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Investigations on the phase stability of Na^+-conducting sodium dysprosium (phospho) silicates

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Abstract

Na^+-conducting sodium dysprosium (phospho) silicates with the compositions $Na_5DySi_4O_{12}$, $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ and $Na_{3.9}Dy_{0.6}Si_3O_{8.85}$ were synthesized by solid state route. The phase evolution in the three systems was studied as a function of heat treatment temperature from 600 °C to 1000 °C by X-ray diffraction technique. It was possible to achieve a NASICON $Na_5DySi_4O_{12}$-type single phase with the compositions $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ and $Na_{3.9}Dy_{0.6}Si_3O_{8.85}$ at 800 °C. Heat treatment at a higher temperature (>850 °C) resulted in the formation of a less conductive $Na_9DySi_6O_{18}$-type phase. Conventional and microwave sintering were carried out on $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ sample at 800 °C and the ionic conductivities were measured as a function of temperature from 75 °C to 325 °C. The microwave sintered sample exhibited better Na^+ ionic conductivity of 0.42×10^{-2} S/cm when compared to that of conventionally sintered sample which was 0.43×10^{-3} S/cm at 325 °C.

Keywords: NASICON; Sodium dysprosium silicates; Na^+-conductivity; Microwave sintering; Na–S battery

1. Introduction

Ever since Maximov et al. [1] discovered sodium ionic conductivity in the skeleton structures of $Na_5RESi_4O_{12}$ (rare earth, RE = Y), intensive research was carried out to synthesize materials having $Na_5RESi_4O_{12}$ (N5) type crystal structure. These materials fall under the category of NASICON (Natrium Super Ionic Conductors) family of solid electrolytes which can be sintered at lower temperatures. NASICON materials possess isotropic ionic conductivity of the order 0.1 S/cm at 300 °C [2] that are comparable to that of sodium beta alumina. The structure of the NASICON is one of the factors that facilitates fast ionic transport through the channels contributing to the ionic conductivity. The possible mechanism for the ionic conduction in $Na_5RESi_4O_{12}$ (RE = Y, Sc) class of compounds was given in [3]. NASICON solid electrolytes find applications in Na–S batteries, gas sensors [4] and in recycling aqueous sodium waste from nuclear reactors [5].

Following this, extensive research was carried on ceramics, glasses and glass ceramics of various compositions of $Na_5RESi_4O_{12}$ and isotypic to N5 with the rare earths Sc, In, Er, Y, Gd, Eu, Sm, Nd, La [6–9]. A new family of Na^+-superionic conductors with composition formula $Na_{3+3x-y}RE_{1-x}P_ySi_{3-y}O_9$ was studied by Yamashita et al. [10]. They obtained polycrystalline N5 type materials with Sc, Y, Gd, or Sm as the rare earth element using the above composition and investigated the thermodynamics and kinetics of the phase transformation in the Na–Y–P–Si–O system of glass ceramics [11]. They had shown that N5 phase was unstable in the Na–Y–Si–O system but phosphorous inclusion aided the formation of N5 phase and found $Na_{3.9}Y_{0.6}P_{0.3}Si_{2.7}O_9$ composition superior to others with regard to ionic conductivity. Balagopal et al. [12] synthesized $Na_5DySi_4O_{12}$ and reported conductivity of 1.1×10^{-2} S/cm at 70 °C. They also tested its use as electrolyte in the electrolysis of an aqueous alkali metal salt solution. Souda and Shimizu synthesized $Na_5DySi_4O_{12}$ and studied its chemical stability [13] and sensing properties in detecting SO_2 gas. They reported an ionic conductivity value of 1.0×10^{-1} S/cm at 300 °C [4]. However detailed study on the formation of various phases in Na–Dy–Si–O system and their stability has not yet been reported.

Microwave processing of ceramic materials has been investigated over the last two decades by various researchers [14–16]. The growing interest in microwave processing over conventional processing methods is due to the fact that the

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electromagnetic wave interacts with ceramic materials leading to volumetric heating by dielectric loss, which enhances rate of densification, decreases densification temperature and improves microstructure uniformity, as well as product properties. Also this unique heating method has the potential for energy savings and cost cutting when compared to conventional heating.

