

Doped MgAl₂O₄ Spinel Screen Print Thick Film as Sensing Material for Humidity Measurement

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Abstract

A low cost humidity sensor in thick film technology was developed based on magnesium aluminate spinel (MgAl₂O₄). The mixed metal oxide was produced using double alkoxide of magnesium and aluminium metals as precursor prepared directly from the reaction of reasonable and available compounds via the oxide one-pot synthesis process. The obtained MgAl₂O₄ powders with high purity can be examined by X-ray diffraction. With this method, the spinel can be easily doped with alkaline metal ions by mixing alkali salts in the alkoxide precursor. As a consequence, even if the lower heat-treatment temperature is employed, the high purity powders with high specific surface area of approximately 55 m²/g are gained. Moreover, the screen printing fabricated thick films of undoped and doped magnesium aluminate spinels on alumina substrate electroded with gold are investigated the humidity sensing properties by conductivity measurement at various relative humidities. It is pointed out that potassium ion doped thick films displays better response to humidity than those without doping and doped with sodium ion.

Keywords: MgAl₂O₄, One-pot synthesis, Double alkoxide precursor, Humidity sensor, Doping, Thick film

1. Introduction

Magnesium aluminate spinel (MgAl₂O₄) material has a wide range of applications in a great number of industrial areas, particularly an insulating material in a fusion reactor and a refractory material in the ceramic industry [1-2]. Due to its high mechanical strength and chemical resistance, MgAl₂O₄ spinel is considered to be one of ceramic materials for using as a ceramic humidity sensor [3-5]. Furthermore, spinel can be prepared as a sensing material in the forms of bulk or film with different requirements for a wide variety of applications [3-5]. There are several methods of preparing spinel materials, such as solid-solid reaction, co-precipitation of hydroxides, and sol-gel method [6-8]. However, the homogeneity, the cost of starting materials, operating temperature, and purity are some significant drawbacks of these synthesis techniques. Therefore, a great number of inexpensive metal precursors

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directly from metal oxides or metal hydroxides have been developed [9]. The oxide one pot synthesis (OOPS) process is of interest for providing an easy and straightforward way [9]. Therefore, this process is developed for preparing double metal alkoxide precursor complex, such as $MgAl_2O_4$ spinel [10].

Recently, Laobuthee and co-workers investigated the porous material of magnesium aluminate ($MgAl_2O_4$) obtained directly from the one pot process and used this powder as a humidity sensing material. The preliminary investigation of magnesium aluminate spinel was performed in the form of pellet. Spinel powder produced by this technique showed a similar performance compared to those produced by others. The material responses to humidity exhibited the relationship with good linearity between the logarithm resistance and the relative humidity. This material also showed the good reproducibility and sensitivity. Furthermore, the microstructure of the pellets influenced the response of their conductivity and humidity [11-12]. Generally, thick film technology is used for a wide range of ceramic oxides to fabricate the solid state sensor. This method has been reported as an appropriate technology for producing the sensing films showing similar microstructure to pellet forms [13-15]. Moreover, the addition of alkali metal ions to ceramic matrix enhancing the conductive and electrical sensing properties has been previously observed [16-18].

In this research, we investigate the preparation of $MgAl_2O_4$ spinel thick film for humidity sensor by screen printing technique using double metal alkoxide precursor synthesized via the one pot process. Moreover, some preliminary humidity sensing studies of the resulting spinel with potassium or sodium ions and without doping are also observed.

2. Experimental

2.1 Materials

Magnesium oxide and aluminum hydroxide hydrate were obtained from Sigma Carlo Erba (Barcelona) and Aldrich Chemical Co. Inc (USA), respectively. They were used as received. Triethanolamine (TEA) (99.5% purity) was purchased from Merck Chemical Co. (Germany) and used as received. Ethylene glycol (EG), purchased from Carlo Erba (Barcelona), was purified by fractional distillation at 200°C prior to use. Potassium nitrate and sodium nitrate were purchased from Fluka Chemical Co. (Switzerland). Butyl-carbitol acetate, α -terpineol, and ethyl-cellulose were obtained from Carlo Erba (Barcelona) and used as received.

