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Study of the Morphological, Electrical and Optical Properties of $Ca_4SrCu_3Ti_4O_{12}$ Ceramic

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Abstract

The objective of this study was to investigate the microstructure, electrical resistivity and optical properties of Calcium strontium copper titanate ($Ca_4SrCu_3Ti_4O_{12}$) ceramic. To achieve this, a two-step milling process was employed in the solid-state method for the preparation of $Ca_4SrCu_3Ti_4O_{12}$ ceramics. The ceramic's morphology was analyzed using Field Emission Scanning Electron Microscopy (FESEM), and the findings indicate a non-uniform microstructure consisting of two distinct grain types: smaller grains and larger grains. The optical properties of the prepared ceramics was determined by UV visible spectroscopy and found that absorption of light decreases at longer wavelength meanwhile the transmittance increases sharply with increasing the light wavelength. The band gap value of CSCTO is 5.91 eV. Resistivity of the ceramic was calculated by utilizing precision impedance analyzer.

Keywords: $Ca_4SrCu_3Ti_4O_{12}$, FESEM, Quality factor, Transmittance and Optical band gap.

1. Introduction

In recent years, there has been significant research focus on inorganic perovskite nanostructures due to their wide range of applications across various disciplines. Numerous environmental compounds exhibit a cubic perovskite structure, characterized by the chemical formula ABO_3. The B cation typically have a coordination number of six, while the A cation have a coordination number of twelve. However, it is common to observe deviations from the ideal structure and stoichiometry in these cases. The ideal perovskite exhibits a frequently observed orthorhombic distortion in which the octahedral arrangement of BO_6 becomes tilted, resulting in a square planar coordination for approximately 75% of the A cation. This particular structure is commonly referred to as $ACu_3M_4O_{12}$. Calcium strontium copper titanate ($Ca_4SrCu_3Ti_4O_{12}$), is a material with a body-centered cubic perovskite structure that falls into the centrosymmetric Im3 space group. Due to a mismatch in atomic sizes and the characteristics of the A cation, the CCTO structure undergoes an octahedral tilt distortion. This distortion leads to a complex perovskite structure where approximately 75% of the A site is filled by the Cu^{2+} cation, while the remaining sites are occupied by calcium atoms. In the case of $Ca_4SrCu_3Ti_4O_{12}$, the Ti-O-Ti angles are decreased to 141º from the ideal angle of 180º due to the tilting of the TiO_6 octahedra. It is worth noting that the tilt or rotation of these octahedra does not impact the connectivity of the corner cations. Nevertheless, the octahedral tilt distortion plays a significant role in determining different fundamental physical properties of perovskite titanates (ACu3M4O12) (Shellaiah, 2020).

$Ca_4SrCu_3Ti_4O_{12}$ possesses several significant features including a temperature- independent high dielectric permittivity, with values reaching approximately 10^5 for single crystals and 10^4 for bulk materials, maintained over a wide temperature range of 100-400 K. Additionally,

$Ca_4SrCu_3Ti_4O_{12}$ exhibits a high melting point, as well as exceptional chemical and mechanical stability. These exceptional properties render $Ca_4SrCu_3Ti_4O_{12}$ a suitable candidate for a diverse range of technological applications, including antennas, switches, microwave devices, capacitors, and sensors. Several synthesis methods for Ca4SrCu3Ti4O12 have been documented so far. High purity $Ca_4SrCu_3Ti_4O_{12}$ has been successfully produced using various techniques such as the solid-state method, sol-gel synthesis method, wet-chemistry method, sonochemical method, and chemical precipitation method. Synthesizing the Ca4SrCu3Ti4O12 bulk powder through the solid-state method results in improved crystallinity. For its utilization in advanced technology, a comprehensive examination of the structure, surface-morphology, and optical properties of $Ca_4SrCu_3Ti_4O_{12}$ is crucial (Puchmark et al., 2011).

