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# $MgWO_4$, $ZnWO_4$, $NiWO_4$ and $CoWO_4$ microwave dielectric ceramics

R.C. Pullar*, S. Farrah, N. McN. Alford

*Centre for Physical Electronics and Materials, Faculty of Engineering, Science and the Built Environment, London South Bank University, 103 Borough Road, London SE1 0AA, UK*

**Abstract**

$AWO_4$ (where $A = Zn^{2+}$, $Mg^{2+}$, $Ni^{2+}$ and $Co^{2+}$) tungstate ceramics were synthesised from a standard ceramic route, and their sintering behaviour and microwave dielectric properties were investigated. All $AWO_4$ powders formed single-phase materials, except $MgWO_4$, and they all had a wolframite-like monoclinic P2/c (13) structure, not the tetragonal scheelite structure found in $CaWO_4$. $MgWO_4$ had a poor *Qf* which deteriorated with further sintering, due to discontinuous grain growth at relatively low temperatures of 1000 °C and over. At higher temperatures, $ZnWO_4$, $NiWO_4$ and $CoWO_4$ have high *Qf* values at 1200 °C of 62,800, 24,900 and 38,600 GHz, respectively, which will all almost certainly be improved with firing at higher temperatures, particularly in the case of $CoWO_4$. Although not at all well sintered, $ZnWO_4$ and $CoWO_4$ have high *Qf* values of 34,000 and 28,900 GHz, respectively, at temperatures below the LTCC limit.

*Keywords:* Sintering; Powders-solid state reaction; Microstructure-final; Dielectric properties; Tungstates

## 1. Introduction

With the continuing growth of mobile telecommunications, there is always an interest in novel ceramics for use as dielectric resonators (DRs) at microwave frequencies (1–20 GHz). An effective DR should have a sufficiently high relative permittivity to allow miniaturisation of the component ($\varepsilon_r > 10$) and low dielectric losses at microwave frequencies to improve selectivity ($Q > 5000$, where $Q = 1/\tan\delta$).[1] Microwave ceramics are currently available with low $\tau_f$ and $Qf > 100{,}000$ ($Qf = Q \times f_r$). However, these are usually made from complex perovskites, such as the mixed metal tantalate perovskites $BaZn_{0.33}Ta_{0.67}O_3$ (BZT) and $BaMg_{0.33}Ta_{0.67}O_3$ (BMT).[2–4] All complex perovskites require high sintering temperatures (>1400 °C), and the structures and properties of the complex perovskites (often with four or more cations) are proving difficult to predict, and depend strongly upon the degree of ordering.[5] The next generation of dielectric ceramic components need to be miniaturised, multilayer devices, packaged in conjunction with conducting layers, with minimal dielectric losses. This has lead to a recent growth in the study of dielectric low temperature co-fired ceramic (LTCC) materials. LTCC technology provides a promising way to realise multi-chip modules and 3D circuits, for use in mobile telecommunication devices and broadband systems. However, to achieve this a new generation of DR materials must be developed, that sinter at sufficiently low temperatures (<960 °C, the melting point of Ag, or <1085 °C if using copper), still have the required dielectric properties at microwave frequencies, and are inexpensive.

The $AWO_4$ compounds are well known. The most common are the minerals scheelite ($CaWO_4$), used for its optical properties (scintillation counters, lasers, optical fibres),[6] and wolframite ([Fe/Mn]$WO_4$), the most common raw material for producing tungsten metal.[7] In the $A^{2+}WO_4$ compounds, if $A^{2+}$ has a small ionic radius <0.77 Å (Mg, Zn) it will have the monoclinic wolframite structure, but larger $A^{2+}$ cations (Ca, Ba) form the tetragonal scheelite structure.[8] Monoclinic $ZnWO_4$ is also a known mineral, named sanmartinite. Recently, Kim et al. reported on the microwave properties of $CaWO_4$ at the Third International Conference on Microwave Materials and their Applications (MMA 2004) conference in October 2004, producing $CaWO_4$ with a low $\varepsilon_r$ of 9.7 but a high *Qf* of 44,200 GHz.[9] Furthermore, Kim et al. reported that when doped with 0.5 wt.% $Bi_2O_3$–9 wt.% $HBO_3$ $CaWO_4$ could be sintered at only 850 °C with an improved *Qf* of 70,000 GHz.[10] Also, at the same conference, Choi et al. reported that $CaMoO_4$ (also scheelite structure) had $Qf = 55{,}000$ GHz and $\varepsilon_r = 11.7$, when sintered at 1100 °C with a slight 1.02 excess of Mo.[11]