2.2 Synthesis of magnesium aluminate spinel powder, $MgAl_2O_4$

The preparation of $MgAl_2O_4$ spinel precursor was described in a previous work [11-12]. For doping process, sodium nitrate or potassium nitrate was added to spinel precursor with the mole ratio of 3%. The thermal behavior of the undoped and doped precursors was investigated by thermogravimetric analyzer (TGA, Netzsch STA 419). 1H -NMR spectrum was obtained on an INOVA VARIAN NMR Spectrometer 400 MHz. Mass spectrum was recorded on FAB mode. The positive fast atom bombardment mass spectrometer (FAB⁺-MS) was a Fison Instrument (707 VG Autospec-ultima mass spectrometer).

Spinel materials were produced by heat treatment of the resulting precursors with and without doping in a furnace at 850°C for 2 h under air atmosphere. Powder X-ray diffraction patterns were examined using a Phillips PW 1830/00 DY 1241 connected with $CuK\alpha$ source of radiation. BET surface area and nitrogen adsorption characterization were performed using a Micromeritics ASAP 2020 surface analyzer.

2.3 Fabrication of $MgAl_2O_4$ spinel thick films

The undoped and doped spinel powders obtained were thoroughly crushed and mixed with the organic vehicle (the mixture of butyl-carbitol acetate, α -terpineol, and ethyl-cellulose) at an approximate ratio by weight of spinel:organic vehicle of 70:30. This weight ratio gave an appropriate paste for the fabrication of thick film by screen printing method. The pastes were further screen printed

on the alumina substrates with comb pattern electrodes (11 fingers, 8.5 mm long and 0.8 mm wide). Then the sensing films were annealed at 850°C with the heating rate of 5°C/min for 3 h. The adhesion of the sensing film to the substrate was examined by qualitative peeling test with scotch tape. The structure of the phases in the pyrolyzed samples was obtained using Field Emission Scanning Electron Microscope (FE-SEM, Leo Supra 1535).

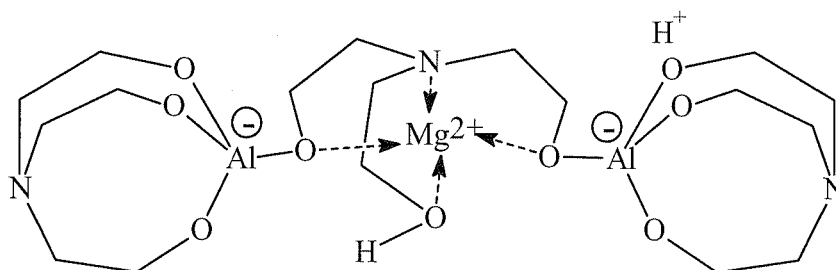
2.4 Investigation of spinel thick film as a sensing material for humidity measurement

The study of the humidity response was carried out using DC impedance spectroscopy. The thick film was carried out in test chamber where both temperature and humidity were monitored. Relative humidity (RH) was detected using a commercial sensor (Honeywell HHH 3602 C) having an accuracy of ~1 %. The evolution of current responses due to the variation of RH ranging from 5 to 95 % with step of 2.5%/100 s. were detected by a Keithley Quasistatic CV meter and recorded. The dry and wet streams for controlling the relative humidity were operated using the MKS mass-flow controller.

