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Wet chemical synthesis and characterization of Na^+-conducting sodium dysprosium silicates

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Abstract

The wet chemical synthesis and characterization of the NASICON family series, based on sodium dysprosium (phopho)silicates namely $Na_5DySi_4O_{12}$, P doped $Na_5DySi_4O_{12}$ ($Na_5DyPSi_4O_{12}$), $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ and $Na_{4.05}Dy_{0.55}P_{0.3}Si_{2.7}O_9$, were carried out. Thermal events of the as-dried mixture were analysed by thermogravimetry/differential scanning calorimetry (TG-DSC). Compacted disks of as-dried powder were subjected to conventional heat treatment from 400 to 1000 °C as well as to non-conventional heat treatments like microwave irradiation and spark plasma sintering at various temperatures. The phase evolution was studied as a function of heat treatment temperature by X-ray diffraction. It was found that the $Na_5DySi_4O_{12}$ type (N_5) crystal structure that was reported to exhibit high Na^+-conductivity could not be achieved using either the conventional or even non-conventional heat-treatment techniques like microwave irradiation and spark plasma sintering, but could be obtained by doping the sodium dysprosium silicate with phosphorous. However, even after doping, the desired N_5 phase was always found to co-exist along with N_9 type ($Na_9DySi_6O_{18}$) phase for $Na_5DySi_4O_{12}$ and with N_3 type ($Na_3DySi_2O_7$) phase for $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ and $Na_{4.05}Dy_{0.55}P_{0.3}Si_{2.7}O_9$ compositions up to a heat treatment temperature of 1000 °C.

Keywords: A. Sol–gel processes; B. X-ray methods; C. Ionic conductivity; E. Batteries

1. Introduction

Solid electrolytes are fast ionic conducting ceramics that promote the transfer of a specific ion through its membrane and are the major subject of research today, since they have a wide range of applications like in batteries, fuel cells, supercapacitors, thermoelectric generators and chemical sensors [1,2]. Of the existing Na^+ conducting solid electrolytes, the well-known is sodium-beta-alumina and was chosen to be the best candidate for use in sodium–sulphur batteries because of its high Na^+-conductivity of $\approx 0.1\ S\ cm^{-1}$ at the temperature of 300 °C [1,2]. But the major disadvantage is that, it has a two-dimensional layered crystal structure because of which it exhibits anisotropic behaviour with respect to ionic conductivity and mechanical properties [3]. In addition, a temperature of ≈300 °C is required to achieve a high Na^+ ion conductivity. When such a high temperature is reached, the corrosive nature of molten sodium which is used as one of the electrodes predominates. In order to overcome these disadvantages, Goodenough et al. [4] introduced NASICON (Natrium Super Ionic Conductor), a series of fast Na^+ ion conductor with the general formula $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 < x < 3$), which was found to exhibit a Na^+ ion conductivity of $\sigma_{300} \geq 0.2\ S\ cm^{-1}$ for $x \approx 2$, competitive to sodium-β-alumina. The advantage of this NASICON over the conventional β-alumina is that it has a three-dimensional framework structure and exhibits comparable Na^+-conductivity at lower temperatures. However, the disadvantage is that NASICON type materials are unstable in acidic and caustic environments due to some species of the NASICON being particularly attacked by acids. From thermodynamic point of view, it could be expected that NASICON-type materials without the phosphorous may exhibit increased stability in corrosive (acidic or caustic) environments. Due to this possibility, investigations were carried out on materials having the formula $Na_5RESi_4O_{12}$, RE = Yttrium or any rare earth metal, for use as electrolyte materials with high

