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YTTRIUM ALUMINUM MONOCLINIC (YAM) SYNTHESIZED BY HIGH ENERGY BALL MILLING

M. K. IKHWAN[1], R. S. AZIS[2], M. HASHIM[3], DIANE HOLLAND[4], M. ZULKIMI[5], A. ZAKARIA[6] & J. HASSAN[7]

[1,2,6,7]Department of Physics, Universiti Putra Malaysia, UPM Serdang, Selangor, Malaysia

[2,3,5,6,7]Institute of Advanced Technology, Universiti Putra Malaysia, UPM Serdang, Selangor, Malaysia

[4]Department of Physics, University of Warwick, CV4 7AL, England, UK

ABSTRACT

The structural of the mixture of Y_2O_3-Al_2O_3 has been studied using X-ray diffraction and ^{27}Al MAS NMR. The sample was synthesized by high energy ball milling process. The polycrystalline YAM powder was form together with impurity YAP and $Y_2O_3$when heated at 1100^{o}C as confirm by XRD and NMR. Increasing heating temperature up to 1400^{o}C did not seem enough to completely transform Y_2O_3 and α-Al_2O_3 into YAM phase as the grain growth occur and increase the diffusion distance in solid state reaction.

KEYWORDS: $Y_4Al_2O_9$, High Energy Ball Milling, XRD, ^{27}Al MAS NMR

INTRODUCTION

According to the literature, there are three important intermediate compounds are known to exist in the Y_2O_3-Al_2O_3 system. These compounds correspond to the compositions of 3Y:5Al ($Y_3Al_5O_{12}$, YAG), Y: Al ($YAlO_3$, YAP) and 2Y: Al ($Y_4Al_2O_9$, YAM). Ceramics based on Y_2O_3-Al_2O_3 system is a promising material in semiconductor technology and also has been applying for numerous advanced applications [1]. For instance, the YAG doped with Nd is widely used as a lasing medium for solid state laser. In addition, the rare earth doped with YAG also excellent material for phosphor use in the development of display devices [2]. YAP is extensively used as gain media, scintillator and acousto-optic [3]. Finally, the least study material which is YAM are suggested to have potential applications in the field of advance plasma display panel [4] and as thermal barrier ceramic [5] due to excellent short decay time, photoluminescence and chromaticity and very low theoretical and experimental thermal conductivities.

There are many ways can be employed to synthesize the material, i.e. solid state method and wet chemical process. However, some chemical process has the intrinsic disadvantages over the conventional solid state reaction. For instance, using chloride or nitrate salt precursor in co-precipitation process will produce the anions that can damage the properties of synthesis powders and enhance the final products. To remove these ions required repeated washing resulted the changing in composition of the precipitates, which in turn makes it difficult to control the stoichiometric composition of the design compound [6].

Solid state reaction assisted by high energy ball milling (HEBM) is industrial important for processing powders at large scale. Basically, high energy ball milling is used to transform coarse-grained materials into nanostructured powders. During the process, the coarse source materials powders are crushed mechanically by collision between the balls and vials. In addition, the high energy ball milling may enhance the reactivity of multicomponent system, thus lowering formation temperature of the materials. In this work, we report the structural analysis of the powders synthesized by high energy ball milling using XRD and ^{27}Al MAS NMR analysis.

METHODS

The Yttrium Oxide (Y_2O_3) 99.9% Alfa Aesar and Aluminum Oxide (α-Al_2O_3) 99.9% Alfa Aesar were weighed according to the stoichiometric ratio. Those powders were then, mixed by dry milling for 24 h using alumina pot and balls. The mixed powder will be further milling by high energy ball milling for 4 hours using a SPEX8000D high energy ball milling machine. SPEX8000D was equipped by hardened steel vials and balls. The raw mixed powders were milled according to 10:1 ball to the powder weight ratio (BPR). The samples obtained were characterized by XRD and ^{27}Al MAS NMR.

XRD analysis was performed on Philips X'pert Diffractometer model 7602 EA Almelo. The polycrystalline powder was used for the test. XRD scans were made from 10° to 80° 2θ, using a scan rate of 12°/min in 0.03° increments and CuKα radiation (1.542 A°) operating at 45 kV and 40 mA. The PAN analytical X'Pert Highscore Plus software (version 2.2d (2.2.4)) was used to identify the crystallographic phases and to determine the relative phase compositions. ^{27}Al magic angle spinning (MAS) NMR experiments were performed using Varian spectrometer at 14.1 T, corresponding to Larmor frequencies, ν_o for ^{27}Al of 156.9 MHz. A 3.2 mm rotor was used with MAS frequency 15 kHz. A single pulse program was used with a pulse width of 1.0 μs to give a small tip angle of 15°; a pre-acquisition delay of 6.0 μs; a recycle delay of 2 s; and a typical acquisition time of 30 mins for each sample. These spectra were referenced against commercial yttrium aluminium garnet (YAG, $Y_3Al_5O_{12}$) as a secondary reference, with the signal corresponding to the octahedral aluminium site [AlO_6] set to 0.7 ppm[7]. The DmFIT2011 program[8] was used to simulate the spectra.

