Novel ultra-low temperature co-fired microwave dielectric ceramic at 400 degrees and its chemical compatibility with base metal

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A novel NaAgMoO\textsubscript{4} material with spinel-like structure was synthesized by using the solid state reaction method and the ceramic sample was well densified at an extreme low sintering temperature about 400°C. Rietveld refinement of the crystal structure was performed using FULLPROF program and the cell parameters are $a = b = c = 9.22039$ Å with a space group $Fd-3M$ (227). High performance microwave dielectric properties, with a permittivity $\approx 7.9$, a Qf value $\approx 33,000$ GHz and a temperature coefficient of resonant frequency $\approx -120$ ppm/°C, were obtained. From X-ray diffraction (XRD) and Energy Dispersive Spectrometer (EDS) analysis of the co-fired sample, it was found that the NaAgMoO\textsubscript{4} ceramic is chemically compatible with both silver and aluminum at the sintering temperature and this makes it a promising candidate for the ultra-low temperature co-fired ceramics technology. Analysis of infrared and THz spectra indicated that dielectric polarizability at microwave region of the NaAgMoO\textsubscript{4} ceramic was equally contributed by ionic displasive and electronic polarizations. Its small microwave dielectric permittivity can also be explained well by the Shannon’s additive rule.

Microwave dielectric ceramics have been widely used as the dielectric resonator, filter, substrate, capacitor etc. in the past half century\textsuperscript{1,2}. Most microwave dielectric ceramics are inorganic, poly-crystal oxides, such as the popular $\text{Al}_2\text{O}_3$, $\text{BaO- TiO}_2$ etc. Usually, the ceramic materials are strong in compression, weak in shearing and tension. Recent years due to the fast development of the electronic devices, the organic has become hot while the ceramic has become “colder”. However, some central passive devices can only be made using ceramic materials. Low temperature co-fired ceramic (LTCC) technology has played an important role in the fabrication of modern electronic devices\textsuperscript{3-4}. Advantage of this technology is that the green tape, consisting of inorganic powders and organic materials, is soft and easy to be processed layer by layer separately in the meantime, and finally passive components can be integrated within a monolithic bulk module with IC chips mounted on the surface. Appropriate permittivity ($\varepsilon_r$), high quality factor (Qf), and lower sintering temperature (S. T.) than the melting point of inner metal electrode are required for the dielectric ceramics to meet LTCC technology.

The most popular method to lower sintering temperature of dielectric ceramic with high microwave dielectric performance is the addition of glass or low melting point oxides ($\text{B}_2\text{O}_3$ based, $\text{SiO}_2$ based etc.)\textsuperscript{5}. The addition usually caused the deterioration of Qf value. In the past decade, a so-called ultra-low temperature co-fired ceramic (ULTCC), which is focused on the microwave dielectric ceramic with intrinsic low sintering temperature, has started a new stage for the LTCC technology. The two classic examples are $\text{BaTe}_4\text{O}_9$ ($\varepsilon_r = 17.5$, Qf = 54,700 GHz and S. T. = 550°C) and $\text{Bi}_2\text{Mo}_2\text{O}_9$ ($\varepsilon_r = 38$, Qf = 12,500 GHz and S. T. = 620°C) ceramics, which was reported in 2005 and 2008, respectively\textsuperscript{5,6}. Both of them are chemically compatible with aluminum, which means that Al can be used as the inner electrode. The search of novel ULTCC in the low eutectic points Mo-rich and Te-rich compounds has attracted more and more attention\textsuperscript{7,8}. In the present work, a novel spinel-like compound NaAgMoO\textsubscript{4} with an extreme low sintering temperature about 400°C was reported. The preparation, sintering...
behavior, microwave dielectric properties and chemical compatibility with both silver and aluminum were studied in detail.

