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Optical properties of nanocrystalline magnesium aluminate spinel synthesized from industrial wastes

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ABSTRACT

In this work, magnesium aluminate spinel (MA) nanoparticles were synthesized via co-precipitation method using industrial wastes of magnesium and aluminum. The obtained powders were calcined at a temperature range of 650–1500 °C. The calcined powders were characterized by XRD, FT-IR, DTA, FE-SEM and HR-TEM. XRD data illustrated that the spinel MA with a crystallite size of ~3.8 nm was formed at 650 °C. Optical properties of the MA spinel revealed that the optical reflectance is highly dependent on calcination temperature. Photoluminescence analysis revealed intrinsic emission bands with high intensity centered at 390, 370 and 485 nm, when the samples are excited by a 350 nm light from a Xe lamp at room temperature. Results suggest that co-precipitation method of aluminum and magnesium wastes at low temperatures is a promising way for the production of highly pure and active nanocrystalline MA spinel with expected unique properties.

1. Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) denoted as MA is one of the most outstanding optically transparent ceramics that exhibits a unique combination of optical and mechanical properties at the ambient and the elevated temperatures [1]. After being shown to be transparent in early 1960's, spinel has received considerable attention and has been the subject of numerous studies [2–8]. It has been considered to be well suited especially for armor applications because of its ideal combination of optical transparency, hardness, impact resistance, strength, modulus, ease of fabrication and crystal size capability [9–11]. In various studies, it has been shown to be superior to other available armor materials such as sapphire, AlON, soda-lime silicate glass and MgF_2 in terms of its excellent balance of performance and affordability [10,11]. Besides being an attractive transparent armor, it is also expected to serve as a high temperature and visible/infrared (IR) window material [4,12] because of its high thermo-mechanical properties with chemical inertness to strong acids and alkali solutions [5] as well as its effective dual optical transparency in the visible and mid-IR wavelength ranges, respectively.

In addition, it possesses a unique combination of desirable properties such as high melting point, high strength at elevated temperature, high chemical inertness, low thermal expansion coefficient and high thermal shock resistance to make it an excellent refractory lining for rotary cement kilns, steel ladles, glass tank furnaces and other ceramic applications [13–17]. Moreover, MA spinel exhibits first deformation under 0.2 MPa at 2000 °C. It does not react with silica until 1737 °C, CaO or MgO until 2000 °C, α-Al_2O_3 until 1927 °C, and can be used for all metals except alkaline earth [18]. Due to its eco-friendly nature, unlike magnesia-chrome based refractories [19], the later ones are constantly being replaced by $MgAl_2O_4$ spinels [20].

Thus, it is important to obtain the spinel of high purity, using a simple and low cost preparation method. The preparation of magnesium aluminate powders with high purity, chemical homogeneity, control of stoichiometry, fine particle size, narrow particle size distribution, and minimum particle agglomeration with high sinter activity has received considerable attention in order to improve the material properties [21]. Numerous wet chemical methods have been employed to synthesize magnesium aluminate fine particles, including sol–gel [22,23], co-precipitation [24–26],

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hydrothermal [27,28], microwave-assisted combustion processing [29], microemulsion [30], metal-organic processing [31–34], spray drying [35], freeze drying [36], and mechanochemical synthesis [37,38] techniques. The chemical co-precipitation method [39–42] ensures proper distribution of various metal ions resulting into stoichiometric and smaller particle sized product compared to some of the others. Moreover, the process is a low cost technique suitable for the mass production compared to the other mentioned methods.

At present, most techniques used to produce MA spinel, whether they are solid state reactions or chemical synthesis, are conducted at high temperature (>800 °C). However, it is known that high temperature processing is detrimental to microstructure and in turn the properties due to the non-uniform grain growth. Therefore, low temperature synthesis of nanocrystalline powders of MA spinel should be investigated.

On the other hand, industrial wastes released from different manufacturing processes and treatment materials are produced in large quantities and have harmful effects on the environment. According to research conducted by the US Environmental Protection Agency, recycling scrap metal wastes can be quite beneficial to the environment. For example, using recycled scrap metal in place of virgin iron ore can yield 75% savings in energy, 90% savings in raw materials used, 86% reduction in air pollution, 40% reduction in water use, 76% reduction in water pollution and 97% reduction in mining wastes [43].

In 1990 total aluminum production was around 28 million tonnes (with over 8 million tonnes recycled from scrap) and today the total is close to 56 million tonnes (with close to 18 million tonnes recycled from scrap). By 2020 metal demand is projected to have increased to around 97 million tonnes (~31 million tonnes recycled from scrap).

