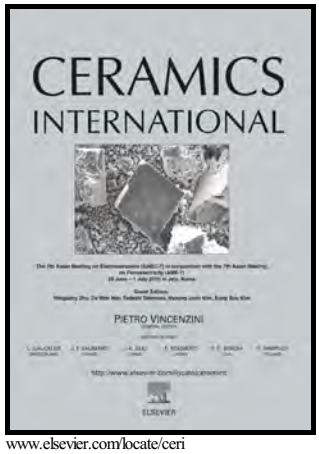

Room-temperature fabrication of microwave dielectric Li_2MoO_4-TiO_2 composite ceramics

Hanna Kähäri, Merja Teirikangas, Jari Juuti, Heli Jantunen

www.elsevier.com/locate/ceri

PII: S0272-8842(16)30475-8
DOI: http://dx.doi.org/10.1016/j.ceramint.2016.04.081
Reference: CERI12699

To appear in: *Ceramics International*

Received date: 2 March 2016
Revised date: 12 April 2016
Accepted date: 14 April 2016

Cite this article as: Hanna Kähäri, Merja Teirikangas, Jari Juuti and Hel Jantunen, Room-temperature fabrication of microwave dielectric Li_2MoO_4-TiO composite ceramics, *Ceramics Internationa* http://dx.doi.org/10.1016/j.ceramint.2016.04.081

Room-temperature fabrication of microwave dielectric Li_2MoO_4-TiO_2 composite ceramics

Hanna Kähäri*, Merja Teirikangas, Jari Juuti & Heli Jantunen

Microelectronics Research Unit, University of Oulu, Oulu 90570, Finland

Abstract

This paper presents the incorporation of large amounts of insoluble additives into a Li_2MoO_4 ceramic matrix fabricated with a room-temperature densification method. Li_2MoO_4-TiO_2 composite ceramics were fabricated by a method based on the water-solubility of Li_2MoO_4, where the densification occurs at room temperature during sample pressing and is followed by further post-processing at 120 °C to remove residual water. As the amount of added rutile TiO_2 rose from 10 to 30 vol%, relative permittivity and loss tangent values at ~9 GHz increased from 6.9 to 10.1 and from 1.1×10^{-3} to 3.8×10^{-3}, respectively, and thermal coefficient of permittivity decreased from 180 ppm/°C to -170 ppm/°C. The Lichtenecker equation used in the analysis of relative permittivity was applicable in this study for Li_2MoO_4-TiO_2 composite ceramics with up to 20 vol% of TiO_2. However, with 25 and 30 vol% additions of TiO_2, correspondence decreased due to increased porosity in the composites. The low post-processing temperature made this material feasible for Ag electrode integration without formation of unwanted extra phases.

Keywords: B. Composites, C. Dielectric properties

1. Introduction

There is a continuous need for new advanced integration, packaging and multimaterial module technologies in wireless communication systems. Electroceramics, which enable creation of light, miniaturised multilayer electronics components, have been widely studied for these purposes. For example, microwave dielectric ceramics are used for antennas, resonators, filters and multilayer substrates that utilise Low Temperature Co-fired Ceramics (LTCC) technology. In ultra-wideband (UWB) antennas operating in a frequency range of 3.1–10.6 GHz, substrate ceramics typically have low relative permittivity (ε_r) and a low dielectric loss value (tan δ)[1-3]. When used in narrow bandwidth antenna applications, a small temperature coefficient of permittivity ($TC\varepsilon_r$)—which is related to the coefficient of resonant frequency (TCF)—is also critical. Usually, densification of these ceramics occurs during a high-temperature sintering step (> 850 °C). Even though there has been much research on electroceramic compositions with intrinsic ultra-low sintering temperatures, the lowest temperature reported is 400 °C [4]. This is still too high for seamless integration with polymer or paper substrates.

