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Preparation of pure cordierite through heat treatment of combustion synthesized magnesium aluminate spinel and silica nanoparticles

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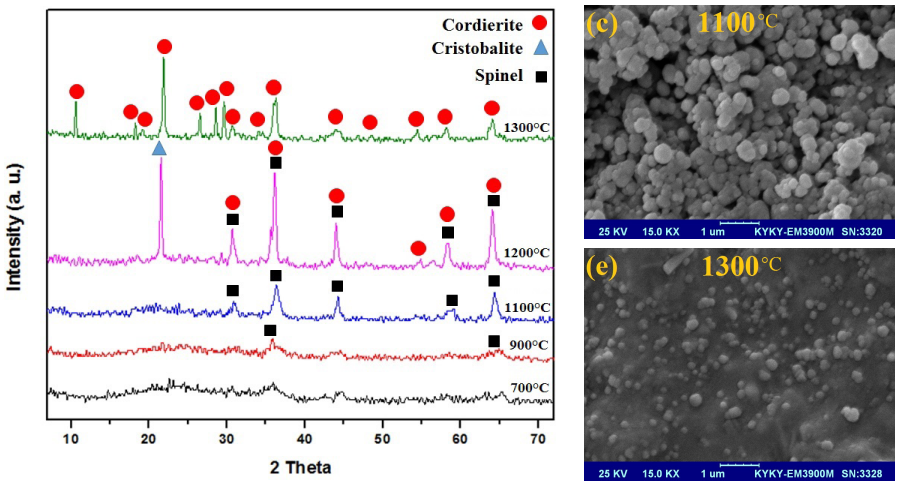
HIGHLIGHTS

- Pure cordierite was synthesized by a two-step process.
- Magnesium aluminate powders were prepared by solution combustion method.
- Cordierite particles were obtained via solid-state reaction of silica nanoparticles and synthesized spinel powders.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, cordierite single-phase powders with high purity were synthesized during a two-step process. First, magnesium aluminate spinel powders were prepared via the KCl-assisted solution combustion route. Then, synthesized spinel particles and nanosilica were planetary milled for 24 h, followed by post-heating at different temperatures for 3 h. Results showed that post-heating at 700 and 900 °C did not change the sample phases. However, a magnesium aluminate spinel phase appeared for particles post-heated at 1100 °C. Further heating up to 1200 °C led to the phase transformation of amorphous silica to cristobalite, which reacted with magnesium aluminate spinel to form a cordierite phase. Finally, at 1300 °C, the remaining spinel and cristobalite reaction was completed, and single-phase cordierite powders without additional phases were obtained. Moreover, there was considerable radial shrinkage, and scanning electron microscope micrographs showed the liquid phase sintering of cordierite occurred.

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1. Introduction

With a chemical formula of $Mg_2Al_4Si_5O_{18}$, Cordierite is an interesting phase in the MgO-Al_2O_3-SiO_2 ternary phase system. Cordierite ceramics have a low thermal expansion coefficient, refractoriness and high resistance to chemical corrosion, and extraordinary thermal shock resistance [1-3]. They have been employed in various important industrial fields, including kiln and furnace tools [2,4], filters for hot gas and molten metals [2], electrical porcelain [4], honeycomb ceramic monolith catalyst support for automobiles [1], diesel engine filters [5,6], complex parts of gas burners [2], gas turbine heat exchanger [4], catalytic converter [4,5], refractory coatings [7], and integrated circuit substrates [1,4]. Since cordierite is naturally very rare, it is mainly synthesized as ceramic powders [8]. Cordierite is usually produced by the solid-state reaction of MgO, SiO_2, and Al_2O_3 single/mixed oxides. The formation mechanism can vary depending on the starting materials [9]. Kronert *et al.* [10] studied the solid-state reaction of talc and kaolinite. They reported a reaction of mullite, cristobalite, and enstatite at 1150 °C. Lamar and Warner [11] also supposed a similar mechanism, but they reported the cordierite formation at 1300 °C. Both research groups, Kronert *et al.* [10] and Lamar and Warner [11] obtained cordierite together with mullite impurity. Benito *et al.* [9] synthesized cordierite powders using kaolin, magnesium hydroxicarbonate, and talc as starting materials. They got cordierite and spinel final products. Redaoui *et al.* [8] used kaolinite and synthetic magnesia as starting materials and concluded from XRD patterns that sapphirine was formed in addition to the cordierite phase. Parcianello *et al.* [5] also synthesized cordierite using nano alumina, nano magnesia, and silicon resin as raw materials. They reported that spinel was formed at 1000 °C and remained as a dominant phase up to 1250 °C, and cristobalite formed at 1250 °C could react with the spinel to obtain the cordierite phase. Additional heating to 1350 °C completed the reaction to produce pure cordierite. The aim of the present study was the synthesis of pure single cordierite powders based on the work of Parcianello *et al.* but with less expensive starting materials. In addition, the effect of initial mechanical activation using high energy ball milling was investigated. A successful new method is presented for the synthesis of fine-grained cordierite particles with high purity.

