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INVESTIGATION ON PURITY AND THERMAL STABILITY OF Ag_2O RAW MATERIAL USED TO SYNTHESIS $Ag_2Nb_4O_{11}$ CERAMICS USING THERMAL AND PHASE ANALYSIS METHOD

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ABSTRACT

This paper reports on the newly found ferroelectric material, $Ag_2Nb_4O_{11}$ ceramics synthesised using solid state reaction and characterised its properties using X-ray powder diffraction, ferroelectric test and impedance spectroscopy. However, the synthesis of phase-pure $Ag_2Nb_4O_{11}$ ceramics was unsuccessful due the presence of other phases such as $AgNbO_3$, Ag metal and un-reacted Nb_2O_5 raw material. The inhomogeneity of the sample was clearly seen in impedance measurement which showed electrical inhomogeneity of bulk and grain boundary capacitances. Difficulties in obtaining phase-pure $Ag_2Nb_4O_{11}$ ceramics has motivated an investigation on the purity and thermal stability of Ag_2O raw material. X-ray diffraction patterns showed that $Ag_2Nb_4O_{11}$ consist of $Ag_2Nb_4O_{11}$, $AgNbO_3$, Ag metal and un-reacted raw material. Studies on Ag_2O raw material was carried out by heating and weighing it after each different temperature. Weight loss observed at temperatures 120°C, 270°C and 400°C correspond to the loss of water and the decomposition of Ag_2O to Ag metal. In this study, the Ag_2O used was mostly contained Ag metal than the Ag_2O. The instability nature of Ag_2O at high temperature may contribute to the difficulties in obtaining phase pure $Ag_2Nb_4O_{11}$ product.

1.0 INTRODUCTION

Research on a newly found ferroelectric material, $Ag_2Nb_4O_{11}$ by Masó et al., (2009) has recently gained interest where it was reported to exhibit a permittivity, ε maximum of ~150 at ~400 K. $Ag_2Nb_4O_{11}$ structure was reported to be monoclinic (*C2/c*) at room temperature with a = 10.7642(1) Å, b = 6.20097(5) Å, c = 12.8581(1) Å, β = 106.183(2) [1]. The polarization, (P) vs. electric field, (E) hysteresis loop at room temperature reported the remnant polarization P_r = 1 cm^{-2} and the coercive field strength E_C = -10 MVm^{-1} [1]. Formerly identified as a secondary phase of well-studied $AgNbO_3$, $Ag_2Nb_4O_{11}$ possesses low thermal stability that only stable up to 800°C before it decomposes to a mixture of $AgNbO_3$ and $AgNb_3O_8$[2]. $Ag_2Nb_4O_{11}$ was previously known for its unique structure for the past 30 years; Jahnberg, (1981) described the crystal structure of $Ag_2Nb_4O_{11}$ consists of layers of pentagonal bipyramids alternating with layers of octahedral. The Nb atoms are positioned between the layers, octahedral surrounded by six apex oxygen atoms of the pentagonal bipyramids above and below the layer, whilst Ag atoms are located between layers and surrounded by six O_2 that form an extremely distorted octahedron [3-6].

Despite all the data reported, they are still insufficient to prove that $Ag_2Nb_4O_{11}$ are ferroelectric; the necessity of structural data is vital to support the statement [1,3]. Therefore, we are interested in studying $Ag_2Nb_4O_{11}$ and explore further on its other potential properties. However, we are facing

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difficulties in synthesizing phase-pure $Ag_2Nb_4O_{11}$ ceramics due to the presence of impurities. Several attempts have been carried out using Ag_2O as starting material, however, the aim to synthesis phase-pure sample were unsuccessful. In this paper, we report on the preliminary results of $Ag_2Nb_4O_{11}$ ferroelectrics characterization as well as studies on the purity and thermal stability of Ag_2O raw material in conjunction to the challenges in obtaining phase-pure $Ag_2Nb_4O_{11}$ samples; no detailed studies on its electrical properties have been reported so far. Therefore, results and discussion part will be divided into two (2) sections: i) preliminary studies on $Ag_2Nb_4O_{11}$ and ii) studies on purity and thermal stability of Ag_2O raw material.

