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Mechanochemical synthesis of $MgTa_2O_6$ ceramic

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Abstract

$MgTa_2O_6$ powders were prepared by mechanochemical synthesis from MgO and Ta_2O_5 in a planetary ball mill in air atmosphere using steel vial and steel balls. High-energy ball milling gave nearly single-phase $MgTa_2O_6$ after 8 h of milling time. Annealing of high-energy milled powder at various temperatures (700–1200 °C) indicated that high-energy milling speed up the formation and crystallization of $MgTa_2O_6$ from the amorphous mixture. The powder derived from 8 h of mechanical activation gave a particle size of around 28 nm. Although at low-annealing temperatures the grain size was almost the same as-milled powder, the grain size increased with annealing temperature reaching to around 1–2 μm after annealing at 1200 °C for 8 h.

Keywords: B. X-ray methods; $MgTa_2O_6$; Mechanochemical synthesis; High-energy milling

1. Introduction

The dielectric ceramics at microwave frequency have been paid much attention for their applications in microwave resonators, filters, antennas and wave guides due to rapid progress of mobile and satellite communication systems such as cellular phones and global positioning satellite devices. These applications require a combination of high-dielectric permittivity ($\varepsilon_r > 15$), near zero temperature coefficient of rersonant frequency (τ_f) and high-quality factor (Q). A higher permittivity value enables the resonator size to be reduced [1]. A very small temperature coefficient of resonant frequency (less than ±10 ppm/°C) is necessary for the stability of the device at room temperature. The quality factor of dielectric resonators determines their frequency selectivity.

Niobium and tantalum-based oxides such as $Ba_3MgNb_2O_9$, $Ba_3MgTa_2O_9$ and $Ba_3ZnTa_2O_9$ are good canditates for dielectric resonators at microwave frequencies [2,3]. Complex perovskite compounds with general formula of $A(B_{1/3}B'_{2/3})O_3$ such as $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Mg_{1/3}Nb_{2/3})O_3$ are also known to posses high-dielectric microwave properties [4,5]. In addition, in a recent study excellent microwave dielectric properties were obtained for $Ba[Mg_{1/3}(Nb_{x/4}Ta_{(4-x)/4})_{2/3}]O_3$ compound ($x = 1$) where Nb and Ta form solid solution [6]. Another type of oxides that contain Nb or Ta and are investigated for their microwave dielectric properties are AB_2O_6 compounds (A = Ca, Mg, Mn, Co, Ni, Zn; B = Nb and Ta) which have columbite or trirutile structure [7,8].

$MgTa_2O_6$ has trirutile structure and it has applications as microwave dielectric materials due to its dielectric properties. $MgTa_2O_6$ has a dielectric constant in the range of 25–30, quality factor of 28.500–58.000 and temperature coefficient of resonant frequency of 22–28.5 depending on the sintering temperatures of 1400–1550 °C.

In this study, $MgTa_2O_6$ ceramic was produced using mechanochemical synthesis. Effect of milling time and annealing temperature on the formation of $MgTa_2O_6$ was investigated in detail. Produced powders were examined using X-ray diffraction and scanning electron microscopy.

2. Experimental

Starting reagents were $Mg(OH)_2$ (Merck, 99.8%) and Ta_2O_5 (Merck, 99.9%) with nominal composition of $MgTa_2O_6$. $Mg(OH)_2$ was converted to MgO at 1200 °C prior to use. The high-energy ball milling was carried out in a planatery ball mill (Fritsch Pulverisette 5) under following milling conditions: stainless steel vial (500 ml) and balls (10 mm in diameter), ball-to-powder ratio was 40:1, air atmosphere, rotation speed of

