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Synthesis, Microstructural and Thermal analysis of inverse spinel compound Mg_2TiO_4

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ABSTRACT

In the present work, the influence of mechanical activation on Mg_2TiO_4 has been studied. High-energy wet ball-mill and post-anneal processing were applied to synthesize Mg_2TiO_4 single phase crystalline material. The mixture of $Mg(NO_3)_2.6H_2O$ and TiO_2 were mechanically activated for 10, 15, 24 and 48 hours in a planetary ball mill and sintered at 1300 ºC for 72 hours. Phase composition, morphological changes and thermal stability of the sample have been analyzed. The thermal analysis of Magnesium Ortho Titanate reveals the exothermic reaction to the abrupt change in two steps.

Introduction:

Ceramic materials which are based on binary magnesium titanates ($MgTiO_3$ and Mg_2TiO_4) can be applied in microwave (MW) engineering [1]. Recent development of microwave communication systems requires materials that can be used at microwave frequencies as oscillators in radar detectors and global positioning satellite devices [2, 3]. Spinels are very attractive minerals for material research and engineering applications. Among the variety of the structural categories of oxides, the spinel, generally denoted by the chemical formula AB_2O_4, has been one of the most familiar structures along with the well-known perovskite. Three stable phases of magnesium titnates (Mg_2TiO_4, $MgTiO_3$, and $MgTi_2O_5$) have been reported in literature [4, 5]. It has been established that $MgTiO_3$ possesses ilmenite structure; $MgTi_2O_5$ has pseudobrookite structure and Mg_2TiO_4 has an inverse spinel structure (space group Fd3m and Z=8) [5, 6]. The magnesium Ortho titanate has the structural formula $(Mg^{2+})[Mg^{2+}Ti^{4+}]O_4$. In this compound half of the magnesium ion lies in the tetrahedral sites and the other half together with titanium occupy octahedral positions [7, 8].

The results of our investigation show the structural changes occurred in the sample by ball-mill processing at different milling timings. In other reports it has been established, that ball milling can facilitate many solid-state reactions, which normally occur only at prominent temperatures [9, 10]. Presumably, a large number of structural defects formed during the milling is capable of driving the structural transformation [11]. It is necessary to reach a temperature of 1300 ºC so as to obtain single phase material (Mg_2TiO_4) [12].

In the present work, we have synthesized single-phase Mg_2TiO_4 material by wet-ball milling with post annealing and characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA) respectively.

Experimental:

The powders $Mg(NO_3)_2.6H_2O$ and TiO_2 from Merk were used for the synthesis of the sample (Mg_2TiO_4). The wet ball milling process was performed in the air for 10, 15, 24 and 48 hours at a basic disc rotation speed of 400 RPM and the mixtures were denoted as A-10 Hrs, B-15 Hrs, C-24 Hrs and D-48 Hrs according to the milling time. The powders were sintered isothermally at 1300 ºC in ambient atmosphere for 72 hours with a heating rate of 3 ºC/min. The X-ray powder diffraction patterns after sintering were obtained using a Philips PW-1050 diffractometer with λCu-Kα irradiation and a step/time scan mode of 0.02 º/sec. Surface morphology was analyzed by Scanning Electron

Microscopy (SEM) model LEO (440), with a resolution of 1.5 μm at 30 kV. Thermal gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were performed in air, during non isothermal heating from 25 ºC to 1100 ºC, with a constant heating rate of 10 ºC/min. For these analyses Metller analyzer has been used at the National Physical laboratory.

Results and discussion:

Microstructural investigation:

X-ray Diffraction (XRD)

In order to investigate the effect of mechanical activation on the sample evolution, Mg $(NO_3)_2.6H_2O$ and TiO_2 powders were grounded for 10 Hrs, 15 Hrs, 24 Hrs and 48 Hrs sintered at 1300 ºC for 72 hours. The evolved microstructure has been presented in fig. 1. Instead of using the present synthesis salts, one can use different salts of hydroxides, sulphates and oxide etc. as starting materials. However, the necessary condition to prepare pure single-phase material (Mg_2TiO_4) is to keep the ratio of Mg and Ti as 2:1. A careful analysis of XRD patterns of samples A, B, C and D reveals that structural changes were induced by ball milling and single phase formation takes place in sample D. The desired peaks are at 111, 222, 311, 400, 333 and 440.

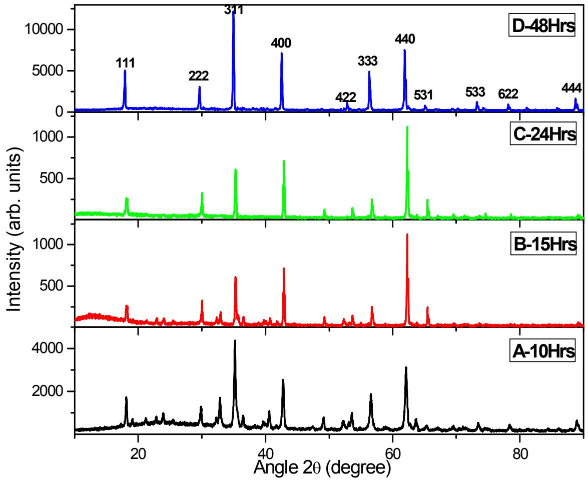

Fig. 1. X- ray diffraction analysis of Mg_2TiO_4

This can be confirmed by the fact that for samples A, B and C, some extra peaks are observed indicating a mixed phase of $MgTiO_3$ and MgO. The XRD pattern was indexed using powder-X software [13] which shows that the sample D-48 Hrs exhibits a cubic spinel structure with space group Fd3m and lattice parameter 8.42 Å.