In this study, $Ca_4SrCu_3Ti_4O_{12}$ powders were produced using a solid-state technique that involved a two-stage milling process. This report also examines how the surface morphology and optical properties are affected by altering the synthesis parameters.

2. Experimental Procedures

The samples of calcium strontium copper titanate were synthesized using the chemical formula $Ca_4SrCu_3Ti_4O_{12}$. The suitable quantities of $CaCO_3$ (Loba Company, India), $SrCO_3$ (Loba Company, India), CuO (Loba Company, India), and TiO_2 (Merck, India) were combined in ethanol through a wet mixing process. This mixture was subjected to 24 hours of mixing using zirconia balls as the medium, with a mass ratio of 2:1 (balls to powder). The slurry underwent an overnight drying process in an oven set at 120°C. Subsequently, it was manually ground in a mortar and pestle for a period of 2 hours. The resulting powdered mixture underwent another round of ball milling using the same method and was dried at the same temperature. The dried powder was placed into a crucible and subjected to calcination in a muffle furnace (Nabertherm GMBH, UK model) at a temperature of 950°C for a duration of 2 hours, while maintaining a heating rate of 3°C/min. The previously calcined powder underwent grinding and was then compressed into pellets using a pellet pressing machine under a pressure of 3-4 kbar. Subsequently, the brownish pellets were sintered in air at a temperature of 1080°C for a duration of 3 hours, while maintaining a heating rate of 5°C/min. With the use of a field emission scanning electron microscope (FESEM, manufactured by Zeiss in Germany), the size distribution and microstructure of the prepared samples were investigated. Before measuring the resistance behaviour of the pellets, the both side of the samples were coated with Ag paste and dried at 120 ºC. Next the electrical properties were carried out employing Impedance analyser (Origin: USA). To collect the optical absorption spectra, a UV-visible spectrometer (Model: SHIMADZU UV/Vis-1650 PC, Japan) was employed. The solution was subjected to UV light scanning across the wavelength range of 200-800 nm.

3. Results and Discussion

Fig. 1. (a) illustrates the sections of SEM picture of Ca4SrCu3Ti4O12 ceramics that were sintered at temperatures of 1080°C. The examination of the microstructure of the sample reveals its inherent heterogeneity, characterized by an unpredictable distribution of