Due to the increasing need for Na^+-conducting solid electrolytes for use at temperatures < 98 °C (melting point of Na) to prevent the problems of corrosion due to liquid Na, which is one of the electrodes when conventional sodium ion conductors are employed as solid electrolytes, investigations were carried out on few compositions in Na–Dy–Si–(P)–O system. In this work, we report the phase evolution in three compositions namely; $Na_5DySi_4O_{12}$, $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ and $Na_{3.9}Dy_{0.6}Si_3O_{8.85}$, as a function of temperature. The phase field stability of superionic conductive N5 phase was also determined. The microwave sintering of $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ has been reported for the first time in literature and ionic conductivities of the microwave sintered material have been compared with those of a conventionally sintered material.

2. Experimental

Ceramic materials with the compositions $Na_5DySi_4O_{12}$, $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ and $Na_{3.9}Dy_{0.6}Si_3O_{8.85}$ were synthesized by solid state reaction method by blending stoichiometric amounts of reagent grade powders of Na_2CO_3 (Merck; assay ≥ 99.5%), Dy_2O_3 (Alfa Aesar; purity – 99.9%), SiO_2 (MK Impex Corp.; purity – 99.9%), and $NH_4H_2PO_4$ (Qualigens; assay ≥ 99%) by ball milling for 24 h using zirconia balls in acetone. The dried powders were compacted into 10 mm diameter disks. The disks were heat treated at various temperatures from 600 °C to 1000 °C for time duration of 6 h, then ground and again pelletized into 6 mm diameter disks for sintering. Microwave sintering was carried out using a 6 kW microwave (MW) sintering furnace (Linn Hightherm GmbH, Germany) at a temperature of 800 °C for 2 h. The sample was placed inside a casket containing SiC susceptors. Conventional sintering was also carried out at 800 °C for 6 h. The densities of conventional and MW sintered compacts were measured using Archimedes principle.

The crystalline phases of the heat treated powders and sintered pellets were identified by X-ray diffraction (XRD) technique using Bruker D8 AXS Advance X-ray diffractometer with Cu K_α radiation (λ = 1.5406 Å). Ionic conductivities of sintered pellets were measured with blocking silver electrodes using Solartron AC impedance analyzer in the frequency range 10 Hz–10 MHz over a temperature range from 75 °C to 325 °C. The microstructure of the conventional and microwave sintered samples was observed under scanning electron microscope (SEM, Hitachi S3400N).

3. Results and discussion

3.1. Phase analysis

Fig. 1 shows the XRD patterns of the samples heat treated at different temperatures corresponding to the composition $Na_5DySi_4O_{12}$ (C-1). It should be mentioned here that the number of XRD patterns present in the JCPDS database corresponding to Na–Dy–Si–O system are less since it is not so well investigated. However since the ionic radius of Dy^{3+} (0.90 Å) is close to that of Y^{3+} (0.89 Å) and Gd^{3+} (0.93 Å), the obtained phases in Na–Dy–Si–O system were analyzed using patterns present in the Na–Y–Si–O and Na–Gd–Si–O systems expecting similarities in crystal structure patterns. Henceforth, the phases $Na_5DySi_4O_{12}$ (PDF # 00-085-0536), $Na_9DySi_6O_{18}$ (iso structural to $Na_9YSi_6O_{18}$; PDF # 00-035-0406), $Na_3DySi_2O_7$ (iso structural to $Na_3YSi_2O_7$; PDF # 00-035-0405) and $NaDySiO_4$ (iso structural to $NaGdSiO_4$; PDF # 04-011-6096) will be referred to as N5, N9, N3 and N1, respectively. It is clear from Fig. 1 that C-1 resulted in N1 + N9 at 800 °C,