3. Results and Discussion

3.1 Synthesis of magnesium aluminate spinel powder, $MgAl_2O_4$

The reaction completion of a mixture of $Al(OH)_3$, MgO , TEA and EG was indicated by the appearance of the clear solution. The residual ethylene glycol was removed by vacuum distillation ($\sim 10^{-2}$ torr) to obtain a viscous product. Then FAB^+ -MS and 1H -NMR were employed to confirm the structure of synthesized precursor. 1H -NMR spectrum display two major triplet peaks at 3.73 ppm and 2.72 ppm. They are assigned to methylene protons adjacent to oxygen ($-CH_2-O-$) and nitrogen ($-CH_2-N-$), respectively. The integration ratio of these peaks observed was 1. The MS spectrum fragmentation pattern also shows a parent peak at $m/z = 518$ (100% intensity) corresponding to a protonated parent ion, as demonstrated in Scheme 1. This pointed out that the spinel precursor is successfully synthesized using OOPS process. The precursor structure has been proposed as trimetallic species which consists of one metal center enfolded with one TEA (Scheme 1) [10-12].



Scheme 1 Protonated precursor as a parent ion ($m/z = 518$, 100% intensity)

A pyrolysis process based on the TGA trace was employed to pyrolyze these precursors. Figure 1 displays the typical TGA curve obtained from those precursors. The weight loss in the temperature range 200-270°C is due to the combustion of organic species. The weight loss ranging from 270-400°C corresponded to the oxidative decomposition of organic residues. Upon further increasing the temperature, the weight loss in the temperature range 400-600°C was caused by the decomposition of magnesium carbonate [10-12]. The percentage ceramic yield of the product was around 37%.

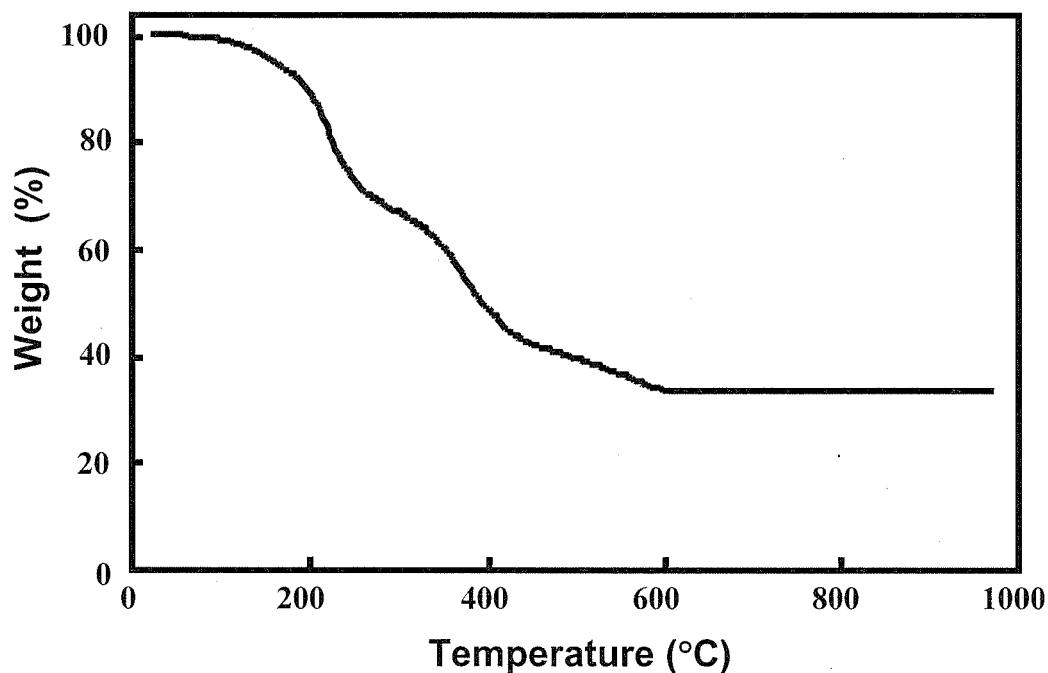


Fig. 1 Thermogram of spinel precursor.

MgAl₂O₄ spinel was obtained from annealing the resulting precursor at 850°C for 2 h. XRD patterns of spinel in Figure 2 shows that all peak positions of product in agreement with JCPDF file No. 21-1152 were consistent with that of magnesium aluminate spinel, particularly two major peaks at 2θ = 36.8° and 44.8°.