During manufacturing of magnesium products, large amount of wastes in the form of chips and discards is produced in the machining process of castings and sheets. Approx. 1/3 of magnesium used to fabricate structural products ends as scrap, so it is really inevitable to find ways for its efficient recycling in order to keep the use of Mg and thus price at a reasonable level.

Nowadays, industrial waste materials are getting a wide exposure to the future generation of the material science world. The novelty and the idea of this work is how to convert unwanted waste materials into something useful or value-added products via an environmental friendly method for advanced applications. In this study, our group reported for the first time, the synthesis of $MgAl_2O_4$ spinel nanoparticles from industrial wastes of aluminum and magnesium scraps released from foundries by co-precipitation method at low temperature. Magnesium aluminate spinel was produced at different temperatures 650–1500 °C. The phase composition, thermal analysis, and microstructure of these compositions were detected using X-ray diffraction (XRD), differential thermal analysis (DTA), infrared spectrum (IR), scanning electron microscope (FE-SEM) as well as transmission electron microscope (TEM). The optical properties of the produced MA were also studied by UV-VIS-NIR spectrophotometer and photoluminescence analysis.

2. Materials and experimental procedure

2.1. Materials and processing

Aluminum and magnesium scrap released from foundries (supplied by Central Metallurgical Research & Development Institute [CMRDI], Helwan, Egypt) were used as starting materials. Ammonia solution [NH_4OH] was used during the co-precipitation to maintain the pH at 10. The chemical composition of aluminum scrap is illustrated in Table 1.

Table 1
Chemical composition of Al scraps.

Elements	Al	Zn	Mg	Cu
Percentage, %	92	3.96	2.35	1.7

An aqueous solution of magnesium nitrate was achieved by dissolving the magnesium scrap in nitric acid. The aqueous solution of aluminum nitrate was achieved by dissolving the aluminum scrap in aqua regia of 20% HCl and 20% HNO_3 acids. The stock solution used for spinel synthesis was made by dissolving magnesium and aluminum nitrates in distilled water with stirring.

In a typical synthesis process, the aqueous solution of the aluminum nitrate was added to a stirring aqueous solution of magnesium nitrate to give MgO/Al_2O_3 molar ratios of 1:1 powder. The aqueous suspended solutions were formed by the addition of NH_4OH drop by drop with constant stirring 500 rpm for 15 min to achieve good homogeneity. pH of the solution was maintained at 10 during the precipitation process. The co-precipitates were filtered off, washed with water and dried in an oven at 110 °C overnight. In order to produce MA spinel, the dry precursor was calcined in a muffle furnace up to different temperatures (650, 750, 850, 950, 1300, 1400 and 1500 °C) with a rate of heating of 10 °C/min for 2 h.

2.2. Characterization

XRD patterns of the resulting products were characterized by a Brucker D8-advance X-ray powder diffractometer with Cu Ka radiation (k = 1.5406 Å). The crystallite sizes of the produced magnesium aluminate spinels were calculated from the most intense peak (311) using the Debye–Scherrer formula:

$$dRX = K\lambda/\beta \cos\theta$$

where dRX is the crystallite size, k = 0.9 is a correction factor to account for particle shapes, β is the full width at half maximum (FWHM) of the most intense diffraction peak (311) plane of MA spinel phase, λ is the wavelength of Cu target = 1.5406 Å, and θ is the Bragg angle.

Fourier transform infrared spectra (FTIR) spectroscopy (Model, Jasco-6300 type A, Japan spectrometer) was used at room temperature in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} to identify functional groups.

Powder morphology and microstructure of the produced magnesium aluminate spinel were examined by using backscattered electron (BSE) in the field emission scanning electron microscopy

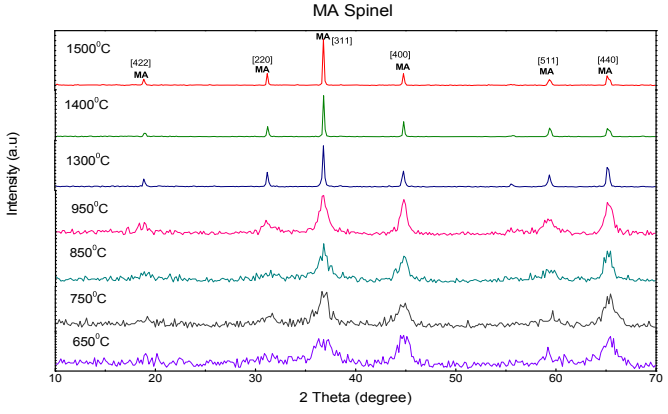

Fig. 1. XRD patterns of MA spinel powders annealed at different temperatures.