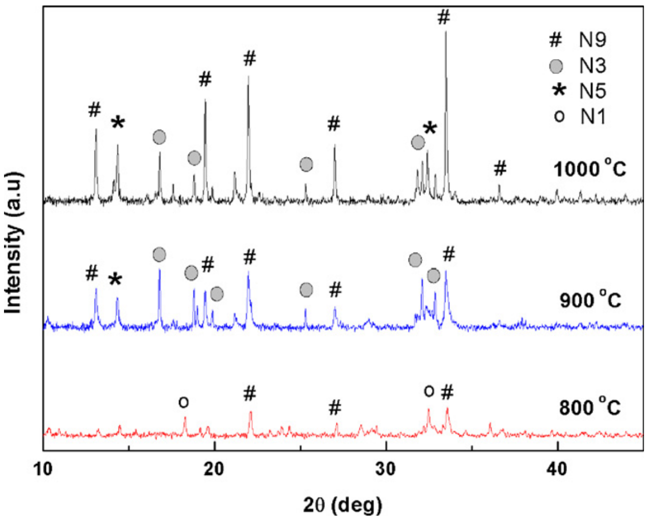


Fig. 1. XRD pattern of powders with $Na_5DySi_4O_{12}$ composition heat treated at temperatures 800 °C, 900 °C and 1000 °C. The phases N1: $NaDySiO_4$, N5: $Na_5DySi_4O_{12}$; N3: $Na_3DySi_2O_7$; N9: $Na_9DySi_6O_{18}$.

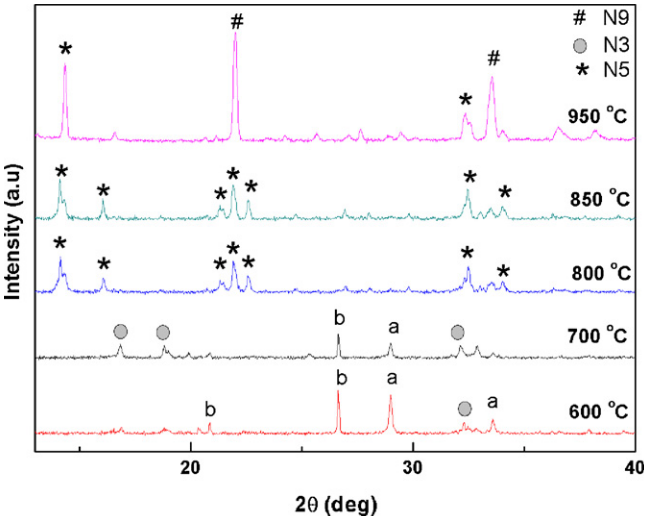


Fig. 2. XRD pattern of powders with $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ composition heat treated from 600 to 950 °C. The phases N5: $Na_5DySi_4O_{12}$; N9: $Na_9DySi_6O_{18}$; a: Dy_2O_3; b: SiO_2.

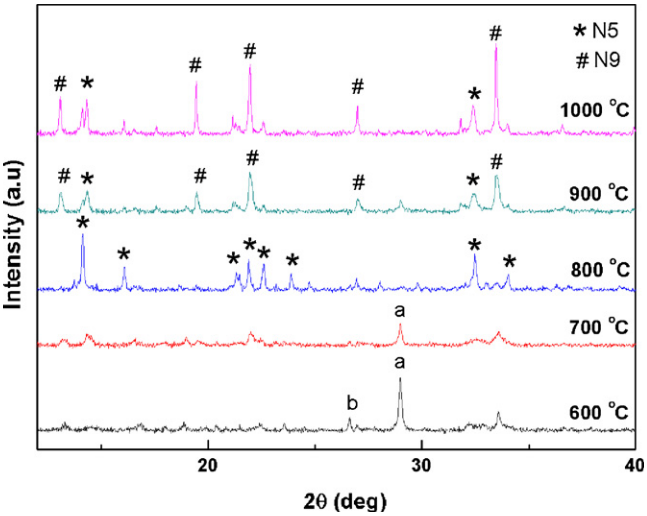
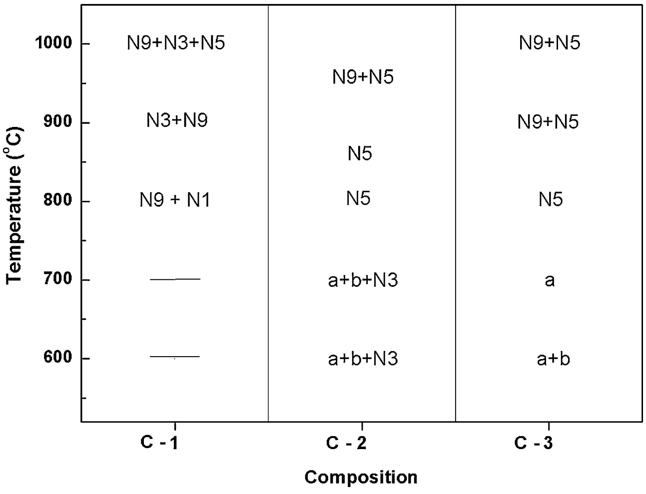


