

## SYNTHESIS OF MAGNESIUM ALUMINATE POWDERS UTILIZING THE SOLUBILITY RELATIONSHIPS IN THE Mg–Al–Oxalic acid–H<sub>2</sub>O SYSTEM

Z. DING, M. ZHANG, J. HAN

*Center for composite materials, Harbin Institute of Technology,  
Harbin 150001, China*

Received 10 November 2001

**Abstract.** In this investigation, oxalic acid and metal nitrates were used to form soluble complexes in the aqueous chemical synthesis of MgAl<sub>2</sub>O<sub>4</sub>. The chelating ability of oxalic acid and the complex formation reactions between metal ions and oxalic acid, which are dependent on the judicious manipulation of solution-chemical variables such as pH and reagent concentrations, as well as the mode of reagent additions, were predicted by using thermodynamic equilibrium constants of the corresponding metals in an aqueous solution. Ultrafine MgAl<sub>2</sub>O<sub>4</sub> powders have been obtained through the thermal decomposition of oxalate precursor at the relatively low temperature of 800°C.

**PACS number:** 81.16.Be, 81.20.Ev

### 1 Introduction

The MgAl<sub>2</sub>O<sub>4</sub> spinel is of technological interest for its good mechanical and optical properties. Its excellent stability under radiation makes it an attractive material for optical transmission applications in the visible and IR portion of the spectrum as transparent plates to electromagnetic windows, radome and armor. Nevertheless, it is not commercially available today as an optical material due to difficulties in reliably obtaining the desired transparency [1]. It is generally recognized that the final material depends essentially on some basic properties of the powders, such as high purity and chemical homogeneity, particle size and narrow size distribution. Thus, various preparation methods have been developed to obtain high quality powders so as to lead to improvements in processing spinel to transparency. Apart from the solid-state

reaction (mixing, grinding and heating at high temperature non-conventional powder elaboration methods recently used are decomposition of metal alkoxides using supercritical ethanol as reactive media [2]; autoignition synthesis of nanocrystalline  $\text{MgAl}_2\text{O}_4$  [3]; the oxide one pot synthesis process [4]; spray drying of a solution of aluminum and magnesium nitrates [5]; controlled hydrolysis of metal alkoxides [6]; hydrothermal synthesis of zinc aluminate spinel [7]; and organic gel-assisted citrate process (complexation) [5]. Although several chemical routes exist for the preparation of fine magnesium aluminate powders, ability to fabricate, crystal size capability and affordability as a major challenge for the material scientists involved in the development of new synthetic routes are taken into consideration.

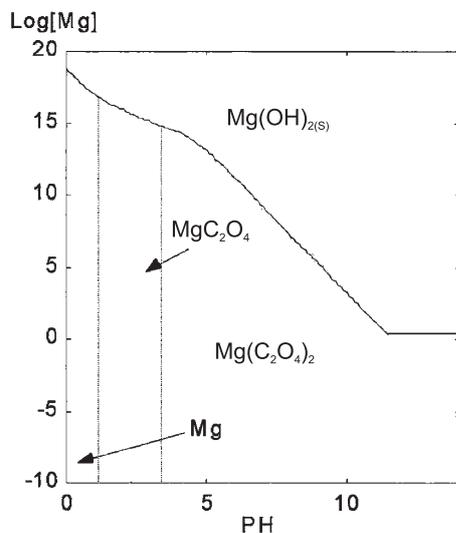
In the present study, our attention was paid to the preparation of ultrafine, pure and reactive  $\text{MgAl}_2\text{O}_4$  spinel starting from comparatively cheap raw materials. That is, our process utilizes only the chelating ability of the oxalic acid and metal nitrates. It is well known that the chelating ability of oxalic acid and the complex formation reaction between metal ions and oxalic acid are highly dependent on the judicious manipulation of solution-chemical variables such as pH and reagent concentrations, as well as the mode of reagent additions. It is, therefore, required to investigate the behavior of ionic species present in an aqueous solution. To optimize the preparation conditions of amorphous precursors, we have carried out theoretical investigations on the behavior of the chemical species based on the thermodynamic equilibrium constants and designed the aqueous stability diagrams [8] which delineate the stability domains of relevant aqueous species and solid compounds.