Figure 1 (a) shows XRD patterns of the NaAgMoO₄ samples calcined at 350 °C/4 h, sintered at 400 °C/4 h, co-fired with 30 wt. % silver at 400 °C/4 h and 30 wt. % aluminum at 450 °C/4 h. It is seen that single phase with spinel-like structure was formed after calculations at 350 °C. However, a weak trace of silver is observed at 38.1 °C and it may be caused by decomposition of the Ag₂CO₃ during calculations process. As seen from XRD patterns of the co-fired samples, only peaks of the metal and NaAgMoO₄ phases were revealed, which means that both silver and aluminum are chemically compatible with the NaAgMoO₄ ceramic at the sintering temperature. To study crystal structure details of the NaAgMoO₄ ceramic, refinements were carried out using Fullprof software based on the fine XRD data. Both the situations of single and composite phases (spinel and silver) were considered. The observed and calculated XRD patterns are shown in Fig. 1 (b). The refined values of lattice parameters are \( a = b = c = 9.22039 \text{ Å} \), with a space group F D \( 3 \text{M} \) (227), according to the data (ICSD #139740) reported by Bouhemadou et al. \(^7\). The \( R_p = 12.1, R_w = 14.8 \) and \( R_{exp} = 6.82 \) were obtained for single phase case as shown in Table I, while the \( R_p = 11.2, R_w = 13.6 \) and \( R_{exp} = 6.79 \) were obtained for the composite phase and the ratio of silver phase is around 1.99%. In fact, due to the limited sensitivity and it may be caused by decomposition of the Ag₂CO₃ during calcination by using a classical harmonic oscillator model as follows:

\[
\varepsilon^*(\omega) = \varepsilon\infty + \sum_{j=1}^{n} \frac{\alpha_j}{\omega_j^2 - \omega^2 - j\gamma_j \omega},
\]

Figure 1 | X-ray diffraction patterns of the NaAgMoO₄ sample calcined at 350 °C/4 h, 400 °C/4 h, co-fired ceramic sample with 30 wt. % silver at 400 °C/4 h and 30 wt. % aluminum at 450 °C/4 h (a), and the experimental (circles) and calculated (line) X-ray powder diffraction profiles for NaAgMoO₄ sample, which was though as a single phase (b) \((R_p = 12.1, R_w = 14.8 \) and \( R_{exp} = 6.82 \). The short vertical lines below the patterns mark the positions of Bragg reflections. The bottom continuous line is the difference between the observed and calculated intensity).

| Atom | Site | Occ. | x     | y     | z     | Biso |
|------|------|------|-------|-------|-------|------|
| Mo   | 8a   | 0.042| 0.12500| 0.12500| 0.12500| 0.534 |
| Na   | 16d  | 0.042| 0.50000| 0.50000| 0.50000| 1.197 |
| Ag   | 16d  | 0.042| 0.50000| 0.50000| 0.50000| 1.197 |
| O    | 32e  | 0.167| 0.23460| 0.23460| 0.23460| 0.777 |

To further study the intrinsic microwave dielectric properties, infrared reflectivity spectra of the NaAgMoO₄ ceramics were analyzed by using a classical harmonic oscillator model as follows:

\[
\varepsilon^*(\omega) = \varepsilon\infty + \sum_{j=1}^{n} \frac{\alpha_j}{\omega_j^2 - \omega^2 - j\gamma_j \omega},
\]

where \( \varepsilon^*(\omega) \) is complex dielectric function, \( \varepsilon\infty \) is the dielectric constant caused by the electronic polarization at high frequencies, \( \gamma_j, \alpha_j \)
and \( \omega_p \) are the damping factor, the transverse frequency, and plasma frequency of the j-th Lorentz oscillator, respectively, and n is the number of transverse phonon modes. The complex reflectivity \( R(\omega) \) can be written as:

\[
R(\omega) = \frac{1 - \sqrt{\frac{\epsilon}{\epsilon_0}} \times (\omega)}{1 + \sqrt{\frac{\epsilon}{\epsilon_0}} \times (\omega)},
\]

(2)

Fitted infrared reflectivity values, complex permittivities and phonon parameters are shown in Fig. 3 (b) and Table II. It is seen that the calculated dielectric permittivity and dielectric loss values are almost equal to the measured ones using TE_01 method, which implies that majority of the dielectric contribution for this system at microwave region was attributed to the absorptions of structural phonon oscillation in infrared region and very little contribution was from defect phonon scattering. The optical dielectric constant calculated from the infrared spectra is about 3.07, which is almost 39% percent of the polarizability contribution at microwave region, and this implies that the contribution from the electronic polarizability can not be ignored in the low k (<10) microwave dielectric materials. The dielectric polarizability contribution of the strongest mode at 809.2 cm\(^{-1}\) is only 0.622, about 8% percentage, and this is due to its much higher frequency than the microwave region. The calculated dielectric loss is almost the same with the measured value and this means that there is no much space for the increase of Qf value by improving sintering process. The small microwave dielectric permittivity of NaAgMoO\(_4\) ceramic can also be explained by the Shannon’s additive rule. At microwave region, the polarizability is the sum of both ionic and electronic components. Shannon\(^{10}\) suggested that molecular polarizabilities of complex substances could be estimated by summing the polarizabilities of constituent ions. Then the polarizabilities \( \alpha \) could be obtained as follows:

\[
\alpha_{NaAgMoO_4} = 2\alpha_{Na^+} + 2\alpha_{Ag^{1+}} + 2\alpha_{Mo^{6+}} + 4\alpha_{O^{2-}} \approx 15.37\, \text{Å}^3,
\]

