

Role of Ti^{4+} and Sn^{4+} ions in spinel formation and reactive sintering of magnesia-rich ceramics

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Abstract

The solid solubility of magnesia in magnesium aluminate spinel and magnesium aluminate spinel in magnesia does not change with temperature thus not creating bonds or precipitation over periclase grains in a single stage sintering process. In comparison, the precipitated spinels in magnesia-chromia refractories form complex spinel due to inversion in the position of bivalent and trivalent cations within the structure, making them more stable at high temperature than either normal or inverse spinel. Additives form low-temperature compounds that diffuse into the spinel structure and create defects that change the properties of spinel solid solution. In the present study, magnesia and alumina powders along with tetravalent oxide additives were analyzed for their role in reactive densification of spinel in a single stage firing process in order to achieve a better binding system for magnesia-based refractories. These tetravalent oxides on reaction with magnesia form spinel solid solution with MgAl_2O_4 as they have similar crystal structure. The spinel solid solution formed using oxide additives is expected to have higher solubility in magnesia than magnesium aluminate spinel, resulting in improvement of the bonding during sintering through increased in solid solubility at elevated temperatures followed by precipitation of secondary spinel phases, similar to the complex spinel in magnesia-chrome refractories. The formation of spinel during firing remains as a second phase that retards the grain growth of periclase. The changes in unit cell dimensions with temperature and amount of additive were analyzed using Reitveld method and correlated with the densification behaviour at different temperatures.

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1. Introduction

The reaction of magnesia and alumina to form spinel [1] is diffusion controlled and accompanied by volume expansion, making it difficult to synthesize in a single stage process. Hence, magnesium aluminate spinel [2] or its precursors [3] have been prepared by different techniques for use as a sintering and binding agent for alumina based refractory compositions, mainly in the preparation of castables [4]. The magnesia-rich refractories need a bonding matrix that is provided by chrome ore forming a direct bonded spinel type composition. The chrome ore contains three trivalent cations (Cr^{3+} , Al^{3+} , Fe^{3+}) that form a spinel structure with the magnesia that bonds the periclase grains after firing. This direct bonding [5] is caused by chrome ore dissolving into periclase at high temperatures

forming spinel that precipitates out on cooling and bonding with the precipitated spinel. The spinel that precipitates out from the solid solution adheres to the grains and the precipitate surrounding it, resulting in bonding of the particles. However, magnesium aluminate spinel [6] does not have a similar solid solubility to chrome ore at high temperatures and thus does not bond periclase grains on cooling.

The spinel formed by the reaction of magnesia with chrome ore has two bivalent cations (Mg^{2+} , Fe^{2+}) and three trivalent cations (Cr^{3+} , Al^{3+} , Fe^{3+}). Further, the bivalent and trivalent cations have individual site preferences and thus form normal, inverse or complex (mix of normal and inverse) spinel [7], depending on the cations present and their characteristics. Thermodynamic studies have shown that the stability of spinel at high temperatures is a result of their inversion (normal to inverse and vice-versa) and ability to form complex spinel, which is more stable than the initial forms. The Fe^{3+} ions predominantly form inverse spinel [8], whereas Cr^{3+} and Al^{3+} form normal spinel, thus resulting in the chrome ore forming a complex spinel on

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reaction with magnesia. In order to achieve a complex spinel using alumina as the base material, some tetravalent oxide additives that form spinel with magnesia may be used. This may result in lower amount of periclase and form complex spinel. The cation size, charge and electronic configuration of the cations in additives result in their occupancy in different sites within spinel structure. It is also observed that ZnO improves densification [9], TiO_2 decreases the synthesis temperature [10] and SnO_2 increases the thermodynamic stability of spinel solid solution containing magnesia and alumina.