2. Experimental

Aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$, Merck), magnesium nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$, Merck), and nanosilica (Fadak Knowledge based Corporation) were used as starting materials. Glycine ($C_2H_5NO_2$, Merck) was used as fuel. Potassium chloride (KCl, Merck) was used as combustion assistant salt.

First, spinel particles were synthesized by the solution combustion method using glycine fuels considering propellant chemistry as Eq. (1).

$$2Al(NO_3)_3.9H_2O + Mg(NO_3)_2.6H_2O + 40/9C_2H_5NO_2 + 2KCl = MgAl_2O_4 + 80/9CO_2 + 316/9H_2O + 56/9N_2 + 2KCl \quad (1)$$

In this regard, 7.336 g glycine, 2.564 g magnesium nitrate hexahydrate, 7.502 g aluminium nitrate nonahydrate, and 1.491 g potassium chloride were dissolved separately in 100 ml of distilled water under magnetic stirring at room temperature. The transparent solution was heated at 350 °C in a heater mantel until gel-like precipitates were obtained, followed by a combustion reaction producing yellowish/white powders. Then, the obtained powders were post-heated at 700 °C for 3 h, washed two times with water at room temperature and one time with hot water for 1 h to remove any remaining KCl salt, and finally, dried at 70 °C for 1 h. Fig. 1 shows the macro-image of the combustion and synthesized spinel powders.

Synthesis of cordierite powders was performed based on Eq (2).

$$5SiO_2\ (s) + 2MgAl_2O_4\ (s) \rightarrow Mg_2Al_4Si_5O_{18}\ (s) \quad (2)$$

First, 5.690 g of synthesized magnesium aluminate spinel and 6.008 g of nanosilica with 0.117 g of stearic acid (as a lubricant) were mixed in a planetary mill (polyethylene cup with 50 hard chromium steel balls) with a ball-to-powder ratio of 10:1 and a rotational speed of 350 rpm for different intervals. The mixed powders were uniaxially pressed in a steel cylindrical die at a loading pressure of 200 MPa at ambient temperature. Finally, the green compact samples were heated in an electric furnace at 700 to 1300 °C for 3 h without any pressure. Heating rates from room temperature

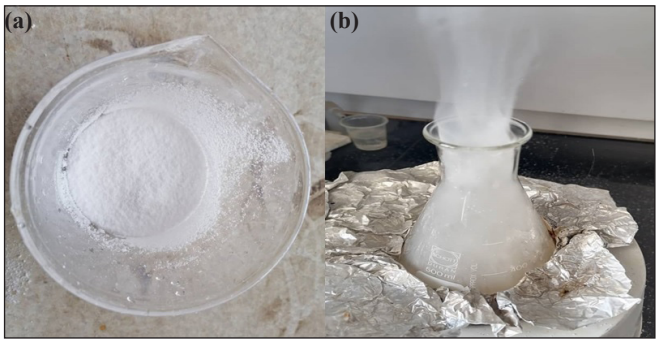

Fig. 1. Macro-image of (a) synthesized spinel powders and (b) combustion.

to 1000 °C and from 1000 °C up to 1300 °C were increased 10 °C.min^{-1} and 5 °C.min^{-1}, respectively. The nanosilica used in this study, an Iranian product produced by the Fadak Knowledge based Corporation, has a purity of 98.6 % and a particle size range of 15 - 20 nm. In the XRD pattern (Fig. 2) of SiO_2 nanoparticles in the range of 2θ angle of 20 - 30 degrees, a broad peak is observed, indicating this material has amorphous structure.