Fig. 3. XRD pattern of powders with $Na_{3.9}Dy_{0.6}Si_3O_{8.85}$ composition heat treated from 600 to 1000 °C. The phases N5: $Na_5DySi_4O_{12}$; N9: $Na_9DySi_6O_{18}$; a: Dy_2O_3; b: SiO_2.



Temperature (°C)	C - 1	C - 2	C - 3
1000	N9+N3+N5		N9+N5
		N9+N5	
900	N3+N9		N9+N5
		N5	
800	N9 + N1	N5	N5
700	——	a+b+N3	a
600	——	a+b+N3	a+b

Fig. 4. Diagram indicating the phase evolution with heat treatment temperature in compositions $Na_5DySi_4O_{12}$ (C-1); $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ (C-2); $Na_{3.9}Dy_{0.6}Si_3O_{8.85}$ (C-3). The phases a: Dy_2O_3; b: SiO_2.

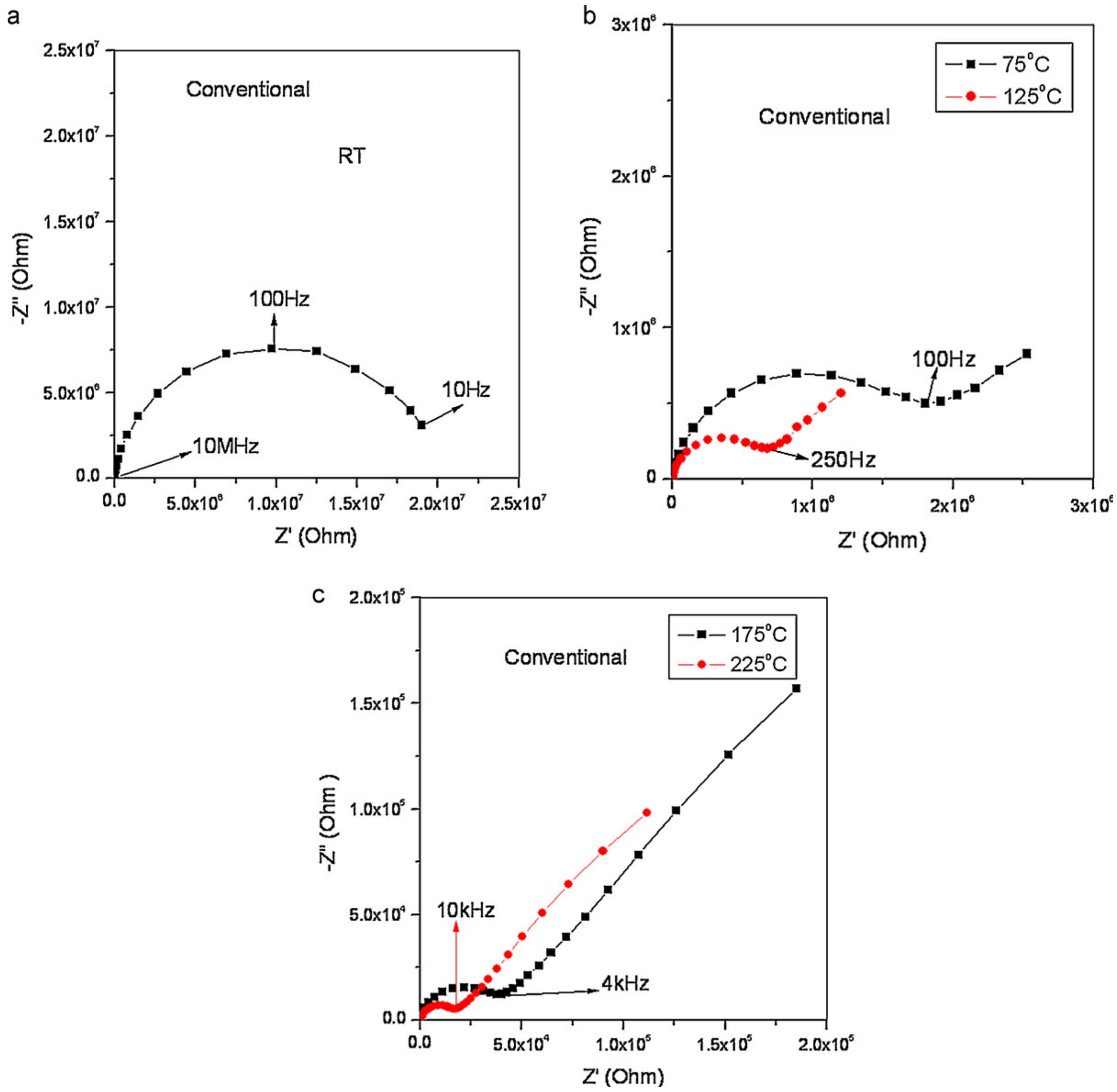


Fig. 5. (a–c) Nyquist plots of conventional sintered $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ samples at different temperatures.

N3 + N9 + N5 at 900 °C and 1000 °C with N9 being the major phase at 1000 °C. There is no single phase obtained between 800 and 1000 °C and is always a mixture of phases obtained at all the three temperatures. A similar kind of result was observed when $Na_5DySi_4O_{12}$ was tried to be synthesized by wet chemical route [17]. Heat treatment beyond 1000 °C also did not result in a single phase. Yamashita et al. [11] reported a similar observation for Na–Y–Si–O system and found that $Na_5YSi_4O_{12}$ type phase could only be stabilized by doping phosphorous in Si^{4+} sites, since undoped $Na_5YSi_4O_{12}$ was thermodynamically unstable phase when compared to $Na_9YSi_6O_{18}$. Keeping this in mind we have synthesized phosphorous doped sodium dysprosium silicate and studied the composition $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ (C-2). Fig. 2 shows the XRD patterns of the samples heat treated at various temperatures corresponding to C-2. We found that there is unreacted Dy_2O_3, SiO_2 and the formation of N3 phase has started at 600 °C. At 700 °C, there is still an unreacted mixture but amount of unreacted components is little compared to the amount present at 600 °C and the N3 phase is developed. The phases at 800 °C and 850 °C correspond to N5 which was reported to have good ionic conductivity in the literature. It is also seen that at 800 °C and 850 °C there are no peaks corresponding to Dy_2O_3, SiO_2 and also the N3 phase which was present at 700 °C has transformed fully to N5 phase. A single phase having N5-type structure was obtained between 800 and 850 °C. Heat treatment at 950 °C resulted in the formation of N9 phase along with N5 phase that was previously formed. A variation to the compositions C-1 and C-2 was taken as $Na_{3.9}Dy_{0.6}Si_3O_{8.85}$ (C-3) by maintaining the ratio of Na/Dy same as to that present in C-2. It is observed from the XRD patterns in Fig. 3 that heat treatment at 600 °C and 700 °C did not result in the formation of any new phase except the unreacted phases. It was found that 800 °C was favorable for the formation of N5 phase in C-3 whereas 900 °C and 1000 °C resulted in N9 phase along with N5. At 1000 °C N9 is the major phase while N5 is the minor one. In one case of study with the rare earth yttrium using $Na_{3.9}Y_{0.6}P_{0.3}Si_{2.7}O_9$ composition by Yamashita, less conducting N3 or N9 phases were formed as the