RESULTS AND DISCUSSIONS

XRD spectra of YAM as milled and heated at 800/1100/1200/1300/1400 ^oC are presented in Figure 1. It is noticed that the as-milled powder (see Figure 1a) consist of Y_2O_3 and α-Al_2O_3 phases, which means that there is no reaction between two components occurring during the milling process. The diffraction peak of Y_2O_3 and α-Al_2O_3 also not greatly broadened and their intensities still significant. This means, the high energy ball milling is not refine the Y_2O_3 and Al_2O_3 particles by means the energy provided by the collision between the highly speeded flying balls and the moving vials during the high-energy ball milling is not high enough to trigger reactions of multi-component systems at near room temperature. According to Kong et al., due to chemical inert property of Y_2O_3 and Al_2O_3, the activation energy is not enough to synthesis YAG at room temperature [6]. Sakura et al. also obtained disordered non-equilibrium phases in as milled sample when they are synthesized $Y_{1-x}Ce_xAlO_3$ by high energy ball milling [9]. There are also no peaks of impuritiesfrom the balls and vials observed from x-ray diffractogram. However, through the X-ray fluorescence (XRF)analysis, it was reveals that the as milled sample contains1.955 % of SiO_2, 0.582 % of SO_3, 0.307% of Fe_2O_3, 0.122 % of CaO and 0.074 % of Sc_2O_3 impurities.

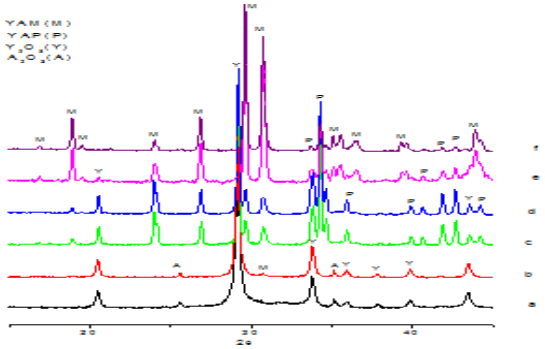
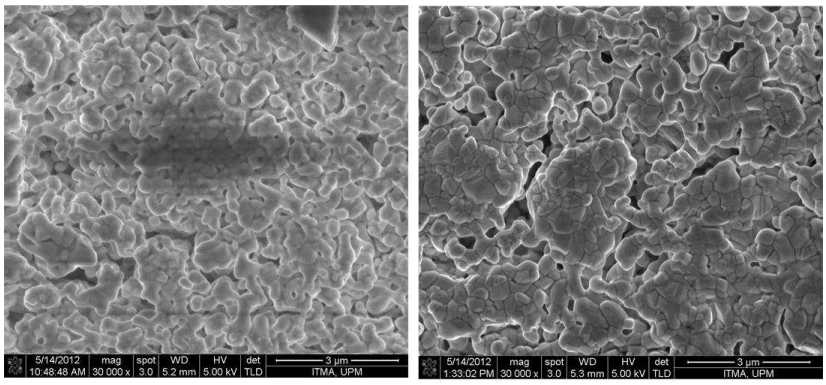


Figure 1: XRD Pattern of (a) the as-Milled Powders and Heated at (b) 800 ^oC, (c) 1100 ^oC (d) 1200 ^oC, (e) 1300 ^oC and (f) 1400 ^oC HEBM for 4 h

After heat treatment at 800 ^{o}C for 10 h, one of the main peaks located at 30.7 θ match perfectly with YAM database (PDF 34-0368), indicating that YAM phase is formed (Figure 1b). Some diffraction patterns of Y_2O_3 are observed for sample heated below 1300 ^{o}C. The impurity of YAP (PDF 87-1288) is observed in the sample heated between 1100 to 1400 ^{o}C. However the diffraction peak of YAP phase had decrease as it reaches certain heating stage. The decreasing of the peaks can be observed started at temperature 1300 ^{o}C. The decreasing of YAP phase occurs due to solid state reaction between YAP with Y_2O_3 phases to form YAM phase. The sample after heat treated at 1400 ^{o}C has shown the major phase of YAM with the minor small impurity phase of YAP. Retaining of YAP phase within the sample is due to the incomplete reaction within the system. So, it is suggested to heat the sample at slightly higher temperature in order to remove the remaining YAP phase. The high heating process is inevitable to produce the YAM phase, moreover when uses the stable α-Al_2O_3 as the alumina source. The uses of the stable α-Al_2O_3 as the alumina source to form YAM phase is not a great deal since the diffusion of Al^{3+} into Y_2O_3 lattice does not occur. Although, the YAM phase may produce at higher temperature, the grain growth of Y_2O_3 and α-Al_2O_3 is inevitable to occur as the temperature was increase. The grain growth will induced the longer diffusion distance of the solid state reaction [10].