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sodium ion conductivity and Na^+-selectivity at low temperatures. The high Na^+-conductivity in Rare earth doped NASICON series having the $Na_5RESi_4O_{12}$ (RE, Rare Earth = Gd) structure was reported by Shannon et al. [5]. This is due to the existence of large channels in the structure, which facilitate ionic transport. Banks and Kim [6] had reported the preparation of $Na_{3.2}M_{0.7}Si_{2.9}P_{0.1}O_{8.7}$ (M = Er, Y, Ho, Dy, Gd, Eu and Sm) and $Na_5MSi_4O_{12}$ (M = Fe, In, Er, Y, Gd, Sm) glasses and glass-ceramics and compared their ionic conductivity values. The reported values were in the range of 10^{-4} S cm^{-1} at 280 °C for the glasses. Due to the poor resistance of NASICON under acidic/caustic conditions, Balagopal et al. [7] reported the use of sodium rare earth silicates with the general formula $Na_5RESi_4O_{12}$ (RE = Y, Dy, Nd, Gd, La, Sm) as electrolytes for caustic recycling. Among all the sodium rare earth silicates, $Na_5DySi_4O_{12}$ was found to exhibit the maximum Na^+-conductivity of ≈0.01 S cm^{-1} at 70 °C and highest current efficiency when used in electrolytic cells. This NASICON structured membrane with dysprosium as rare earth element was also reported as an electrolyte for caustic recycling from Hanford tank waste by Fountain et al. [8], which was found to have highest sodium transport efficiency >90% with high sodium ion selectivity. Yamashita et al. [9] had also identified a new family of Na^+ super ionic conductors with the composition formula $Na_{3+3x-y}RE_{1-x}P_ySi_{3-y}O_9$ (RE = Y, Gd, Sm) and carried out extensive investigations on the phase stabilities of different sodium yttrium silicates namely $NaYSiO_4$, $Na_3YSi_2O_7$, $Na_5YSi_4O_{12}$, and $Na_9YSi_6O_{18}$. They had synthesized $Na_5YSi_4O_{12}$ with stable N_5-type ($Na_5RESi_4O_{12}$) crystal structure that exhibited very high Na^+ ion conductivity of ≈0.1 S cm^{-1} at 300 °C with an activation energy $E_a = 20$ kJ mol^{-1}. They had also studied the effects of different rare earth elements such as Sc, Y, Gd, Sm, and La on the crystallization of sodium rare earth phosphosilicates with the general formula $Na_{3+3x-y}RE_{1-x}P_ySi_{3-y}O_9$ and their conduction properties were also discussed [10]. Since, there is no such detailed investigation on the phase evolution and stability of phases in Na–Dy–Si–O system, the aim of the present work was to study this system in order to obtain high Na^+ ion conducting sodium dysprosium silicates with stable N_5-type structure. The present investigation reports for the first time, the synthesis of sodium dysprosium silicates with and without phosphorous doping, by wet-chemical route and a systematic study of the phase evolution as well as phase stability was carried out as a function of heat-treatment temperature.

2. Experimental

2.1. Materials and synthesis

Sodium trisilicate ($Na_2Si_3O_7$, Sigma–Aldrich; Assay (NaOH) ≥ 10%, assay (SiO_2) ≥ 27%), dysprosium nitrate pentahydrate (Dy $(NO_3)_3 \cdot 5H_2O$, Alfa Aesar; purity – 99.9%.), sodium hydroxide (NaOH, Qualigens; Minimum assay 97%), tetra ethoxy silane (TEOS, ABCR, GmbH; Minimum assay 97%), ethanol (C_2H_5OH, Minimum assay 99.9%) and ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$, Qualigens; Minimum assay 97%) were used as starting materials. Stoichiometric amounts of $Dy(NO_3)_3 \cdot 5H_2O$, $Na_2Si_3O_7$ and NaOH were dissolved in water and added to appropriate amounts of C_2H_5OH, TEOS and $NH_4H_2PO_4$ (for phosphorous doping), to synthesize $Na_5DySi_4O_{12}$, $Na_5DyPSi_4O_{12}$, $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ and $Na_{4.05}Dy_{0.55}P_{0.3}Si_{2.7}O_9$. The precursors were stirred at room temperature for 5 h till a homogeneous mixture was obtained. The mixture was dried at 150 °C for 3 h to remove solvent, water and then ground into fine powder and compacted into 15 mm diameter disks. The disks were subjected to heat treatment at various temperatures from 400 °C to 1000 °C for time periods varying from 1.5 h to 10 h. In some cases non-conventional heat treatments like microwave irradiation and spark plasma sintering (SPS) were also employed. Heat treatment using microwaves was carried out by placing the sample inside a casket containing SiC susceptor pieces. The process was carried out using a 6 kW microwave sintering furnace (supplied by Linn Hightherm GmbH, Germany) at a temperature of 1130 °C for varying time period of 0.5 h, 1 h, and 2 h. Further experimental details about microwave irradiation are given in [11]. SPS was carried out using a Dr Sinter 1050, Japan, by placing required amounts of powder (as-dried powder heat treated at 800 °C) between the graphite punches and applying a DC source of 600–800 A for 5 min simultaneously with applied pressure of 50 MPa. Further experimental details regarding spark plasma sintering are given in [12]. The SPS experiments were carried out for different temperatures of 700 °C, 750 °C and 950 °C.