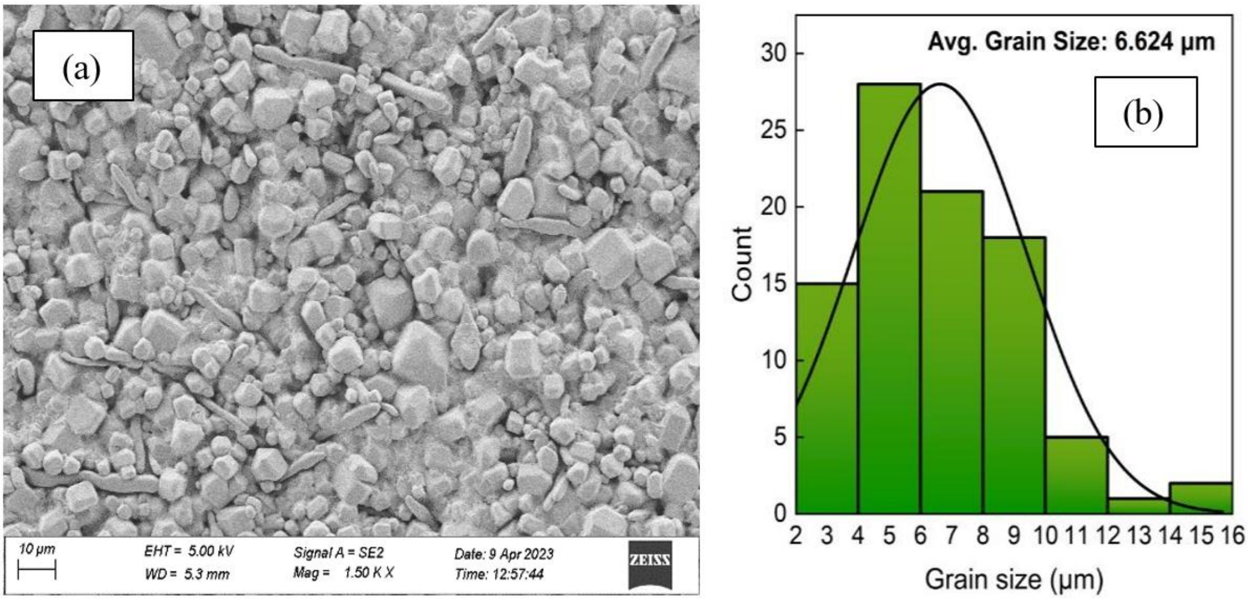

Figure 1: (a) FESEM photograph of Ca4SrCu3Ti4O12 and (b) SEM histrogram.

grain sizes. While the shapes of the grains are not uniform, in certain instances, they exhibit a bimodal size distribution. The image also exhibited a well-developed microstructure comprising a multitude of smaller and larger grains that are distinctly separated by visible grain boundaries. In some regions the grains are almost square in shape. There is a trace amount of pororsity is noticed in the microstructure of the Ca4SrCu3Ti4O12 sample (Gouitaa, 2022). The SEM histogram was obtained using imageJ software and is represented in Figure 1. (b), which also allowed for the determination of the average grain size. The calculated average grain size using this software was found to be 6.62 µm which is lower than CCTO ceramic.

Fig. 2 illustrates the UV-visible absorbance and transmittance spectra of Ca4SrCu3Ti4O12 powder that was calcined at 950 oC. Upon analyzing the spectra in the UV-visible range, it was seen that the Ca4SrCu3Ti4O12 ceramic exhibits a sharply