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* Corresponding author. Tel.: +44 20 7815 7540; fax: +44 20 7815 7699.
*E-mail address:* r.c.pullar@lsbu.ac.uk (R.C. Pullar).

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However, no one has looked at the microwave dielectric properties of any other related $AWO_4$ or $AMoO_4$ compounds. To this end series of ceramics based upon wolframite ($CaWO_4$) and scheelite ($CaMoO_4$) were made and characterised by microwave measurements, dilatometry, XRD and SEM. This paper details the synthesis and investigation of $A^{2+}WO_4$ ceramics where $A^{2+}$ = Mg, Zn, Co and Ni, their sintering behaviour, and quality factor (*Q*), and dielectric permittivity ($\varepsilon_r$) at microwave frequencies. It was also hoped that some of these materials could be useful candidates for LTCC dielectrics. Results on $A^{2+}MoO_4$ compounds will be reported in the future.

## 2. Experimental

All $A^{2+}WO_4$ samples were prepared by a standard ceramics mixed-oxide route (oxides atleast 99% pure), from MgO, $WO_3$, ZnO, NiO and $Co_3O_4$. A stoichiometric mix of the oxides needed to form each compound was ball milled in deionised water with zirconia milling media for 1 day to mix the powders, and then dried on a rotary evaporator. The resultant powder was then calcined at 900 °C for 12 h in air, and then milled in water at 300 rpm/3 h on Fritsch Pulverisette high-energy planetary ball mill to reduce particle size to <3 μm. The resultant fine powders were again dried on a rotary evaporator, and then used to make all samples, without any further processing or addition of an organic binder. The powders were uniaxially pressed to form pellets under a pressure of 100 MPa using a 13 mm diameter die. All samples were then sintered in air, at temperatures between 900 and 1200 °C/2 h, heated and cooled at a rate of 5 °C $min^{-1}$. The density of the samples was calculated from their measured volume and mass, and theoretical maximum densities were obtained from the Philips JCPDF files.

The change in length of a cylindrical sample, $dL/L_0$, with increasing temperature was measured at a rate of 5 °C $min^{-1}$ using a Netzsch 402C dilatometer. This was expressed as a % change in length with temperature, to study the sintering behaviour of the samples.

X-ray diffraction patterns of the samples treated at various temperatures were recorded in the region of $2\theta = 20–75°$ on a PANalytical X'Pert MRD diffractometer using Cu $K_\alpha$ radiation, with a PANalytical X'cellerator detector. The results were analysed and manipulated using PANalytical X'Pert software.

The microstructure and grain size of the samples were investigated using a field emission electron microscope (Hitachi S-4300), on unpolished samples.

The quality factor (*Q*) and relative permittivity ($\varepsilon_r$) were measured at frequencies of 8.5–10 GHz, using the resonant $TE_{01\delta}$ mode of the sample,[12] in an oxygen-free high-conductivity copper cavity, whose diameter was three times that of the sample, as recommended by Kajfez and Guillon.[12] The $TE_{01\delta}$ mode was examined using a Hewlett-Packard HP8720D Vector Network Analyser, and the surface resistance of the copper was calculated from the *Q* value of the $TE_{011}$ resonance of the empty cavity, to allow the results to be corrected for any loss due to the cavity walls.[12] The *Q* values are corrected for losses due to the measurement equipment, and so can be assumed to be the *Q* of the dielectric ceramic. Measurements were made on the as-fired samples, at room temperature. The results are given as *Qf*, that is $Q \times$ resonant frequency ($f_r$), and $f_r$ was between 8.5 and 10 GHz in all cases.