2.0 METHODOLOGY

Preliminary work on $Ag_2Nb_4O_{11}$ ceramics sample was prepared by solid state reaction using Ag_2O (99%, Sigma Aldrich) and Nb_2O_5 (99.9%, Sigma Aldrich) raw materials based on the following chemical equation: $Ag_2O + 2(Nb_2O_5) \rightarrow Ag_2Nb_4O_{11}$. Dried raw materials were weighed according to the stoichiometric formula. The powders were mixed manually in acetone using a mortar and pestle for 30 minutes, dried, pelleted and fired at increasing temperatures with final firing at 800°C overnight in air and cooled naturally by switching off the furnace. The phase of $Ag_2Nb_4O_{11}$ was analysed using X-ray powder diffraction, XRD at room temperature using StoePSD diffractometer, Cu $K\alpha_1$ radiation, λ = 1.5406 Å. The instrument was calibrated using Si external standard.

For electrical property measurements, pellets (~1.2 mm thick and ~10 mm diameter) were prepared by uniaxial pressing with pellet densities were ~56%. Electrodes were fabricated on opposite pellet faces from Au paste, which was dried, decomposed and hardened by gradually heating to 800°C. Samples with electrodes attached were placed into a conductivity jig and fixed frequencies measurement data recorded using HP 4284A Inductance, Capacitance, Resistance (LCR) meter at fixed frequency range 1 KHz, 10 KHz, 100 KHz and 1 MHz and temperature range 30°C to 700°C. Impedance data were recorded using HP 4192A impedance analyser over the standard frequency range 10 Hz to 1 MHz. Data analysis was carried out using the software program ZView version 2.1B.

Hysteresis studies used an RT-66A Standardize Ferroelectric Test System linked to a computer. A high voltage amplifier was connected to a ferroelectric test system via an RT66A high voltage interface. Pellets were dropped in a silicone oil bath and aligned under the pin holder and the measurements were recorded from low to high applied of electric field (0.5 MVm^{-1} to 2.5 MVm^{-1}) at room temperature.

For raw material studies, Ag_2O (99% pure, Sigma Aldrich) powder weighed 1.1316 g was heated in electric muffle furnace for 30 minutes at temperatures in the range 30°C – 800°C, intermittently; exceeding 800°C will possibly leads to reaction of Ag_2O raw material. Powder was removed from the furnace and let cool in vacuumed desiccator before the remaining powder was weighed after each temperature. Investigation was conducted at two different temperature ranges: i) 30°C to 800°C to provide general information on the decomposition trend of Ag_2O powder reagent with temperatures and, ii) 30°C to 300°C to study the stability trend at low temperatures. Phase analysis by X-ray powder diffraction, XRD was carried out using Phillips PW1710 measured in the 2θ range 10° to 70°.

3.0 RESULTS AND DISCUSSION

3.1 Preliminary Studies On $Ag_2Nb_4O_{11}$ Ceramics: Analysis Phase

Figure 1 shows the XRD pattern of $Ag_2Nb_4O_{11}$ sample using Ag_2O as starting material. Relative peak intensities of $Ag_2Nb_4O_{11}$ correspond well with the $Ag_2Nb_4O_{11}$ pattern reported in the ICDD card (21-1086) and by matching these reflections with those of known structures, sample contained impurity phases identified as $AgNbO_3$ observed 2θ = 28°, 46.45°, 57.43°, 57.78°, Ag metal at 38.31°, 44.1°, 64.4°, and un-reacted Nb_2O_5 at 22.8°, 42.6°. Upon further heat treatment, the impurities peaks became prominent whilst $Ag_2Nb_4O_{11}$ structure was gradually diminished; this confirms that $Ag_2Nb_4O_{11}$ is stable up to only 800°C and decomposes to form a mixture of $AgNbO_3$ and another compound [2]. $Ag_2Nb_4O_{11}$ ceramics was found monoclinic, space group *C2/c* at room temperature with unit cell dimensions obtained: a = 10.807(3) Å; b = 6.295(3) Å; c = 13.18(5) Å; β = 103.31° (3) compared to literature: a = 10.745(3) Å; b = 6.201(2) Å; c = 12.843(4) Å; β = 106.18(2)° [3] due to the presence of impurities. The existence of Ag metal as one of the impurity phases was not known; Rozier and Szajwaj, 2009 reported that some points

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need to be considered when using Ag compound as raw material since spontaneous reduction of Ag oxide may occur and/or the formation of Ag metal during heat treatment [2].

