Direct integration of dielectric all-ceramic thick films on a polymer substrate using room temperature fabrication

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A B S T R A C T
Direct integration of all-ceramic thick films and a polymer substrate has been realized for the first time without high temperature processing using the Room Temperature Fabrication method.

Printable Li$_2$MoO$_4$-BaTiO$_3$ composite pastes with 0, 10, and 20 vol.% of BaTiO$_3$ were fabricated from the respective ceramic powders and water without organic additives or vehicles. The pastes were stencil printed on a polyimide substrate and dried at 120 °C without pressing or lamination.

Using scanning electron microscopy, the films were observed to be in seamless contact with the substrate and to have a uniform microstructure. Relative permittivities of the ceramic films increased from 4.2 to 7.2 (at 2.5 GHz) and 4.5 to 7.5 (at 9.9 GHz) according to the vol.% content of the added BaTiO$_3$, with corresponding dielectric losses from 10$^{-3}$ to 10$^{-2}$.

The results show that the room temperature fabrication method enables 2D printing of all-ceramic thick films on temperature-sensitive substrates.

1. Introduction
Printed electronics technology offers the means for the easy and cost-efficient manufacture of electronic devices with a high output. The various techniques are all additive by nature which minimizes the material waste. The most simple, adaptable and cheap technique is screen printing. Using viscous paste-like materials, 0.1–100 μm thick layers called thick films are produced on top of a substrate. [1–3]

In general, thick films are polymer composites, where the functional ceramic particles are bound by the polymer matrix enabling easy processing at relatively low temperatures [4–6]. However, there is a clear requirement, from the component point of view, for all-ceramic thick films due to their versatile electrical properties. On the other hand, all-ceramic films require a high manufacturing temperature (hundreds or over 1000 °C) which hinders their integration with temperature-sensitive substrates.

The Room Temperature Fabrication method (RTF) has previously been introduced for bulk structures [7]. It offers the means for low-temperature ceramics processing without the use of polymeric matrixes or organic additives. In these studies, the RTF utilized the water solubility of a ceramic material to form an aqueous phase, which aided the packing of the solid ceramic particles during pressing. The ceramic material studied for the RTF was lithium molybdate (Li$_2$MoO$_4$), a non-toxic dielectric material with low relative permittivity ($\varepsilon_r$) and loss tangent (tan $\delta$). The results showed $\varepsilon_r$ of 5.1 and tan $\delta$ of 0.0004 measured at 9.6 GHz [7].

In this paper, the RTF was adapted to the 2D printing of all-ceramic thick films on a polymer substrate for the first time. This offers a simple route to the manufacture of a printing paste without organic vehicles or solvents and, consequently, without a binder burnout stage. In addition, the process does not require any additional steps such as pressing or lamination. Li$_2$MoO$_4$-based pastes with different amounts of insoluble barium titanate (BaTiO$_3$) were prepared to modify the dielectric properties of the films. The pastes were characterized by their viscosity and yield properties. The surface roughness and microstructure of the resulting all-ceramic thick films were studied as well as the dielectric properties at 2.5 and 9.9 GHz.

2. Materials and methods

2.1. Preparation and characterisation of the pastes
Three different Li$_2$MoO$_4$-based pastes with BaTiO$_3$ contents of 0, 10, and 20 vol.% were fabricated. The starting powders for the pastes were prepared according to Ramachandran et al. [8], except that a smaller mesh size of 90 μm was chosen to be used in sieving due to the stencil...
was to keep the amount of water as low as possible without compromising printability of the paste and the surface smoothness of the printed films. Extra water increases the drying time, resulting in larger shrinkage, and can increase porosity [10]. When suitable compositions were found, the viscosities of the pastes were studied and matched. As a result, recipes for optimized pastes were established (Table 1). Careful mixing with a spatula produced uniform viscous pastes.

A study of the viscosities and yielding behaviour of the pastes was conducted using a rheometer (Discovery HR-1, TA Instruments, New Castle DE) with a 40 mm parallel steel plate geometry and a 1 mm gap between the plates. To prevent drying of the pastes during the measurements, a plastic cover was employed. First, the pastes were preconditioned to 22 °C. Then pre-shear with a 5 s⁻¹ shear rate for 1 min and a subsequent equilibrium period of 2 min was applied. To study the viscosity, flow ramps with shear rates of 1 to 200 s⁻¹ were measured. Yielding behaviour analyses were conducted at 1 Hz changing the oscillation stress from 0.1 to 3000 Pa.

The powders were characterized with a laser diffraction particle size analyzer (Beckman Coulter LS13320, Brea, CA) in isopropanol. For the powders containing 0, 10, and 20 vol.% BaTiO₃, mean particle sizes of 10, 8.8, and 7.2 μm were measured, while 99% of the particles were smaller than 31, 27, and 23 μm, respectively. No ultrasonic mixing was applied prior to the analysis because previously it had been observed to break down larger particles [9].