Microwave dielectric lithium molybdate (Li_2MoO_4) ceramic can be conventionally sintered at the ultra-low sintering temperature of 540°C, exhibiting ε_r ~ 5.5 and a tan δ value of 2.8×10^{-4} at 13.051 GHz, and a large negative TCF of -160 ppm/°C [5,6]. An effective way to modify these electrical properties is to design ceramic-ceramic composites. Guo *et al*. have produced Li_2MoO_4-TiO_2 composites [7], since rutile TiO_2 provides temperature stabilisation and an increase in permittivity due to its large positive value of TCF ~465 ppm/°C and ε_r ~105 [8]. For example, the temperature-

stable compositions of microwave dielectric $0.55Li_2MoO_4$-$0.45TiO_2$ sintered at 700 °C and $0.50Li_2MoO_4$-$0.50TiO_2$ sintered at 720 °C exhibit low loss behaviour with permittivities of 10.6 and 12.3, respectively [7]. Although there was no reaction between these two phases, the high sintering temperature led to the formation of unwanted extra phases during co-firing with Ag particles, thus making the use of Ag electrodes problematic.

Recently, an alternative room-temperature fabrication method based on utilising a small amount of an aqueous phase of Li_2MoO_4 and subsequent recrystallisation was presented [9, 10]. While in a typical sintering process densification of material occurs by diffusion or viscous flow, for which temperature provides an energy source, it is thought that in this alternative method material is transported through the aqueous phase during dissolution and recrystallisation of Li_2MoO_4, and compacting pressure is the driving force. When residual water from the dense uniaxially pressed samples was removed at a temperature of 120°C, Li_2MoO_4 ceramics exhibited relative permittivity of 5.1 and a tan δ value of 3.5×10^{-4} at 9.6 GHz. The results also indicated that the post-processing temperature is not critical in this fabrication method, as it mainly affects the time needed to remove residual water from the samples. This gives moderately wide freedom of choice of the fabrication temperature of the components according to the other materials (such as the substrate or electrodes) being co-fired [10]. Furthermore, since typical sintering temperatures destroy temperature-sensitive materials such as polymers or silicon, and can cause reactions and extra phases in composites, the proposed fabrication method with a low post-processing temperature provides an opportunity to overcome this challenge. Even though Li_2MoO_4 is water-

soluble, the samples do not hydrolyse easily, unlike what is reported for $Li_2Mo_4O_{13}$ ceramics from the same binary system [5]. It is stated that Li_2MoO_4 is slightly hygroscopic [11], but it is also noted that even when it is fabricated in the presence of water, no constitutional water is present in the crystal structure [12].

In order to fully benefit from low-temperature processing of Li_2MoO_4 ceramic in actual components, it would be beneficial to be able to greatly modify its electrical properties. The dielectric properties of Li_2MoO_4 fabricated at room temperature were modified with 10 vol% of rutile TiO_2 and $BaTiO_3$ already in our previous study, where relative permittivities of 6.7 and 8.2 were obtained, respectively [10]. However, according to Guo *et al*. [7] addition of more than 10 vol% of rutile TiO_2 is needed for temperature stabilisation of resonance frequency. Thus, there is a need to investigate in more detail the feasibility of this room-temperature densification method from the larger addition point of view.

In this work, the incorporation of large amounts of insoluble additives into a ceramic matrix fabricated with the room-temperature densification method was studied. The effect of rutile TiO_2 loading up to 30 vol% on the dielectric properties of Li_2MoO_4-TiO_2 composite ceramics, fabricated with a method based on dissolution and recrystallisation, was investigated. The influence of the particle size of Li_2MoO_4 and the loading level on the microstructure and processibility of Li_2MoO_4 composite ceramics is discussed. Phase compositions, microstructures and chemical compatibility with Ag were investigated.