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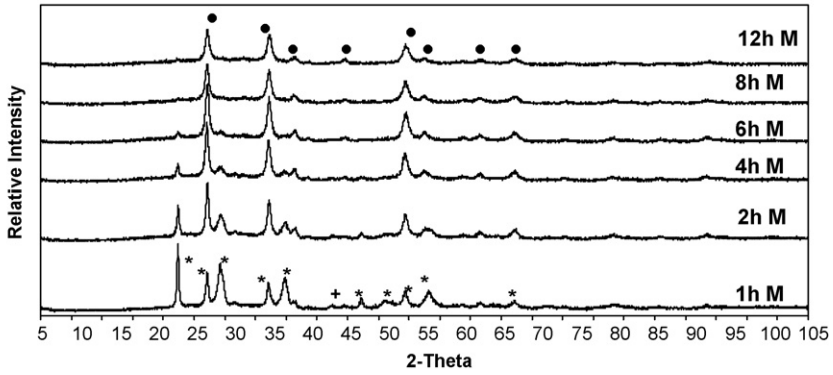

Fig. 1. Effect of milling time on the formation of $MgTa_2O_6$ phase in mechanochemical synthesis after high-energy milling of 1, 2, 4, 6, 8 and 12 h ('*' tantalum oxide; '+' MgO; '●' $MgTa_2O_6$).

discs with vials was 280 min^{-1} and milling time was 1, 2, 3, 4, 8 and 12 h. The milled powder was annealed for 8 h at temperatures from 900 to 1200 °C in air.

Phase composition of the milled and annealed powders was determined by X-ray powder diffraction analysis (XRD) on Rigaku powder diffractometer using Cu Kα radiation. The average crystallite size of the milled powder was estimated using the Scherrer formula [9]:

$$D = \frac{k\lambda}{B\cos\theta}$$

where D is the mean particle size (nm), k a constant (taken as 0.9), $\lambda = 0.15406$, the wavelength of Cu Kα, B the full width at