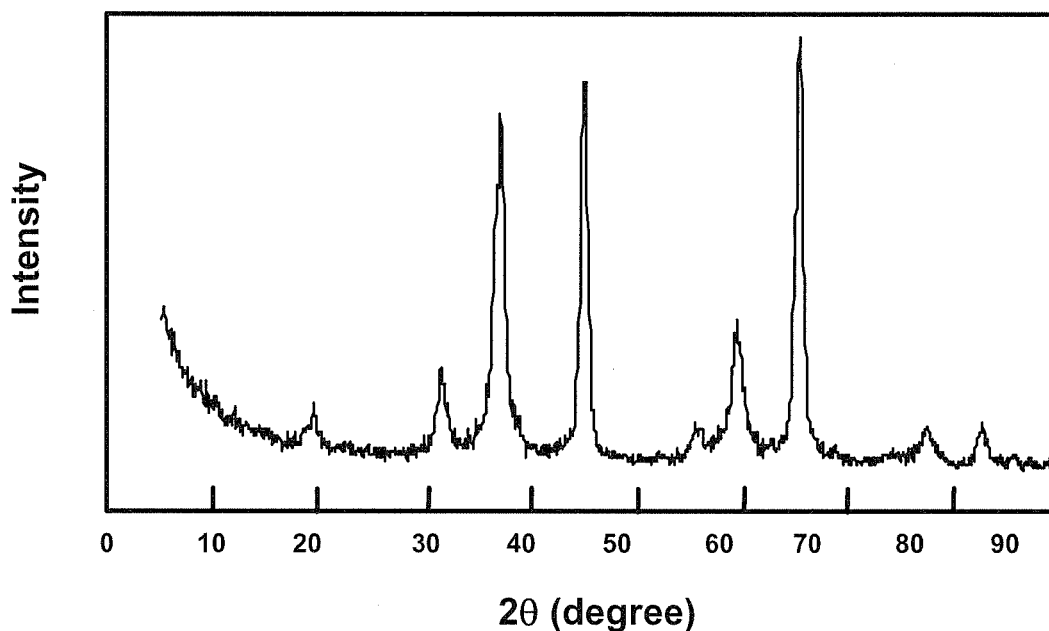


Fig. 2 XRD patterns of spinel pyrolyzed at 850° for 2 h.

BET surface area for spinel materials obtained after thermal treatment was also considered. The BET specific surface area of the obtained spinel was approximately $44 \text{ m}^2 \text{ g}^{-1}$ whereas that of spinel obtained previously (heated at 1100°C for 2 h) by Laobuthee and co-workers was $11 \text{ m}^2 \text{ g}^{-1}$ [11-12]. This observation was identified by SEM technique, as illustrated in Figure 3. The microstructure of powder was nanoparticles with low agglomeration as comparing with previous work [11-12]. As the results, the thermal treatment at 850°C for 2 h was the appropriate condition for preparing spinel. Reasonably, it could be implied that not only the high purity spinel with high surface area was acquired, but also the decrease of particle agglomeration was observed.