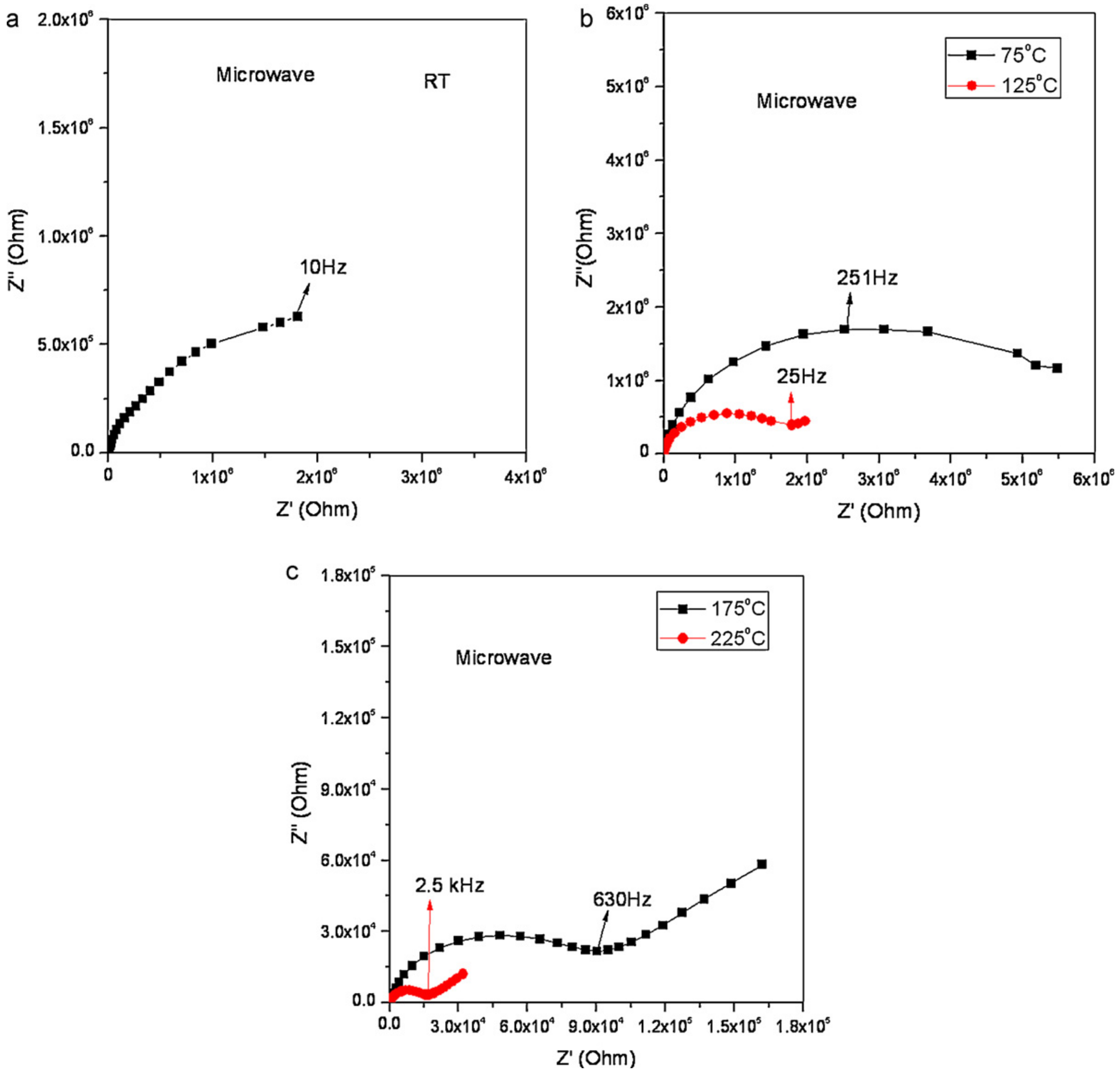


Fig. 6. (a–c) Nyquist plots of microwave sintered $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ samples at different temperatures.