## 3. Results and discussion

There are few reports on the synthesis of these materials, but $NiWO_4$ and $ZnWO_4$ have been made at 700 °C from amorphous powders,[6] and $W^{6+}$ has been shown to diffuse well in $CaWO_4$ at 900 °C,[13] so it was decided to calcine the oxides at 900 °C for 12 h. The XRD patterns of the calcined powders are shown in Fig. 1. As expected, all formed a monoclinic wolframite-like structure, with space group P2/c (13). All were pure single phase, except for $MgWO_4$, which had a small amount of an unidentified second phase with a peak at 37.5°. The $ZnWO_4$ and $MgWO_4$ powders were white, while $NiWO_4$ was deep yellow and $CoWO_4$ was a rich blue colour.

The shrinkage behaviour of the pressed powders is shown in Fig. 2, heated continuously at 5 °C $min^{-1}$. None have sintered below the LTCC target temperatures of 1050 °C (Cu) or 950 °C (Ag), and $MgWO_4$ does not sinter much at all below 1250 °C. At that temperature the material suddenly expands and de-densifies, typical of a phase change, and any $MgWO_4$ pellets fired to this temperature disintegrate into a fine powder. Both $ZnWO_4$ and $NiWO_4$ appear fairly well sintered by 1200 °C, whereas $CoWO_4$ has barely begun sintering at this temperature, but then rapidly sinters over the next hundred degrees, seemingly needing temperatures of over 1250 °C to become dense. Samples were fired between 900 and 1200 °C, and held for 2 h at that temperature, and the changes in density are shown in Fig. 3. It can be seen that the density of $MgWO_4$ levels out and remains roughly constant above1050 °C, at a density of around 6.00 g $cm^{-3}$, only 87.0% of the maximum theoretical density (MTD = 6.896 g $cm^{-3}$). $ZnWO_4$ (MTD = 7.872 g $cm^{-3}$) and $NiWO_4$ (MTD = 7.954 g $cm^{-3}$) have low densities of 4.47 g $cm^{-3}$ (56.8%) and 4.90 g $cm^{-3}$ (61.6%), respectively, at 900 °C, but they sinter steadily up to 6.86 g $cm^{-3}$ (87.1%) and 7.29 g $cm^{-3}$ (91.7%) at 1200 °C, and should sinter further at higher temperatures. $CoWO_4$ (MTD = 7.760 g $cm^{-3}$) has only increased in density from 4.40 g $cm^{-3}$ (56.7%) at 1050 °C, the lowest firing temperature at which the pellets were sufficiently reacted to be handleable, to 5.39 g $cm^{-3}$ (69.5%) at 1200 °C. The dilatometer results suggest that $CoWO_4$ requires atleast a further 50 °C rise in firing temperature to become a well sintered sample. Unfortunately, due to extreme furnace contamination issues from vaporisation of $WO_3$, $MoO_3$ and other components from $AWO_4$ and $AMoO_4$ samples above 1200 °C, we have had to temporarily suspend firing these samples above 1200 °C.

The plots of $\varepsilon_r$ and *Qf* against sintering temperature are shown in Figs. 4 and 5. As expected, $\varepsilon_r$ closely follows density in all cases, and is higher than $CaWO_4$ ($\varepsilon_r = 9.7$)[9] for all well sintered samples, reaching 12.1 for $MgWO_4$, 13.5 for $ZnWO_4$ and 13.3 for $NiWO_4$. Even the poorly sintered $CoWO_4$ achieves $\varepsilon_r$ higher than $CaWO_4$, with a value of 10.7, in a ceramic that is only 69.5% dense.