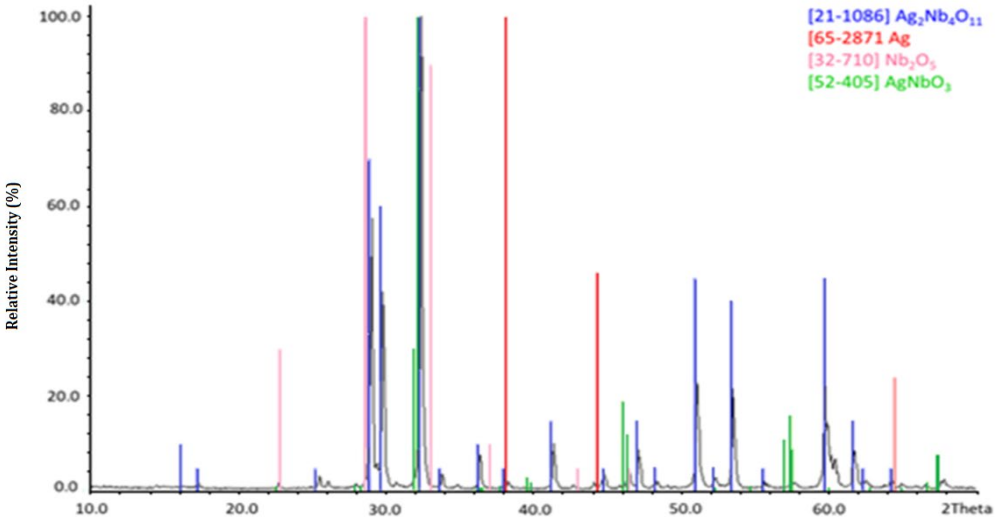

Figure 1. XRD pattern of mixture phases containing $Ag_2Nb_4O_{11}$, $AgNbO_3$ and other impurity phases fired at 800°C for overnight

3.2 Preliminary Studies On $Ag_2Nb_4O_{11}$ Ceramics: Ferroelectric Measurement

Figure 2 shows fixed frequencies measurements as a function of temperature for 100 kHz and 1 MHz data where a shoulder is observed at Curie temperature, $T_c \sim 120^oC$. $Ag_2Nb_4O_{11}$ sample exhibited lower value of maximum permittivity ~110 compared to literatures ~150 [1,3] which most likely due to the non-phase pure sample of $Ag_2Nb_4O_{11}$. Polarisation, (P) vs. electric field, (E) hysteresis loop at room temperature shown in Figure 3, does not show unambiguous evidence of ferroelectricity; the 'ellipsoidal' shape of hysteresis loop was attributed to the poor insulating properties of $Ag_2Nb_4O_{11}$ [3] with the value of remnant polarization, $P_R = 1\ cm^{-2}$ and coercive field strength, $E_C = -10\ MVm^{-1}$.

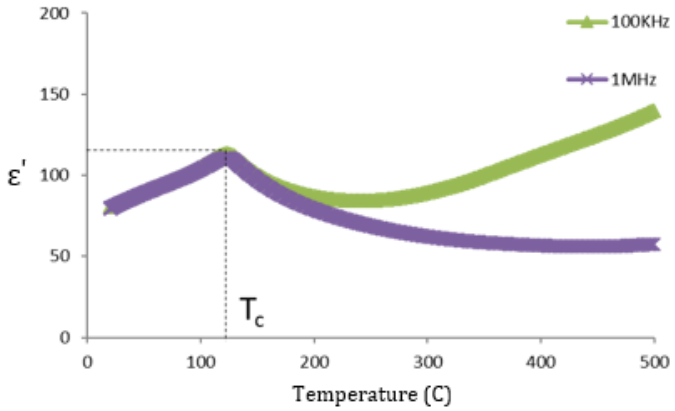

Figure 2. Permittivity, ε' versus temperature at fixed frequencies of 100 KHz and 1 MHz