Scanning electron microscopy (SEM, KYKY EM3900) and the X-ray diffraction method (Bruker, Advance D8) were used to determine the microstructure and phase characterizations, respectively. Thermal behaviors of the synthesized particles were studied using a simultaneous thermal analysis apparatus (NETZSCH STA 449F3) in the air atmosphere with a heating rate of 10 Ks^{-1}. The steps of cordierite synthesis are briefly shown as a flowchart in Fig. 3.

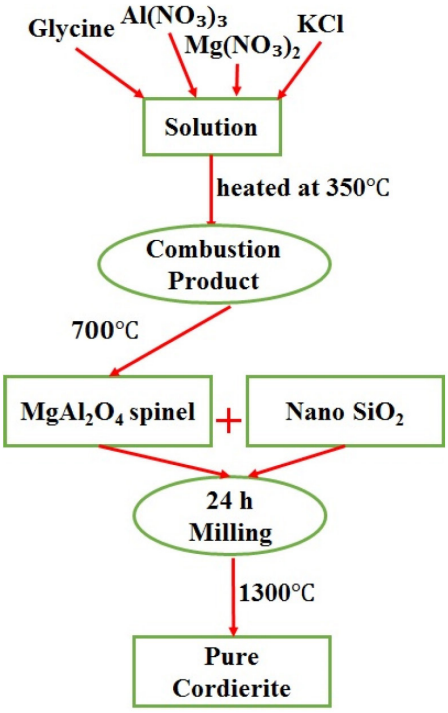

Fig. 3. Flowchart of cordierite synthesis.

3. Results and disscusion

3.1. Synthesis and characterrization of magnesium aluminate spinel powders

Fig. 4 shows the XRD pattern of the sample synthesized in the presence of glycine fuel and post-heated at 700 °C for 3 h. As illustrated, the crystalline magnesium aluminate phase with spinel structure (Card no. 96.900.2136) was obtained as the predominant phase.

Fig. 5 shows SEM micrographs of magnesium aluminate spinel particles synthesized and post-heated at 700 °C for 3 h at two different magnifications. As can be seen, a porous spongy microstructure containing highly agglomerated particles was obtained due to the strong combustion of Glycine fuel and the high volume of the exhaust of gases during the combustion reaction. Several researchers reported this type of microstructure for spinel structure ceramic powders [12-16].

3.2. Synthesis of cordierite powders

For the synthesis of cordierite, the mechano-chemical treatment of the magnesium aluminate spinel and silica powders as starting materials was studied.

Fig. 6 shows the XRD patterns of samples that were planetary milled for different intervals. As can be seen, the reaction of mixed powders and the formation of cordierite powders did not occur. In other words, the crystalline

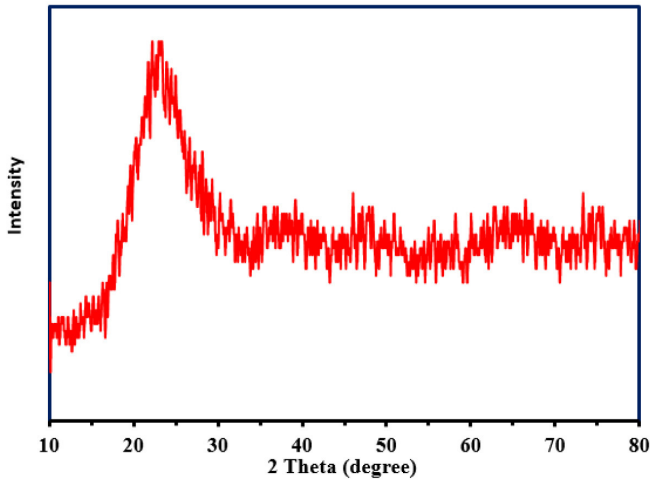

Fig. 2. XRD pattern of nanaoilica purchased from Fadak Knowledge based Corporation.