For all $MgWO_4$ samples *Qf* is low, but unusually with a maximum of 5400 GHz in the least sintered sample at 950 °C (only

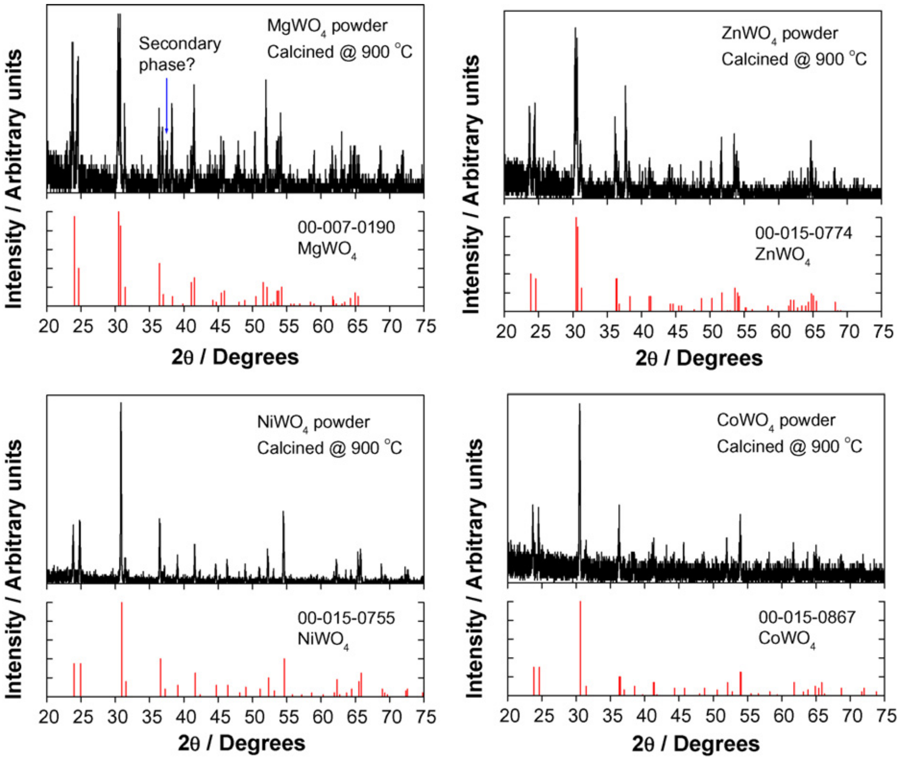

Fig. 1. XRD patterns of calcined Mg, Zn, Ni and CoWO$_4$ powders.

71.2% dense). After this poor start, the *Qf* then decreases with increasing temperature and density to under 1000 GHz. This can be explained by the microstructure—the sample appears well sintered at 950 °C, despite its low density (Fig. 6(a)), but with further increases in temperature large grain growth occurs, resulting in the existence of some very large grains due to discontinuous grain growth (DGG) (Fig. 6(b)). This DGG has been shown to be the cause of very poor *Q* in over sintered niobate ceramics,[14] and once it occurs *Q* values can decline sharply even as density and $\varepsilon_r$ continue to rise.

ZnWO$_4$ has good *Qf* values even at low temperatures (26,000 GHz at 950 °C), and very high *Qf* at 1200 °C (63,000 GHz). Almost no grain growth has occurred between 950 and 1200 °C, and density is <90%, so *Q* may still improve with further sintering. NiWO$_4$ has low *Qf* values at lower temperatures, achieving a poor minimum of only 3200 GHz at 1050 °C, but *Qf* rises suddenly above 1150 °C to 25,000 GHz. Again, this can be explained by the microstructure—the ceramic is clearly