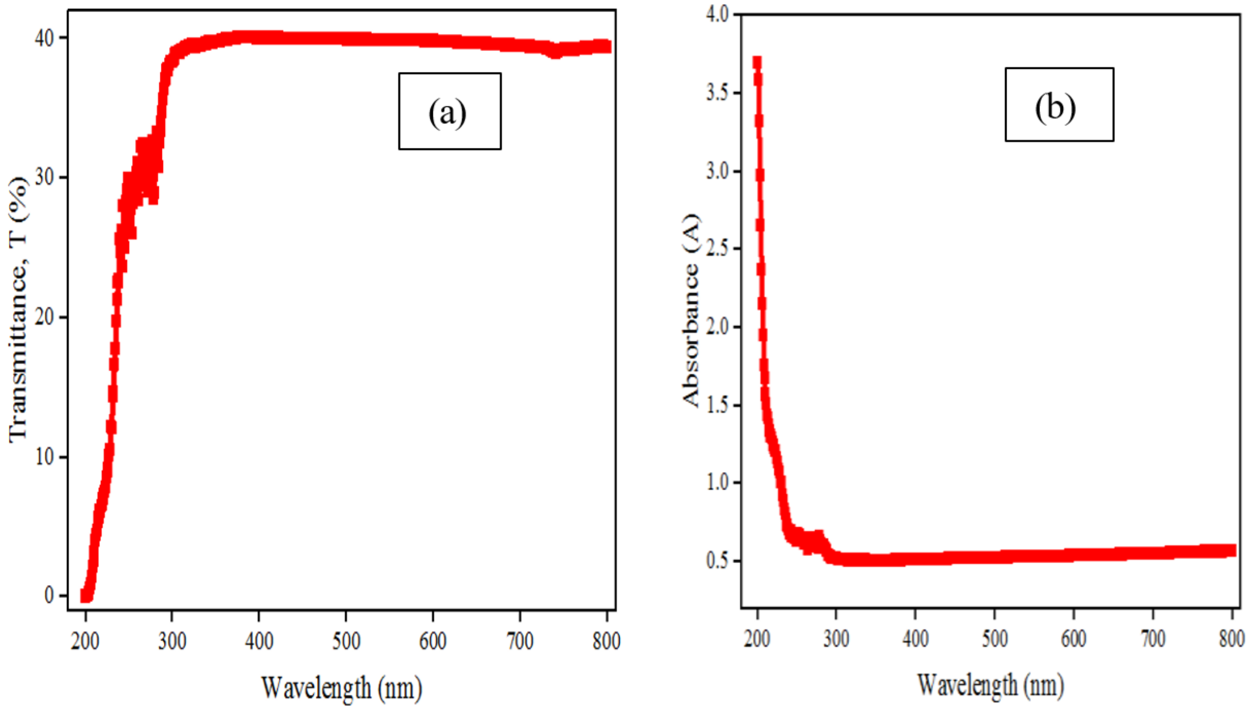

Figure 2: (a) Optical transmittance and (b) absorbance spctra of Ca4SrCu3Ti4O12.

increasing transmission behaviour at lower wavelength (200 nm) which rises to transmittance percentage of 38 at 300 nm wavelength and it becomes stable at visible.

and longer wavelength of light. This suggests that the Ca4SrCu3Ti4O12 compound possesses significant optical transparency (Anamitra et al., 2022). The absorbance spectra indicates that the absorption intensity greatly decreases at shorter wavelength and falls to around the magnitude of 0.5 at 250 nm and maintain the same value upto the longer wavelength (800 nm). This demonstrates the stability of the sample in the longer wavelength region.

The absorption coefficient (α) can be quantified by utilizing the equation (1) given below for measurement.

$$\alpha = \frac{2.303 \times A}{t}$$

Where A is the absorbance and t is the thickness of the sample. The Kubelka-Munk model along with the Tauc plot are used to calculate the band gap energy for indirect transition (Ahmadipour, 2017).

$$\alpha hv = A(hv - Eg)$$

Where h is plank's constant, hυ is photon energy and E_g is the optical band gap. The band gap was measured by extrapolating the linear region of the plot to $\alpha^2 = 0$ in the plot of the square of α vs hυ (Fig. 3). The calculated energy band gap values for the $Ca_4SrCu_3Ti_4O_{12}$ powder are 5.91 eV which indicates that this material can be used as an electrical insulator.

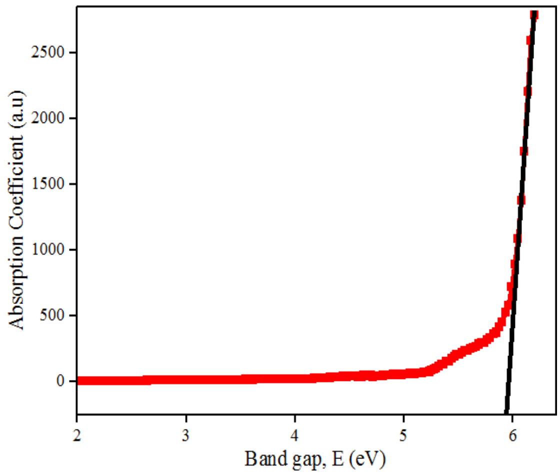

Figure 3: Band gap measurement of $Ca_4SrCu_3Ti_4O_{12}$.

Fig. 4 displays the quality factor (Q) and resistivity behaviour of Ca4SrCu3Ti4O12 sample throughout the frequency range of 40 Hz to 1000 kHz which is determined by Precision Impedance analyzer. Clearly it is viewed from the Figure that the Q value at first decreases in the low frequency region and then start increasing rapidly after 200 kHz and reaches around the magnitude of 2.4 at 500 kHz and next followed by sharp reduction of the Q value at the high frequency region. The sample also displays a declining resistance characteristics. It shows high resistance magnitude of over 105 ohm at lower frequency of 40 Hz and next sharply decreases to around 10 ohm at the radio wave and microwave frequency. This behaviour of decreasing resistance with increasing frequency is in good aggrement with literature (Omar et al., 2014).