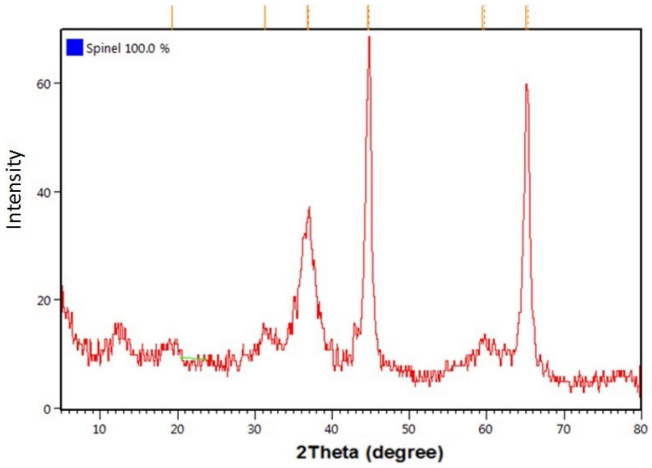

Fig. 4. XRD pattern of a sample synthesized and post-heated at 700 °C for 3 h.

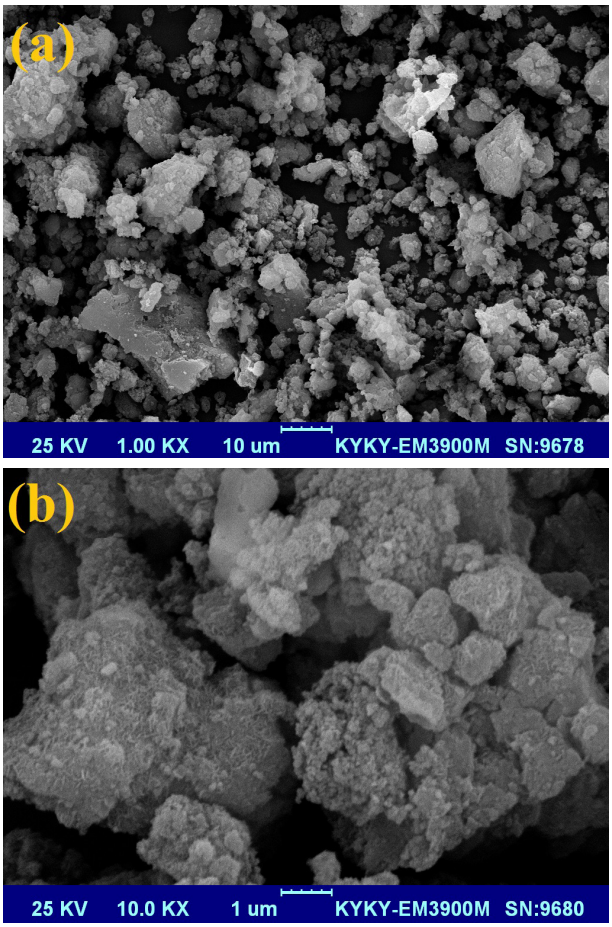

Fig. 5. SEM micrographs of magnesium aluminate spinel particles synthesized and post-heated at 700 °C for 3 h at different magnifications.

magnesium aluminate phase with a spinel structure (Card no. 96.900.2136) remained the predominant phase, even after 24 h milling. However, the broadening of peaks in the XRD patterns and decreased peak intensities could be observed after 18 and 24 h milling. This is due to the partial transformation of crystalline spinel to an amorphous phase. The energy released during milling seemed insufficient to initiate a reaction between spinel and silica particles to obtain the cordierite phase as expected.

Fig. 7 shows SEM micrographs of mixtures of magnesium aluminate spinel and silica powders milled for different intervals. As expected, by increasing milling periods up to 18 h, agglomerated particles were broken into smaller elements and uniformly distributed. However, further milling (up to 24 h) caused the particles to re-agglomerate due to more activation of the powders' surface. So, milling for more than 24 h was not necessary.

Therefore, the mixtures of synthesized magnesium aluminate and silica powder activated by milling for 24 h were compacted and post-heated at different temperatures for 3 h.