## 2 Theoretical Calculation of Stability Diagrams

In order to gain a better understanding and control of the synthesis process or to predict the behavior of the formation and dissolution of chemical species present in the Mg-Al-Oxalic acid- $\text{H}_2\text{O}$  system, it is necessary to establish the thermodynamic constraints which govern the chemical reactions taking place. The solution chemistry of the Mg-Oxalic acid- $\text{H}_2\text{O}$  and Al-Oxalic acid- $\text{H}_2\text{O}$  systems is analyzed in terms of aqueous stability diagrams, which delineate the conditions of thermodynamic stability for the Mg-Oxalate complex and Al-oxalate complex. Various chemical equilibria and their equilibrium constants used in this Mg-Al-Oxalic acid- $\text{H}_2\text{O}$  system are listed in Table 1 [9]. The Matlab computer program was used to calculate and plot the stability relationships.

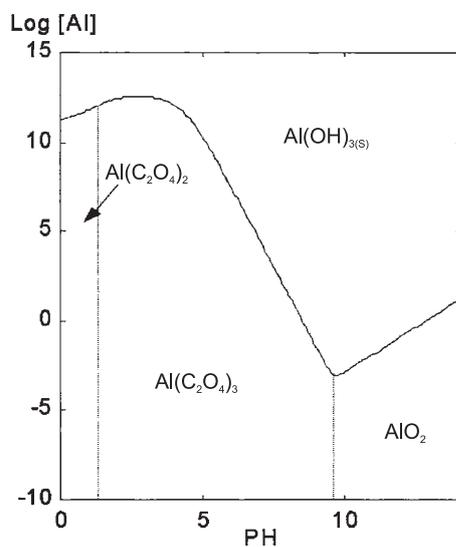
Log[Me]-pH diagram at 25°C for the Mg-Oxalate- $\text{H}_2\text{O}$  and Al-Oxalate- $\text{H}_2\text{O}$  systems are presented in Figs. 1 and 2. As shown in Fig. 1, at high metal concentrations, various chemical species exist as major ones depending upon the solution pH; free  $\text{Mg}^{2+}$  ion at  $\text{pH} < 1.18$ ,  $\text{MgC}_2\text{O}_4$  at  $1.18 < \text{pH} < 3.38$ ,  $\text{Mg}(\text{C}_2\text{O}_4)_2^{2-}$  at  $3.38 < \text{pH} < 11.44$ . Thus, in the Mg-Oxalate- $\text{H}_2\text{O}$  system, the best PH region for the formation of pure Mg-Oxalate complexes is  $1.2 < \text{pH} < 11.44$ .

Fig. 2 shows that the aluminum oxalate complex is predominant at  $\text{pH} < 8.8$  ( $[\text{Al}^{3+}] = 0.1\text{M}$ ). The precipitation of  $\text{Al}(\text{OH})_{3(s)}$  could occur at  $\text{pH} = 9.552$  ( $[\text{Al}^{3+}]$



**Fig. 1.** Log [Mg]-pH diagram for the Mg-Oxalate-H<sub>2</sub>O system at 25°C. [Oxalate] = 1 mol.l<sup>-1</sup>.

= 10<sup>-3.241</sup>M). Therefore, the optimum pH condition for the formation of pure aluminum oxalate complex could be estimate to be pH < 8.8. Based upon the above stability diagram for Mg-Oxalate-H<sub>2</sub>O and Al-Oxalate-H<sub>2</sub>O systems, we could predict



**Fig. 2.** Log [Al]-pH diagram for the Al-Oxalate-H<sub>2</sub>O system at 25°C. [Oxalate] = 1 mol.l<sup>-1</sup>.

**Table 1.** Thermodynamic equilibrium constants for the possible species present in the Mg-Al-Oxalic acid-H<sub>2</sub>O system.