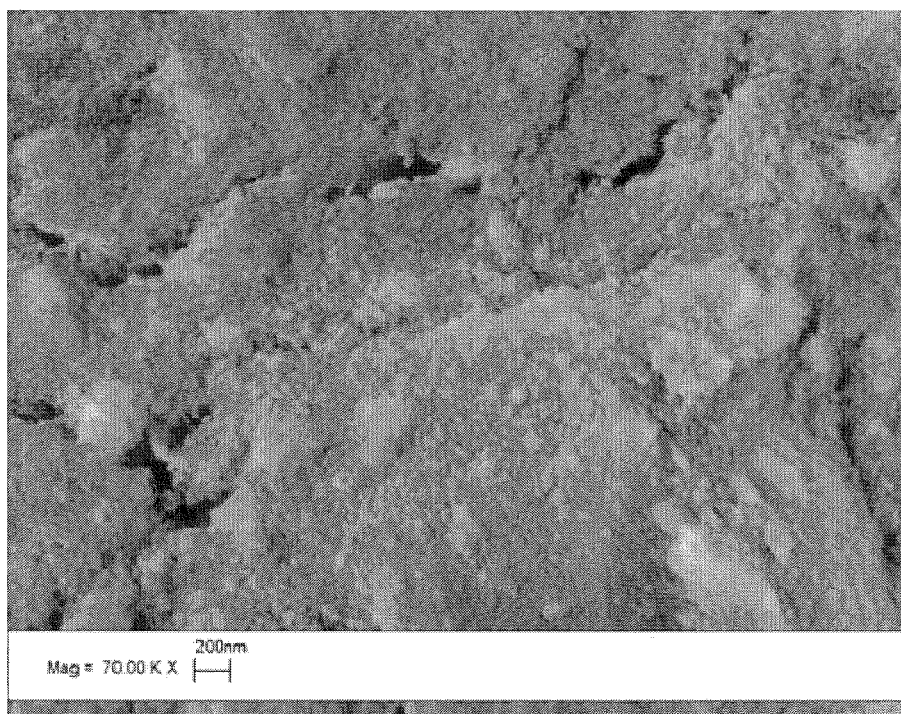


Fig. 3 Scanning electron micrograph of spinel powder obtained after thermal treatment at 850° for 2 h.

Afterwards, the precursor was doped with alkaline metal ions by dissolving precursor and metal nitrate salt (sodium nitrate or potassium nitrate) in isopropanol to obtain a homogeneous solution. After dissolution completion, isopropanol in this system was then removed under vacuum. The doped precursor, after removal of isopropanol, has the appearance of a viscous liquid. The structure of doped precursor was identified by $^1\text{H-NMR}$ and $\text{FAB}^+\text{-MS}$ methods. It can be seen that $^1\text{H-NMR}$ spectra do not show any variation in all peak positions of $-\text{CH}_2\text{-O}-$ and $-\text{CH}_2\text{-N}-$ including the integration ratio of both peaks. Moreover, mass spectra fragmentation pattern (Figure 4) show the parent peak at $m/z = 556$ and 540 assigned to parent peaks of potassium doped precursor and sodium doped precursor, respectively. However, the protonated parent ion peak was still existed in the fragmentation pattern of salt doped complexes. It is probably due to the addition of a small amount of metal nitrate in spinel precursor.

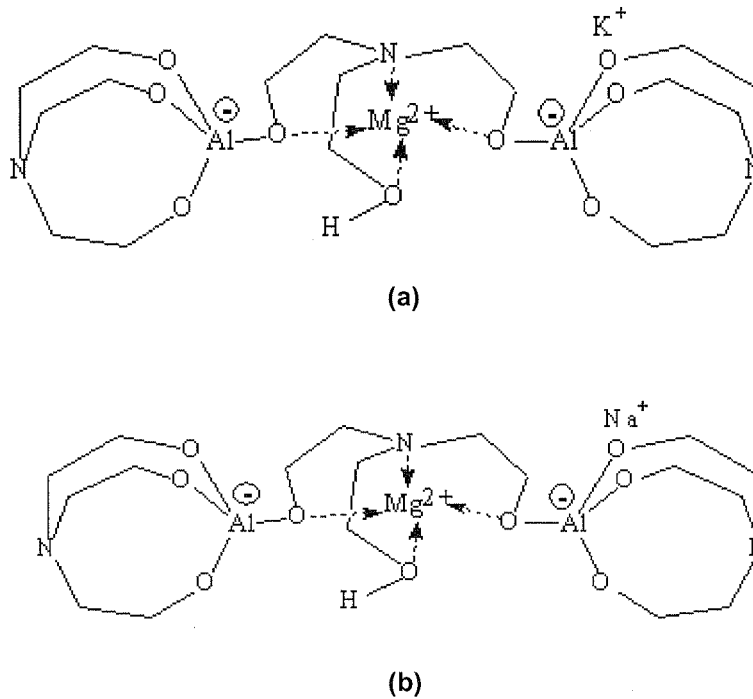


Fig. 4 Proposed structures of salt doped precursor parent ions: (a) precursor parent ion doped with potassium ($m/z = 556$) and (b) precursor parent ion doped with sodium ($m/z = 540$)