2. Materials and methods

For the Li_2MoO_4-TiO_2 composites with 10 and 15 vol% of TiO_2 (99.8%; 97% min rutile phase, 0.9–1.6 Micron APS Powder, Alfa Aesar, Karlsruhe, Germany), Li_2MoO_4 powder (99+%; Alfa Aesar) was ground with a mortar and pestle and sieved (<180 μm). For the Li_2MoO_4-TiO_2 composites containing 20, 25 and 30 vol% of TiO_2, the Li_2MoO_4 powder particle size was reduced by milling in ethanol with ZrO_2 milling media and sieving with a mesh size of 45 μm. A laser diffraction particle size distribution measurement (LS13320; Beckman Coulter) showed that at least 95% of the particles were smaller than the chosen mesh size. Sieved Li_2MoO_4 powders were mixed in ethanol with a predetermined amount of TiO_2, first with an ultrasound mixer to remove possible agglomerates, and then with a mortar and pestle. The slurries were dried in an oven at 100 °C and the resulting powders were sieved again. To study chemical compatibility with silver as an electrode material, 20 wt% of silver powder (99.9%; Alfa Aesar) was mixed in ethanol with the Li_2MoO_4 composite powder with 30 vol% of TiO_2, comparable with the powder processing method used by Guo *et al.* [7] for sintered ceramics. For the room-temperature densification, all powders were moistened by spraying with deionised water and mixed with a spatula until a thick uniform paste was formed, after which the paste was pressed uniaxially in a steel mould at a pressure of 150 MPa to produce disks (diameter 20 mm, height 2–3 mm). To remove residual water, the disks were dried in a laboratory oven at 120 °C for 24 h. Density of the disks was calculated from the dimensions measured by a micrometre screw (Mitutoyo Co., Japan) and the weight measured by a precision scale (XT620M, Precisa, Switzerland). The phase composition of the samples was analysed by x-ray diffraction (XRD) over angular range of 10-70° (2θ) with a step size of 0.01° and step time of 0.75 s using CuK_α

radiation (Bruker D8 Discover X-Ray Diffractometer, Karlsruhe, Germany), divergence slit of 1.5 mm, and secondary slit of 1.2 mm. Microstructural studies were done with a field-emission scanning electron microscope (FESEM; Zeiss Sigma, Carl Zeiss, Germany) equipped with an energy-dispersive spectrometer for chemical composition examination. For microstructure imaging the samples were polished at first with water-free diamond solution and then coated with thin layer of carbon. Dielectric properties were measured with a resonant mode technique using a Split Post Dielectric Resonator (QWED, Warsaw, Poland) with a nominal resonant frequency of 9.97 GHz. To determine the temperature coefficients of permittivity ($TC\varepsilon_r$), measurements were performed every 10 degrees between temperatures of 25 °C and 85 °C.

3. Results and discussion

Table 1 presents the densities and dielectric properties of the ceramics fabricated by a room-temperature densification method and post-processed at 120 °C. In our previous studies [9,10], Li_2MoO_4 powder was sieved with a mesh size of 180 µm, producing a mean particle size of 87 µm. With this particle size it was easy to press the moistened powders into dense samples, and only a small amount of aqueous phase was left in the mould. The results of this work show that the particle size of Li_2MoO_4 powder has a significant effect on the densification of Li_2MoO_4-TiO_2 composite ceramics fabricated at room temperature, especially when the amount of TiO_2 is increased above 10 vol%. Figure 1 presents backscattered electron images of a Li_2MoO_4-TiO_2 composite ceramic with 15 and 20 vol% of TiO_2, fabricated by the room-temperature densification method from Li_2MoO_4 powders sieved with mesh sizes of 180 and 45 µm, respectively. The

light-coloured particles are Li_2MoO_4 phase and the dark grey ones rutile TiO_2 phase. It is apparent that the larger Li_2MoO_4 particle size used also in our previous studies [9,10] results in uneven distribution of TiO_2 because the surface area of the Li_2MoO_4 powder is not large enough to accommodate all of the TiO_2 powder particles as the amount of TiO_2 increases. This can be seen from Fig. 1 a), where distinctive areas of TiO_2 are visible. According to a laser diffraction based particle size distribution measurement, the powder sieved with mesh size of 180 µm has a mean particle size of 87 µm which is considerably larger than that of the used rutile TiO_2 powder (0.9 – 1.6 µm according to the manufacturer).

A mean particle size of 14 µm was measured for the powder sieved with mesh size of 45 µm and about 43 % of particles were smaller than 10 µm. The use of Li_2MoO_4 with a smaller particle size, and thus a larger surface area, led to more homogeneous distribution of TiO_2 (Fig. 1 b). This also improved the attachment between the particles and decreased the size of voids.

Problems related to the use of Li_2MoO_4 with a small particle size have been reported [10]: Use of Li_2MoO_4 powder sieved with a mesh size of 45 µm, having a mean particle size of 14 µm, led to formation of clay-like clusters during moistening, resulting in a non-uniform density leading to sample warpage and cracking during drying. In this paper the problem was solved by providing more solution phase between the particles with an increased amount of water. This resulted in a thick uniform paste, which was then pressed into the desired form, although fabrication problems like flashing of the material to the pistons of the mould still continued. To achieve dense samples with a uniform microstructure, it is clear that a compromise between the processibility and

the particle size of Li_2MoO_4 is required, especially in the case of high loading levels of an insoluble additive like TiO_2.

