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Microwave dielectric properties of mineral sillimanite obtained by conventional and cold sintering process

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ABSTRACT

The sillimanite (Al_2SiO_5) mineral has been sintered by conventional ceramic route and by cold sintering methods. The mineral has very poor sinterability and transformed to mullite on sintering above 1525 °C. The dielectric properties of sillimanite mineral (Al_2SiO_5) are investigated at radio and microwave frequency ranges. The mineral sintered at 1525 °C has low ε_r of 4.71 and tanδ of 0.002 at 1 MHz and at microwave frequency ε_r = 4.43, $Q_u \times f$ = 41,800 GHz with τ_f = −17 ppm/°C. The sintering aid used for cold sintering Al_2SiO_5 is sodium chloride (NaCl). The Al_2SiO_5—NaCl composite was cold sintered at 120 °C. XRD analysis of the composite revealed that there is no additional phase apart from Al_2SiO_5 and NaCl. The densification of the Al_2SiO_5—NaCl composite was confirmed by using microstructure analysis. The Al_2SiO_5—NaCl composite has ε_r of 5.37 and tanδ of 0.005 at 1 MHz whereas at microwave frequency it has ε_r = 4.52, $Q_u \times f$ = 22,350 GHz with τ_f = −24 ppm/°C. The cold sintered NaCl has ε_r = 5.2, $Q_u \times f$ = 12,000 GHz with τ_f = −36 ppm/°C.

1. Introduction

Microwave dielectric materials conquer today's wireless communication industry by providing a wide variety of applications such as broadcasting satellites, cellular phone, global positioning systems etc. [1]. New microwave substrate materials with low relative permittivity and high performance are desired for high speed communication devices [2]. For microwave substrate applications the dielectric materials should possess low dielectric constant (ε_r), low loss(tanδ), low temperature coefficient of permittivity (τ_ε), high thermal conductivity and low coefficient of thermal expansion [3]. Low ε_r materials offer the advantage of fast signal propagation [3,4]. Sillimanite (Al_2SiO_5) is a naturally occurring alumino silicate polymorph which is obtained as a byproduct during the extraction of rare earths from beach sand minerals [5,6]. The most well-known alumino-silicate polymorphs are sillimanite (Al_2SiO_5), andalusite (Al_2SiO_5) and kyanite (Al_2SiO_5) [7,8]. In 1928, Taylor first resolved the crystal structure of sillimanite while the cell dimensions and space group was determined by Mark and Rosband in 1926 [9,10].Sillimanite decomposes into mullite ($Al_6Si_2O_{13}$) and cristobalite (SiO_2) on heating between 1500 °C and 1650 °C [11,12]. The decomposition temperature may differ depending on the region of its occurrence. Sillimanite and mullite are compounds of alumino silicates with Si-Al tetrahedral chains [13]. The main applications of Al_2SiO_5 are in the fabrication of high tension insulators, spark plugs, glass furnaces, combustion chambers etc [14].

Recently Kahari et al. reported [15,16] a novel method to prepare Li_2MoO_4 ceramics at room temperature by moistening the water soluble Li_2MoO_4 powder using deionized water and pressing the sample at about 130 MPa. The samples were then dried at room temperature or at 120 °C. There was no appreciable difference in the sintered density of the samples dried at room temperature, dried at 120 °C or sintered at 540 °C. The amount of water in the pressed samples was about 2–3 wt% before drying or sintering. It is believed that the densification of the samples occurred during pressing. X-ray diffraction study showed that the crystal structure remains the same and water did not react to form any hydrates. The room temperature dried samples showed a $Q_u \times f$ value slightly less than that prepared by conventional sintering method and is attributed to the presence of small amount of residual water. It was found [16] that ceramic powder particle size has great influence on preparation; densification and dielectric properties. Larger particles are advantageous in fabricating Li_2MoO_4 ceramics by

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moistening and pressing method. Smaller particles lead to clay like clusters leading to non-uniform densification, warpage and cracking. Kahari et al. [17] tailored the dielectric properties by adding TiO_2 and $BaTiO_3$ in Li_2MoO_4 with optimized room temperature preparation method. More recently Randall and co-workers have done extensive work [18–28] on room temperature or sintering below 200 °C by the same technique and introduced the term cold sintering process (CSP). CSP is primarily based onthe solid particle rearrangement with the help of liquid phase followed by densification by dissolution-precipitation [19]. The temperature, pressure, the particle size of the ceramic powder,amount of solvent added are the key factors that control the CSP process [19]. CSP technique has been utilized for achieving dense ceramic, ceramic-polymer composites at temperature less than 200 °C. Simplicity as well as energy saving are the attractive features of CSP process [15,23]. Owing to the low temperature sintering, CSP method offers the advantage of integrating polymers with ceramics. The CSP method was successfully applied to NaCl, alkali molybdates, KH_2PO_4, $NaNO_2$, zirconia, ZnO, $BaTiO_3$ and V_2O_5 [22,25–28]. The possibility of incorporating ceramics with polymers in single step sintering using the emerging CSP method for the study of Li_2MoO_4–(-CF_2-)n(PTFE), electrolyte $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (-CH_2CF_2)$_x$[$CH_2CF(CF_3)_y$(PVDF-HFP) and semiconductor V_2O_5–poly(3,4-ethylenedioxythiophene)polystyrene sulfonate (PEDOT:PSS) composites was also exploited [20]. Baker et al. fabricated monolithic capacitorusing lithium molybdenum oxide ceramic material by CSP method [24].