Scanning Electron Microscopy (SEM)

The morphological images of Mg_2TiO_4 samples grinded for (a) 10 Hrs (b) 15 Hrs (c) 24 Hrs and (d) 48 Hrs are shown in fig. 2.

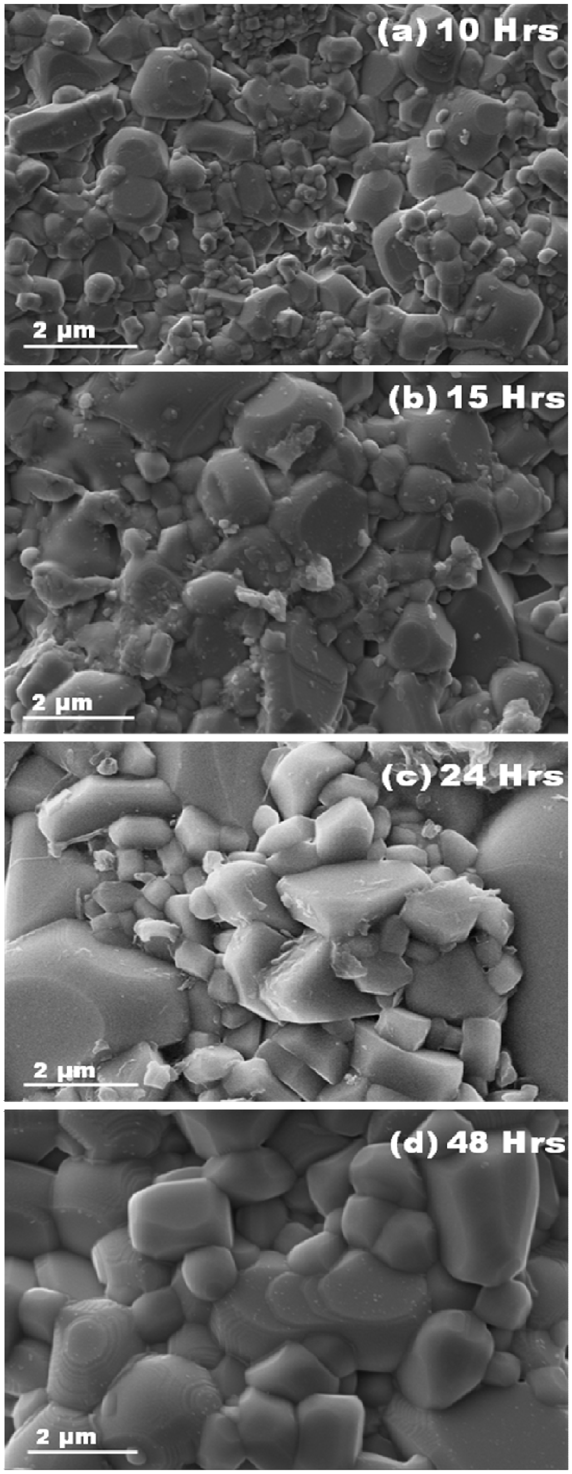

Fig. 2. SEM images of pattern evolution in Mg_2TiO_4 samples grinded for (a) 10 Hrs (b) 15 Hrs (c) 24 Hrs and (d) 48 Hrs.

It has been observed in the micrographs that scattered and irregular structures of the material are becoming organized and well defined shape of three-dimensional structure as we proceed to the higher grinding time from 10 hrs to 48 hrs. The SEM results give the supporting evidence to the XRD results and shows that the increase in grinding time increases the refinement in the construction of the sample.

Thermo Gravimetric Analysis and Differential Scanning Calorimetry:

The thermal behaviour of sample D has been studied by Thermo Gravimetric analysis & Differential Scanning Calorimetry (fig. 3). TG analysis reveals that the compound decomposes into two basic steps to produce the final binary oxide on heating in air. Fig. 3 also shows weight percentage and mass loss of the sample versus temperature. Two exothermic peaks appear at 244.71 ºC and 934.82 ºC. A residue of about 94.4922 % remains due to the elimination and suggestive of an abrupt mass loss assigned to the combustion of compounds. In the temperature range of about 450-550 ºC we find the Magnesium ortho titanate (Mg_2TiO_4) phase. The material stabilizes at 600 ºC and complete conversion of the molecular compounds takes place and a single phase binary oxide Mg_2TiO_4 forms.

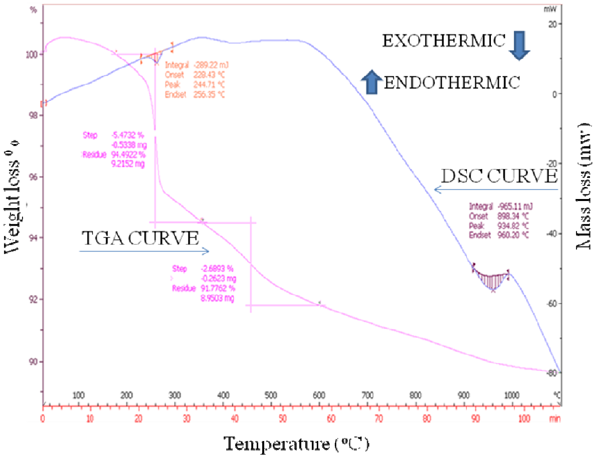

Fig. 3. Thermo Gravimetric Analysis and Differential Scanning Calorimetry of Mg_2TiO_4

Conclusions:

On the basis of our X-ray diffraction, SEM and thermal analysis results, we may conclude that wet ball milling is an efficient processing method for the synthesis of single phase compounds with cubic structure. The Thermal Gravimetric analysis shows the complete exothermic reaction (heat is evolved) and decomposes into two basic steps to produce the final binary oxide on heating in air.

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