The tetravalent cation oxides form both spinel [7] ($\text{A}^{2+}_2\text{B}^{4+}\text{O}^{2-}_4$) and perovskite [11] ($\text{A}^{2+}\text{B}^{4+}\text{O}^{2-}_3$). Both these structures have close packing of oxygen that forms a cubic lattice. The cations, being smaller in size than the oxygen anion, occupy positions in the interstices formed by surrounding oxygen ions. The spinel and perovskite are similar in terms of their cubic structure and the cations are in tetrahedral and octahedral sites with free interstices of the oxygen ions in the respective lattices, but have different arrangements within the unit cell. The spinel formed using tetravalent oxides form solid solution with spinel containing trivalent oxides that creates inversion through bivalent cations in the octahedral sites. This is similar to the positioning of the bivalent ions in the presence of ferric ion in the spinel structure, which occupies the tetrahedral site forming an inverse spinel structure. It has been reported that ZnO improves sintering of spinel [9]. We have previously reported [12] that there is no change in the unit cell dimensions or change in the maximum peak intensity with increase in additive content and firing temperature, thus not affecting the synthesis of spinel using ZnO as additive. TiO_2 has been reported [10] to improve the sintering and single stage synthesis of magnesium aluminate spinel and is used as a sintering aid. Our studies [12,13] indicate that TiO_2 increases the solubility of magnesia in stoichiometric and magnesia rich spinel improving the densification at relatively low temperatures. The reaction of SnO_2 [14] with MgO results in a stable spinel as compared to other tetravalent cations that form both perovskite and spinel. The use of zirconia [15] as an additive has shown to improve the mechanical properties of stoichiometric spinel, although it remains as a separate phase and does not form a solid solution with magnesium aluminate spinel.

In the present study, we have used MgO and Al_2O_3 for formation of magnesia-spinel with SnO_2 or TiO_2 additives that were pressed and fired at 1500 °C to 1800 °C for 3 h. The samples were then analyzed for their physical properties and unit cell dimensions using Reitveld method on the X-ray diffraction pattern for the samples.

2. Experimental procedure

The magnesia-spinel experimental compositions were designed such that the magnesia (NEDMAG Industries, NEDMAG-99 DBM) remained constant at 60% by weight as in most magnesia-chrome bricks [5]. The amounts of Al_2O_3 (Almatis A 16 SG) and either TiO_2 (SIGMA Chemicals, T-8141) or SnO_2 (Alpha Aesar, Product No. 36302) were varied so as to have theoretically different molar amounts of MgAl_2O_4 replaced by either Mg_2TiO_4 or Mg_2SnO_4 in the spinel phase. The mix compositions and the calculated amount of different spinel compounds are shown in Table 1.

These compositions were mixed in a ball mill at 50 rpm for 1 h for homogenisation using acetone as the liquid media and poly-vinyl alcohol as the binder. The mixes were then air-dried 24 h, pressed to form pellets (25 mm in diameter, ~15 mm thick) pressed at 0.25 T/cm², dried at 110 °C for 8 h in laboratory oven before firing at 1500 °C to 1800 °C (heating rate 10 °C/min to 1200 °C, 8 °C/min to maximum temperature) with a soaking period of 3 h. The samples are allowed to cool in the furnace before characterization in terms of their physical properties (bulk density, apparent porosity and apparent specific gravity by boiling in water) and X-ray diffraction technique for phase analysis and Rietveld refinement for calculation of lattice parameter.

3. Results and discussions

3.1. Sintering study without additives

Sintering of magnesia-spinel without any tetravalent cation shows the presence of only magnesia and spinel phases, even when fired at 1500 °C. The lattice parameters for both spinel

Table 1
Experimental Compositions.

Batch	Weight% MgO	Weight% Al_2O_3	Weight% TiO_2	Weight% SnO_2	Mole% MgAl_2O_4 in spinel	Mole% Mg_2TiO_4 in spinel	Mole% Mg_2SnO_4 in spinel
M-0	60.0	40.0	–	–	100	–	–
MS-1	60.0	38.8	–	1.2	98	–	2
MS-2	60.0	37.7	–	2.3	96	–	4
MS-3	60.0	36.6	–	3.4	94	–	6
MS-4	60.0	35.4	–	4.6	92	–	8
MS-5	60.0	34.3	–	5.7	90	–	10
MS-6	60.0	31.7	–	8.3	85	–	15
MT-1	60.0	39.4	0.6	–	98	2	–
MT-2	60.0	38.7	1.3	–	96	4	–
MT-3	60.0	38.1	1.9	–	94	6	–
MT-4	60.0	37.4	2.6	–	92	8	–
MT-5	60.0	36.8	3.2	–	90	10	–
MT-6	60.0	35.1	4.9	–	85	15	–

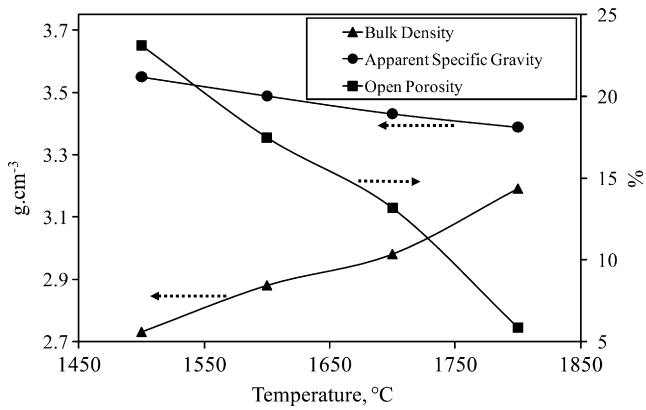


Fig. 1. Physical properties vs. firing temperature for magnesia–alumina system without additives.