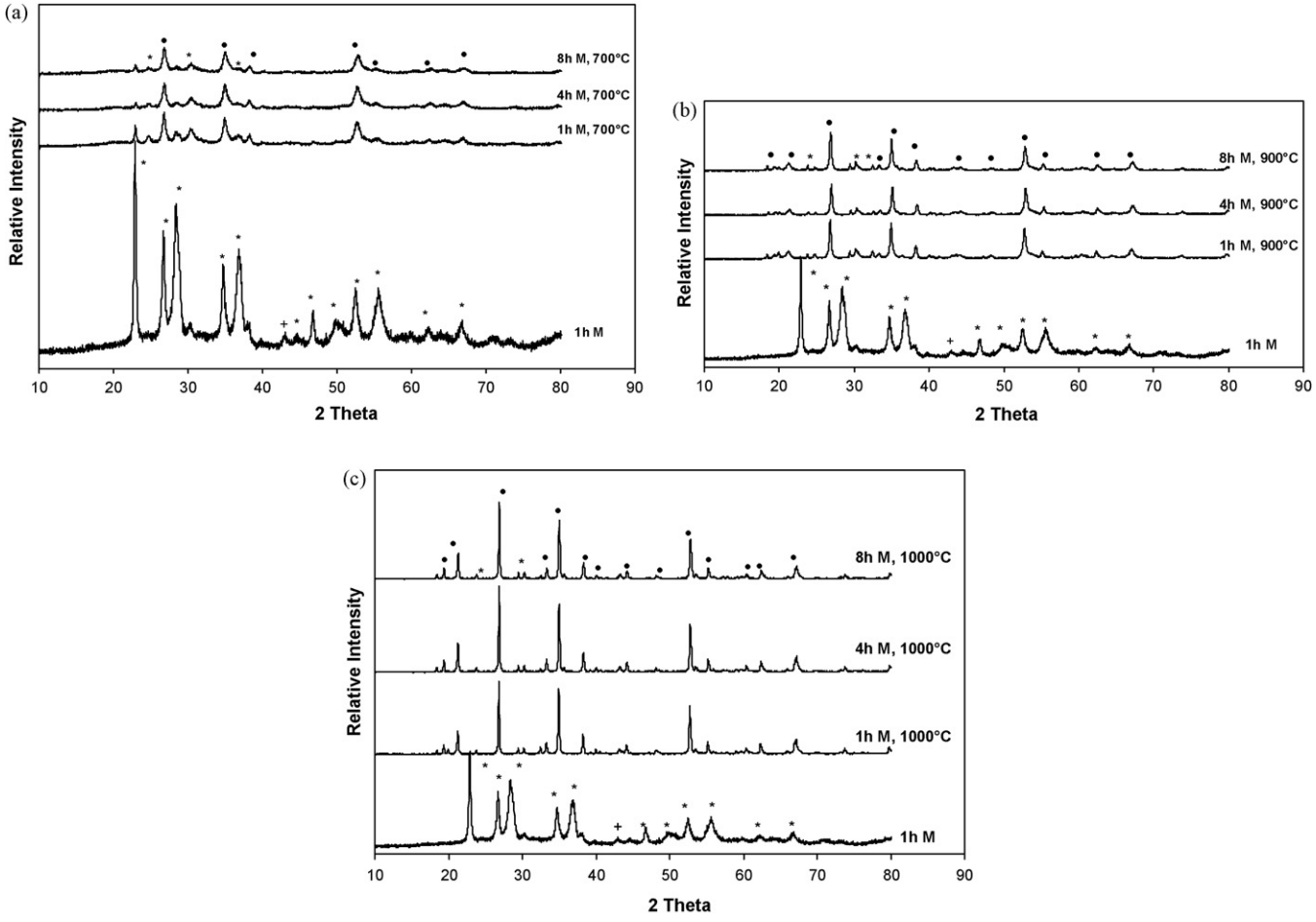

Fig. 2. Phase development in powders milled for 1 h, 4 h and 8 h and heat treated for 1, 4 and 8 h: (a) 700 °C, (b) 900 °C and (c) 1000 °C ('*' tantalum oxide; '+' MgO; '●' $MgTa_2O_6$).