2.2. Characterization

Thermal events like water loss, decomposition of nitrate, reaction temperature and phase transitions were analyzed by subjecting the as-dried powders to TG-DSC measurements (Netzsch STA 449 analyzer). It was carried out from room temperature to 1250 °C with a heating rate of 5 °C/min. X-ray diffraction was carried out (Bruker D8 Axs Advance X-ray diffractometer), $\lambda = 1.5406$ Å, using Cu K_α radiation in the 2θ range of 5°–80° to analyse the phase formation. The heat treated samples were subjected to SEM (Hitachi S3400 N) analysis for studying the microstructure. Ionic conductivity of the sintered samples was measured using a Solartron impedance analyzer. Silver paste was applied on the parallel surfaces of the densified compact as blocking electrodes. The measurements were carried out for the samples from room temperature to 350 °C, over a frequency range of 10 MHz–1 Hz.

3. Results and discussion

3.1. Thermal analysis

The TG–DSC analysis of the as-dried $Na_5DySi_4O_{12}$ powder, as shown in Fig. 1, indicates that there was a mass loss starting from a temperature of ~100 °C corresponding to an endotherm, which could be attributed to evaporation of ethanol and water. These are part of reactants and also get formed as a by-product of the hydrolysis and condensation of TEOS. The sharp

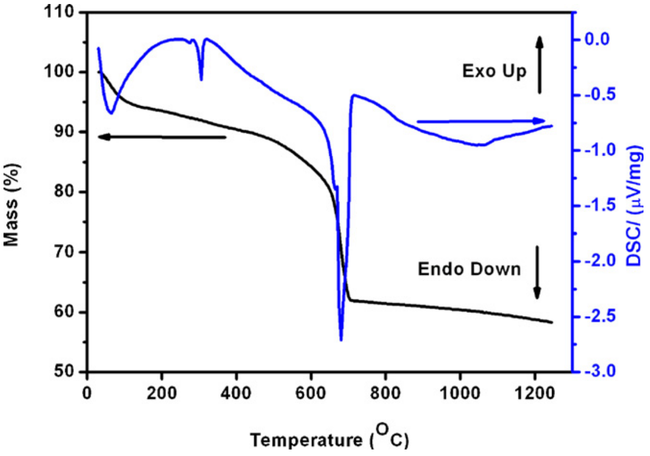

Fig. 1. TG–DSC of as-dried $Na_5DySi_4O_{12}$ powder.

endotherm around 300 °C could be due to loss of any chemically bound water molecules and the endotherm with $T_{onset} \approx 600$ °C accompanied by large mass loss can be attributed to the decomposition of dysprosium nitrate which in turn leads to reaction with other reactants to form sodium dysprosium silicate. Above 700 °C, there was no appreciable mass loss as well as no sign of phase change as seen from the DSC curve.

The TG–DSC curves of as-dried phosphorous doped sodium dysprosium silicate powders corresponding to compositions $Na_5DyPSi_4O_{12}$ and $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ were similar to each other and almost similar to that of the as-dried $Na_5DySi_4O_{12}$ powder, as shown in Fig. 2 (TG–DSC of $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$). In addition to the peaks present in Fig. 1, a large mass change in the range of 200 °C was observed in Fig. 2 and can be attributed to the decomposition of ammonium dihydrogen phosphate. The sharp endotherm with $T_{onset} \sim 580$ °C accompanied by a large mass loss can be attributed to the decomposition of dysprosium nitrate leading to formation of phosphorous doped sodium dysprosium silicate.

