Na$_2$CaV$_4$O$_{12}$: a low-temperature-firing dielectric with lightweight, low relative permittivity, and dielectric anomaly around 515 °C

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Abstract

A low temperature fired Na$_2$CaV$_4$O$_{12}$ ceramic was synthesized via a solid-state reaction route at a temperature range of 350-550 °C. The Thermal analysis confirmed the densification and melting temperature of Na$_2$CaV$_4$O$_{12}$ to be 530 °C and 580 °C, respectively. Dielectric properties together with the electrical conductivity were characterized at a broad frequency and temperature range. A super-low relative permittivity of $\varepsilon_r = 7.72$ and loss tangent of $\tan\delta = 0.06$ were obtained at 1 MHz at room temperature. A dielectric anomaly peak took place around 515 °C, which was associated with the phase transition from $P4/nbm$ to $P\bar{4}b2$. ac impedance spectrum coupled with complex modulus plots unveiled the electrical conduction mechanism, which was dominated by the short-range movement of the charge carriers at low temperatures ($T \leq 220$ °C) however long-range migration of charge carriers emerged at higher temperatures.

Keywords: Ceramics; Dielectric properties; Thermal analysis; ac impedance spectrum

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1. Introduction

Vanadates are inorganic compounds that consist of polyatomic oxovanadium ions. These materials have been extensively researched owing to their wide range of potential applications in phosphors, catalysts, chemical sensors, wireless telecommunications, and solid-state batteries\textsuperscript{[1-8]}. The functional diversity of vanadates is due to their structural uniqueness, with VO\textsubscript{4} polyhedral being the major building unit. The VO\textsubscript{4} tetrahedrons, like silicates, are linked by shared oxygens (polymerization). Depending on how vanadates are polymerized, they can take on a range of structural shapes, including chains, sheets, and three-dimensional blocks.\textsuperscript{[9-11]} Among them, a complex structural configuration, which is built by four isolated and double four-common-shared tetracyclic units [V\textsubscript{4}O\textsubscript{12}] in a unit cell, has been specialized because of the arrangement of all tetracyclic units in (101) plane\textsuperscript{[9]}. Only a few reports of such materials have been published so far, the majority of those reports are based on a generic formula M\textsubscript{2}M'(XO\textsubscript{3})\textsubscript{4}, e.g., Na\textsubscript{2}Sr(VO\textsubscript{3})\textsubscript{4}, CaY\textsubscript{2}(GeO\textsubscript{3})\textsubscript{4}\textsuperscript{[12]}. 

Initially, Krasnenko \textit{et al.} determined the crystal structure of Na\textsubscript{2}CaV\textsubscript{4}O\textsubscript{12} based on single-crystal and powder X-ray diffraction\textsuperscript{[13]}. Afterward, several authors confirmed the synthesis and crystal structure of Na\textsubscript{2}CaV\textsubscript{4}O\textsubscript{12}\textsuperscript{[10]} which has a tetragonal structure with space group \textit{P4/lbnm}. Based on the temperature dependence of relative permittivity, a ferroelectric phase transition was previously reported\textsuperscript{[14]}. However, the space group of Na\textsubscript{2}CaV\textsubscript{4}O\textsubscript{12} (\textit{P4/lbnm}) features a nonpolar centrosymmetric structure\textsuperscript{[9]}, which contradicts the ferroelectric state previously reported\textsuperscript{[12]}. Therefore, it is necessary to systematically study the dielectric of Na\textsubscript{2}CaV\textsubscript{4}O\textsubscript{12} to further understand this phenomenon and develop a better understanding of the structure-property relationship. Therefore, in this paper, extensive exploration of the phase formation, sintering behavior, microstructure evolution, and
electrical properties were carried out to link these fundamental aspects of Na$_2$CaV$_4$O$_{12}$ with properties.

2. Experimental procedure

Sample preparation: High purity-raw materials of Na$_2$CO$_3$ (99.99%), CaCO$_3$ (99.99%), and NH$_4$VO$_3$ (99.99%) were used to synthesize Na$_2$CaV$_4$O$_{12}$ ceramics via a conventional solid-state reaction route. Stoichiometrically weighted powders were mixed with ethanol and zirconia balls in a nylon jar using a planetary ball milling for 6 h and calcined subsequently in the air at 300 °C for 4 h in an alumina crucible. The calcines powders were re-milled using a planetary ball mill for 4 h to break the agglomerates to generate homogenous and fine particle size. The calcined and re-milled powders were dried and cold-pressed into disks of 10 mm in diameter and 1 mm in thickness. Finally, these disks were covered with powders of the same composition and sintered at 350-550 °C for 6 h inside a box furnace.