(8.082 Å) and periclase (4.210 Å) are low at 1500 °C when compared to firing at high temperature and then remain constant at 8.086 Å and 4.212 Å respectively when fired at 1600 °C to 1800 °C. This may be a result of intrinsic defects and vacancies that can result densification or because magnesia (lattice parameter 0.4212 nm) has diffused into the spinel structure. The low solubility [6] of magnesia and alumina in spinel and the low solubility of MgAl_2O_4 spinel in magnesia make it difficult to create a high reaction rate and the volume increase during spinel formation renders it difficult to reaction sinter without any additives. The similar lattice parameters at 1600–1800 °C denote complete reaction, resulting in solid-state sintering at these temperatures.

Fig. 1 depicts the decrease in apparent porosity and apparent specific gravity as the firing temperature is increased. The increase in firing temperature results in better consolidation of particles and entrapment of pores within the grains indicating that magnesia-spinel formed with low apparent porosity needs high temperature in a single step firing process. The decrease in apparent specific gravity indicates that more pores are entrapped within the grains as the firing temperature is increased with decrease in the volume of open pores.

3.2. Phase analysis of compositions containing SnO_2

The samples fired at 1500 °C have two spinel phases with different unit cell dimensions (Table 2) showing that Mg_2SnO_4 forms two solid solutions with MgAl_2O_4 . The dimensions of the unit cell of spinel solid solution varies with the composition suggest that the solid solutions have different amount of cations at different mix compositions.

The samples fired at 1600–1800 °C result in dimensions for a single spinel phase and are greater than the dimensions observed for the composition without SnO_2 additive. Fig. 2(a)

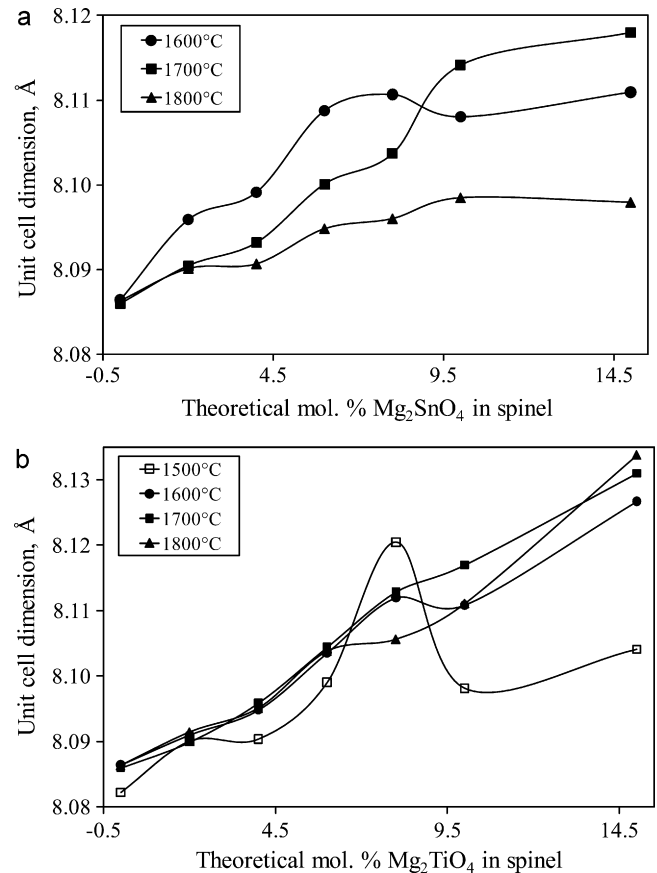


Fig. 2. Variation of unit cell dimensions with theoretical (a) Mg_2SnO_4 and (b) Mg_2TiO_4 content fired for 3 h.