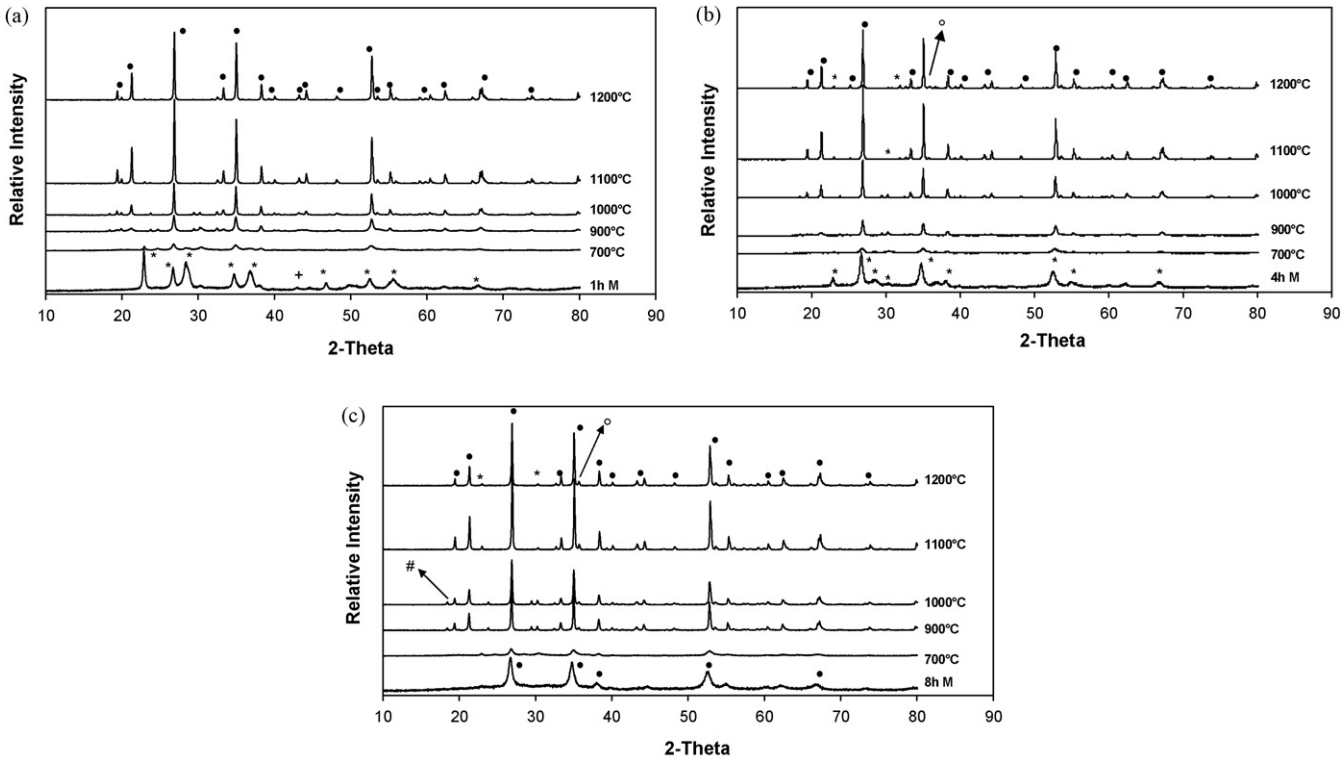

Fig. 3. Effect of annealing temperature on the phase development of powders milled for 1, 4 and 8 h and annealed at (a) 700 °C, (b) 900 °C and (c) 1000 °C ('*' tantalum oxide; '+' MgO; '●' $MgTa_2O_6$; '#' unidentified peak; '○' iron oxide).

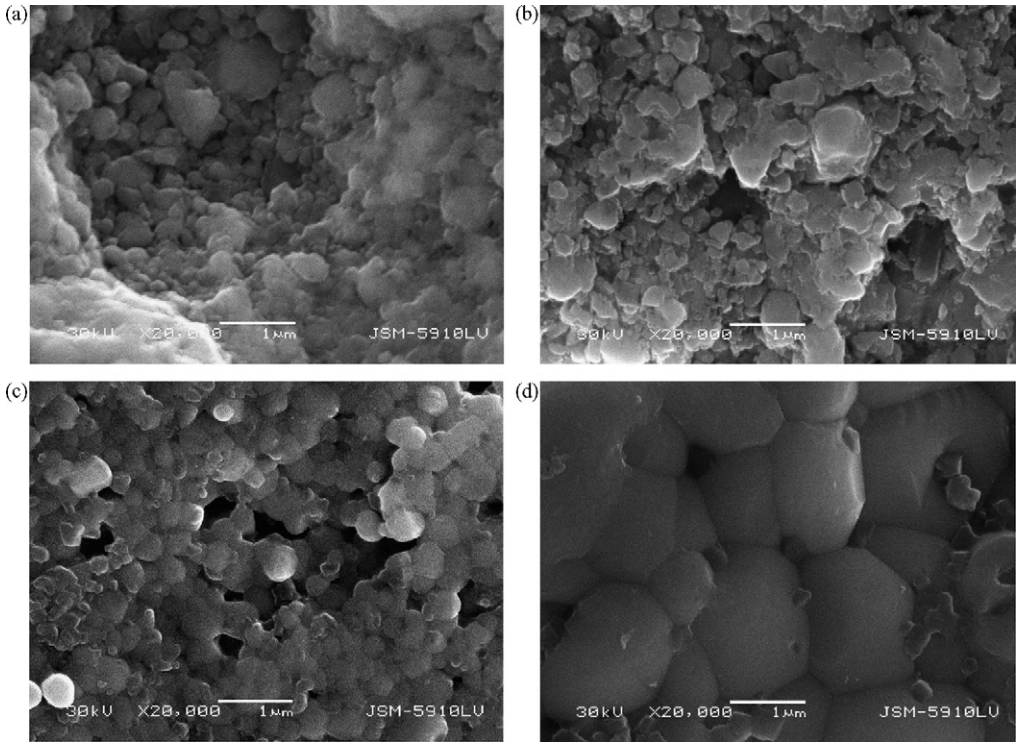

Fig. 4. Scanning electron micrographs of 8 h milled powders annealed for 8 h at various temperatures: (a) 8 h milled powder without annealing, (b) powder annealed at 700 °C, (c) powder annealed at 1000 °C and (d) powder annealed at 1200 °C.

half (rad), and θ is the angle between the incident and diffracted beams (°).