Detailed microstructural information for the grain growth process was examined by FeSEM and the obtained photograph is shown in Figure 2. It can be seen in Figure 2, the grain growth was increase as the temperature increase. The average grain size determined by FeSEM are 292.5 and 328.5 nm for the samples heated at 1200 ^{o}C and 1300 ^{o}C respectively.



(a) **(b)**

Figure 2

^{27}Al MAS NMR is very helpful in discussing the aluminium-oxygen environment in the sol-gel derived YAM. In the YAM lattice, aluminium ions are known to occupy two types of tetrahedral site (AlO_4) in the ratio of 1:1 [11]. Florian *et.al* [11] determined the quadrupolar parameters for single crystal YAM: the quadrupole coupling constant C_Q is 10.8 MHz and 10.4 MHz and asymmetry parameter η_Q = 0.48 and 0.77 for each AlO_4 site. Figure 3 show the ^{27}Al MAS NMR spectra for YAM obtained at 14. T with the sample spinning speed at 15 kHz.

The spectrum was fitted using DmFIT[12], with AlO_6 and AlO_4 sites being simulated using Gaussian-Lorentzian (G-L) and Q_{MAS} lineshapes, respectively. For as milled and heated sample at 800 ^{o}C, the peak at 13.6 ± 1.0 ppm and 10.1 ± 1.0 ppm are from AlO_6 site corresponding to impurity α-Al_2O_3, agreeing with XRD. The sample heated at 800 ^{o}C also consists of small amount of YAM which is difficult to fit by DmFIT due to small peak intensity. For the sample heated at 1400 ^{o}C (Figure 4), AlO_6 peak belonging to YAP occur at 9.4 ± 1.0 ppm, whilst peaks at 77.3 ± 1.0 ppm and 79.7 ± 1.0 ppm represent the AlO_4 of YAM. All the NMR parameters from the fits are listed in Table 1.

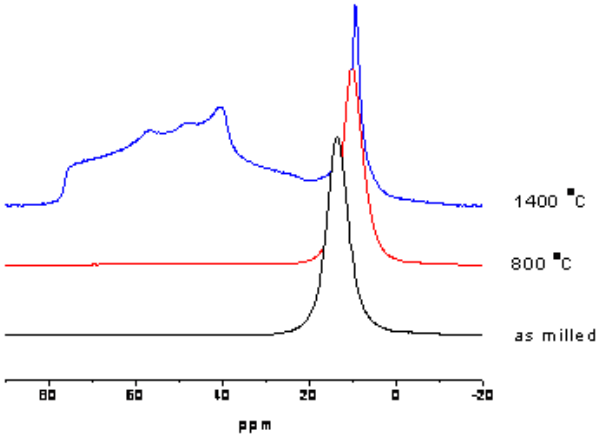


Figure 3: ^{27}Al MAS NMR of YAM Acquired at 14.1 T

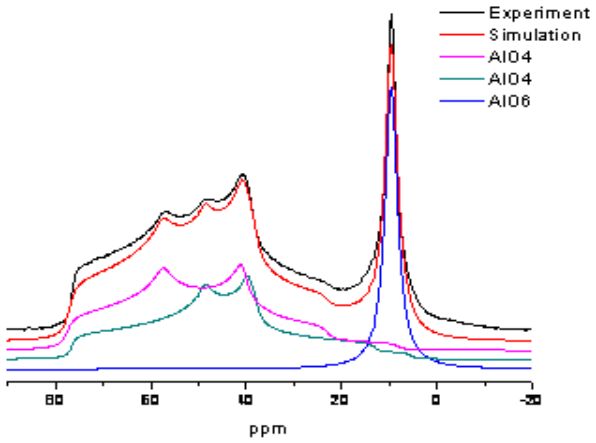


Figure 4: Experiment and Simulation of ^{27}Al MAS NMR of $Y_4Al_2O_9$ Heated at1400 ^{o}C

Table 1: ^{27}Al MAS NMR Parameters of YAM, as Milled and Heated at 800 and 1400 ^{o}C

Sample (^{o}C)	Site	Crys %	δ_{iso} ($\pm$1ppm)	C_Q ($\pm$0.1 MHz)	η_Q $\pm$0.05	% Calc. $\pm$1
As-milled	$AlO_{6(I)}$	100	13.6	-	-	100
800^{o}C	$AlO_{6(I)}$	100	10.1	-	-	100
1400^{o}C	$AlO_{6(II)}$	-	9.4	-	-	20.3
	AlO_4	50	77.3	10.4	0.74	35.9
	AlO_4	50	79.7	10.6	0.51	43.7

CONCLUSIONS

The structural of the mixture of $2Y_2O_3$: Al_2O_3 have been studied by XRD and ^{27}Al MAS NMR The high energy ball milling for 4 h did not seem able to completely refine the materials as strong diffraction patterns was observed from as prepared powders. Perhaps, need longer milling time. There are some contaminations introduced into the samples as the steel milling media was used. From the structural analysis, the presence of minor impurity YAP had been trace appear together with YAM and retain even the heating temperature was increase up to 1400 ^{o}C.

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