of real part of capacitance, C’, vs frequency, f for ZnWO₄ at temperature range room temperature to 400°C. At 30°C, the capacitance data is independent of frequency and temperature that the capacitance value of plateau ~ 1.8 pF/m. As the temperature increased to 100°C, the data showed C’ drop effects where two distinct capacitance plateaus were observed. The low-frequency dielectric response is perhaps dominated by grain boundary and the high-frequency response by the bulk contributions. As the temperatures raised, the time constant of the low-frequency plateaus shift to higher frequencies, and it is apparent that these plateaus values are independent of temperatures and frequencies.

The conductivity, σ’ data as a function of frequency for selection of higher temperatures in the range of 250°C to 400°C for ZnWO₄ is also presented in Figure 5(b). At temperatures below 300°C, frequency-dependence of ac conductivities at high frequency are observed where the data sets do not show a frequency-independent conductivity plateau at lower frequencies. The dc conductivity could be observed and measured only at temperatures ≥ 300°C. It shows evidence of lower frequency dc plateau which changes to temperature- and frequency-dependent behaviour of power law response at higher frequencies.

Figure 5: (a) The frequency dependence of the capacitance, C’ data of ZnWO₄ covering range of temperatures 30°C to 400°C and (b) conductivity, σ’ vs frequency, f for 250° to 400°C.

4. Conclusion

Single-phase MgWO₄ and ZnWO₄ ceramics have been successfully prepared using solid state conventional technique. Both compounds were phase-pure at temperatures 1000°C for 24 hours and 1000°C for 12 hours, respectively; all samples show monoclinic unit cell, space group P2/c (13) structure, which are comparable to literatures. The purity of these compositions has been confirmed by X-ray diffraction and EDX analysis indicating the absence of impurity. Scanning electron microscopy pictures of ZnWO₄ composition sintered at 1000°C for 24 hours reveals the uniform rock-like structures, meanwhile for MgWO₄ composition sintered at 1000°C, 12 hours, a low densification of
MgWO₄ may be seen in the micrograph. IS response shows that ZnWO₄ exhibits low permittivity, $\varepsilon_r \sim 20$ at room temperature; two distinct capacitance plateaus at low-frequency and high-frequency are observed, which may indicate grain boundary and bulk response. At temperatures below 300°C, frequency-dependence $ac$ conductivities are only observed at high frequency and with further increment in temperature, $dc$ conductivities appeared. Further investigations in electrical as well as microwave properties of MgWO₄, ZnWO₄-doped and MgWO₄-doped compositions will be carried out soon. Substitution of other element at A-site of AWO₄ is expected to enhance properties such as the permittivity, $\varepsilon_r$, quality factor, $Q_f$ and the temperature coefficient of frequency, $TC_f$ of the composition.

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