

Rapid synthesis of nanocrystalline magnesium chromite and ferrite ceramics with concentrated sunlight



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ABSTRACT

High-temperature refractory ceramics and catalysts such as MgM_2O_4 ($M = Cr, Fe$) are produced conventionally via energy-intensive solid-state syntheses (using 0.44–10 GJ electricity for sintering per ton oxide, equivalent to combustion of 48–1088 kg coal per ton oxide). This article reports rapid production of 17 ± 2 mol% $MgFe_2O_4$ and 8.6 ± 0.9 mol% $MgCr_2O_4$ after 30 min at $1200^\circ C$ employing 0.82 kW m^{-2} sunlight concentrated at a geometric ratio of about $900 \text{ m}^2 \text{ m}^{-2}$ using a Fresnel lens. Solar radiation promotes the diffusion-limited ferrite formation ($42 \pm 5 \mu\text{mol MgFe}_2\text{O}_4$ per mol $\text{Fe}_2\text{O}_3 \text{ s}^{-1}$ vs. $26 \pm 3 \mu\text{mol mol}^{-1} \text{ s}^{-1}$ in absence of sunlight) while the transition metals promote the reduction of Mg^{2+} . The nanocrystalline and macroporous spinel has a specific surface area of $9.7\text{--}11.9 \text{ m}^2 \text{ g}^{-1}$ (in the order of sol-gel synthesis methods) and is stable under extreme conditions, i.e., high temperature, solar radiation, and reducing agents.

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1. Introduction

Spinel is a cubic double oxide with the general formula AB_2O_4 ($A =$ divalent metal ion, e.g., Mg^{2+} , $B =$ trivalent metal ion, e.g., Fe^{3+} or Cr^{3+}). Their unique chemical properties (such as high-temperature stability and flexible lattice structure [1–3] and exchange capacity for cations of various sizes and oxidation state [1]) make them industrially important refractory materials [4,5], useful catalysts under extreme conditions [6–9], or high-temperature reactive materials [10–12]. Magnesium chromite (MgCr_2O_4 , normal spinel ion ordering [13], p-type semiconductor [5,14]) and magnesium ferrite (MgFe_2O_4 , inverse spinel ion ordering [1,13], n-type semiconductor [14,15]) are chemically stable refractories [4,5], resistant to slag attack [16]. MgCr_2O_4 has been used as selective oxidation catalyst (e.g., as efficient complete combustion catalyst for the oxidation of propane and propene) [6,7], while MgFe_2O_4 has been utilized for various electromagnetic, catalytic [9,15] and medical

applications (e.g., for achieving local hyperthermia [17], i.e., localized heating of tumors [18]).

Cr- and Fe-containing ores are mined extensively, e.g., for chromium, ferrochrome and steel production [19,20]. To achieve uniform and reproducible materials properties, such as purity [20] and lattice structure (e.g., for memory and switching circuits applications [9,21]) as well as density [21] and morphology (e.g., for use as electrocatalysts) [15], metal oxides are extracted from natural ores and further processed into synthetic spinel [9]. Conventionally, synthetic spinel is produced via the energy-intensive and slow reaction of MgO and transition metal oxide (TMO, i.e., Cr_2O_3 or Fe_2O_3) particles [1–3] near $1200^\circ C$ [6,13] which controls the materials properties of the product [22]. The sintering step of this process alone [23,24] consumes in the order of 0.44–10 GJ electricity per ton product [23,25,26], equivalent to combustion of 48–1088 kg coal per ton product (assuming a conversion efficiency of chemical energy in coal to electricity of 0.35 and a higher heating value of 26.27 GJ per ton coal) [27]. Although a number of alternative synthesis techniques at lower temperatures have been developed to increase the specific surface area [6,16], such as sol-gel methods with calcination at $500\text{--}1100^\circ C$ [6,8,15,28,29], co-precipitation in reverse microemulsion [6,9,30], mechanical activation [9], or high-pressure hydrothermal methods [9], these techniques are energy-intensive, may require catalysts, and consume costly chemicals such as solvents, surfactants, and complexing agents [6,9]. High-temperature synthesis methods utilize inexpensive and readily available raw