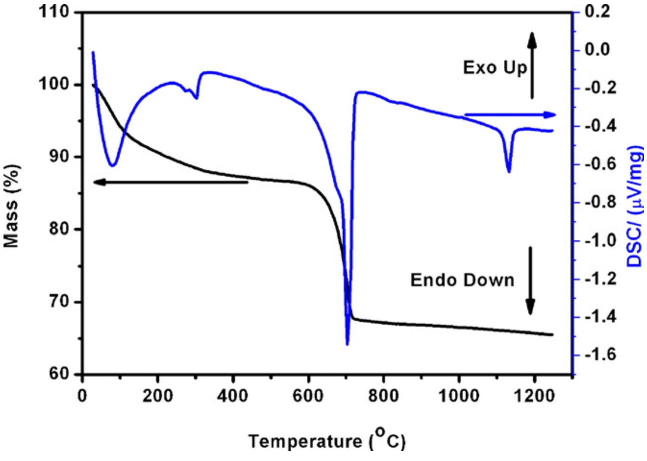

Fig. 2. TG–DSC of as-dried $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ powder.

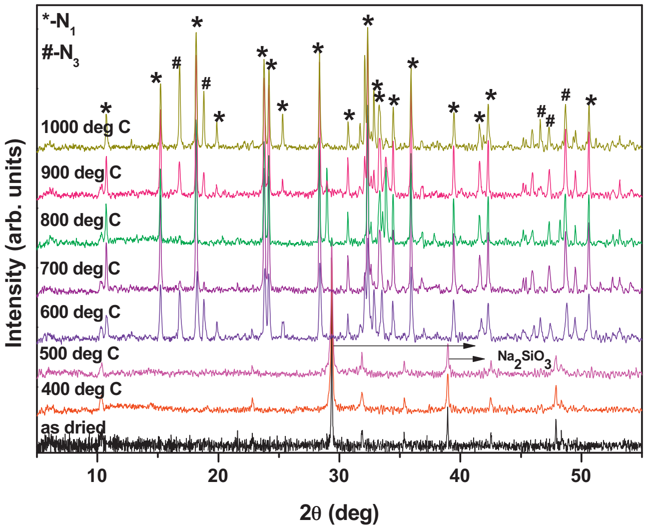

Fig. 3. XRD patterns of conventionally heat treated $Na_5DySi_4O_{12}$ from 400 °C to 1000 °C.

3.2. X-ray diffraction analysis

Fig. 3 shows the XRD patterns of conventional heat treated $Na_5DySi_4O_{12}$. The as-dried powder and samples heat treated at 400 °C and 500 °C revealed a similar pattern. The observed peaks correspond to that of sodium silicate (Na_2SiO_3, PDF# 00-082-0604) and no required N_5 ($Na_5DySi_4O_{12}$) phase was obtained by heat treating the sample up to 600 °C. Above 600 °C, the reaction was found to have taken place as seen from the XRD and TG–DSC, leading to the formation of sodium dysprosium silicate phase. It must be mentioned here that there is very limited information on phases in Na–Dy–Si–O system. No pattern could be found in the JCPDS database that could be matched with the XRD patterns obtained in the present investigation. Since the ionic radius of Y^{+3} (0.89 Å) closely matches with that of Dy^{+3} (0.90 Å), an analogous system Na–Y–Si–O was analyzed which was well studied and so a similarity in crystal structures for phases in Na–Dy–Si–O and Na–Y–Si–O could be expected. Accordingly, the phase formed at 600 °C was found to be corresponding to $NaDySiO_4$ (similar to $NaYSiO_4$, PDF # 00-020-1180 and will be henceforth abbreviated as N_1) and at 700 °C there was a phase formation of $Na_3DySi_2O_7$ (similar to $Na_3YSi_2O_7$, PDF# 00-035-0405 and will be henceforth abbreviated as N_3). It was also seen that over the temperature range from 800 °C to 1000 °C, the phases present were $N_1$and N_3 with no N_5 phase formation even at 1000 °C. Therefore, it was concluded that conventional heat treatment of the $Na_5DySi_4O_{12}$ samples could not yield the required N_5 phase and so efforts were made to see if the phase formation could be achieved with the help of non-conventional heat treatments, e.g. microwaves and spark plasma sintering.