The powder morphology after high-energy milling was characterised using scanning electron microscopy (JEOL 5910LV).

3. Results and discussion

Fig. 1 shows the XRD patterns of the MgO and Ta_2O_5 mixture after mechanochemical treatment for 1, 2, 4, 6, 8 and 12 h. After milling for 2 h, there were still only Ta_2O_5 peaks but with reduced intensities as compared to 1 h milled powder. After 4 h milling the first $MgTa_2O_6$ peaks were observed and as the milling time increased the Ta_2O_5 peak intensties decreased and they disappeared after 8 h milling. Only single-phase $MgTa_2O_6$ was observed after milling for 8 h. This indicates that the mechanochemical reaction between MgO and Ta_2O_5 is triggered by mechanical energy resulting in $MgTa_2O_6$ phase. As the milling time increased, the broadening in the Ta_2O_5 peaks increased which indicated a reduction in crystallite size and amorphization due to the mechanical energy. The line broadening observed in $MgTa_2O_6$ peaks were also due to small particle size and low crystallinity of the phase. The size of $MgTa_2O_6$ particles was around 28 and 26.5 nm for powders milled for 8 and 12 h, respectively.

The effect of milling time and annealing temperature on the synthesis of $MgTa_2O_6$ from the milled powder was investigated by annealing the samples milled for 1, 4 and 8 h at various temperatures (Fig. 2). $MgTa_2O_6$ was the dominant phase in samples milled for various times and annealed at 700 °C (Fig. 2a). However, at annealing temperature of 700 °C the crystallinity was still low and the $MgTa_2O_6$ peaks were broad. When the temperature increased to 900 °C, the major phase was $MgTa_2O_6$ but there was tantalum oxide phase in all samples milled for 1, 4 and 8 h (Fig. 2b). At all annealing temperatures, as the milling time increased, the intensity of $MgTa_2O_6$ peaks also increased while the intensity of tantalum oxide peaks decreased. This indicates that higher energy milling speed up the formation of $MgTa_2O_6$. In addition, rise in milling time at the same annealing temperature also caused an increase in the crystallization of $MgTa_2O_6$. This result implies that mechanochemical processing during high-energy ball milling can promote the crystallization of $MgTa_2O_6$ from the amorphous mixture. At annealing temperature of 1000 °C, even powders milled for 1 h had a high crystallinity (Fig. 2c). Although these powders (milled for 1 h and annealed at 1000 °C) had major phase of $MgTa_2O_6$, they also contained tantalum oxide but with lower contents than 900 °C.