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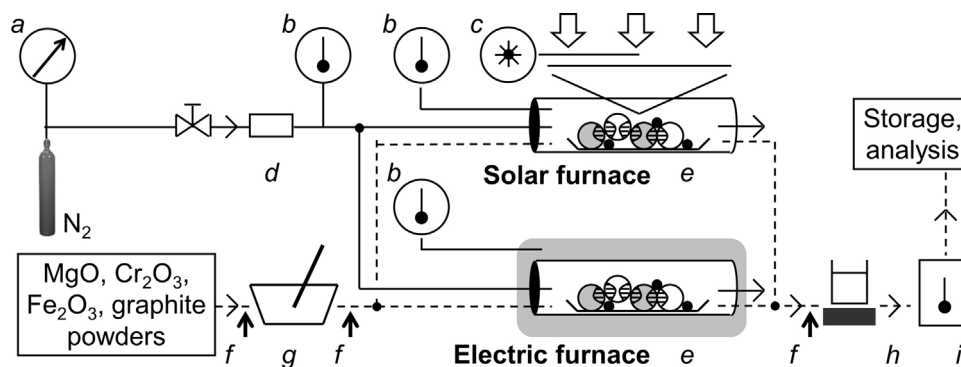


Fig. 1. MgM_2O_4 ($M=Cr, Fe$) synthesis: (a) N_2 , (b) thermometer, (c) Fresnel-lens and solar meter, (d) flow meter, (e) white: MgO particles, gray: TMO particles, black-dashed: particle contact and MgO/TMO diffusion, (f) solid state analysis, (g) powder mixing, (h) powder separation, (i) drying.

materials and may allow for rapid production up to ton per day scale.

Solar energy has been used at industrial scale as environmentally benign source of elevated temperatures and process heat [31,32]. Sunlight is essentially unlimited and can be concentrated, theoretically, up to the surface temperature of the sun of about $5500^\circ C$. Practical processes are limited to less than $5500^\circ C$ by radiation losses from solar concentrators and heat losses from the solar receivers and reactors [33]. Solar-driven synthesis of metal carbide and nitride refractories has been reported [34–38]. Here we report a novel method for producing MgM_2O_4 ($M=Cr, Fe$) via rapid solid-state synthesis at $1200^\circ C$ with concentrated solar radiation.

Section 3.1 assesses the chemical composition of the solids formed during the reaction of MgO , graphite, and Cr_2O_3 or Fe_2O_3 , respectively. The experimental data suggests reduction of Mg^{2+} in presence of the transition metals, graphite, and N_2 to Mg vapor, rather than the previously proposed formation of Mg_3N_2 [10]. Section 3.2 characterizes the morphology of the nanocrystalline ceramics with specific surface areas comparable to those of materials synthesized at lower temperatures or via sol-gel methods. Sections 3.3 and 3.4 assess the effect of varying graphite concentrations and the presence or absence of solar radiation. While understanding the formation of chromite or ferrite in reducing environments is important when studying the natural formation of these minerals in carbonaceous sediments or in presence of coal depositions/feedstock, the resistance to reducing environments becomes relevant in the industrial production of ferrochrome or stainless steel [19] or in refractory applications such as for solar-driven carbothermal production of aluminum or silicon [40,41].