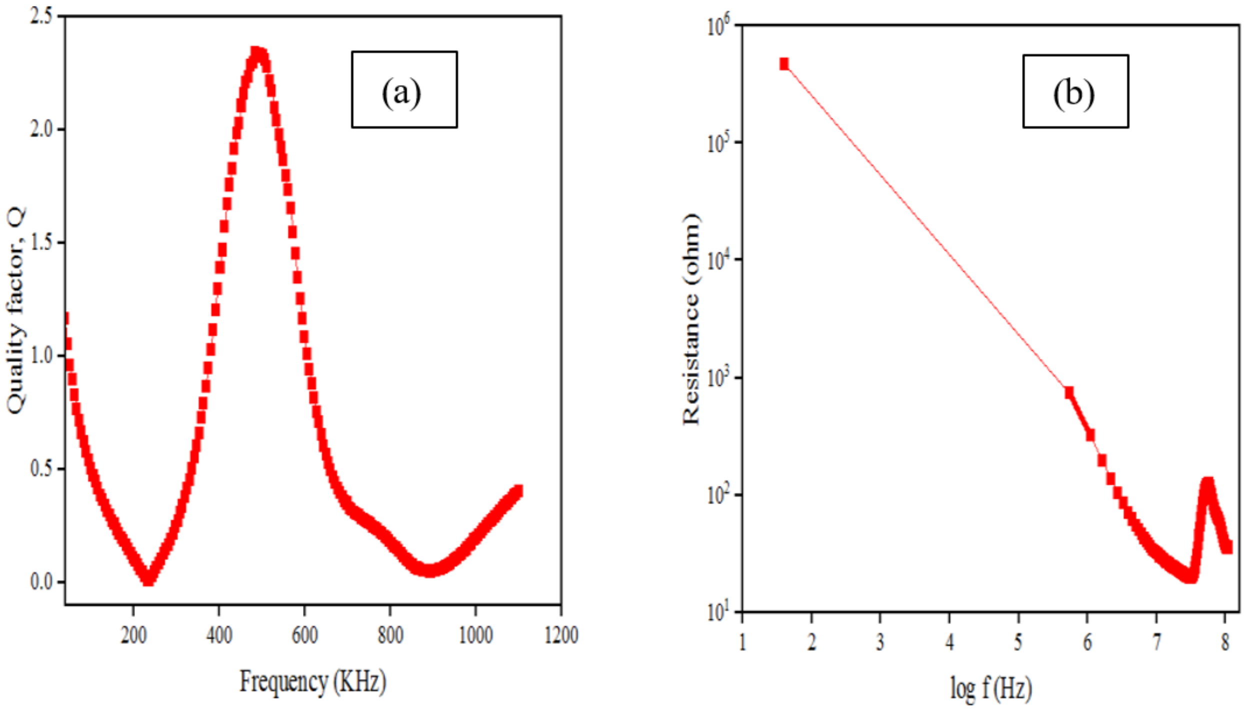

Figure 4: (a) Quality factor and (b) Resistivity of $Ca_4SrCu_3Ti_4O_{12}$ ceramic.

4. Conclusions

The $Ca_4SrCu_3Ti_4O_{12}$ ceramic was effectively produced using the conventional solid- state route, and an analysis was conducted to examine its microstructural, electrical and optical properties. FESEM revealed a significant increase in the size of the grains observed in the samples that were subjected to sintering temperatures of 1080°C, indicating a substantial natural growth process. The grain size decreased with the addition of Sr in the $Ca_4SrCu_3Ti_4O_{12}$ ceramic. The UV-Visible spectra indicated increased absorption at shorter wavelengths and a consistent line, indicating high transmission at longer wavelengths of UV light. The measurement of electrical properties suggests that the sample exhibits a high level of electrical insulation along with good quality factor.

5. References

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