equation	reaction	Symbol constants	for Log k
I Mg system			
(1)	$\text{Mg(OH)}_{2(S)} = \text{Mg}^{2+} + 2\text{OH}^-$	$\text{Log } k_{sp}$	-9.22
(2)	$\text{MgC}_2\text{O}_4(S) = \text{Mg}^{2+} + \text{C}_2\text{O}_4^{2-}$	$\text{Log } k_{sp}$	-4.1
(3)	$\text{Mg}^{2+} + \text{OH}^- = \text{MgOH}^+$	$\text{Log } \beta_1$	2.58
(4)	$\text{Mg}^{2+} + \text{C}_2\text{O}_4^{2-} = \text{MgC}_2\text{O}_4$	$\text{Log } \beta_2$	3.43
(5)	$\text{Mg} + 2\text{C}_2\text{O}_4^{2-} = \text{Mg(C}_2\text{O}_4)_2^{2-}$	$\text{Log } \beta_2$	4.38
II Al system			
(6)	$\text{Al(OH)}_{3(S)} = \text{Al}^{3+} + 3\text{OH}^-$	$\text{Log } k_{sp1}$	-32.89
(7)	$\text{Al(OH)}_{3(S)} = \text{AlOH}^{2+} + 2\text{OH}^-$	$\text{Log } k_{sp2}$	-23
(8)	$\text{Al(OH)}_{3(S)} = \text{AlO}_2^- + \text{H}^+ + \text{H}_2\text{O}$	$\text{Log } k_{sp3}$	-12.80
(9)	$\text{Al}^{3+} + \text{OH}^- = \text{AlOH}^{2+}$	$\text{Log } \beta_1$	9.27
(10)	$\text{Al}^{3+} + 4\text{OH}^- = \text{Al(OH)}_4^-$	$\text{Log } \beta_2$	33.03
(11)	$\text{Al}^{3+} + \text{C}_2\text{O}_4^{2-} = \text{AlC}_2\text{O}_4^+$	$\text{Log } \beta_1$	7.26
(12)	$\text{Al}^{3+} + 2\text{C}_2\text{O}_4^{2-} = \text{Al(C}_2\text{O}_4)_2^-$	$\text{Log } \beta_2$	13
(13)	$\text{Al}^{3+} + 3\text{C}_2\text{O}_4^{2-} = \text{Al(C}_2\text{O}_4)_3^{3-}$	$\text{Log } \beta_3$	16.3
III Dissociation of oxalic acid			
(14)	$\text{H}_2\text{C}_2\text{O}_4 = \text{H}^+ + \text{HC}_2\text{O}_4^-$	$\text{Log } k_1$	-1.25
(15)	$\text{HC}_2\text{O}_4 = \text{H}^+ + \text{C}_2\text{O}_4^{2-}$	$\text{Log } k_2$	-4.27

Log  $k_{sp}$ : solubility product; Log  $\beta_i$ : overall stability constant; Log  $k_i$ : stepwise stability constant

that the optimum pH condition for the simultaneous formation of oxalate complexes of Mg and Al ions can be determined as  $2 < \text{pH} < 8$  and for high metal concentration in aqueous solution.

### 3 Experimental Procedure

A solution of aluminum and magnesium nitrates ( $\text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Mg(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) in stoichiometric proportion were chelated by oxalic acid, and ammonia was added to adjust the pH to  $\sim 6$ . The resulting clear solution was heated until the viscous liquid mixture was formed, which was dried on a hot plate between  $100^\circ\text{C}$  and  $120^\circ\text{C}$  leaving behind a fluffy gel powder. These gel powders were calcined at various temperatures to obtain the desired phase.

X-ray diffraction patterns of the products were recorded by a Rigaku D/max-rB diffractometer using  $\text{Cu K}\alpha$ , radiation. In order to prepare TEM samples, powders were ultrasonicated in high purity ethanol for 10 min to disperse uniformly.

The as-dispersed samples were examined using a transmission electron microscope JEM-200CX at 200 KV.

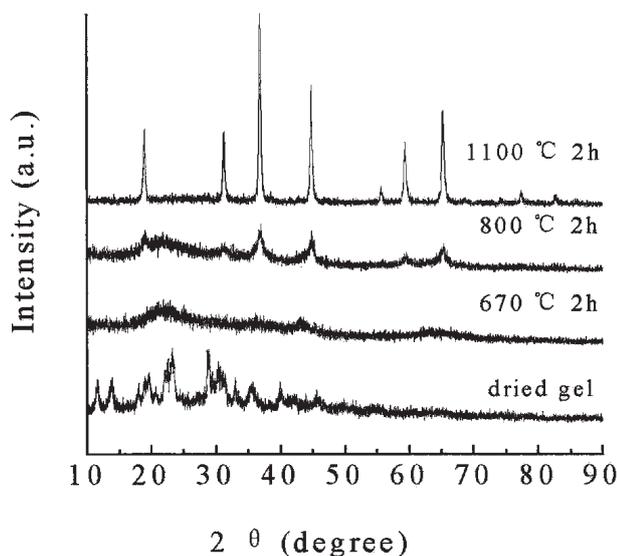


Fig. 3. XRD patterns of the MgAl<sub>2</sub>O<sub>4</sub>.