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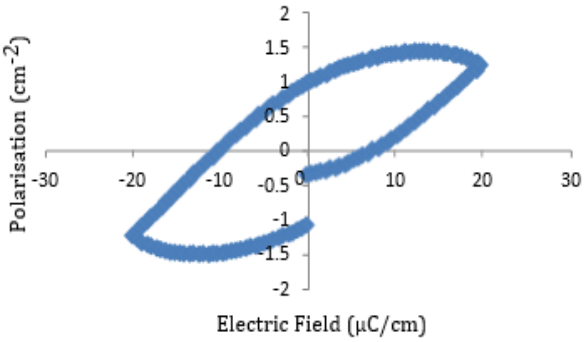
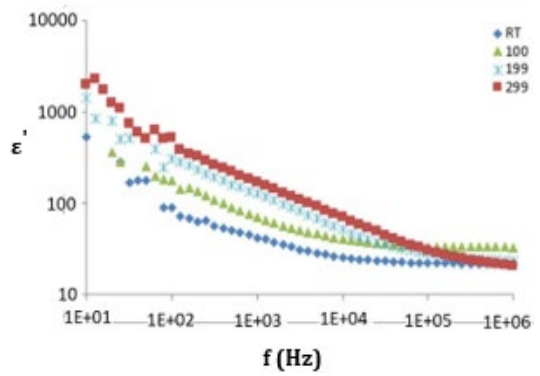


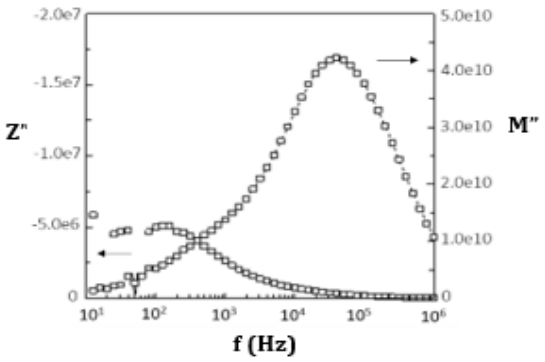
Figure 3. P-E hysteresis loop of $Ag_2Nb_4O_{11}$ ceramics at room temperature

3.3 Preliminary Studies On $Ag_2Nb_4O_{11}$ Ceramics: Impedance Measurement

Preliminary studies of electrical properties for $Ag_2Nb_4O_{11}$ ceramics were carried out using impedance spectroscopy. Capacitance, C' measurement from 28°C to 300°C were converted to permittivity's, ε' as a function of frequency, where at room temperature, the permittivity is ~ 30, as shown in Figure 4(a). At these temperature ranges, permittivity data demonstrates low frequency dispersion of temperature- and frequency-dependent behaviour which perhaps attributed to complex interplay of: i) contribution from the impurity phases that present in the sample, as shown in Figure 1, ii) electrical inhomogeneity of the samples which consists of bulk and grain boundary as shown in Figure 4(b) and iii) the non-idealist of the bulk response which may be represented by a constant phase element, (CPE). Figs. 4(c) and (d) show the variation of electrical conductivity as a function of frequency at low and high temperatures of $Ag_2Nb_4O_{11}$ ceramics sample, respectively. Plateau region at low frequencies corresponds to bulk or dc conductivity, σ_{dc} which increases with the increasing temperature, whilst at high frequencies the conductivity is governed by $A_\omega{}^n$, where n is a constant and ω is the angular frequency. Generally, the conductivity behaviour of $Ag_2Nb_4O_{11}$ increases with the increasing temperature and fall within the range between 10^{-8} Ω^{-1} and 10^{-5} Ω^{-1} which demonstrates that the electrical conductivity of the material is thermally activated. However, the real properties of $Ag_2Nb_4O_{11}$ ceramics were not able to be measured due to the presence of other impurity phases. We believe that the purity of raw materials used contribute to the quality of samples produced therefore, we decided to investigate the purity of Ag_2O raw material to necessarily understand the issue in producing phase-pure $Ag_2Nb_4O_{11}$ ceramics. In this work, thermal method was used to determine the purity and thermal stability of Ag_2O raw material by monitoring the weight change that occurred at a constant heat rate of 5°C/min.