The thermal behavior of salt doped precursors was investigated by TGA measurement. The TG profiles of salt doped precursors (Figure 5) show three transitions similar to that of undoped precursor. The salt doped products gave the ceramic yields of ~31-37% which are not so different from that of undoped precursor. It can be implied that the addition of metal nitrate salt at 3 mol.% to precursor shows no significant influence on ceramic yield.

Similarly, metal salt doped precursors were then sintered at 850°C for 2 h to attain doped spinel materials. XRD measurement was employed to observe spinel powders by comparing with JCPDF file No. 21-1152. It was found that the XRD patterns of doped spinel powders were not altered as comparing with that of undoped spinel, as presented in Figure 6. It can be said that the addition of metal to precursor show no significant effect on spinel structure. The specific surface area of salt doped spinel materials increased to around 55 %, especially at 3% by mole of potassium.

3.2 Investigation of spinel thick film as a sensing material for humidity measurement

In order to investigate the humidity response, the sensing films deposited by screen printing technique were measured using DC impedance spectroscopy. The increase of relative humidity leads to the increment of the measured current. The film with the best response to humidity shows the highest current at each relative humidity. It was found that the humidity response of metal salt doped films increased as comparing with that of undoped films. MgAl₂O₄ spinel doped with 3 mol.% potassium gave the highest response at every relative humidity. It is probably due to higher metallic property of potassium than that of sodium leading to higher conductivity. In forthcoming works, the effect of the concentration and type of metal ion on humidity sensing properties will be discussed in detail.