Na^+-conducting sodium beta alumina has been reported to be a good absorber of microwaves and capable of getting heated and sintered in a microwave field [13]. Hence, it could be expected that Na^+-conducting sodium dysprosium silicate will also absorb and get heated when irradiated with microwaves. Fig. 4 shows the XRD patterns of samples heat treated using

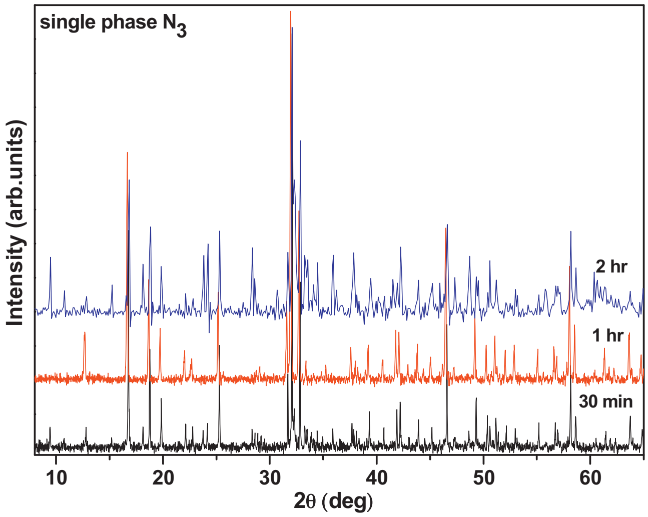

Fig. 4. XRD patterns of microwave heat treated $Na_5DySi_4O_{12}$ at 1130 °C.

microwaves. The samples were heated to a temperature of 1130 °C with varying soaking times of 0.5 h, 1 h and 2 h. From all the XRD patterns, it was seen that, phase formation of only single phase N_3 takes place. Thus, heat treatment with microwaves though helped in achieving a single phase N_3, irrespective of soaking times, the formed phase was not the required N_5 phase. Therefore, another non-conventional heating method, namely, spark plasma sintering was carried out as an attempt to stabilize the required N_5-type crystal structure. Samples were sintered using spark plasma sintering and the XRD patterns obtained on samples subjected to spark plasma sintering using 3 different conditions are shown in Fig. 5. The patterns revealed the presence of an amorphous background for the samples sintered at 700 °C and 750 °C. This can be attributed to the formation of glassy phase along with a crystalline phase. In the case of samples sintered at 950 °C, there was no such amorphous background. This can be because the temperature used for sintering was high enough to completely crystallize the phase. Here also, there always existed a mixture of N_1 and N_3 phases along with an unknown phase. Thus the required N_5 phase could not be obtained even with the help of spark plasma sintering. It should be mentioned here that Yamashita et al. reported that in the series of compositions $Na_{3+3x-y}Y_{1-x}P_ySi_{3-y}O_9$ belonging to the Na–Y–(P)–Si–O system, the N_5 structure could not be stabilized without addition of phosphorous due to the high free energy of the N_5 phase with $[P] = 0$ [14]. Since in the present investigation also, the N_5 phase could not be obtained with the composition $Na_5DySi_4O_{12}$, and considering the similarities in ionic radii of Dy^{3+} and Y^{3+}, it was expected that phases in Na–Dy–Si–O and Na–Y–Si–O had similar thermodynamic stabilities. Since Si^{4+} and P^{5+} have similar ionic radii (42 pm and 35 pm respectively), P^{5+} is generally used for aliovalent doping of silicates. Hence, further studies were carried out on phosphorous doped Na-dysprosium silicate system. Fig. 6 shows the XRD of conventional heat treated $Na_5DyPSi_4O_{12}$. Similar to $Na_5DySi_4O_{12}$, heat treatment at 400 °C and 500 °C revealed the presence of peaks of Na_2SiO_3 and also peaks corresponding to silica (SiO_2 PDF# 00-013-0026). When samples were heated to a temperature of 600 °C, as seen in $Na_5DySi_4O_{12}$, phase formation of sodium dysprosium silicate takes place. But, in this case, it was seen that addition of phosphorous favoured the formation of the required N_5 phase, though however a single N_5 phase (PDF# 00-085-0536) was not formed. The XRD patterns revealed the presence of another sodium dysprosium silicate phase $Na_9DySi_6O_{18}$ (similar to $Na_9YSi_6O_{18}$, PDF# 00-035-0406 and will henceforth be abbreviated as N_9) as well as an unknown phase at $2\theta = 10.32°$ with the major phase being N_5. The unknown phase at $2\theta = 10.32°$ was observed to disappear when the sample was heat treated at a temperature of 1000 °C. The XRD patterns of $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ and $Na_{4.05}Dy_{0.55}P_{0.3}Si_{2.7}O_9$ obtained at various heat treatment temperatures were