The starting point for the optimization of the paste compositions was to keep the amount of water as low as possible without compromising printability of the paste and the surface smoothness of the printed films. Extra water increases the drying time, resulting in larger shrinkage, and can increase porosity [10]. When suitable compositions were found, the viscosities of the pastes were studied and matched. As a result, recipes for optimized pastes were established (Table 1). Careful mixing with a spatula produced uniform viscous pastes.

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The pastes densities were measured with a pycnometer in 1-octanol (≥ 99.4 %, Sigma-Aldrich, St. Louis, MO) at the prevailing temperature of 22.3 °C. Because 1-octanol is immiscible in water it is thus suitable to use with pastes containing an aqueous phase. The density of 1-octanol at this temperature was measured to be 0.822 g/cm³.

### Table 1

| BaTiO₃ content (vol.%) | Li₂MoO₄ (g) | BaTiO₃ (g) | Deionized water (g) |
|-----------------------|------------|-----------|---------------------|
| 0                     | 10         | 0         | 2.4                 |
| 10                    | 10         | 2.2       | 2.6                 |
| 20                    | 10         | 5.0       | 3.4                 |
Table 2
Solids contents and densities of the printing pastes.

| BaTiO3 content (vol.%%) | Solids content (vol.%%) | Paste density (g/cm³) |
|-------------------------|-------------------------|-----------------------|
|                         | Before mixing           | After mixing          |
| 0                       | 58                      | 48                    |
| 10                      | 58                      | 48                    |
| 20                      | 55                      | 44                    |

water upon the preparation of the paste determined how much Li2MoO4 was dissolved.

An important property of a printing paste is to flow during printing and then to set immediately afterwards, meaning that the viscosity of the paste must decrease upon shear and again increase again when the shear is released [1,15]. In the current case, the pastes expressed this shear-thinning behaviour (Fig. 1a) even without the use of organic solvents or other additives. The pastes exhibited similar viscosities at low shear rates (< 20 s⁻¹). At higher rates, the paste with 20 vol.% BaTiO3 had a lower viscosity due to the slightly lower solid content.

The amount BaTiO3 particles had an effect on the yielding behaviour of the pastes (Fig. 1b). The disruption of the paste network occurred at different oscillation stresses because of the differences in the paste composition. The yield point for the pastes increased with increasing BaTiO3 content. It was observed to be at 21, 145, and 440 Pa for the pastes containing 0, 10, and 20 vol.% BaTiO3, respectively (Fig. 1b). This meant that 10 or 20 vol.% addition of BaTiO3 particles was able to make the paste network significantly stronger.

Previously, a similar Li2MoO4-based paste was designed for 3D printing using extrusion [9]. Compared to the pastes presented here, the 3D printing paste exhibited similar shear-thinning behaviour but a higher viscosity because of the larger solid content (60.0 vol.%). Differences in the optimal paste composition resulted from the printing technique used: with extrusion, the pressure forcing the paste to flow is larger, which is why a more viscous paste suffices in this case.

3.2. Ceramic thick films

The average thickness of the ceramic films was 73 μm. The films were slightly thicker at the edges, especially at the edge where the squeegee exits the aperture during printing. This indicated an accumulation of the paste against the stencil edge and its subsequent lifting with the stencil releasing back to the gap position after printing. Compared to the stencil height of 100 μm, the films were somewhat thinner because of shrinkage. With increasing BaTiO3 content, the surface roughness decreased from 3.5 μm to 2.0 μm. This was due to the different water content (Table 2) and the mean particle size in the pastes. Smooth surfaces are desirable when dimensionally accurate conductive lines on top of the film are needed. The surface microstructures showed no cracking upon drying, however, some pinholes were observed (Fig. 2b).

The densities of the ceramic films were measured as 2.02, 2.29, and 2.45 g/cm³ with BaTiO3 contents of 0, 10, and 20 vol.%, respectively, which corresponded to relative densities of 66–69 %.

Microstructural analysis of the sample cross-sections showed that the ceramic films were in seamless contact with the substrate (Fig. 3a). Furthermore, the BaTiO3 particles were evenly distributed between the Li2MoO4 particles as agglomerate-like clusters while some porosity could also be observed (Fig. 3b-d).

The dielectric properties of the samples are presented in Tables 3 (at 2.5 GHz) and 4 (at 9.9 GHz). For the plain polyimide substrate, εr of 3.4 was measured at both frequencies with tan δ values of 0.007 at 2.5 and 0.008 at 9.9 GHz. The substrate affected the measured overall dielectric properties of the samples (ceramic film and substrate). The values of εr and tan δ increased with respect to the amount of added BaTiO3. This was expected since BaTiO3 is commonly used to adjust the dielectric properties of composites [4,6–8,16–20].