(a)



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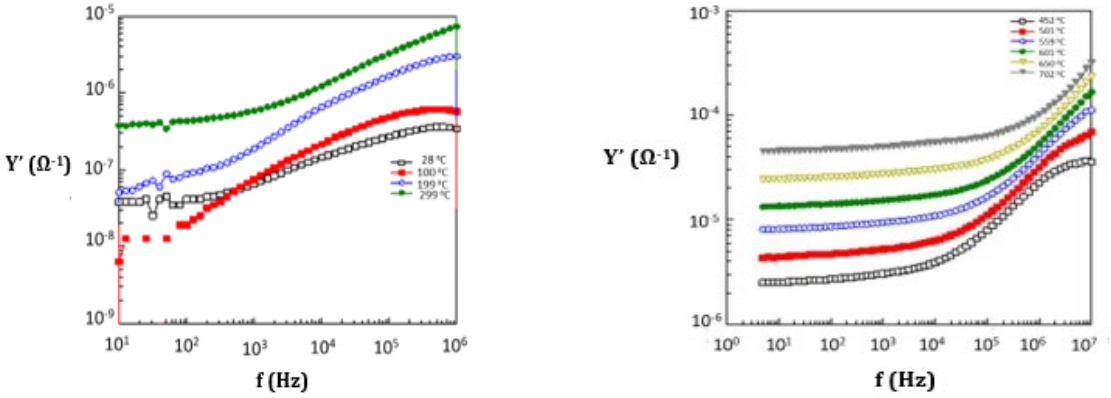

(c) (d)

Figure 5: (a) graph permittivity, ε' vs frequency, f for $Ag_2Nb_4O_{11}$ sample from 28°C to 300°C, (b) impedance, Z" and modulus, M" vs. frequency, f measured at 200°C, (c) admittance, Y' data vs frequency, f from 28°C to 300°C and (d) admittance, Y' data vs frequency, f from 450°C to 700°C

3.4 Studies On The Purity And Thermal Stability Of Ag_2O Raw Material

The graph of weight (g) versus temperature for Ag_2O powder upon heat treatment from 30°C to 800°C is shown in Figure 6 while Table 1 displays the details of cumulative weight loss and its percentage, as well as variation of colour changes as temperatures applied. From 30°C to 300°C, the oxide's weight decreased gradually from 1.1316 g to 1.1208 g however, when temperature of 400°C was applied, a sharp decrease observed before remained constant at 1.089 g throughout the temperatures. Changes in colour variation was also observed with the application of heat treatment; blackish brown of Ag_2O powder gradually changes its colour to grey at ~ 210°C before finally changes to whitish as the temperature increased to 400°C.

For detailed observation trend at low temperatures, the experiment was repeated from 30°C to 300°C. The oxide specimen gave reproducible results where the shapes of weight- temperature plots were similar. It is observed that the decomposition occurred in two steps i.e. 120°C and 270°C, as shown in Figure 7. Weight loss details of Ag_2O powder at low temperature ranges in Table 2 shows that the cumulative weight loss for 120°C and 270°C are 0.0005 g and 0.0083 g, respectively and the difference is pronounced. Figs. 8 (a) and (b) show the XRD patterns of Ag_2O powder at 30°C and 250°C. Relatively, no changes of XRD patterns detected and the powder remained to consist of Ag_2O, Ag metal and small amount of other impurity, until the temperature of 400°C was applied; the oxide undergoes decomposition which resulted to pure Ag metal phase, Figure 8(c).

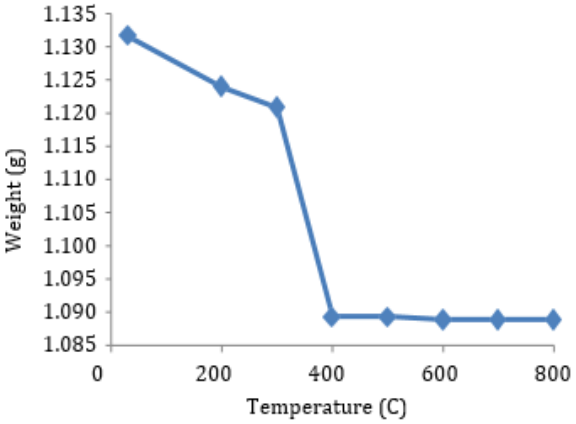

Figure 6. Weight loss vs. temperature for Ag_2O powder from 30°C to 800°C

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Table 1. Data on weight loss of Ag_2O from 30°C to 800°C

