



Low firing temperature zinc molybdate ceramics for dielectric and insulation applications

Zijing Wang, Robert Freer*

School of Materials, University of Manchester, Manchester M13 9PL, United Kingdom

Received 23 February 2015; received in revised form 16 April 2015; accepted 17 April 2015

Abstract

Low temperature firing, non-stoichiometric zinc molybdate ($11\text{ZnO}-10\text{MoO}_3$) dielectric ceramics (NSZM) were prepared by the mixed oxide route with additions of B_2O_3 . All products were sintered at $850-950^\circ\text{C}$ to over 96% theoretical density with co-existence of ZnMoO_4 and $\text{Zn}_3\text{Mo}_2\text{O}_9$ phases. The addition of B_2O_3 reduced the proportion of $\text{Zn}_3\text{Mo}_2\text{O}_9$ secondary phase. The relative permittivities of NSZM samples ranged from 9.2 to 11.1; the breakdown strength was between 14.3 and 17.6 kV/mm. Impedance spectroscopy suggested that charge transport in the grain boundary region governed the breakdown strength. NSZM prepared with 1.0 wt% B_2O_3 exhibited a relative permittivity of 11.1, dielectric strength of 17.6 kV/mm, thermal expansion coefficient of 4.7 ppm/K and thermal conductivity of 1.3 W/(m K). The results indicate that NSZM is a promising candidate for dielectric and high temperature insulation applications.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Keywords: Dielectric; Relative permittivity; Breakdown strength; Thermal conductivity; Insulator

1. Introduction

The modern aviation industry is moving towards the concept of the ‘More Electric Aircraft (MEA)’ which involves replacing on-engine pneumatic and hydraulic systems with electrical machines [1]. In this way the reliability of the aircraft is improved by reducing the number of gearboxes and fuel efficiency is improved by the reduction of weight [2]. As a consequence there is growing interest in the use of electrical machines (motors and generators) at temperatures higher than 350°C [3]. Conventional polymeric coated wires are not suitable for the electrical windings because the insulation cannot withstand such high temperatures for extended periods.

Traditional ceramic insulators [4] (e.g. Al_2O_3 and AlN) are candidates for high temperature wire insulation because of their excellent dielectric and thermal properties. Unfortunately, the high temperatures [5] required to produce dense coatings of these materials would prohibit co-firing with the Cu conductors.

However, low temperature co-fired ceramic (LTCC) technology may offer a solution [6]. Any LTCC candidate material for the insulation applications should have (i) sintering temperature lower than the melting point of Cu (1081°C) to enable co-firing with the conductor materials, (ii) low relative permittivity (ϵ_r) to suppress discharges under high-voltage conditions, (iii) adequate dielectric strength ($>10\text{ kV/mm}$) to enable its operation at high voltage levels, (iv) thermal expansion coefficient close to that of Ni (13 ppm/K) to minimize the thermal stress under thermal-cycle conditions and (v) high thermal conductivity to dissipate the I^2R heat generated (by the conductor) quickly to ambient environments [4]. Molybdate based ceramics meet many of these requirements; they can be sintered at low temperatures and exhibit good microwave dielectric properties [7–10]. Zhou et al. [7] showed that $\text{Li}_2\text{Zn}_2\text{Mo}_2\text{O}_{12}$ ceramic sintered at 650°C exhibits a low relative permittivity of 11.1 and a high dielectric quality factor (product of Q and measurement frequency f) of 55,000 GHz. Although the lithium molybdates have ultra-low sintering temperatures, Sebastian et al. [8] suggested that for the Mg analogue ($\text{Li}_2\text{Mg}_2\text{Mo}_3\text{O}_{12}$) highly mobile Li^+ ions can cause increased conductivity at 400°C ; this may limit the use of such materials in high temperature insulating

* Corresponding author. Tel.: +44 161 306 3564.

E-mail address: Robert.Freer@manchester.ac.uk (R. Freer).

applications. Choi et al. [9] investigated the family of AMoO_4 ceramics ($A = \text{Ca, Sr, Ba, Mg, Zn, Mn}$), and found that ZnMoO_4 , sintered at 950°C , exhibits acceptable microwave dielectric properties: $\epsilon_r < 15$, $Qxf > 30,000$ GHz. Whilst the LTCC material ZnMoO_4 is considered to be a good candidate for microwave dielectric applications [9], there are no published data for dielectric strength, thermal expansion or thermal conductivity. In a subsequent study, Guo et al. [10] was not able to sinter ZnMoO_4 to greater than 94% theoretical density; the resulting porosity would have an impact on both dielectric strength and thermal conductivity of the ceramic insulator.

B_2O_3 has frequently been employed as a fluxing agent for preparation of LTCC materials. By adding 3 wt% B_2O_3 to CaWO_4 , Kim et al. [11] were able to reduce the optimum sintering temperature from 1100 to 900°C . Sarkar et al. [12] reported a beneficial increase in the dielectric strength of BaTiO_3 prepared with borate additions. Thus, B_2O_3 is a valuable sintering additive that can simultaneously reduce the sintering temperature and improve breakdown strength.

The objective of the present study was to investigate the processing and properties of ZnO-MoO_3 based ceramic materials, with a view to exploring their suitability as low temperature firing materials for dielectric and high temperature insulation applications.