Characterization: PerkinElmer STA8000 was used to characterize thermal properties from room temperature to 600 °C. The phase purity and crystal structure of Na$_2$CaV$_4$O$_{12}$ were identified using X-ray diffraction (XRD, PANalytical, X-Pert-PRO, Almelo, Netherlands) technique with Cu Ka radiation. The results along with the Rietveld refinement were already published in our recent work $^{[15]}$. The microstructure was analyzed using scanning electron microscopy (SEM, JSM-6380, Japan). Raman-scattering measurements were used to examine spectroscopic characteristics using a Linkam MDS600 (Linkam, Tadworth, UK). The dielectric performance was measured via an impedance analyzer (Agilent Hyogo, USA) over the frequency range from 40 Hz to 1 MHz at various temperatures. The Z-View software was used to analyze the complex impedance data.
3. Results and discussion

3.1 Thermal analysis and sintering behavior

Figure 1 Thermogravimetric analysis/differential scanning calorimetry (TG/DSC) analysis of the Na_2CaV_4O_{12} sample: a) uncalcined mixed precursors; b) Na_2CaV_4O_{12} sample of fired at 550 °C.

Thermal analysis was used to investigate the chemical reaction and, in particular, probe the densification and melting of the target phase which is Na_2CaV_4O_{12}. This was carried out by monitoring the mass loss (TG) and heat flow (DSC) upon increasing temperature. For the un-calcined precursors, TG-DSC curves (Figure 1a) show complex processes of physical and chemical reactions. An endothermic peak at 108 °C in the DSC profile is related to the evaporation of water [8], which was also confirmed by a weak weight loss of about 2%. Two subsequent endothermic processes peaking at 196 °C and 232 °C with a total mass loss of about 11% were assigned as the decomposition of carbonates with the release of carbon dioxide [16]. Two exothermic peaks at 246 °C and 284 °C with a further ~ 10% weight loss resulted from the chemical reaction between raw materials [16]. Figure 1b shows a DSC curve of Na_2CaV_4O_{12} which was heated to a temperature of 550 °C. Upon further increasing temperature, a continuous exothermic process was observed till 532 °C. XRD analysis verified the single-phase nature of the sample sintered at 550 °C [13], suggesting the complete reaction.
taking place between the raw materials. Thus, this exothermic process was attributed to the solidification of \( \text{Na}_2\text{CaV}_4\text{O}_{12} \) ceramics and was regarded as the optimal densification temperature at 532 °C. Beyond this temperature, a subsequent endothermic process emerged along with a sharp endothermic peak at 580 °C, which was due to the melting of the \( \text{Na}_2\text{CaV}_4\text{O}_{12} \) sample.

![Figure 2a](image)

**Figure 2a** shows the variation in density (relative and bulk) with increasing sintering temperature. The sintering temperature plays a significant role in the densification of \( \text{Na}_2\text{CaV}_4\text{O}_{12} \) ceramics. The bulk density increased linearly from a low value of 2.72 g/cm\(^3\) at 490 °C (~91.5% of theoretical density) to a saturation value of 2.87 g/cm\(^3\) (~96.4 % of theoretical density) at 550 °C. The corresponding relative density of 96.4 %, is consistent with the compact microstructure, as shown in **Figure 2b**. The grain size distribution (in the inset of **Figure 2b**) is uniform and homogeneous, most of which (70%-80%) lies in the range of 0.8-1.2 μm, with an average grain size of 0.92 μm. The high relative density and dense microstructure ruled out some extrinsic contributions (e.g., pores, cracks, density, and second phase) to dielectric and electrical behaviors [8]. It should be highlighted that the subsequent dielectric and electrical characterizations were performed for the samples having the highest relative density at 550 °C to have reliable dielectric and electrical measurement values.
3.3 Spectroscopic characteristics