shows the variation in unit cell dimension with theoretical Mg_2SnO_4 content in spinel. The spinel solid solution shows decrease in the lattice parameter with increase in firing temperature, unlike the analysis for no additive. Compositions with 10 and 15 mol.% Mg_2SnO_4 show increase in length of unit cell on increasing the firing temperature from 1600 to 1700 °C and decreases thereafter. Compositions with maximum 6 mol.% Mg_2SnO_4 show a gradual lowering in lattice parameter and higher SnO_2 content in the mix result in large reduction in the size of spinel unit cell with increase in firing temperature from 1700 °C to 1800 °C. The unit cell dimensions increase with SnO_2 content for the samples fired at 1700 °C, but have inflexions at 8 mol.% theoretical Mg_2SnO_4 in spinel solid solution when fired at 1600 °C and 6 mol.% for 1800 °C firing. The change in unit cell dimension from 4 to 6 mol.% theoretical Mg_2SnO_4 is comparatively the highest over all temperatures. It is assumed that the increase in lattice parameter is a result of substitution defects in the spinel structure as Mg_2SnO_4 [16] has a larger unit cell than MgAl_2O_4 [17].

Table 2

Unit cell dimensions of spinel phases at different theoretical Mg_2SnO_4 content fired at 1500 °C, 3 h.

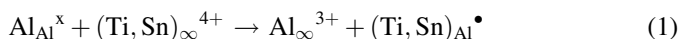
Mol.% Mg_2SnO_4	Phase	0	2	4	6	8	10	15
Unit cell dimensions (Å)	MgAl_2O_4	8.082	8.092	8.095	8.094	8.093	8.086	8.088
	Mg_2SnO_4	–	8.680	8.568	8.582	8.607	8.549	8.552

3.3. Phase analysis of compositions containing TiO₂

The unit cell length of spinel solid solution increases with TiO₂ content and decreases with firing temperature, similar to the result for SnO₂. Compositions containing TiO₂ had one lattice parameter for spinel solid solution. The unit cell size increased for all compositions with increase in temperature from 1500 °C to 1600 °C, except for theoretically 8 mol.% Mg₂TiO₄. This composition showed a gradual decrease in the size of unit cell, unlike the compositions with lower TiO₂ that had almost the same unit cell size for firing at 1600 °C to 1800 °C. 10 mol.% Mg₂TiO₄ showed increase in the size of unit cell from 1500 °C to 1700 °C, followed by reduction at 1800 °C and 15 mol.% had an increase unit cell with increasing temperature. The formation of perovskite at low temperatures in the initial stage may increase the reactivity of Mg²⁺ ions into the system resulting in the formation of bonding during reaction sintering to form spinel. The increased lattice parameter of spinel solid solution as compared to MgAl₂O₄ [17] may be a result of defect structure caused by the Ti⁴⁺ ion that forms Mg₂TiO₄, with a larger unit cell [18].

3.4. Comparative analysis of phases containing tetravalent cations

Spinel structure consists of bivalent and trivalent cations occupying tetrahedral and octahedral sites respectively. Replacement of trivalent cation Al³⁺ by tetravalent cation (Ti⁴⁺ or Sn⁴⁺) results in additional replacement of the trivalent cation by bivalent cation Mg²⁺ to maintain the charge neutrality in the spinel structure. Hence, the bivalent cations substituting for the trivalent cations are in the octahedral site.



In the case of Fe³⁺ ions having a half-filled stable d-orbital, tetrahedral sites are favourably occupied, thus forming an inverse spinel [8]. The Sn⁴⁺ also has a stable d-orbital, being completely filled, and thus occupies the tetrahedral sites in the spinel structure. This may result in all the bivalent cations being in the octahedral site and Sn⁴⁺ being in tetrahedral site, forming an inverse spinel structure both through substitution and the position of the electrons in stable configuration of the cation.

Among the spinels formed by tetravalent cations, Mg₂SnO₄ [16] has larger unit cell dimension than Mg₂TiO₄ [18]. However, the increase in lattice parameter using TiO₂ is more than that of using SnO₂ although the spinel phase Mg₂TiO₄ has a smaller unit cell than Mg₂SnO₄. This may be due to TiO₂ creating more interstitial and substitution defects in spinel solid solution formed in solid solution and the ability of TiO₂ to take more ions into the structure, making it a better sintering aid than SnO₂. The comparatively low increase in the unit cell dimensions for compositions containing Sn⁴⁺ ions compared to those with Ti⁴⁺ ions may result in solid solution with lower defects in the structure.