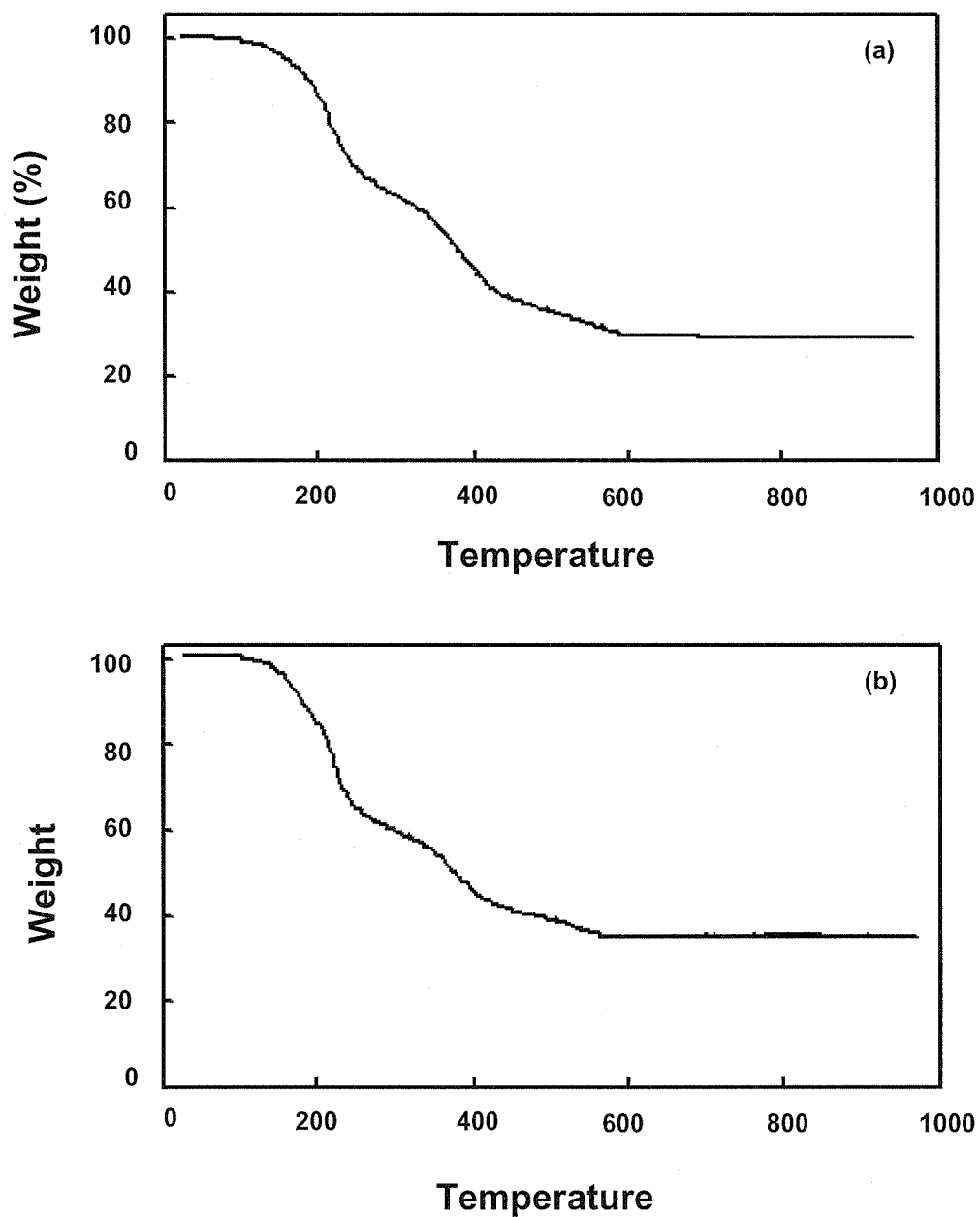


Fig. 5 TGA thermograms of salt doped precursors: (a) precursor doped with 3 mol.% potassium and (b) precursor doped with 3 mol. % sodium