Previously, Li2MoO4 ceramics have been manufactured with RTF using pressing in a mould and extrusion based 3D printing [7,9]. At 9.6 GHz these samples exhibited εr of 5.1 and 4.4, and tan δ of 0.0004 and 0.0006, respectively. Compared to the ceramic film with 0 vol.% of BaTiO3 measured at a similar frequency of 9.9 GHz (Table 4), the value of εr matched that of the 3D printed sample. However, tan δ was twice as high.

RTF manufacture of Li2MoO4-based composites from 10 vol.% of BaTiO3 using pressing in a mould resulted previously in εr of 8.2 and tan δ of 0.026 at 9.2 GHz [7]. Here, the corresponding sample, a ceramic film with 10 vol.% of BaTiO3, exhibited somewhat lower εr, while tan δ was the same magnitude of 10⁻² at a similar frequency of 9.9 GHz (Table 4). Similar samples with 9 vol.% of nanosized BaTiO3 have also been manufactured for a weight optimized antenna, which exhibited εr of 10.5 and tan δ of 0.006 at 1 GHz [8].

Despite the fact that RTF was applied in all of the above-mentioned cases, different manufacturing techniques were used for the sample.

Fig. 1. a) Viscosity of pastes at different shear rates showing shear-thinning behaviour, and b) dynamic mechanical analysis at 1 Hz showing the yield points of the different pastes.
preparation and thus different paste compositions were needed. As a result, the dielectric properties of the resulting samples differed from case to case. This was due to the different densities. Moreover, the dielectric properties of BaTiO$_3$ depend on the measurement frequency as well as on the particle and grain sizes [21] which makes comparison of dielectric properties between different BaTiO$_3$ containing composites difficult.

Fig. 2. a) Surface profile of a corner of a sample with 20 vol.% BaTiO$_3$ (yellow to red) showing the accumulated paste at the sample edge (white arrow). b) Secondary electron microscope image of the same sample demonstrating the typical crack-free surface microstructure with a pinhole (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

Fig. 3. Electron microscope images of a sample cross-sections at the polyimide substrate interface. a) Secondary electron image of a sample with 10 vol.% BaTiO$_3$ shows the seamless contact with the substrate. Back-scattered electron images of samples with b) 0, c) 10 with an inserted image of Li$_2$MoO$_4$-BaTiO$_3$ interface, and d) 20 vol.% BaTiO$_3$, where the grey particles represent Li$_2$MoO$_4$ and the small white dots BaTiO$_3$, respectively. Black areas between the particles denote porosity.

| BaTiO$_3$ content (vol. %) | Ceramic film and substrate | Ceramic film |
|----------------------------|----------------------------|--------------|
|                            | $\varepsilon_r$ | $\tan \delta$ | $\varepsilon_r$ | $\tan \delta$ |
| 0                          | 3.6 ± 0.1 | 0.005 ± 0.001 | 4.2 ± 0.3 | 0.005 ± 0.001 |
| 10                         | 4.3 ± 0.1 | 0.008 ± 0.002 | 6.1 ± 0.4 | 0.012 ± 0.002 |
| 20                         | 4.7 ± 0.1 | 0.014 ± 0.002 | 7.2 ± 0.3 | 0.022 ± 0.003 |

Table 3
The average values of dielectric properties of the samples measured at 2.5 GHz.

| BaTiO$_3$ content (vol. %) | Ceramic film and substrate | Ceramic film |
|----------------------------|----------------------------|--------------|
|                            | $\varepsilon_r$ | $\tan \delta$ | $\varepsilon_r$ | $\tan \delta$ |
| 0                          | 3.8 ± 0.2 | 0.006 ± 0.001 | 4.5 ± 0.6 | 0.001 ± 0.001 |
| 10                         | 4.5 ± 0.1 | 0.010 ± 0.002 | 6.6 ± 0.3 | 0.011 ± 0.003 |
| 20                         | 4.9 ± 0.1 | 0.016 ± 0.001 | 7.5 ± 0.6 | 0.022 ± 0.001 |

Table 4
The average values of dielectric properties of the samples measured at 9.9 GHz.

4. Conclusions

The Room Temperature Fabrication method, used earlier to fabricate bulk ceramics with pressing in a mould and with 3D printing, is now shown for the first time to be feasible also in the 2D printing of all-ceramic thick films.

The compositions of the Li$_2$MoO$_4$-based printable pastes were optimized without organic additives or vehicles, just by controlling the
amount of water. Composite manufacture with 10 and 20 vol.% of BaTiO₃ allowed adjustment of the dielectric properties. These results indicate that this approach allows the fabrication of all-ceramic composite thick films with a very broad variety of electrical properties by the selection of different ceramic fillers. Further investigations should also include detailed adhesion testing although the ceramic film and polymer substrate appeared to be in seamless contact.

Declaration of Competing Interest

None.

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