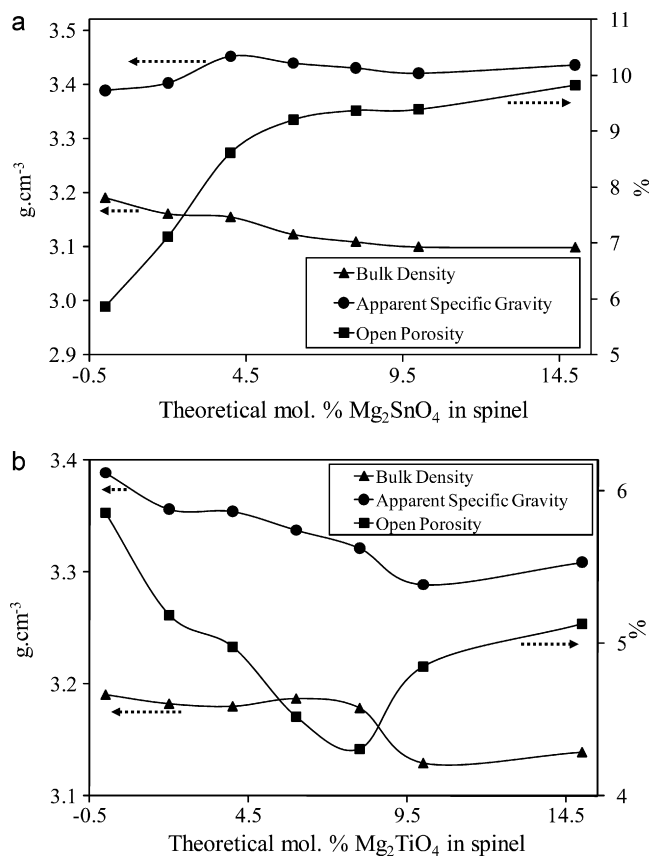


Fig. 3. Physical properties of pellets vs. theoretical (a) Mg₂SnO₄ and (b) Mg₂TiO₄ content fired at 1800 °C, 3 h.

3.5. Densification behaviour

The substitution of Al₂O₃ by SnO₂ shows an increase in the open porosity (Fig. 3a) for pellets fired at 1800 °C, accompanied by a decrease in the density. The apparent specific gravity increases with incremental increase in SnO₂ content to 4 mol.% Mg₂SnO₄ in spinel solid solution calculated theoretically from the oxide composition. Further increase in SnO₂ content reduces the apparent specific gravity. The theoretical density of Mg₂SnO₄ (4.77 g cm⁻³) [16] is higher than both magnesia (3.59 g cm⁻³) [19] and magnesium aluminate spinel (3.584 g cm⁻³) [17] and theoretically the batches containing SnO₂ would have a higher specific gravity. The reduction in apparent specific gravity may be because of a phase of lower true density or due to closed pores within the grains. The increase in open porosity leads to the hypothesis that SnO₂ alone is not a good sintering additive, but it may be thermodynamically more stable because of its ability to form complex spinel structure [7].

Fig. 3b shows the decrease in apparent specific gravity with increasing TiO₂ content. The open porosity decreases to theoretically calculated 8 mol.% Mg₂TiO₄ in the spinel phase. Further TiO₂ addition increases the open porosity. The decrease in apparent specific gravity may be related to the true density of Mg₂TiO₄ (3.54 g cm⁻³) [18] and the creation of closed pores within the grains. The open porosity at 6–8 mol.% calculated