According to the group theory prediction, Na$_2$CaV$_4$O$_{12}$ with space group $P4/nbm$ should have 38 Raman-active modes ($\Gamma_{\text{Raman}} = 6A_{1g} + 7A_{2g} + 5B_{1g} + 7B_{2g} + 13E_g$)$^{[17-18]}$. At room temperature, collected Raman spectra showed 11 Raman active modes, as shown in Figure 3a. The strongest Raman peaks were in the range of 920-960 cm$^{-1}$ which arose from the symmetric vibrations of the individual [VO$_4$] tetrahedra, while those in the range of 500-800 cm$^{-1}$ were attributed to the symmetric vibrations of [V$_4$O$_{12}$] rings. The low-band Raman modes originated from the asymmetric vibrations of VO$_2$, such as scissoring, twisting, wagging, and rocking modes$^9$. The spectra's profile remained unchanged as the temperature increased, although a phase transition was expected to occur at temperatures $\geq 510^\circ$C.

This anomaly can be explained by the stable building units of VO$_4$ tetrahedral and V$_4$O$_{12}$ rings in both the low and high temperature Na$_2$CaV$_4$O$_{12}$ phases, as aforementioned. On the other hand, all the observed modes exhibited a red-shift feature (Figure 3b), which revealed the decreasing phonon energy because of the thermal expansion of the lattice.

3.4 Dielectric and electrical properties
Figure 4 a, b) Temperature dependence of dielectric properties of Na$_2$CaV$_4$O$_{12}$ ceramics over a broad temperature range from -150°C to 550°C; c, d) Frequency dependence of the real and imaginary parts of permittivity at room temperature. The red solid lines are fitting results by Eq. (2). (The green and orange dashes reflect the dielectric response contributed by Cole-Cole relaxation and UDR, respectively.)

Figure 4 shows the dependence of the real and imaginary parts of relative dielectric constant over a broad frequency (40-10$^6$ Hz) and temperature range (-150°C to 550°C). As the temperature increased in the range of -150°C to 150°C, both dielectric constant and loss tangent increased gradually (Figure 4a). No dielectric anomaly was observed, suggesting no phase transition took place over the measured temperature range. This agrees with the room-temperature inversion symmetry of the Na$_2$CaV$_4$O$_{12}$ ceramics. Upon further increasing the temperature, however, a dielectric anomaly peak was observed at ~515°C (Figure 4b), which coincided with the previously determined phase transition at 510°C via various-temperature XRD$^{[15]}$. This proves that the origin of the dielectric anomaly is associated with the phase transition from $P4/nbm$ to $P4b2$. 
Figures 4 c and d show the room temperature real and imaginary permittivity ($\varepsilon'$ and $\varepsilon''$) as a function of frequency from 40 Hz to $10^6$ Hz. Both $\varepsilon'$ and $\varepsilon''$ showed strong frequency dependence as both dramatically decreased with the increasing frequency. This decrease is a characteristic of interfacial polarization caused by the Maxwell-Wagner phenomenon, which is linked to electrical heterogeneity in ceramic grains and grain boundaries.\(^{[19-20]}\).

The polarization dependence of frequency can be described by dielectric relaxation models such as the Cole-Cole (CC) formula, which is widely used to describe the frequency dependence of dielectric permittivity to follow:

$$\varepsilon^* = \varepsilon_\infty + \left[ (\varepsilon_s - \varepsilon_\infty) / \left(1 + (j \omega \tau)^{1-\alpha}\right) \right]$$

where $\varepsilon_s$ is the static permittivity, $\varepsilon_\infty$ is the permittivity at very high frequency, $\omega$ is the angular frequency, $\tau$ is the mean relaxation time, and $\alpha$ is the Cole-Cole parameter. The Cole-Cole equation does not take into account the effect of the electrical conduction; however, Eq. (1) alone is not enough to describe the experimental data. The rapid increase of both the real and imaginary parts of dielectric permittivity appeared at low frequency, which was caused by the DC electrical conductivity of the Universal dielectric response (UDR)\(^{[22-24]}\). As a result, the total dielectric contribution from interface polarization, UDR, and DC conductivity can be described as:

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \frac{1+(\omega \tau_o)^{1-\alpha} \sin \frac{\pi}{2} \alpha}{1+2(\omega \tau_o)^{1-\alpha} \sin \frac{\pi}{2} \alpha + (\omega \tau_o)^2(1-\alpha)} + A \left(\frac{n\pi}{2}\right) \omega^{n-1}$$

$$\varepsilon'' = (\varepsilon_s - \varepsilon_\infty) \frac{(\omega \tau_o)^{1-\alpha} \cos \frac{\pi}{2} \alpha}{1+2(\omega \tau_o)^{1-\alpha} \sin \frac{\pi}{2} \alpha + (\omega \tau_o)^2(1-\alpha)} + \frac{\sigma_{dc}}{2\pi \varepsilon_\infty \omega} + A \omega^{n-1}$$

where $\omega = 2\pi f$ is an angular frequency, $\sigma_{dc}$ is the DC electric conductivity, and parameters $A$ and $n$ are temperature-dependent parameters. A close fit was achieved to the experimental data using Eq. (2) as
shown in Figure 4c and Figure 4d. It is possible to investigate each relaxation mechanism that contributes to the material's dielectric response separately using Eq (2). According to the fitting result, high-frequency dielectric response was dominated by the electronic and atomic polarization. Another significant contribution was from the UDR with $n = 0.124$. As a result, the main contribution to the dielectric relaxation came from the Cole-Cole polarization. The dielectric response contributed by the Cole-Cole relaxation and UDR plots are shown in Figures 4c and 4d. The Cole-Cole relaxation mechanism has a significant contribution to the mid-frequency and high-frequency dielectric responses, suggesting the existence of electrical heterogeneity structure in the ceramic.

Figures 5 a and b show the variations of the real ($Z'$) and imaginary ($Z''$) parts of complex impedance as a function of frequency (in log scale, 100 Hz-10$^6$ Hz) at various temperatures (60-220$^\circ$C). A typical electrical relaxation, characterized by a sharp decrease in $Z'$ accompanied by a peak value in $Z''$ at a feature frequency (denoted as relaxation frequency, $\omega_\ell$), was observed with increasing frequency. The magnitudes of both $Z'$ and $Z''$ values decreased as temperature increased, revealing a normal feature of a semiconductor [25-26]. The frequency and temperature dependence of impedance suggested a thermally activated conductivity process. The Arrhenius law (Eq. 3) is used to describe the relaxation behavior:

$$
\omega_\ell = \omega_o \exp\left(-\frac{E_a}{k_BT}\right)
$$

where $\omega_o$ is a pre-exponential factor and $k_B$ is the Boltzmann constant. A linear correlation was observed in the $\ln(\omega_\ell)$ vs $1/T$ curve. The activation energy $E_a \sim 0.16$ eV was obtained by the linear fitting (in the inset of Figure 6b).

For complex impedance plots (Figure 6c), only a certain area in which the arcs approaching zero intercepts in the horizontal axis is presented for each temperature over the frequency range of 40-10$^6$ Hz.
Figure 5 (a, b) Frequency dependence of the real part \(Z\) and imaginary part \(Z''\) of Na\(_2\)CaV\(_4\)O\(_{12}\) at selected temperatures (60-220 °C); (c) Complex impedance plots as a function of frequency at the same temperature range (the equivalent circuit and the fitting curves are also shown in the inset); (d) Temperature dependence of the fitted \(R\) values (\(R_g\) for grains and \(R_{gb}\) for grain boundary) obtained from the impedance plots for Na\(_2\)CaV\(_4\)O\(_{12}\).

To understand the contribution of this arc which can arise from bulk, grain boundary, or overlapping of bulk and grain boundary effects (if the relaxation time constant is close), different equivalent circuit models were proposed and employed to fit the experimental curves. It is pertinent to mention that employing equivalent circuit with only one RC is not enough to describe the experimental data because of the large deviation at low-frequency regions (Figure S1 in Supplementary information). As shown in Figure 5 existence of an electrical heterogeneity structure in the ceramic was observed while fitting the data. The fitted curves based on an equivalent circuit model consisting of two parallel RC components in series (in the inset of Figure 5c) exhibited an excellent agreement with the measured curves, suggesting the proposed equivalent circuit is valid. The separated grain resistances (\(R_g\)) and boundary resistances (\(R_{gb}\)) are plotted in Figure 5d as a function of reciprocal temperature. It was observed that grain boundaries resistance was slightly higher than the resistance of the grain, giving clear evidence for the higher oxidation degree of the grain boundary. Both grain resistance and grain boundary resistance decreased gradually with increasing temperature due to the thermal activation behavior. The change in magnitude of \(R_g\) (\(E_g = 0.29\) eV) was greater than that of \(R_{gb}\) (\(E_{gb} = 0.12\) eV).
with the increase of temperature, suggesting more thermal-activated carriers in grains.