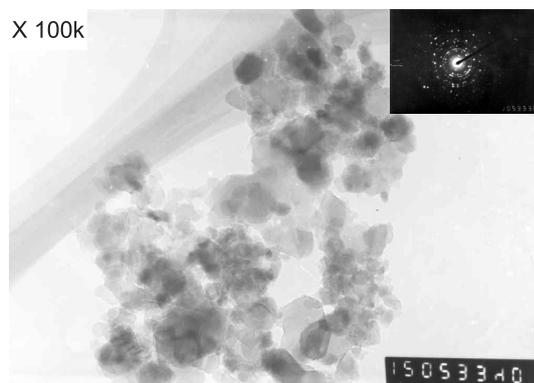
#### 4 Results and Discussions

The XRD study of precursor powder at different calcination temperatures is shown in Fig. 3. The powders remain amorphous even after calcination at 670°C for 2 h. With increasing temperature, gradual increases in the peak intensities accompanied by sharpening of the peaks is observed, which is an indication that the quantity of the crystalline spinel phase is increasing. No extra diffraction lines associated with the presence of single metal oxides are evinced for the calcinated powders at 1100°C for 2 h. Additionally, the average crystallite size of spinel powder obtained after pyrolysis of the precursor at 1100°C for 2 h was 24.8 nm by using the Scherrer's equation from a line broadening technique, which measures the full width at half-intensity of the largest intensity reflection of XRD pattern.

Fig.4 shows a bright field (BK) TEM micrograph of the as-synthesized powder and the corresponding selected area diffraction (SAD) pattern, respectively. The BK image shows that spinel grains are equiaxed in nature. Grain sizes are about 20–30 nm, which is in good agreement with the XRD result (*e.g.* 24.8 nm). The SAD shows polycrystallinity.

#### 5 Conclusions

The homogeneous stoichiometric MgAl<sub>2</sub>O<sub>4</sub> precursors were prepared by using oxalic acid as a chelating agent. Through the theoretical consideration of thermodynamic equilibrium of the corresponding metals in an aqueous solution and establishment of



**Fig. 4.** Bright field (BK) TEM micrography of the as-synthesized powder and the corresponding selected area diffraction (SAD) pattern.

the stability diagrams in the Mg-Oxalate- $H_2O$  systems, the optimum  $2 < \text{pH} < 8$  for the formation of metal oxalate complexes could be obtained. Nanometer-sized  $\text{MgAl}_2\text{O}_4$  ( $\approx 25$  nm) could be obtained through the thermal decomposition of oxalate precursor at  $1000^\circ$ .

## References

- [1] R.W. Tustison, Window and Dome Technologies and Materials VI, proceedings of spie. Orlando, Florida: the international society for optical engineering. (1999) 94–104.
- [2] M. Barj, J.F. Bocquet, Submicronic MgAlA powder synthesis in supercritical ethanol, *Journal of materials science* **27** (1992) 2187–2192.
- [3] S. Bhaduri, S.B. Bhaduri, Auto ignition synthesis of nanocrystalline  $\text{MgAl}_2\text{O}_4$  and related nanocomposites, *Journal of Material Research* **14** (9) (1999) 3571–3580.
- [4] A. Laobuthee, S. Wongkasemjit,  $\text{MgAl}_2\text{O}_4$  spinel powders from oxide one pot synthesis (oops) process for ceramic humidity sensors, *Journal of the European Ceramic Society* **20** (2000) 91–97.
- [5] V. Montouillout, D. Massiot, Characterization of  $\text{MgAl}_2\text{O}_4$  precursor powders prepared by Aqueous Route, *Journal of the American Ceramic Society* **82** [12] (1999) 3299–3304.
- [6] J. Parmentir, M. Richard-Plouet, Influence of the Sol-gel synthesis on the formation of spinel  $\text{MgAl}_2\text{O}_4$  *Materials Research Bulletin* **33** [11] (1998) 1717–1724.
- [7] M. Zawadzki, J. Wrzyszc, Hydrothermal synthesis of nanoporous zinc aluminate with high surface area, *Materials Research Bulletin* **35** (2000) 109–114.
- [8] E. Hogfeldt, Graphic presentation of equilibrium data, Chapter 15 in *Treatise on analytical chemistry*, part 1, vol. 2  $2^{nd}$  Ed. John Wiley & sons. Inc., 1983.
- [9] Central south institute of mining and metallurgy, department of analytical chemistry, *Handbook of analytical chemistry*, science publishing house, China, 1997.