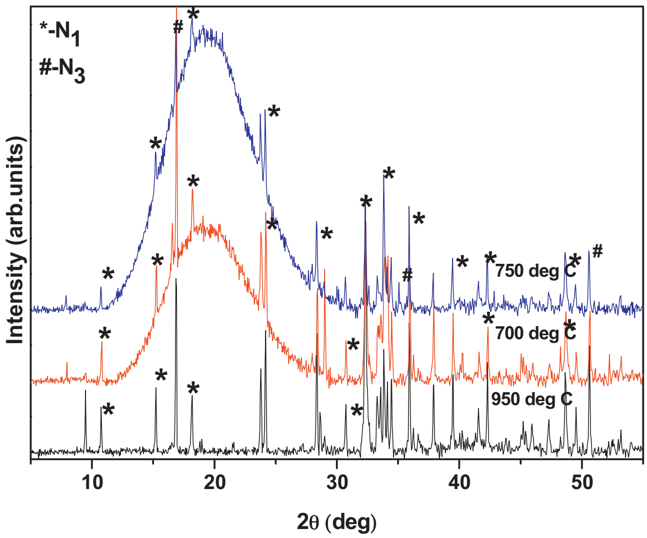

Fig. 5. XRD patterns of spark plasma sintered $Na_5DySi_4O_{12}$ at different temperatures.

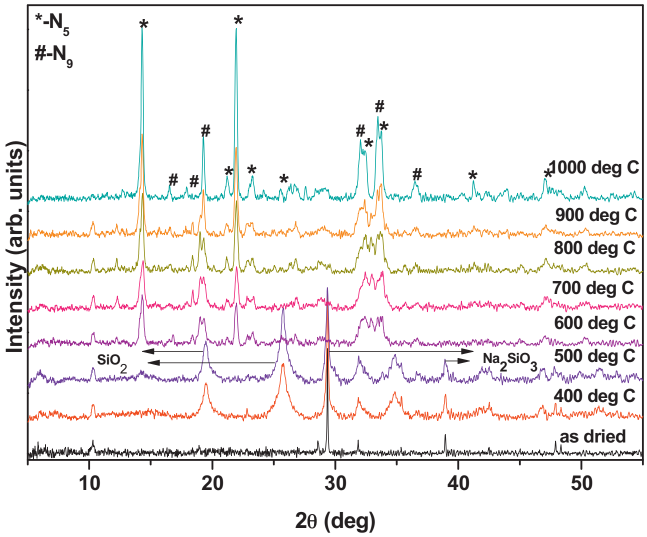

Fig. 6. XRD patterns of conventionally heat treated $Na_5DyPSi_4O_{12}$ from 400 °C to 1000 °C.