The x-ray diffraction patterns of the fabricated composites in Fig. 2(a) are consistent with previous studies of Li_2MoO_4-TiO_2 ceramic composites [7,10], and show only diffraction lines of Li_2MoO_4 [powder diffraction file 12-0763] and rutile TiO_2 [powder diffraction file 34-0180] phases, indicating that Li_2MoO_4 does not react with TiO_2. The intensity of the TiO_2 diffraction lines increases as the amount of TiO_2 increases in the fabricated composites, as can be expected. However, it has been reported elsewhere that when Li_2MoO_4-TiO_2 composites were co-fired with Ag to study its chemical compatibility as an electrode material, small amounts of $LiTi_2O_4$ and Ag_2MoO_4 phases were formed [7]. Allegedly, this partial reaction was caused by the relatively high sintering temperatures of the composites (700–730°C), which were close to the melting temperature of Li_2MoO_4 (705°C). In our earlier study [10] we thought this reaction could be prevented by using the room-temperature fabrication method with a low post-processing temperature. Figure 2 (b) shows the XRD patterns of the Li_2MoO_4-TiO_2 composite with 30 vol% of TiO_2, as well as a composite with the same amount of TiO_2 and 20 wt% of Ag powder. Only Li_2MoO_4, rutile TiO_2 and Ag phases are observed, confirming that at the low post-processing temperature used in this study, no reaction between Ag and Li_2MoO_4-TiO_2 composite materials occurs. Therefore, electrode fabrication is possible, for example, by screen printing a commercial nano-Ag ink like DuPont 5064H.

The dielectric properties of the Li_2MoO_4-TiO_2 composites are presented in Fig. 3. The ε_r and tan δ values of the Li_2MoO_4-TiO_2 ceramic composite with 10 vol% of TiO_2 are

similar to the results we achieved in our previous study [10]. There are several models for calculating the effective permittivity of a two-phase ceramic composite. An earlier study by Guo *et al.* [7] showed that the measured relative permittivities of sintered Li_2MoO_4-TiO_2 composites are generally in accordance with the empirical Lichtenecker logarithmic rule for a two-phase composite

$$lg\varepsilon = y_1 lg\varepsilon_1 + y_2 lg\varepsilon_2 \qquad (1)$$

where y_1 and y_2 refer to the volume fractions of materials 1 and 2, and ε_1 and ε_2 define the permittivities of the materials, respectively. As expected, also in this study the relative permittivity of the fabricated Li_2MoO_4-TiO_2 composites increased from 6.9 to 10.1 at ~9 GHz as the amount of TiO_2 was increased from 10 vol% to 30 vol% due to the higher permittivity of rutile TiO_2 (~105) [8].

On the other hand, Fig. 3 shows that as the amount of TiO_2 phase exceeds 20 vol%, the correspondence between Lichtenecker's equation (1) and the measurements of the composites decreases. The effect of Li_2MoO_4 particle size on the dielectric properties can also be seen in Fig. 3. The relative permittivity and dielectric losses of the composite material with 15 vol% of TiO_2 are not in line with the others, further proving that using a smaller Li_2MoO_4 powder particle size is advantageous for composite materials fabricated with the method presented in this paper.

Considering that the dielectric loss value of rutile TiO_2 is of the same magnitude (10^{-4}) [13] as that of Li_2MoO_4, the measured loss values of the composites are higher than expected, rising at ~9 GHz from 1.1×10^{-3} to 3.8×10^{-3} as a function of the amount of

TiO_2. Such behaviour has been reported with Li_2MoO_4-TiO_2 composites sintered at 700–730 °C, and it was assumed to be due to the difference in the sintering temperatures of the two phases [7]. This difference in the sintering temperatures cannot be the cause for the growing dielectric loss values in this study. Since the room-temperature fabrication method depends on the solubility of Li_2MoO_4 in water, the increase in loss value may be attributed to the difference in the solubilities of the two phases. TiO_2 is not water soluble, thus an increased amount of aqueous Li_2MoO_4 solution is needed to incorporate the space between the insoluble particles during pressing. Therefore, the amount of residual water in the samples directly after pressing increases with the amount of TiO_2 phase. As the residual water evaporates from the samples during post-processing, it leaves very small pores in the samples. The effect of this increased porosity is a plausible cause for the decrease in permittivity and the increase in dielectric losses. However, these finely distributed, very small pores did not seem to affect the processing of the ceramic composite samples, as they were still hard and durable even with 30 vol% of TiO_2.