(3)

where the ionic polarization of Ag\(^+\) was set to be 2.25 Å\(^3\) as suggested in our previous work\(^{11}\). The ionic polarization of Na\(^+\), Mo\(^{6+}\) and O\(^{2-}\) were set to be 1.80 Å\(^3\), 3.28 Å\(^3\) and 2.01 Å\(^3\), respectively\(^{10,12}\). Considering the Clausius–Mosotti relation as follow:

\[
\varepsilon = \frac{3V + 8\pi N}{3V - 4\pi N},
\]

(4)

where the V is the cell volume, 783.88/Å\(^3\). The calculated dielectric permittivity is about 6.75, which is a little smaller than the measured value 7.9 and the extrapolated value 7.85. A 14.5 percent deviation of permittivity from the measured value is considered acceptable considering the simplicity of additive rule and the uncertainty of ionic polarization of Ag\(^+\).

**Summary**

In conclusion, a novel NaAgMoO\(_4\) ceramic with high microwave dielectric performance, with a permittivity \(\sim 7.9\), a Qf value \(\sim 33,000\, \text{GHz}\) and a temperature coefficient of resonant frequency \(\sim -120\, \text{ppm/°C}\), can be well densified at 400 °C with grain size lying between 2 ~ 5 μm. From XRD and EDS analysis of the co-fired sample, it was found that the NaAgMoO\(_4\) ceramic is chemically compatible with both silver and aluminum at the sintering temperature and this makes it a candidate for the ultra-low temperature co-fired ceramics technology. Specifically, its densification temperature is almost half of that of the most popular low-fired Al\(_2\)O\(_3\) material with glass addition and it might be promising in the dielectric substrate application.

**Methods**

Reagent-grade Na\(_2\)CO\(_3\), Ag\(_2\)CO\(_3\), and MoO\(_3\) (>99%, Fuchen Chemical Reagents, Tianjin, China) were weighted according to the stoichiometric formulation NaAgMoO\(_4\). Powders were mixed and milled for 4 h by using a planetary mill. The calcined powders were set to be 1.80 Å\(^3\), 3.28 Å\(^3\) and 2.01 Å\(^3\), respectively\(^{10,12}\). Considering the simplicity of additive rule and the uncertainty of ionic polarization of Ag\(^+\).}

**Table II | Phonon parameters obtained from fitting of the infrared reflectivity spectra of NaAgMoO\(_4\) ceramic**

| Mode | \(\omega_{oj}\) | \(\omega_{pj}\) | \(\gamma_j\) | \(\Delta \gamma\) |
|------|---------------|---------------|-------------|--------------|
| 1    | 68.184        | 39.665        | 16.946      | 0.338        |
| 2    | 91.072        | 75.964        | 30.928      | 0.696        |
| 3    | 134.830       | 156.640       | 43.058      | 1.350        |
| 4    | 181.560       | 191.420       | 33.449      | 1.110        |
| 5    | 208.990       | 127.450       | 24.380      | 0.372        |
| 6    | 295.420       | 160.830       | 15.216      | 0.296        |
| 7    | 809.200       | 638.130       | 19.468      | 0.622        |

\(\omega_{oj} = 3.070\)  \(\epsilon_0 = 7.854\)

**Figure 2 | Bulk density of the NaAgMoO\(_4\) ceramic as a function of sintering temperature, and SEM image of NaAgMoO\(_4\) ceramic sintered at 400°C/2 h (a), BSE image of co-fired sample with 30 wt.% Ag at 400°C/4 h and EDS results (b).**
Dielectric properties at microwave frequency were measured and gate respectively two GaAs photoconductive antennas for the generation and detection of THz wave. Dielectric properties at microwave frequency were measured with the TE01 dielectric resonator method with a network analyzer (HP 8720 Network Analyzer, Hewlett-Packard) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The temperature coefficient of resonant frequency TCF ($\Delta f / f_0$) was calculated with the following formula:

$$\text{TCF} = \frac{f_T - f_0}{f_0 \times (T - T_0)} \times 10^6,$$

where $f_T$ and $f_0$ are the TE01, resonant frequencies at temperature T and T0, respectively.

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