T (°C)	Weight (g)	Cumulative Weight Loss (g)	Percentage of Weight Loss (%)	Colour
30	1.1316	-	-	Black brown
200	1.1239	0.0077	0.681	Grey
300	1.1208	0.0108	0.954	Grey
400	1.0893	0.0423	3.738	Off white
500	1.0893	0.0423	3.738	Off white
600	1.0888	0.0428	3.782	Off white
700	1.0888	0.0428	3.782	Off white
800	1.0887	0.0429	3.791	Off white

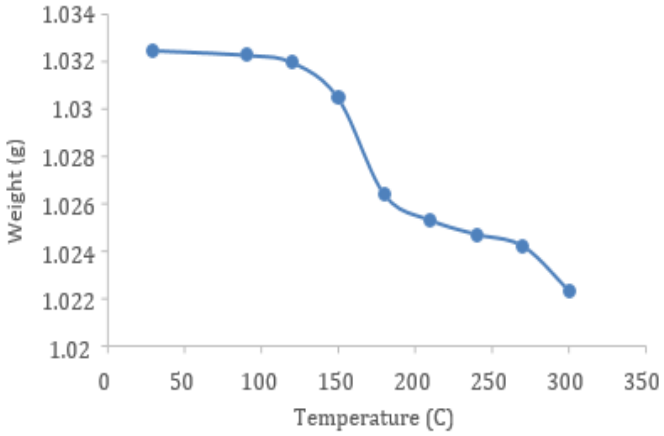
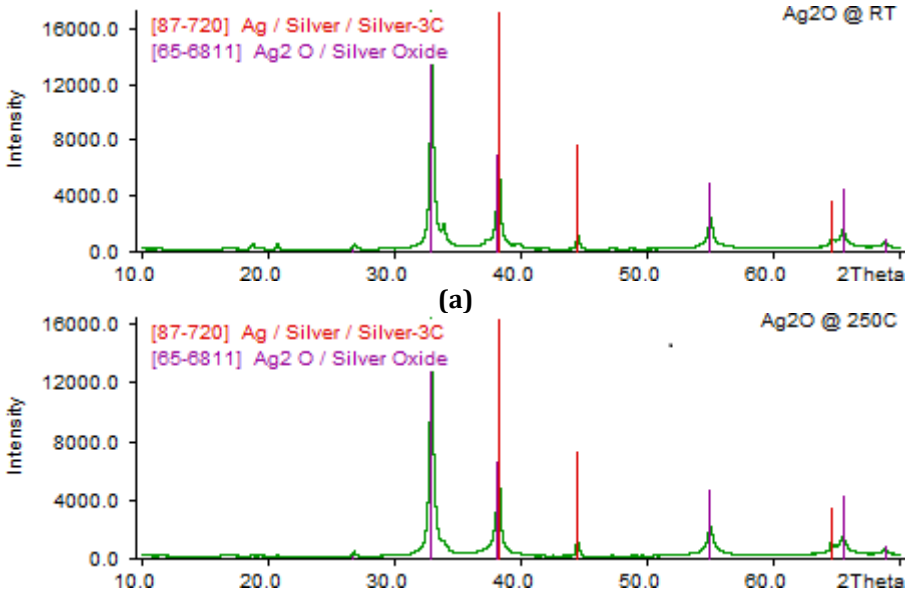


Figure 7. Weight loss vs. temperature for Ag_2O powder at 30°C to 300°C

Table 2. Data on weight loss of Ag_2O from 30°C to 300°C

T (°C)	Weight (g)	Cumulative Weight Loss (g)	Colour
30	1.0325	-	Black brown
90	1.0323	0.0002	Black brown
120	1.0320	0.0005	Black brown
150	1.0305	0.002	Black brown
180	1.0264	0.0061	Black brown
210	1.0253	0.0072	Grey
240	1.0247	0.0078	Grey
270	1.0242	0.0083	Grey