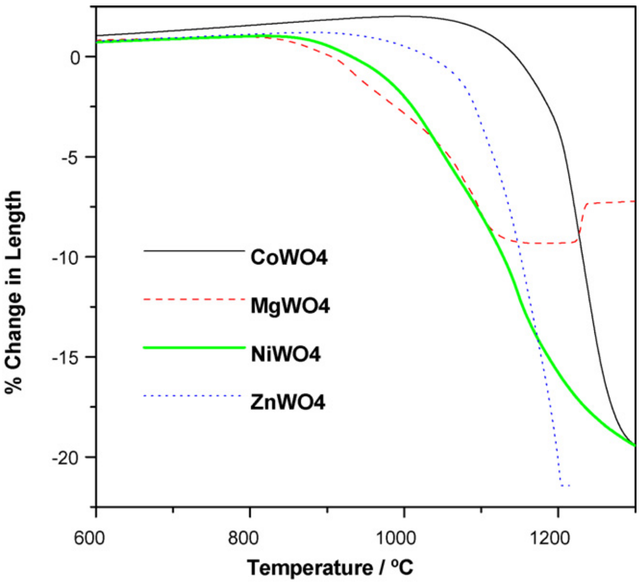

Fig. 2. Shrinkage measurements of AWO$_4$ pellets pressed from calcined powders, fired at 5 °C min$^{-1}$.

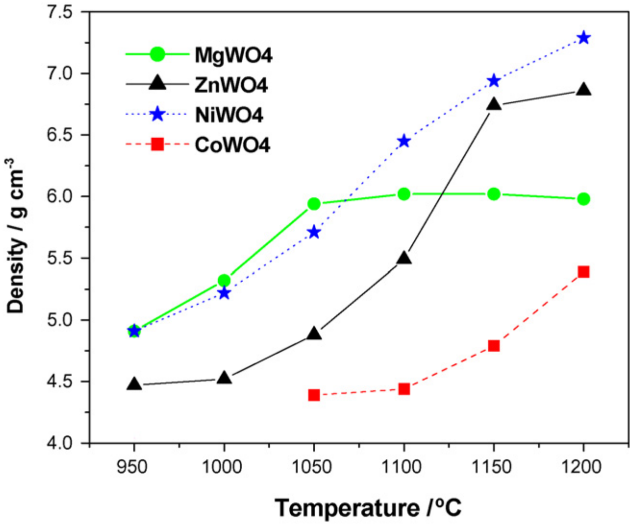

Fig. 3. Variation of density with sintering temperature for AWO$_4$ ceramics.

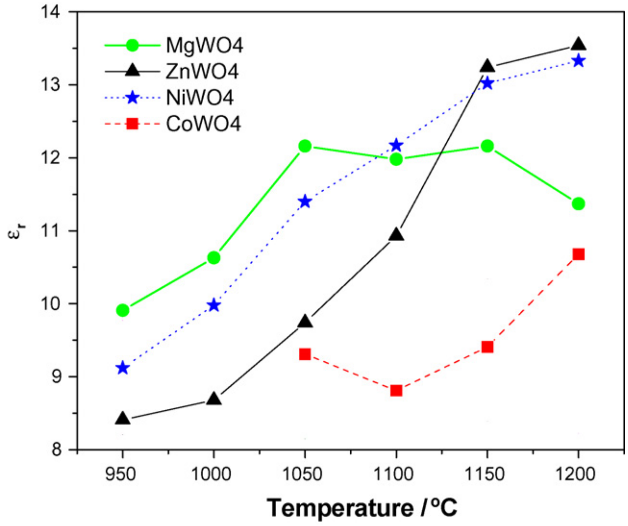

Fig. 4. Variation in $\varepsilon_r$ with firing temperature for $AWO_4$ ceramics.

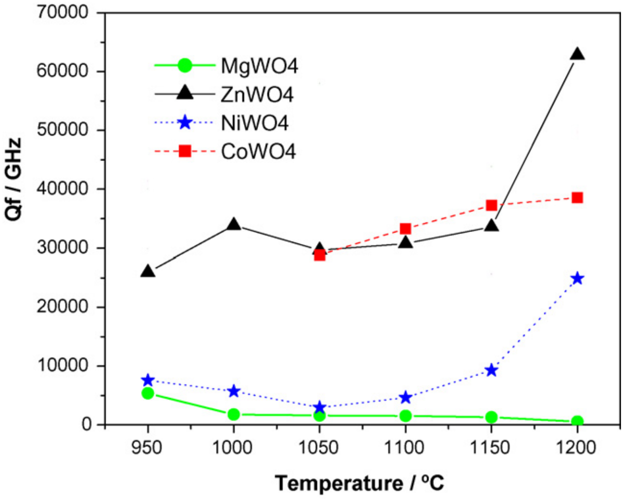

Fig. 5. Variation in *Qf* with firing temperature for $AWO_4$ ceramics.