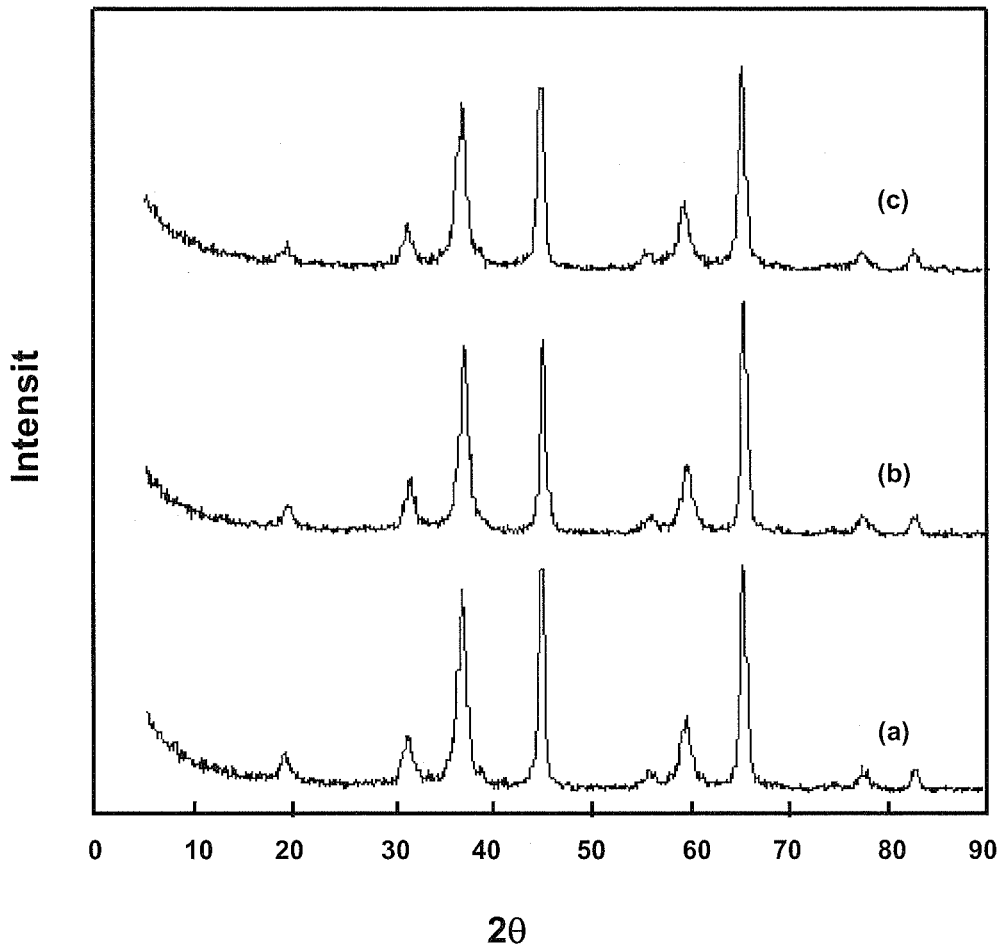


Fig. 6 XRD patterns of spinel materials after heat treatment at 850° for 2 h prepared from: (a) precursor, (b) precursor doped with 3 mol.% sodium, and (c) precursor doped with 3 mol.% potassium.

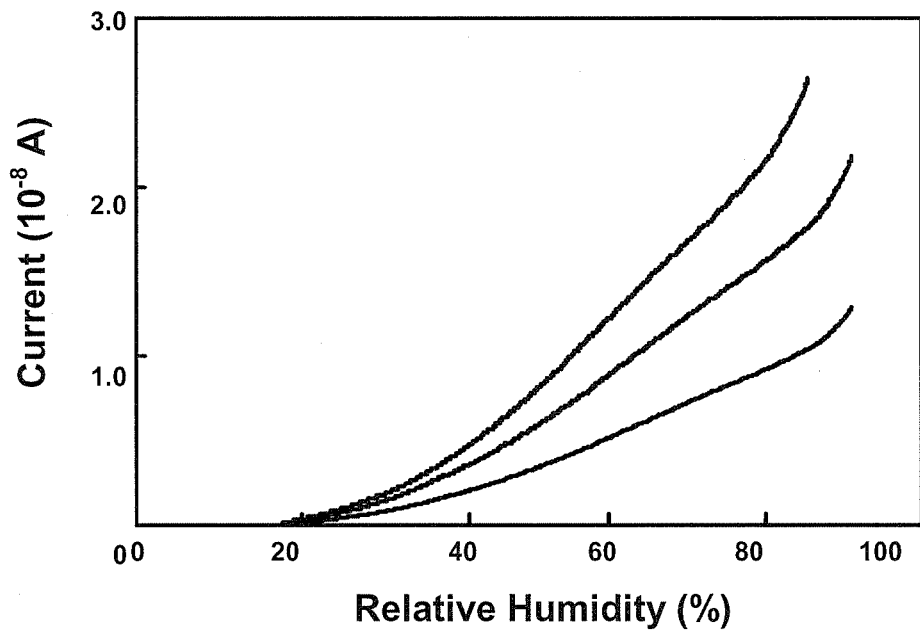


Fig. 7 Humidity response of thick films: (a) without doping, (b) doped with 3 mol.% potassium, and (c) doped with 3 mol.% sodium

Conclusions

Double metal alkoxide of aluminium and magnesium metals, obtained via the one pot process using inexpensive and readily available reactants, can be used as precursor for producing high purity magnesium aluminate spinel ($MgAl_2O_4$). We have also exhibited a simple way to dope alkali metal ion to $MgAl_2O_4$ spinel by direct mixing of alkali metal salt to spinel precursor solution. Heat treatment of the resulting precursor with and without doping at $850^\circ C$ for 2 h produces the high specific surface area spinel. Additionally, screen printed thick films of magnesium aluminate spinel doped with potassium ion presents better response to humidity than those of spinel without doping as well as doped with sodium ion.

Acknowledgments

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