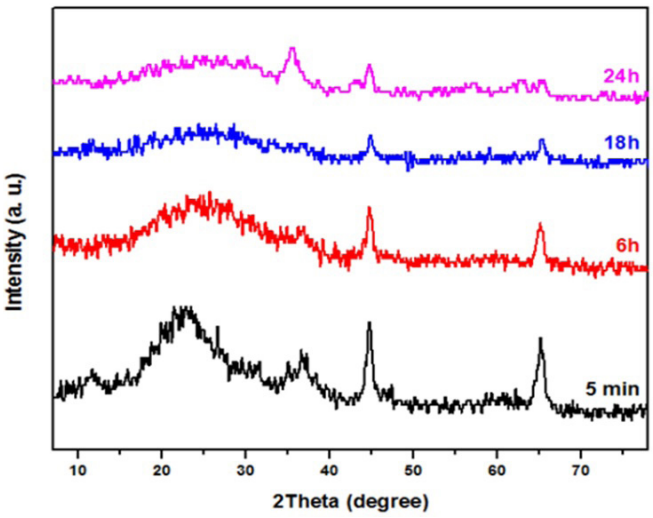

Fig. 6. XRD patterns of mixtures of magnesium aluminate spinel and silica powders planetary milled for different intervals.

Fig. 8 shows the XRD patterns of samples post-heated at different temperatures for 3 h. As seen, significant phase variation after post-heating at 700 and 900 °C was not observed. This is because reactants, i.e., spinel and silica, could not obtain enough energy to initiate/progress the reaction of cordierite formation. Moreover, heating to 1100 °C led to a decrease in the amorphous phase and more formation of spinel structure magnesium aluminate (card no. 96-900-2119). Furthermore, post-heating to 1200 °C transformed amorphous silica into cristobalite (card no. 01-089-3435). Finally, the remaining spinel and cristobalite reacted, and the cordierite phase was formed (card no. 96-900-5807).

To better understand the mechanism of cordierite formation, simultaneous thermal analyses (STA) were performed on the mixtures of synthesized magnesium aluminate and silica powder activated by milling for 24 h (Figs. 9(a), (b)). As illustrated in the thermogravimetry analysis (TGA) curve, weight loss occurred in three stages:
i) from room temperature to 150 °C due to adsorbed/absorbed water removal (about 2 wt%),
ii) as a result of the organic removal of stearic acid and structural water remaining from the raw materials reaction, and
iii) negligible evaporation of products at about 1200 °C.

Moreover, the exothermic peak at differential scanning calorimetry (DSC) analysis at 1180 °C is associated with the nucleation of cristobalite from amorphous silica, followed by an endothermic peak at 1266 °C that can be attributed to the formation of cordierite. The latter broad peak shows that the formation of cordierite from the magnesium aluminate spinel and nano silica is a diffusional process.