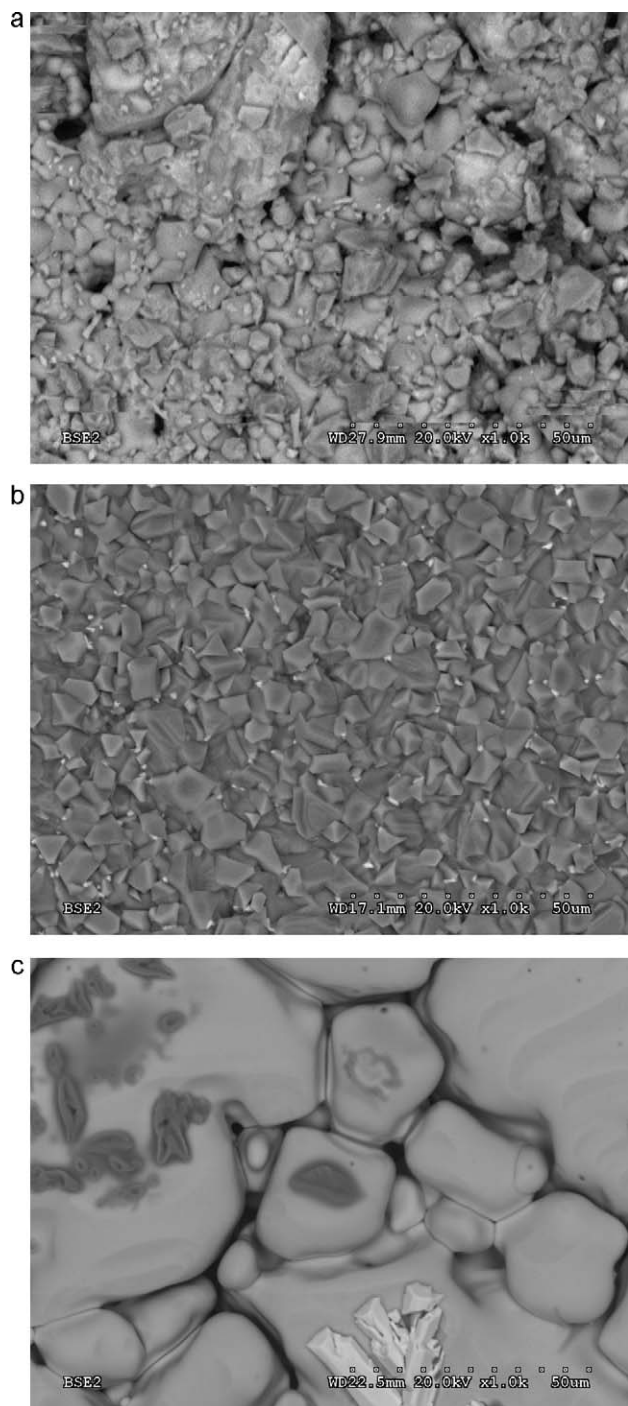


Fig. 4. Scanning electron micrographs of (a) M-0, (b) MT-4, (c) MS-3 fired at 1800 °C, 3 h.

Mg_2TiO_4 in spinel solid solution has apparent porosity less than 5%. The improvement in physical properties with increase in TiO_2 content is in agreement with other studies [10,13].

The change in apparent porosity on correlation with the change in lattice parameters indicate that 8 mol.% Mg_2TiO_4 with large variation from MT-3 and MT-5 compositions and minor decrease with increase in firing temperature give optimum results. The composition MS-3 has the same kind of variation in the lattice parameter of spinel and may have

more closed pores than those with lower SnO_2 content. Fig. 4 shows the microstructure of M-0, MT-4 and MS-3 that shows that MT-4 has a dense structure with lowest pores. The brighter regions for MT-4 are homogeneous and around the boundaries of the darker regions, indicating that titania has created better bonding through precipitation and this may be similar in bonding to magnesia-chrome bricks [5]. In comparison, the microstructure of MS-3 shows that the formation of fine spinel around the darker periclase grains and consolidation around pores, this may be attributed to the volatility of SnO_2 forming spinel around the grain boundary of periclase. This results in the compositions containing SnO_2 to have more open pores in spite of improved bonding mechanism. The variation of bulk density is comparable to the results for the unit cell dimensions, showing that decrease in the unit cell dimensions with increase in firing temperature a direct correlation between change in the unit cell parameter and densification pattern of the compositions.

4. Conclusions

1. The absence of alumina peaks in all compositions indicates complete spinel formation at 1500 °C.
2. The Mg_2SnO_4 does not form a single-phase solid solution with MgAl_2O_4 at 1500 °C although there is an increase in unit cell dimensions for MgAl_2O_4 . One spinel phase solid solution is estimated at 1600 °C to 1800 °C.
3. Single-phase spinel solid solution is observed for all compositions containing Mg_2TiO_4 for firing at 1500 °C to 1800 °C.
4. Spinel solid solution containing theoretically 6 mol.% Mg_2SnO_4 shows maximum variation in unit cell dimension with composition and small reduction with increasing sintering temperature indicating that it may be the optimum concentration.
5. Spinel containing 8 mol.% Mg_2TiO_4 as solid solution has the maximum density and minimum open porosity indicating that it is the optimum concentration. This is further supported by decrease in unit cell dimensions with increase in temperature and a large change from 6 and 10 mol.% Mg_2TiO_4 compositions.

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