poorly sintered at 950 °C, and remains so at 1150 °C, despite achieving 88% density (Fig. 7(a) and (b)). The ceramic is better sintered at 1200 °C (Fig. 7(c)), but shows little grain growth, indicating that higher *Qf* values may well be attainable at higher sintering temperatures. $CoWO_4$ has a surprisingly high *Qf* for such a poorly sintered ceramic—up to 39,000 GHz in a sample only 69.5% dense at 1200 °C, which can certainly be improved upon with higher firing temperatures.

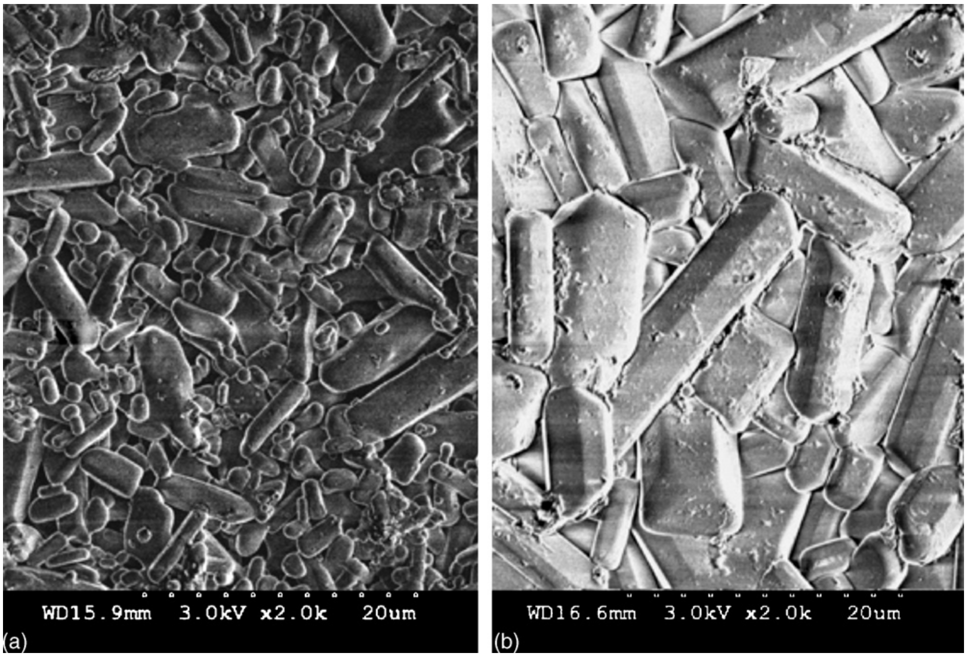

Fig. 6. SEM micrographs (2K magnification) of unpolished $MgWO_4$ fired to (a) 950 °C/2 h and (b) 1200 °C/2 h.

Table 1
Properties of $AWO_4$ samples with the highest *Qf* values

| Material | Temperature (°C) (fired 2 h) | *Qf* (GHz) | $\varepsilon_r$ | Density (g cm$^{-3}$) | X-ray density[a] | Maximum density (%) |
|---|---|---|---|---|---|---|
| $MgWO_4$ | 950 | 5400 | 9.9 | 4.91 | 6.896 | 71.2 |
| $ZnWO_4$ | 1200 | 62800 | 13.5 | 6.86 | 7.872 | 87.1 |
| $NiWO_4$ | 1200 | 24900 | 13.3 | 7.29 | 7.954 | 91.7 |
| $CoWO_4$ | 1200 | 38600 | 10.7 | 5.39 | 7.760 | 69.5 |
| $CaWO_4$[b] | 1200 | 44200 | 9.7 | n/a | 6.120 | n/a |

[a] From Philips JCPDF files.