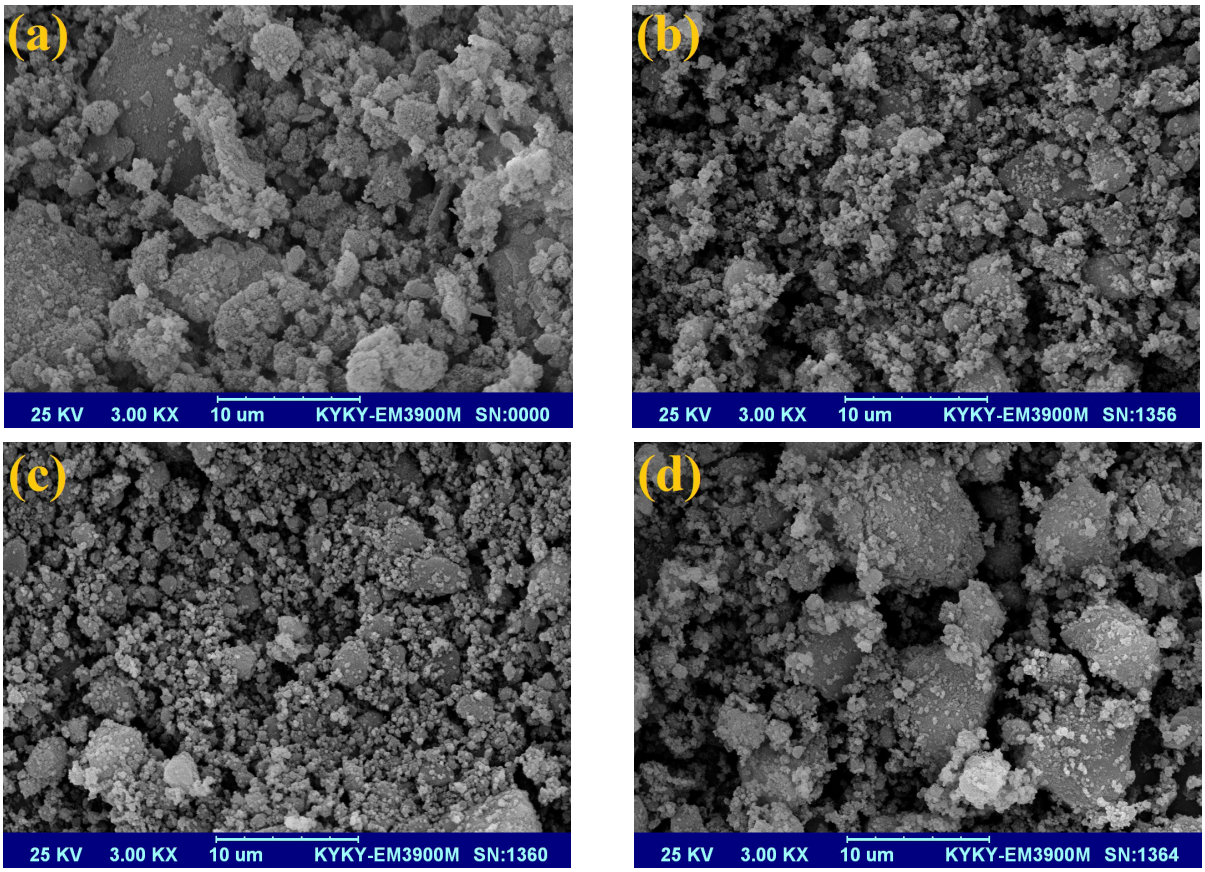

Fig. 7. SEM micrographs of mixtures of magnesium aluminate spinel and silica powders milled for (a) 5 min, (b) 6 h, (c) 18 h, and (d) 24 h.

Fig. 10 shows the SEM micrographs of post-heated compacts of the mixture of activated synthesized magnesium aluminate and silica powders. As shown, by increasing post-heating from 700 to 1100 °C, particles were attached and porosity decreased. This means that in addition to the

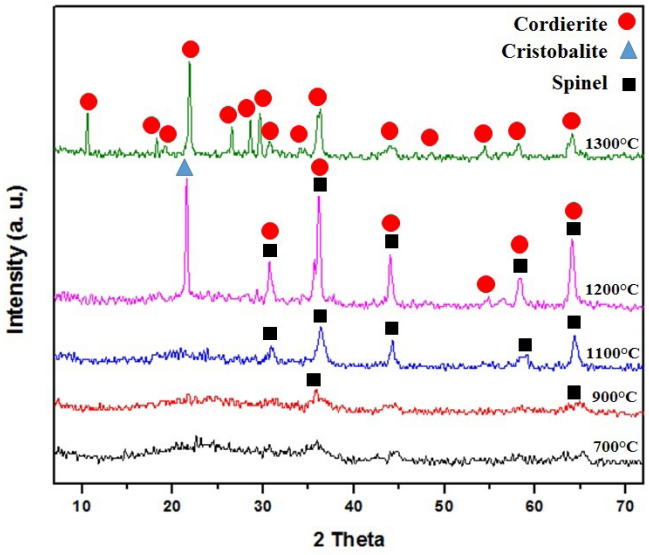

Fig. 8. XRD patterns of compacts of the mixture of activated synthesized magnesium aluminate and silica powders post-heated at different temperatures for 3 h.