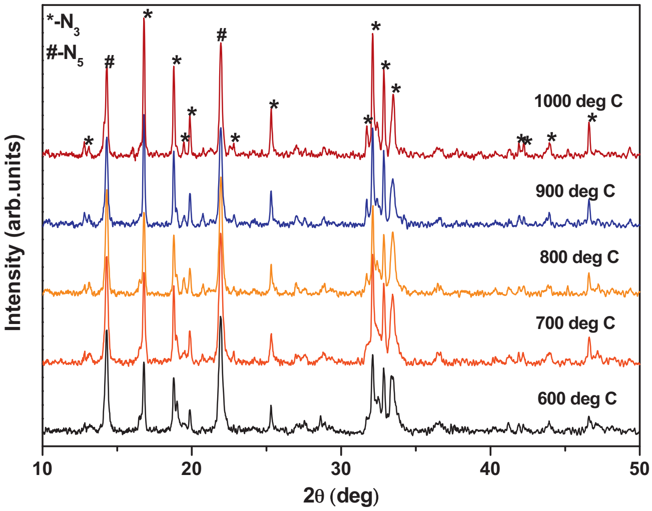

Fig. 7. XRD patterns of conventional heat treated $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ from 600 °C to 1000 °C.

seen to be similar. The XRD of $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ as shown in Fig. 7 revealed that the samples heat treated from 600 °C to 1000 °C exhibited a similar pattern with each other. It was observed that, here also, N_5 phase was achieved by preparation of samples with the above mentioned composition. But again the material obtained was not a single phase but always a mixture of phases corresponding to N_5 and N_3 with N_3 phase being the major phase, irrespective of heat treatment temperatures.

From the obtained XRD patterns, it was seen that sodium dysprosium silicate samples with phosphorous doping were found to exhibit the required N_5 phase. Although the required phase was obtained, it was always a mixture of phases, i.e. N_5 phase co-existing along with either N_1/N_3/N_9 phase. Fig. 8 shows a schematic representation of the phases of sodium dysprosium silicate system when different compositions were conventionally heat treated at different temperatures. The results of the present investigation were highly reproducible and provided insight into the phase stabilities of phases in Na–Dy–Si–O system on which very little information exists in the literature.

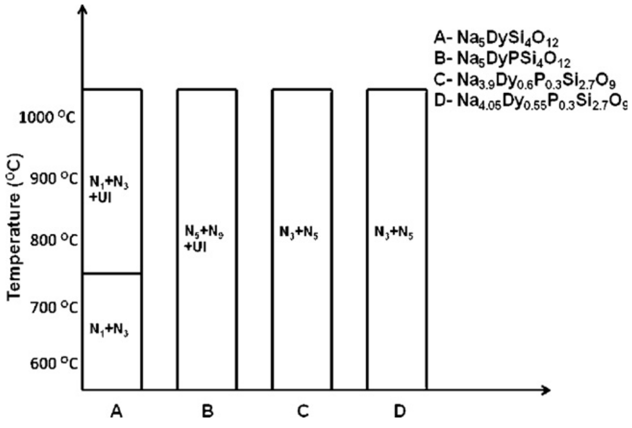

Fig. 8. Schematic showing phases of sodium dysprosium silicate present when different compositions were conventionally heat treated at various temperatures. UI, unknown phase.

3.3. Conductivity measurement and scanning electron microscope analysis

Though a single phase N_5 could not be obtained in the present study, it was of immense interest to find out the ionic conductivities of the phases obtained by different heat treatment techniques. Hence, impedance measurements were carried out for conventionally heat-treated, microwave irradiated and spark plasma sintered $Na_5DySi_4O_{12}$ samples. The room temperature (25 °C) conductivities of microwave heat treated samples were found to be 8.7e−6 S cm^{-1}, 15.8 e−6 S cm^{-1} and 4.1 e−6 S.cm^{-1} for soaking times of 0.5 h, 1 h and 2 h respectively. The room temperature conductivity of conventionally heat treated sample at 1130 °C for 8 h was found to be 2.4e−6 S cm^{-1}. In case of spark plasma sintered samples, conductivities measured at a slightly higher temperature of 150 °C for samples sintered at 750 °C and 950 °C were found to be 1.3e−7 S cm^{-1} and 7e−6 S cm^{-1} respectively. It can be seen that the pure N_3 phase obtained by microwave heat treatment is more conducting than a mixture of N_1 and N_3