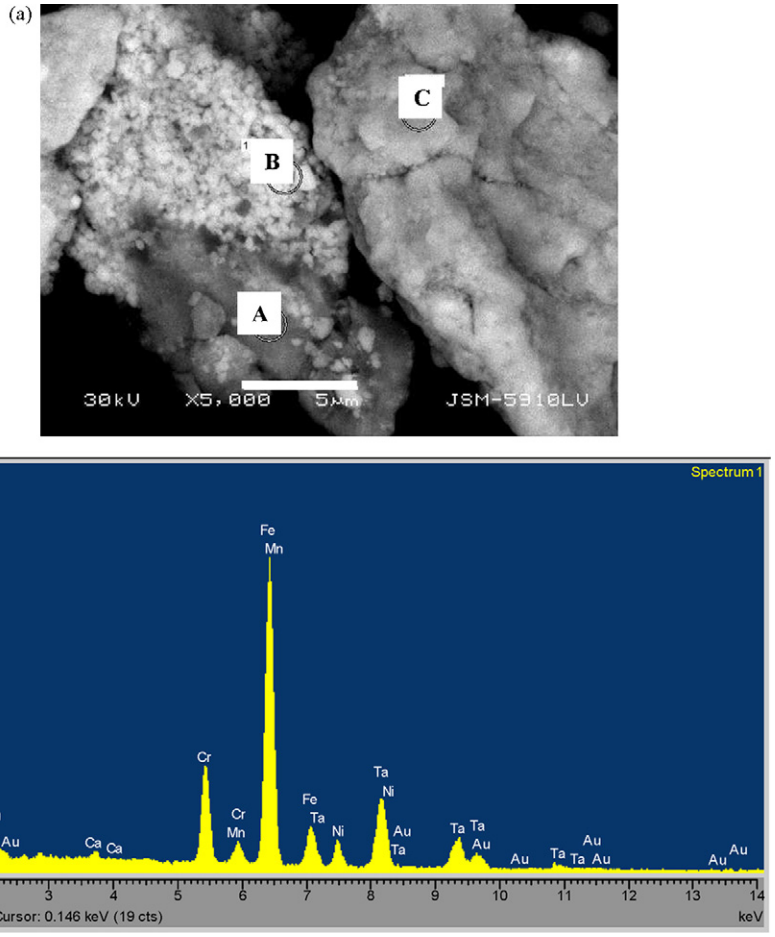

Fig. 5. Backscattered electron images and EDS analysis of powders milled for 8 h: (a) backscattered electron micrograph, (b) EDS analysis of Fe-rich phase (region A), (c) EDS analysis of $MgTa_2O_6$ phase (region B) and (d) EDS analysis of Ta-rich phase (region C).

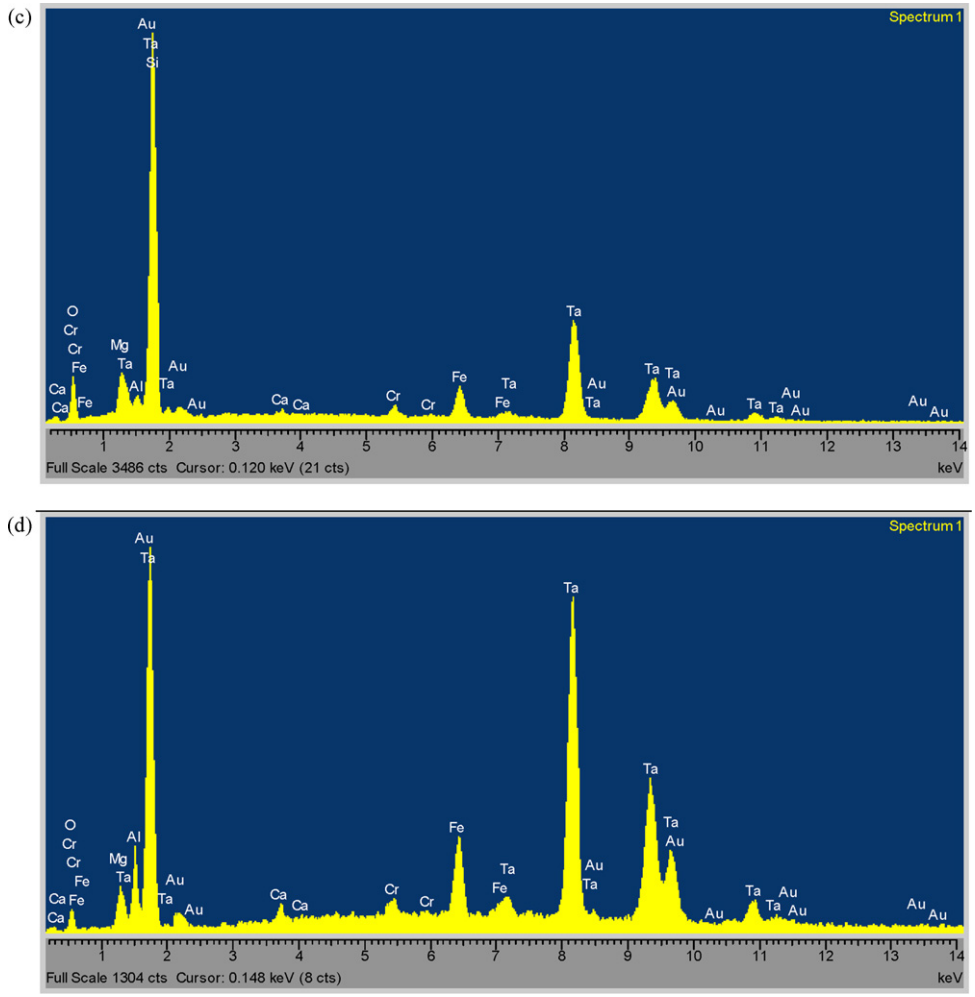

Fig. 5. (*Continued*).