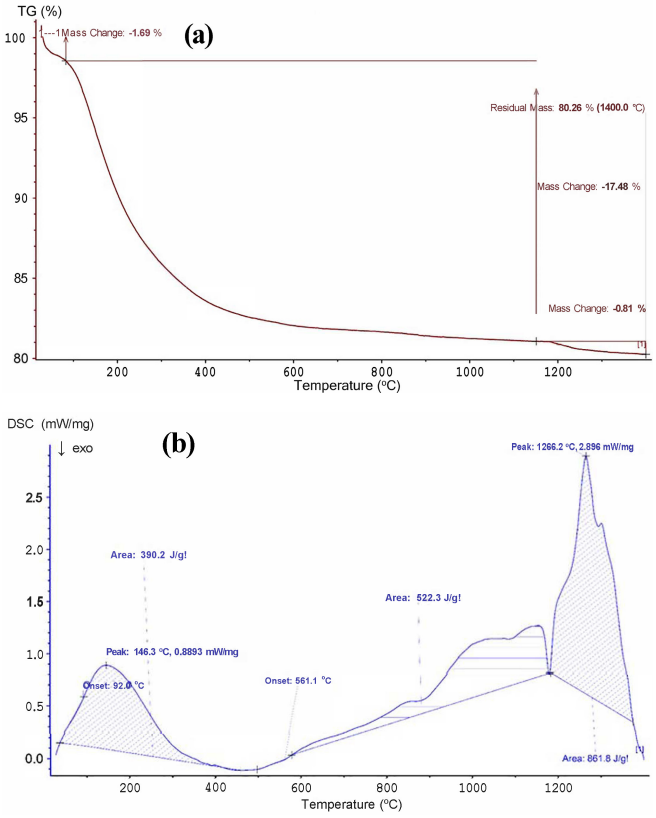

Fig. 9. Simultaneous thermal analyses (STA) of the mixtures of synthesized magnesium aluminate and silica powder activated by milling for 24 h (a) TGA and (b) DSC.