2. Experimental

Zinc molybdate ceramics ZnMoO_4 (abbreviated as ZMO) were synthesized via conventional mixed oxide route. Stoichiometric ZnO and MoO_3 powders (both 99.95%, from Alfa Aesar) were mixed and wet milled for 24 h using propan-2-ol and yttria-stabilized zirconia media. The mixture was dried in an oven, calcined at 600°C in air for 16 h, then re-milled for 24 h and dried. The resulting powder was pressed into pellets of 10 mm diameter and sintered in air at $650\text{--}850^\circ\text{C}$ for 2 h. To improve densification of zinc molybdate, the ZnO and MoO_3 powders were mixed in a non-stoichiometric ratio of 11:10 (denoted as NSZM). The mixed powders were processed in a similar way to the stoichiometric formulation, but milled, dried and calcined at 700°C for 16 h, re-milled, dried and pressed into pellets which were sintered at $800\text{--}950^\circ\text{C}$ in air for 2 h. In additional batches, 0.5, 1.0 and 2.0 wt% B_2O_3 was added to calcined NSZM powders (denoted as NSZM05B, NSZM10B and NSZM20B, respectively) and ball milled for a further 24 h. These powders were dried, pressed into pellets and sintered in air at $850\text{--}950^\circ\text{C}$ for 2 h.

Bulk densities of the sintered pellets were determined by the Archimedes' method. Phase identification and crystal structure analysis of the sintered products were undertaken using a Philips X'PERT X-ray diffraction (XRD) system (PW1700) over the 2θ range $10\text{--}60^\circ$ in steps of 0.05° . All sintered specimens were ground using 1200 grade SiC paper before analysis. The lattice parameters and phase composition were determined using the Rietveld refinement method [13] using Topas 4.1 software. Before microstructural analysis, samples were ground on 2500 and 4000 SiC papers, and polished using colloidal silica suspension. The microstructures of the polished specimens were

examined by a Philips XL 30 Field Emission Gun Scanning Electron Microscope (SEM) equipped with energy dispersive spectroscopy facility for chemical analysis.

The relative permittivity was determined at room temperature as a function of frequency from 1 kHz to 1 MHz using a Hewlett Packard 4192A LF impedance analyser. Measurements were made in parallel plate capacitor mode; specimens were in the form of discs, 10 mm diameter and 1 mm thick. The planar surfaces of the specimens were sputtered with a thin layer of platinum. For impedance analysis the same type of specimens were instead coated with silver paste and annealed at 550°C for 30 min in air. Impedance spectra were collected from 5 Hz to 12 MHz at temperatures of $25\text{--}600^\circ\text{C}$ (in steps of 25°C) using the HP 4192A LF impedance analyser.

The dielectric strength was determined by a method based on the ASTM standard [14]. Specimens were 10 mm diameter discs and 1 mm thick. Planar surfaces were ground on SiC down to 4000 SiC grade, polished on $0.25\ \mu\text{m}$ diamond cloth and cleaned in acetone. Newly polished, hemispherical shaped brass electrodes (40 mm diameter) were clamped to planar faces, and the test unit was immersed in an oil bath to suppress corona effects. The electrodes were connected to an 80 kV Ferranti step up transformer operating at 60 Hz. The applied voltage was increased uniformly at $500\ \text{V s}^{-1}$ until electrical breakdown occurred.

The coefficient of thermal expansion of sintered NSZM samples was determined using a Netzsch DIL-420 PC dilatometer. Samples 10 mm diameter and 10 mm long were heated from 25°C to 500°C at a rate of 3°C min^{-1} . Thermal diffusivity was determined using the laser flash technique (in-house facility); heat capacity was determined using a Netzsch STA-449-C Differential Scanning Calorimeter, with measurements made up to 500°C using a sapphire standard. From the heat capacity (C_p), thermal diffusivity (λ), and bulk density (ρ), the thermal conductivity (κ) was calculated from Eq. (1):

$$k = C_p \lambda \rho \quad (1)$$

3. Results and discussion

3.1. Densification

Stoichiometric ZnMoO_4 ceramics (ZMO) sintered at $650\text{--}850^\circ\text{C}$ achieved a maximum density of only $3.82\ \text{g/cm}^3$ (88% theoretical), consistent with the findings of Guo et al. [10]. In contrast for the non-stoichiometric ceramics, densities in excess of 96% theoretical were readily achieved (Fig. 1 and Table 1). The density of NSZM samples increased with sintering temperature, reaching 96.2% theoretical by 950°C . Addition of B_2O_3 to the starting formulations enabled liquid phase-assisted sintering, and a reduction in the sintering temperature; for samples prepared with 1 wt% B_2O_3 (NSZM10B), for example, the optimum sintering temperature was 850°C (Fig. 1).

3.2. Phase analysis

X-ray diffraction spectra for sintered bodies of ZMO, NSZM and NSZM prepared with additions of B_2O_3 are shown

Download English Version:

<https://daneshyari.com/en/article/10629370>

Download Persian Version:

<https://daneshyari.com/article/10629370>

[Daneshyari.com](https://daneshyari.com)