In order to clearly indicate the effect of temperature on the phase development and on the crystallization of $MgTa_2O_6$, powders fabricated by mechanochemical synthesis annealed between 700 and 1200 °C for 8 h. In powders milled for 1 h, although $MgTa_2O_6$ was the prodominat phase, some peaks belong to tantalum oxide were also identified (Fig. 3a). As the temperature increased the intensity of tantalum oxide peaks decreased while the intensity of $MgTa_2O_6$ increased. At 1200 °C, nearly pure $MgTa_2O_6$ phase was obtained. In terms of crystallinity, at 700 °C the powders were mostly amorphous in nature and the crystallinity increased with temperature. At 1100 °C, all the peaks were sharp indicating possibly no any amorphous phase was left and also an increase in the particle size of $MgTa_2O_6$ powders. For powders milled for 4 and 8 h, no single $MgTa_2O_6$ phases was obtained even at 1200 °C and there were additional tantalum oxide peaks (Fig. 3b and c). At low temperatures, the tantalum oxide peaks were high in intensity and the intensities decreased with temperature. But even at high temperatures of 1200 °C, all the tantalum oxide did not convert to $MgTa_2O_6$. In additon, an unidentified peak was appeared at 900 °C and disappeared at 1100 °C in powders milled for 4 and 8 h (Fig. 3b and c). Iron oxide peak (at about 38°) was also observed in powders milled for 4 and 8 h due to contamination effect (Fig. 3b and c) but no any iron impurity was observed in powders milled for 1 h (Fig. 3a). Although the iron oxide content was very low, its amount increased as the milling time increased.

Fig. 3 also clearly indicated that milling time had a significant effect on the crystallinity of $MgTa_2O_6$ phase. Although high crystallinity was obtained at 1000 °C for powder milled for 1 and 4 h, it was obtained at 900 °C for powders milled for 8 h.

Micrographs of scanning electron microscopy of the milled powders before and after annealing between 700 and 1200 °C for 8 h are shown in Fig. 4. Although at low-annealing temperatures the grain size was almost the same as-milled powder, the grain size increased with annealing temperature. The size of the sub-micron particles obtained from milling for 8 h before annealing reached to around 200–500 nm and 1–2 μm after annealing at 1000 and 1200 °C, respectively.

Scanning electron microscopy investigation also revealed various phases in the microstructure (Fig. 5). Fig. 5a gives the backscattered electron images of as-milled powders that indicate three different phases. Fe-rich phase was observed in the microstructure (region A in Fig. 5a) as it was observed in XRD pattern (Fig. 3b). This was due to contamination during