[b] From Kim et al.,[9] included here for comparison.

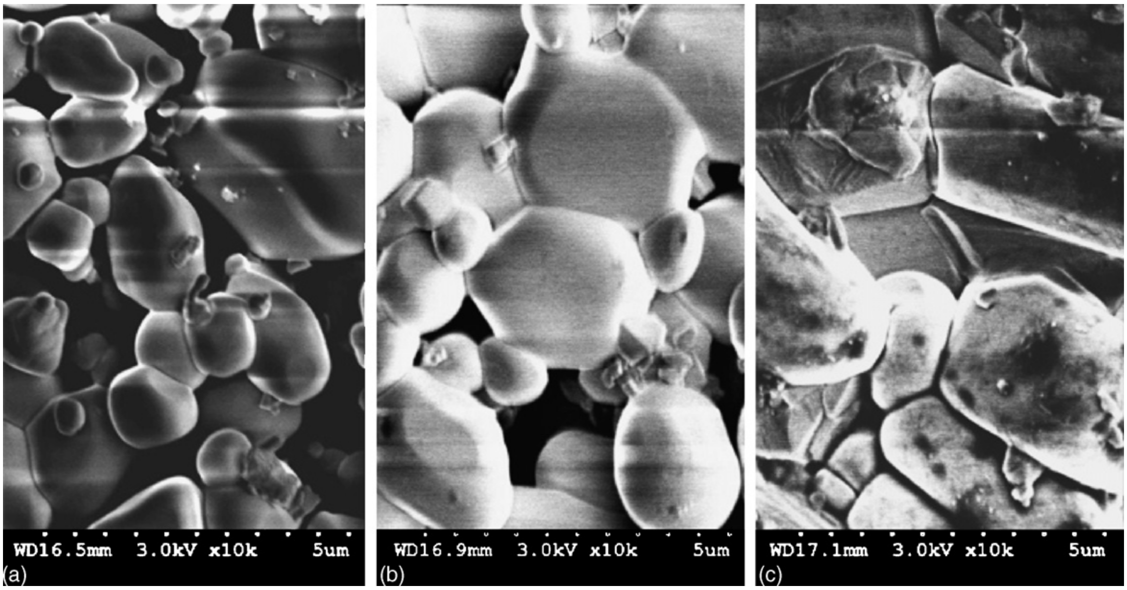

Fig. 7. SEM micrographs (10K magnification) of unpolished $NiWO_4$ fired to (a) 950 °C/2 h, (b) 1150 °C/2 h and (c) 1200 °C/2 h.

It should be noted that although they are not at all well sintered, $ZnWO_4$ and $CoWO_4$ have high *Qf* values of 34,000 and 28,900 GHz, respectively, at temperatures below the LTCC limit, although porosity could be a problems regarding any possible applications of such materials. Table 1 shows the properties of the sample of each ceramic with the highest *Qf* values, compared to $CaWO_4$ for comparison.

## 4. Conclusion

All $AWO_4$ powders were formed as single-phase materials, except maybe $MgWO_4$ which had a small amount of an unidentified second phase, and they all had a wolframite-like monoclinic P2/c (13) structure. All sintered above the LTCC temperature limits, but although not at all well sintered, $ZnWO_4$ and $CoWO_4$ have high *Qf* values of 34,000 and 28,900 GHz, respectively, at temperatures below the LTCC limit. $MgWO_4$ had a poor *Qf* which deteriorated with further sintering, due to discontinuous grain growth at relatively low temperatures of 1000 °C and over. At 1250 °C $MgWO_4$ undergoes a phase change, resulting in disintegration of the sintered ceramic sample to a fine powder. At higher temperatures, $ZnWO_4$, $NiWO_4$ and $CoWO_4$ have high *Qf* values developing at 1200 °C of 62,800, 24,900 and 38,600 GHz, respectively, which will all almost certainly be improved with firing at higher temperatures, particularly in the case of $CoWO_4$.

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