Pure Li_2MoO_4 showed a large positive temperature coefficient of permittivity ($TC\varepsilon_r$) of ~320 ppm/°C. With an increasing amount of TiO_2 addition, the value of $TC\varepsilon_r$ decreased, as shown in Fig. 3, and it was closest to zero (~20 ppm/°C) with the loading level of 20 vol%. Since $TC\varepsilon_r$ is related to TCF according to

$$TCF = -\alpha_L - 0.5TC\varepsilon_r \qquad (2)$$

where α_L refers to linear expansion coefficient, it can be concluded that the temperature behaviour of the composites is comparable with the ones fabricated by Guo *et al.* [7] and sintered at close to 700 °C.

From the application point of view, the proposed Li_2MoO_4-TiO_2 composites also provide interesting ε_r and tan δ values. Commercially available LTCC substrates from Ferro, Heraeus and CeraTec, with ε_r values of 5.9–8.5, tan δ values up to 0.0026 and sintering temperatures above 800 °C, have earlier been reported to be feasible for UWB antennas operating in the frequency range of 3.1–10.6 GHz [1-3]. Therefore, Li_2MoO_4-TiO_2 composites fabricated with the room-temperature densification method are good candidates, for example, for UWB antennas.

One should also note that in these kinds of room-temperature methods there is no measurable change in the sample size after pressing. This can be considered an advantage, since the size of the components can easily be managed by controlling the mould dimensions.

4. Conclusions

By utilising different Li_2MoO_4 particle sizes, Li_2MoO_4-TiO_2 composite ceramics with up to 30 vol% of TiO_2 were fabricated using a method based on the dissolution of Li_2MoO_4 in water and its recrystallisation, where densification occurs during sample pressing. The permittivity of the composites was modified by utilising TiO_2 additions with fairly good predictability up to 20 vol%. The dielectric properties of the ceramics fabricated in this study were somewhat different from those reported for similar ceramics fabricated with conventional methods. Nevertheless, the composites show dielectric properties that may be used, for example, in UWB antennas. In addition, the results indicate that nano-Ag inks could be used for embedded electrodes, since due to the low processing temperature, no reactions with Ag could be detected. Another

advantage of the proposed method is the controllability of the dimensions of the components during fabrication. The mould precisely determines the dimensions of the final component because there is no measurable shrinkage after pressing. Low temperatures will also enable seamless integration of the ceramic components with polymers.

Acknowledgements

The work leading to these results has received funding from the European Research Council (ERC) under the ERC grant agreement n° 291132. Author H.K. gratefully acknowledges the financial support from the Seppo Säynäjäkangas Foundation, the Riitta and Jorma J. Takanen Foundation, the Tauno Tönning Foundation, the Ulla Tuominen Foundation, the Finnish Foundation for Technology Promotion and the KAUTE foundation. Author J.J. acknowledges the funding by the Academy of Finland (project number 267573).

References

[1] S. Mei and Z.Y. Ping, A chip antenna in LTCC for UWB radios, IEEE T. Antenn. Propag. 56 (2008) 1177 – 1180.

[2] M.K. Mandal, Z.N. Chen, X. Qing, Compact ultra-wideband filtering antennas on low temperature co-fired ceramic substrate, Asia Pacif. Microwave (2009) 2084 – 2087.

[3] B. Hussain, I. Kianpour, V. Grade Tavares, H.S. Mendonca, G. Miskovic, G. Radosavljevic, V.V. Petrovic, Design considerations for LTCC based UWB antennas for space applications, Wireless for Space and Extreme Environments (WiSEE), 2014 IEEE Conference on (2014) 1 – 5.

[4] D. Zhou, L.-X. Pang, Z.-M. Qi, B.-B. Jin, X. Yao, Novel ultra-low temperature co-fired microwave dielectric ceramic at 400 degrees and its chemical compatibility with base metal, Sci. Rep. 4 (2014) 5980.