In the present paper we report the microwave dielectric properties of sillimanite mineral sintered by the conventional solid state method and by cold sintering process using NaCl as sintering aid.

2. Experimental

The mineral sillimanite obtained from Indian Rare Earths Limited (IRE) was planetary ball milled for 6 h using distilled water medium in order to reduce its particle size. The average particle size of the Al_2SiO_5 after ball milling was found out using dynamic light scattering instrument (Malvern Zetasizer, Nano-ZS, UK). The slurry was dried at 100 °C. The dried Al_2SiO_5 powder was ground well and polyvinyl alcohol (PVA) was added prior to pelletizing the bulk sample. The bulk Al_2SiO_5 was sintered at 1525 °C and the structural, micro structural analysis and dielectric studies were carried out. Sodium chloride (NaCl) from SDFCL, Mumbai, India was used for the present study. NaCl was moistened using deionized water and then transferred into suitable die set and hot pressed at 120 °C by applying a pressure of 200 MPa. After several trial and errors, a 1:1 ratio (in weight% (wt%)) was maintained between Al_2SiO_5 and NaCl for cold sintering Al_2SiO_5. For preparing the composite containing Al_2SiO_5 – NaCl, first NaCl was moistened with deionized water and Al_2SiO_5 was added into it. The mixture was thoroughly mixed using deionized water to make a paste. In the present work, 4 wt% deionized water was added to make the paste of Al_2SiO_5—NaCl depending upon the weight of the composite taken. The paste was in semi solid form.The Al_2SiO_5 – NaCl composite was then hot pressed using die set at a temperature of about 120 °C (50 min) and pressure 200 MPa. In order to remove the moisture content, the cold sintered NaCl and Al_2SiO_5—NaCl composite was kept in hot air oven at 120 °C for 24 h. The phase composition of bulk Al_2SiO_5, Al_2SiO_5—NaCl was studied using XRD (CuKα radiation, PANalyticalX'Pert PRO diffractometer, Netherlands). The room temperature FT-IR spectrum of cold sintered Al_2SiO_5—NaCl was recorded using Agilent Technologies, 600ATR, UK using the KBr pellet method. The microstructure of the fractured bulk Al_2SiO_5 sintered using the conventional high temperature sintering method and Al_2SiO_5—NaCl cold sintered at 120 °C was recorded using scanning electron microscopy (JOEL-JSM 5600LV, Tokyo, Japan and Zeiss, Germany). The density of the bulk Al_2SiO_5, cold sintered NaCl andAl_2SiO_5—NaCl composite was determined using dimensional method with the help of a digital screw gauge and weight measured using a semi-micron weighing balance (Shimdazu, AUW220D, Japan). The radio frequency dielectric properties were measured by parallel plate capacitor method using an LCR meter (Hioki 3532-50 LCR Hi Tester, Japan). For radio frequency measurements of bulk Al_2SiO_5, cold sintered NaCl and the Al_2SiO_5 – NaCl composite samples having 11 mm diameter and

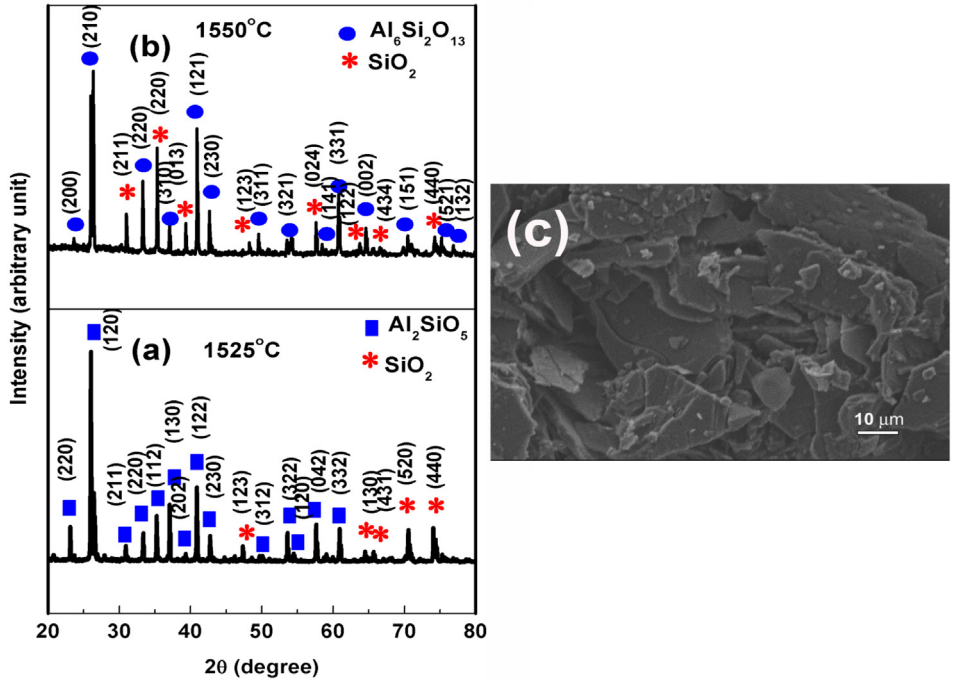

Fig. 1. (a) XRD pattern of bulk sillimanite sintered at (a) 1525 °C and (b) 1550 °C and (c) microstructure of fractured surface of sillimanite sintered at 1525 °C using the conventional solid state ceramic method.

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