Figure 6a) Complex modulus plots of ceramics measured at different temperatures. b) Frequency dependence of the imaginary parts of the electric modulus for ceramics at different temperatures.

To reveal the polarization behaviors of grains and grain boundaries, complex modulus plots of the ceramic at different temperatures are shown in Figure 6a. The transformation relationship between modulus plots and impedance plots is as follows:

\[ M = i\omega C_0 Z = M' - iM'' \]  \hspace{1cm} (4)

where \( C_0 \) is vacuum capacitance, \( \omega \) is the angular frequency. The peak value of \( M'' \) moves to high frequency with the gradual increase of temperature from 60 °C to 220°C, which indicates that the relaxation is closely related to temperature. To understand the modulus plots of the relaxation mechanism, the Fourier transform formula is used:

\[ M^* = M_\infty \left[ 1 - \int_0^\infty \exp(-\omega t)(-\frac{d\varphi}{dt}) dt \right] \]  \hspace{1cm} (5)

According to Bergman et al. proposed the modified Kohlraush Williams Watts (KWW) formula, the imaginary part of the modulus plots can be described:

\[ M'' = (1 - \beta) + \frac{\beta}{1 + \beta \left[ \frac{\omega_{\text{max}}}{\omega} + \left( \frac{\omega_{\text{max}}}{\omega} \right)^{\frac{1}{\beta}} \right]} \]  \hspace{1cm} (6)

where \( M''_{\text{max}} \) is the peak of \( M'' \), \( \omega_{\text{max}} \) is the corresponding frequency of \( M''_{\text{max}} \). \( \beta \) is the parameter characterizing dielectric relaxation of polarization. Equation (6) was used to fit the frequency dependence of \( M'' \) but failed by one relaxation process. Considering the dielectric spectroscopy and impedance spectroscopy, two KWW formulas were used to get a best fitting result. The two relaxation times were very close, which agreed with the previous results[14]. The value of \( \beta_1 \) and \( \beta_2 \) increased with the increasing temperature (the inset of Figure 6b), indicating that the polarization process induced by
thermal activation was close to Debye relaxation with the increasing temperature.

**Figure 7 (a-d)** Normalized imaginary parts of the impedance and modulus vs. the frequency (in log scale) for at various temperatures (60-260 °C)

It is reported that the combined $Z''$ and $M''$ plots were used to scale the extent of charge carriers being localized\(^{27}\). The coincidence of peak frequencies between $Z''$ and $M''$ suggests a long-range movement of charge carriers. If, on the other hand, separation occurs, it means that the charge carriers are locally refined and can only undertake short-range hopping movements. **Figure 7** shows the combined spectroscopy of $Z''$ and $M''$, in which obvious separation of the peak frequencies between $Z''$ and $M''$ was observed at $T \leq 220$ °C. However, the separation magnitude decreased with increasing temperature. Particularly, at $T = 260$ °C, the maximum peaks coincide with each other. Therefore, it is proposed that in the current samples, short-range movement of the charge carriers was dominant at low temperatures and the long-range migration of charge carriers emerged at higher temperatures.
4. Conclusions

A low-temperature fired ceramic Na$_2$CaV$_4$O$_{12}$ was synthesized and its sintering behavior, thermal stability, and dielectric properties were extensively investigated. Dense ceramics with a low density (~2.87 g/cm$^3$) were obtained at relatively low temperatures (500-550 °C). Na$_2$CaV$_4$O$_{12}$ remained thermally stable up to 550°C as evidenced by thermal analysis and various-temperature Raman spectrum, while it melts at 580 °C. Room-temperature dielectric properties with a low relative permittivity of $\varepsilon_r = 7.72$ and loss tangent of $\tan\delta = 0.06$ were obtained at 1 MHz. A dielectric anomaly peak took place around 515 °C, which was associated with the phase transition from $P4/nbm$ to $P4\bar{2}2$. Dielectric spectroscopy, impedance spectroscopy, and electrical modulus revealed a weak electrical heterogeneity structure in the ceramic. The thermally activated conductivity process in grains and grain boundaries was also studied and found that with the increasing temperature, more thermal-activated carriers were found in grains.

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