[5] D. Zhou, C.A. Randall, H. Wang, L.-X. Pang, X. Yao, Microwave dielectric ceramics in Li_2O-Bi_2O_3-MoO_3 system with ultra-low sintering temperatures, J. Am. Ceram. Soc. 93 (2010) 1096 – 1100.

[6] L. He, D. Zhou, H. Yang, Y. Niu, F. Xiang, H. Wang, Low-temperature sintering Li_2MoO_4/$Ni_{0.5}Zn_{0.5}Fe_2O_4$ magneto-dielectric composites for high-frequency application, J. Am. Ceram. Soc. 97 (2014) 2552 – 2556.

[7] J. Guo, D. Zhou, S.-L. Zou, H. Wang, L.-X. Pang, X. Yao, Microwave dielectric ceramics Li_2MO_4 – TiO_2 (M = Mo, W) with low sintering temperatures, J. Am. Ceram. Soc. 97 (2014) 1819 – 1822.

[8] K. Fukuda, R. Kitoh, I. Awai, Jpn. J. Appl. Phys. 32, Microwave characteristics of TiO_2-Bi_2O_3 dielectric resonator (1993) 4584 – 4588.

[9] H. Kähäri, M. Teirikangas, J. Juuti, H. Jantunen, Dielectric properties of lithium molybdate ceramic fabricated at room temperature, J. Am. Ceram. Soc. 97 (2014) 3378 – 3379.

[10] H. Kähäri, M. Teirikangas, J. Juuti, H. Jantunen, Improvements and modifications to room-temperature fabrication method for dielectric Li_2MoO_4 ceramics, J. Am. Ceram. Soc. 98 (2015) 687 – 689.

[11] O.P. Barinova, F.A. Danevich, V.Ya. Degoda, S.V. Kirsanova, V.M. Kudovbenko, S. Pirro, V.I. Tretyak, First test of Li_2MoO_4 crystal as a cryogenic scintillating bolometer, Nucl. Instrum. Meth. A 613 (2010) 54 – 57.

[12] T.W.S. Yip, E.J. Cussen, C. Wilson, Spontaneous formation of crystalline lithium molybdate from solid reagents at room temperature, Dalton T. 39 (2010) 411 – 417.

[13] S.B. Cohn, Microwave bandpass filters containing high-Q dielectric resonators, IEEE T. Microw. Theory 16 (1968) 218 – 227.

Figure captions

Figure 1. Backscattered electron images of Li_2MoO_4-TiO_2 composite ceramics fabricated by the room-temperature densification method and post-processed at 120 °C with a) 15 vol% of TiO_2 and fabricated from larger particle sized Li_2MoO_4 powder (sieved with a mesh size of 180 µm) b) 20 vol% of TiO_2 and fabricated with smaller particle sized Li_2MoO_4 powder (sieved with a mesh size of 45 µm).

Figure 2. X-ray diffraction patterns of a) fabricated Li_2MoO_4-TiO_2 (rutile) ceramic composites, and b) Li_2MoO_4-TiO_2 ceramic composites with 30 vol% of rutile TiO_2 and 20 wt% of Ag.

Figure 3. Calculated and measured relative permittivity, loss tangent values and temperature coefficient of permittivity of the Li_2MoO_4-TiO_2 composite ceramics fabricated at room temperature at ~9 GHz. Composites with 10–15 vol% and 20–30 vol% of TiO_2 were fabricated from Li_2MoO_4 powder sieved with mesh sizes of 180 µm and 45 µm, respectively.

Table 1. Densities and microwave dielectric properties of Li_2MoO_4-TiO_2 composite ceramics fabricated by a room-temperature densification method and post-processed at 120 °C for 24 h

vol% of rutile TiO_2	Sample density (g/cm^3)	Density (% of theoretical)	Measurement f (GHz)	ε_r	tan δ	$TC\varepsilon_r$ (ppm/°C)
0	2.83	93	9.50	5.1	0.0004	320
10	2.82	89	9.42	6.9	0.0011	180
15	2.83	88	9.41	7.2	0.0020	125
20	2.88	88	9.22	8.7	0.0023	20
25	2.88	86	9.13	9.5	0.0027	-85
30	2.90	86	9.10	10.1	0.0038	-170