precursor phases (in the synthesis of N5 phase) and transformed to N5 phase at higher temperatures [18]. In our case, we found that N9 phase started to appear at about 900 °C in C-2, C-3 and the percentage amount of that phase increased with increasing temperature in both the cases. We can expect a single N9 phase at higher temperatures, which is in contrast to the results reported in [18]. The above observation imposed a restriction on the sintering temperature to get dense, single phase N5-type structure. The effect of heat treatment temperature in three compositions is summarized in Fig. 4. In order to study the ionic conductivities, a dense compact with single phase N5-type structure was necessary since it has been reported that a single phase material with N5-type structure exhibited high Na^+-ionic conductivity [4,5,12] at low temperatures (~70 °C), when compared to conventional sodium ion conductors. Hence, sintering was carried out at 800 °C by conventional and microwave heating methods on green samples of dimensions 10 mm diameter; 3 mm thick and 6 mm diameter; 4 mm thick, respectively. The dimensions of samples after sintering were 9.2 mm diameter; 2.7 mm thickness and 5.5 mm diameter; 3.9 mm thickness for conventional and microwave sintering. The active area considered for evaluation of ionic conductivity was 0.66 and 0.237 cm^2 for the conventional and microwave sintered samples, respectively. The densities of the samples were found to be 3.01 g/cm^3 (conventional) and 2.97 g/cm^3 (MW) which were 93% and 92% of theoretical density, respectively.

3.2. Conduction properties and microstructural analysis

Figs. 5(a–c) and 6(a–c) shows Nyquist plots of conventional and microwave sintered $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ samples at different temperatures in the frequency range (10 Hz–10 MHz). At all temperatures, a single semicircle with a straight line in the low frequency region was observed. The low frequency intercept made by the semicircle on the real impedance axis could be used to determine the bulk resistance of the sample. The bulk electrical conductivity (σ_B) is written $\sigma_B = (t/R_B \times A)$, where t is the thickness and A is the area of the electrode deposited on the sample. Fig. 7 shows the Nyquist plot of conventional and microwave sintered samples at 325 °C. The microwave sintered sample was seen to show lower resistance when compared to that of conventional sintered sample. Electrical conductivities were evaluated for the two samples at 325 °C. The ionic conductivity of microwave sintered sample (0.42×10^{-2} S/cm) is higher than conventional sintered sample (0.43×10^{-3} S/cm). Fig. 8 shows the Arrhenius plot of the AC conductivity evaluated from the impedance plots of $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ samples as a function of temperature. The log (σT) versus $1/T$ plot consists of two straight lines for both the samples. The activation energy for electrical conduction (E_a) can be calculated from the slopes of straight lines. It was found that the activation energy was less up to 125 °C and increased above 125 °C. The E_a values were found to be 0.73 eV and 0.87 eV (>125 °C), 0.24 eV and 0.22 eV (<125 °C) for conventional and microwave sintered samples, respectively.

The surface morphology of the samples was observed under SEM and is presented in Fig. 9(a and b). Microwave sintering is seen to have resulted in a product with uniform grain structure. The ionic conductivity values for microwave sintering are higher than the conventionally sintered counterparts though the activation energy for microwave sintering is higher. In order to find out the cause for improved conductivity in case of the MW sintered sample, XRD analysis was carried out on the sintered pellets to verify whether the phases were still retained after sintering at 800 °C. It was observed that conventionally sintered pellet consisted of N5 and N9 phases almost in equal proportions where as the microwave sintered pellet has N5 as the major phase with trace amounts of N9 phase. This must have been the major contribution for the higher ionic

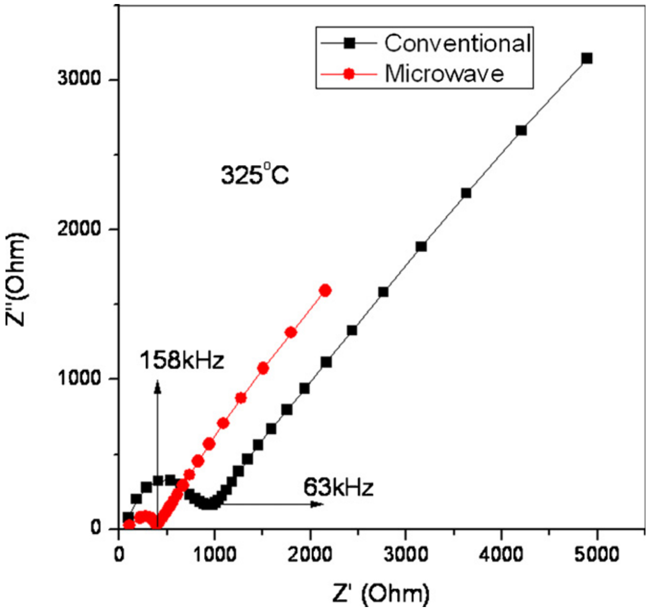


Fig. 7. Nyquist plots of conventional and microwave sintered $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ sample at 325 °C.