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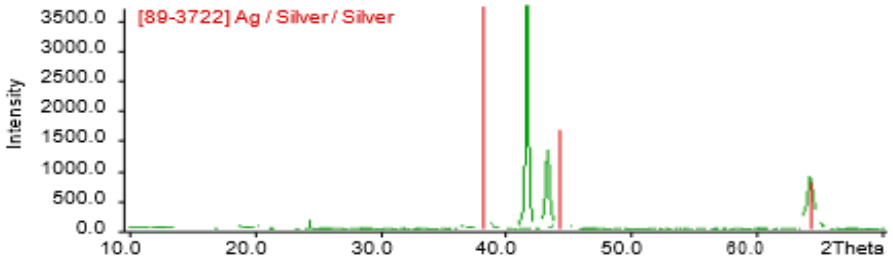

(c)

Figure 8. XRD patterns of Ag_2O powder at (a) 30°C, (b) 250°C and (c) 400°C matched with Ag metal (red lines) and Ag_2O (purple lines)

At low temperature, the difference of weight loss at 120°C and 270°C is large ~ 0.0078 g which possibly attributed to the loss of H_2O or decomposition of hydroxide phase. As the temperature increased to 400°C, cumulative weight loss increased to 0.042 g which corresponds to the loss of oxygen in which half an oxygen molecule is released as oxygen gas to produce Ag residue according to the following reaction:

$$Ag_2O \rightarrow 2Ag + 1/2\ O_2 \quad (1)$$

The amount of Ag_2O and Ag metal have been calculated theoretically, using molar equation, where each compound is 0.4004 g and 0.3728 g, respectively. However, in this experiment the amount of Ag metal found was 0.3902 g, which 0.00174 g more than the calculated value whilst for Ag_2O, the amount of experimental and calculated are consistent with each other. This leads to an indication that the Ag_2O (99% pure, Sigma Aldrich) raw material contains Ag_2O with large amounts of Ag metal that contributed to the undesired excessive Ag metal found in $Ag_2Nb_4O_{11}$ sample, Figure 1. It is clear, that Ag_2O is stable only at low temperatures as reported widely in literatures [5-6]. Literature reported similar observation on the formation of Ag residue at 400°C using Ag_2O reagent [2]. In this study, it is presumed that the Ag_2O powder decomposes at 400°C to give Ag residue and re-oxidizes at higher temperatures during the reaction that occurs simultaneously among three phases: Nb_2O_5, Ag and O_2.

The colour contrast with the heat treatment may be used as initial indicator of Ag_2O decomposition process. Black brownish colour of Ag_2O raw material corresponds to its feature which spontaneously oxidizes at room temperature. The change from black brownish to grey colour indicates that the oxide is in the middle decomposition process before finally turned to whitish metallic of Ag metal. In this study, the instability of Ag_2O (99% pure, Sigma Aldrich) raw material may be responsible to the failure in synthesizing phase pure $Ag_2Nb_4O_{11}$ ceramics; content inspection of a raw material and its purity are essential prior using it [9-10].

4.0 CONCLUSION

Synthesis of phase-pure $Ag_2Nb_4O_{11}$ ceramics has not been achieved using solid state reaction method. XRD pattern confirmed that the sample contained mixtures of $Ag_2Nb_4O_{11}$, $AgNbO_3$, Ag metal and un-reacted Nb_2O_5 raw material therefore, initiated further investigation in purity and thermal stability of Ag_2O starting material. In this work, thermal method was used to investigate the raw material; upon firing, weight loss occurred in two steps at ~ 120°C and 270°C which due to loss of H_2O or decomposition of a hydroxide phase. At 400°C Ag_2O powder decomposed to give Ag metal and re-oxidizes as the temperature increased further during the reaction with Nb_2O_5, Ag and O_2 for the case of synthesizing $Ag_2Nb_4O_{11}$ composition. Ag_2O commercial material, nominally 99% pure contained significant amounts of Ag metal together with unidentified crystalline phase(s) and therefore, contribute to the impurity of $Ag_2Nb_4O_{11}$ phase. It is of great importance to use high purity starting materials (99.9% purity and above) to ensure the production of good samples.

5.0 ACKNOWLEDGEMENT

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