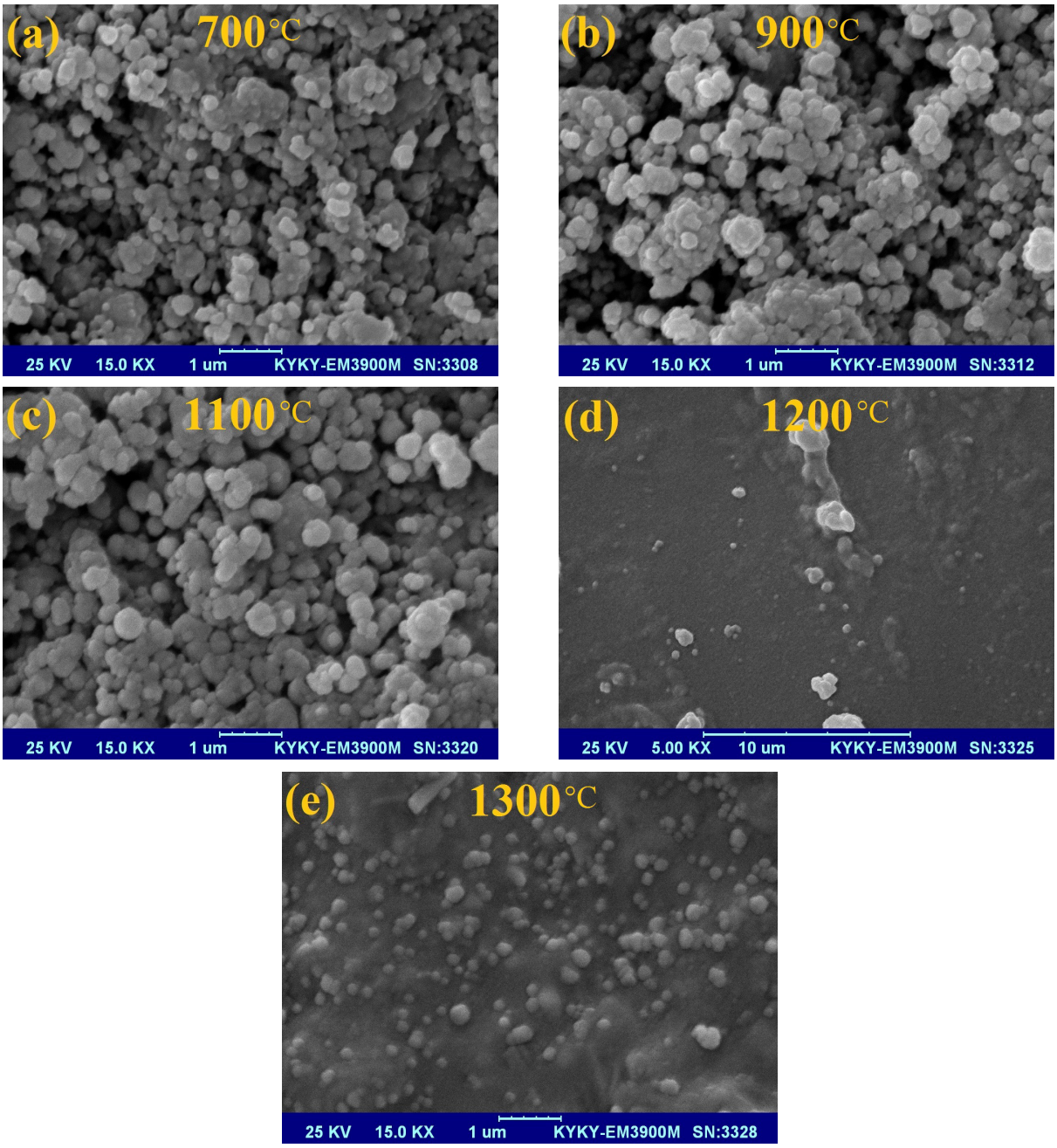

Fig. 10. SEM micrographs of compacts of the mixture of activated synthesized magnesium aluminate and nanosilica powders post-heated at (a) 700 °C, (b) 900 °C, (c) 1100 °C, (d) 1200 °C, and (e)1300 °C.

recrystallization of magnesium aluminate spinel (Fig. 8), the initial state of sintering has occurred. Post-heating at the higher temperature of 1200 °C led to a considerable increase of the liquid phase (Fig. 10(d)). Finally, further heating to 1300 °C resulted in a sintered sample with a uniform microstructure containing semi-sphere cordierite particles (Fig. 10(e)).

Fig. 11 shows the radial shrinkage (%) of activated magnesium aluminate and nano silica compact powders post-heated at different temperatures. As illustrated, a considerable continuous trend of sample shrinkage was observed as the post-heating temperature increased. Spongy, highly porous synthesized magnesium aluminate and very fine silica powders led to porous initial compacts with low green density values. Thus, post-heating of samples caused significant shrinkage. At 1200 °C and higher, liquid phase sintering was dominant, leading to a higher shrinkage rate.

4. Conclusion

In the present work, cordierite single-phase particles were synthesized using synthesized magnesium aluminate and silica reactants. The main results can be concluded as follows:

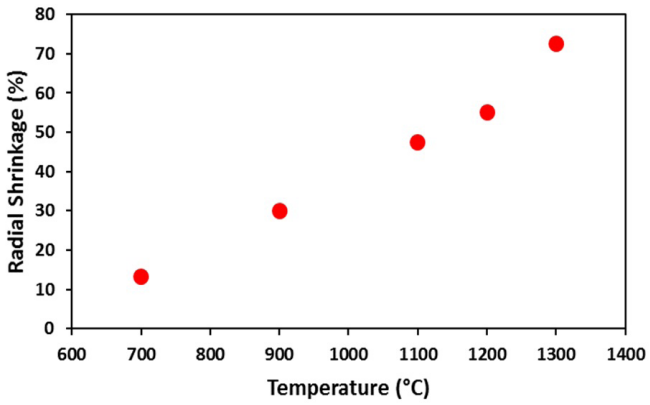

Fig. 11. Radial shrinkage (%) of compacts of the mixture in activated synthesized magnesium aluminate and nano silica powders post-heated at different temperatures.

1) Proper spongy porous high pure magnesium aluminate spinel powders could be obtained via a KCl-assisted solution combustion synthesis method and post-heating at 700 °C for 3 h powders.

2) A mechanochemical process of up to 24 h did not provide enough energy to form the cordierite phase from the synthesized spinel and nano silica mixture. However, milling led to amorphization of crystalline spinel and, consequently, obtaining more active powders.

3) Post-heating compacts of a mixture of synthesized magnesium aluminate and nano silica powders at 1200 °C led to the partial formation of the cordierite phase. Further heating to 1300 °C resulted in the formation of pure single-phase cordierite as well as liquid phase sintering of samples.

Disclosure statement

No potential conflict of interest was reported by the authors.

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Additional information

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