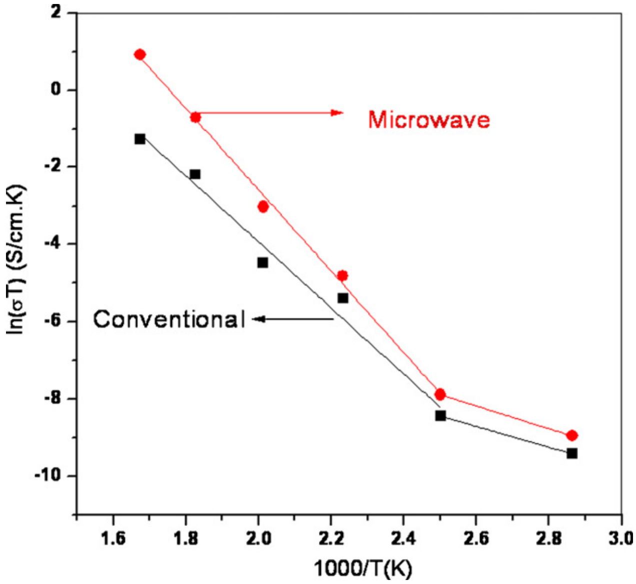


Fig. 8. Arrhenius plots of conventional and microwave sintered $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ sample.

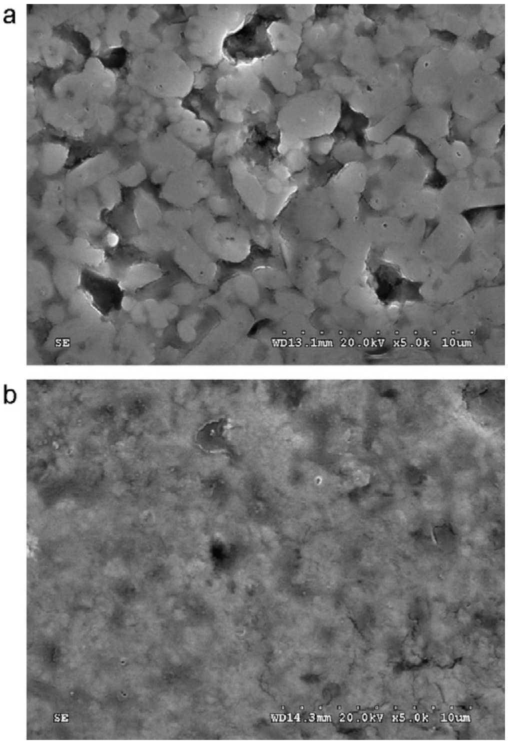


Fig. 9. SEM images of: (a) microwave and (b) conventional sintered $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ sample.

conductivity in MW sintered sample due to rapid and volumetric heating. Thus it could be inferred that microwave sintering helped in maintaining the highly Na^+-conducting N5 phase. Furthermore, MW sintering could also lead to a uniform microstructure, contributing to higher ionic conductivity in the MW sintered sample. Further research is in progress to stabilize and retain the highly conductive N5 phase even after sintering.

4. Conclusions

Single phase with N5 type crystal structure could successfully be synthesized with the compositions $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ and $Na_{3.9}Dy_{0.6}Si_3O_{8.85}$ which was stable over a narrow temperature range 800–850 °C. The conventional composition $Na_5DySi_4O_{12}$ yielded a multiphasic mixture irrespective of the heat treatment temperature. Conventional sintering of $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ led to a phase change whereas microwave sintering helped in retaining the phase of the sintered compact. The microwave sintered $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ samples revealed uniform microstructure compared to conventional sintered as well as exhibited higher ionic conductivity of 0.42×10^{-2} S/cm when compared to 0.43×10^{-3} S/cm at 325 °C.

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