2. Experimental

2.1. Solar radiation experiments

To study the formation of MgM_2O_4 ($M=Cr, Fe$) under solar radiation and in reducing environments, oxides were mixed using mortar and pestle with graphite at molar $MgO:M_2O_3:C$ ratios of 1:1:4, 1:1:8, 2:1:5, or 2:1:10 (Table 1). This includes equimolar oxide mixtures [1,7] or mixtures containing an excess of MgO [2], as suggested previously. Typically, 0.37 ± 0.05 g of a mixture was placed into a quartz boat and heated under 30 ± 2 ml_(STP) s⁻¹ N_2 flow at $1200 \pm 100^\circ C$ (Fig. 1) by concentrated solar radiation (peak heating rate in the order of $100^\circ C$ s⁻¹, 0.82 ± 0.02 kW m⁻² normal insolation, SP1065, measuring between 300 and 1100 nm, EDTM Glass, Window & Film Test Equipment). The radiation was concentrated with a Fresnel lens-based solar furnace (tubular flow-through quartz reactor, sunlight tracking was manually via incremental adjustment of the focal point alignment at least once

per 5 min heating) that had been described previously [34]. A thermocouple (High Temperature Flexible Ceramic Fiber-Insulated Probe, Type K; ThermoWorks) was used to determine the furnace temperature before the experiment. After the reaction the furnace was moved out-of-focus to cool the reactor down to ambient temperature within about 15 min.

2.2. Electric resistance heat experiments

Typically, 0.36 ± 0.01 g $MgO:M_2O_3:C$ (1:1:8 molar ratio) or 0.16 ± 0.03 g $MgO:C$ (1:8 molar ratio) as reference respectively were placed into a quartz boat and heated for 30, 60, or 120 min under 31 ± 2 ml_(STP) s⁻¹ N_2 flow at $1200 \pm 1^\circ C$ (Fig. 1) using an electric resistance furnace (tubular flow-through quartz reactor, model HTF55347C, temperature controller CC58434C, Lindberg/Blue). Samples were introduced into the furnace at about $305 \pm 45^\circ C$, heated at $0.79 \pm 0.03^\circ C$ s⁻¹ to $1200^\circ C$, and cooled at a mean rate of $-4 \pm 1^\circ C$ s⁻¹ to ambient temperature.

2.3. Solid state analysis

All solid samples were stored under air at $4^\circ C$. Powder X-ray diffraction (XRD) was performed using a Miniflex II diffractometer ($5-80^\circ 2\theta$ range, $1^\circ 2\theta$ /min scan speed, 0.02 data points/ $^\circ 2\theta$, $CuK\alpha$ radiation, 30 kV/15 mA output, diffracted beam monochromator, Rigaku) for quantitative solid phase identification. All powder mixtures were weighed before and after the experiment (AE260 DeltaRange balance, ± 0.1 mg, Mettler). The average particle diameter (Table 1) was determined using scanning electron microscopy (SEM, 20 kV, S-3500 N Scanning Electron Microscope, Hitachi). The specific BET surface area (6-multi point analysis) was analyzed by NanoScale Inc., Manhattan, KS (Table 1). To characterize the spinel morphology, selected samples were washed with 5–10 ml water and acetone, separated from the liquid via sedimentation ($MgCr_2O_4$) or by a magnetic field ($MgFe_2O_4$, using a neodymium disk magnet, 13,200 Gauss residual induction,

Table 1
Characterization of solid reactants.

Reactant	MgO	Cr_2O_3	$\alpha-Fe_2O_3$	Graphite
Space group	$Fm\bar{3}m$	$R\bar{3}c$	$R\bar{3}c$	$P6_3/mmc$
d_p^a (μm)	4 ± 4	6 ± 4	17 ± 11	24 ± 15
A_s^b ($m^2 g^{-1}$)	20.5 ± 0.2	1.45 ± 0.02	8.0 ± 0.1	12.4 ± 0.2
Φ^c ($m^3 m^{-3}$)	0.882 ± 0.004	0.81 ± 0.01	0.87 ± 0.01	0.839 ± 0.006

^a Average particle diameter.

^b BET surface area.

^c Void space fraction $\Phi = 1 - \rho_{bulk}/\rho_p$, ρ_i is the density in $kg m^{-3}$, powder bed surface: 2.4 ± 0.2 or 33 ± 2 cm² for solar or electric experiments respectively, bed thickness < 1 mm.

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