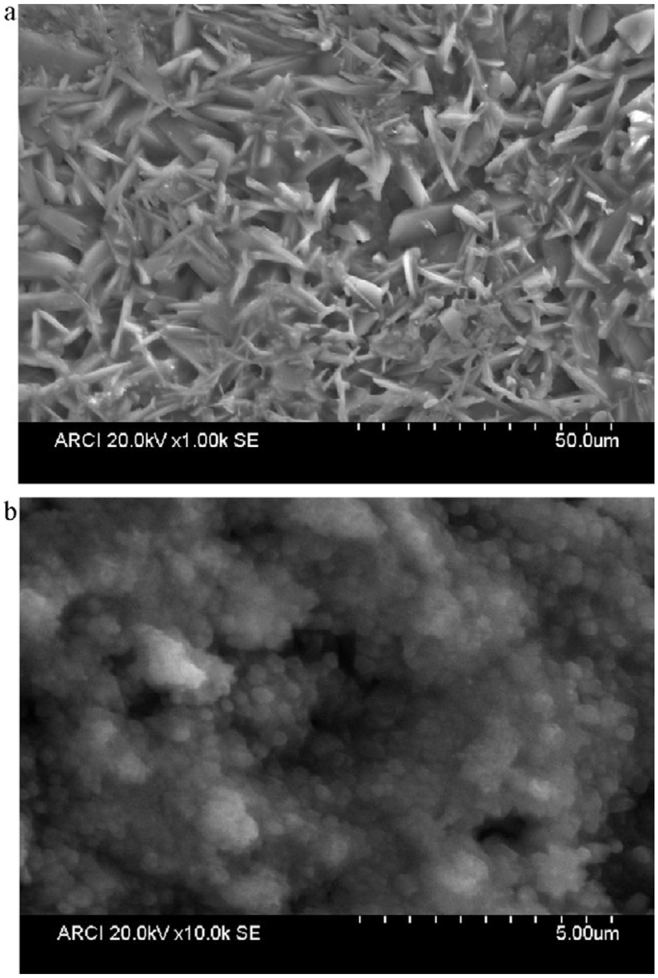

Fig. 9. SEM images of spark plasma sintered $Na_5DySi_4O_{12}$ sintered at (a) 750 °C and (b) 950 °C.

phases obtained by conventional heat treatment and spark plasma sintering. The difference in conductivity values of 750 °C and 950 °C spark plasma sintered samples is nearly of one order and such a large difference can be attributed to the presence of glassy sodium silicate as seen from Fig. 9a which is the SEM image for sample sintered at 750 °C that reveals needle-like structures. This can also be confirmed by the presence of broad amorphous background in XRD (Fig. 5). The surface morphology of samples sintered at 950 °C (Fig. 9b) reveals considerably higher amount of sintering though there still exists some porosity.

4. Conclusions

Sodium dysprosium silicate samples with/without phosphorous doping were synthesized using sodium silicate, dysprosium nitrate and TEOS precursors along with ammonium dihydrogen phosphate. Four different compositions of sodium dysprosium (phospho)silicates such as $Na_5DySi_4O_{12}$, $Na_5DyPSi_4O_{12}$, $Na_{3.9}Dy_{0.6}P_{0.3}Si_{2.7}O_9$ and $Na_{4.05}Dy_{0.55}P_{0.3}$-$Si_{2.7}O_9$ were prepared. It was found that the highly Na^+-conducting N_5-type crystal structured phase could be stabilized by phosphorous doping of the sodium dysprosium silicate. This study showed for the first time in literature, stabilization of the required N_5 structure in Na–Dy–Si–O system by doping phosphorous into the sodium dysprosium silicate. From the results of conductivity measurements, it was realized that the conductivity values of compositions measured over the temperature range from 25 °C to 150 °C were of the order $\sim 10^{-6}\ \mathrm{S\ cm^{-1}}$ for conventional, microwave heat treated and spark plasma sintered samples. Further studies are in progress in order to probe deep into the sodium dysprosium silicate system to achieve a stabilized single phase with N_5 crystal structure.

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