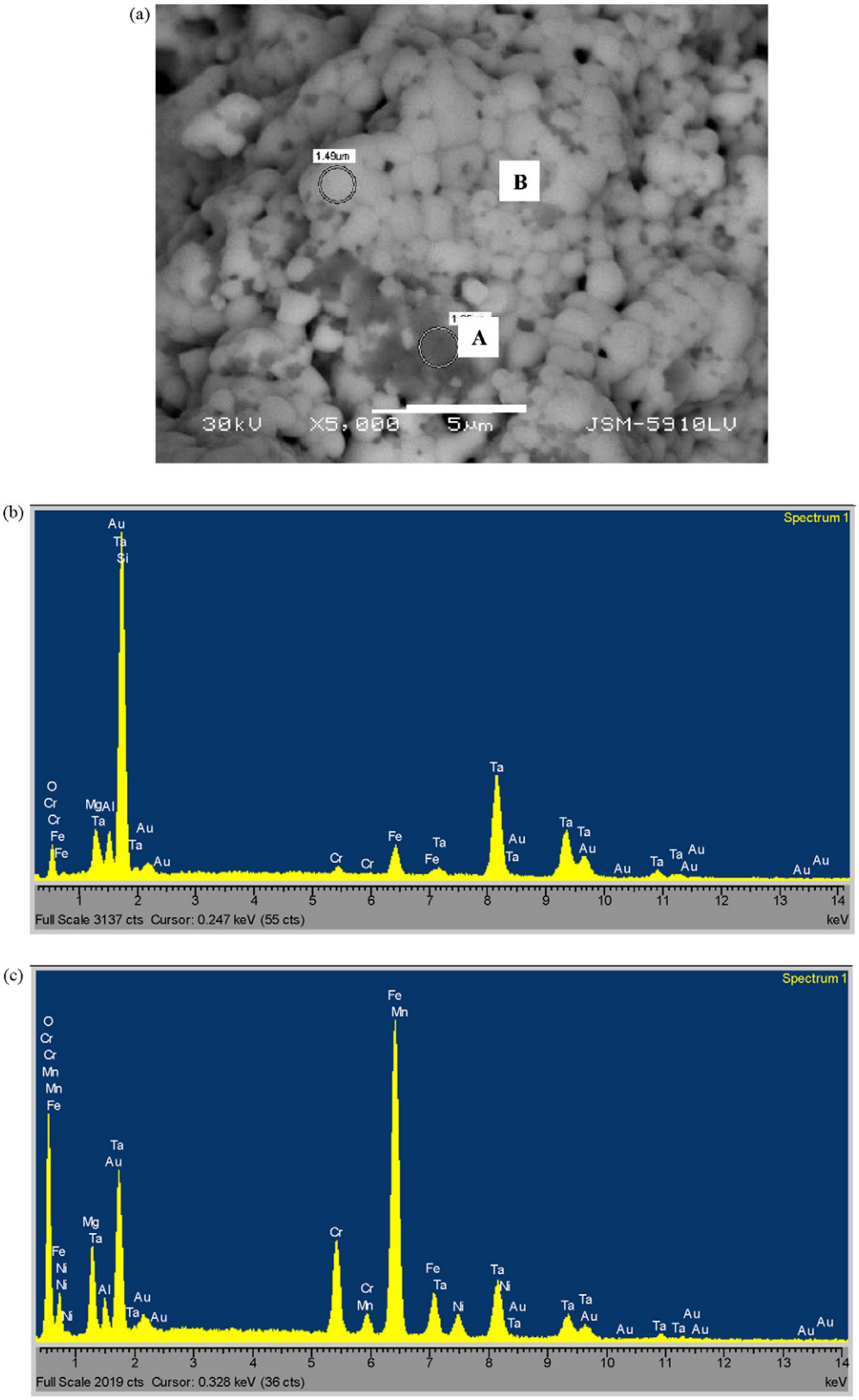

Fig. 6. Backscattered electron images and EDS analysis of powders milled for 8 h and annealed at 1200 °C for 8 h: (a) backscattered electron micrograph, (b) EDS analysis of $MgTa_2O_6$ phase (region A) and (c) EDS analysis of Fe-rich phase (region B).

milling. In addition, $MgTa_2O_6$ (region B in Fig. 5b) and a Ta-rich phase (region C in Fig. 5b) were also identified. Microstructural investigation also indicated that the amount of Ta-rich phase decreased significantly in samples annealed at 1200 °C for 8 h (Fig. 6).

4. Conclusions

The mechanochemical synthesis was successfully used to produce nanostructure $MgTa_2O_6$ powders from stoichiometric MgO and Ta_2O_5 mixtures. Nearly single phase $MgTa_2O_6$ was obtained after milling for 8 h with particle size of around 28 nm. High-energy milling increased the reactivity of milled powders which promote the formation of $MgTa_2O_6$ phase at lower temperatures. Milling time had a significant effect on the crystallinity of $MgTa_2O_6$ phase during annealing. Low-temperature annealing did not have almost any effect on the grain growth but increasing annealing temperature significantly increased the $MgTa_2O_6$ grain size. Scanning electron microscopy investigation also indicated Fe-rich phase due to contamination during milling and Ta-rich phase due to unreacted tantalum oxide in addition to $MgTa_2O_6$ phase.

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