SYNTHESIS OF DIOPSIDE BY SOLUTION COMBUSTION PROCESS USING GLYCINE FUEL

BABURAO N. SHERIKAR* A. M. UMARJI

Materials Research Centre, Indian Institute of Science, Bangalore, India 560 012.
*shantbabu@gmail.com

Nano ceramic Diopside ($\text{CaMgSi}_2\text{O}_6$) powders are synthesized by Solution Combustion Process (SCS) using Calcium nitrate, Magnesium nitrate as oxidizer and glycine as fuel, fumed silica as silica source. Ammonium nitrate (AN) is used as extra oxidizer. Effect of AN on Diopside phase formation is investigated. The adiabatic flame temperatures are calculated theoretically for varying amount of AN according to thermodynamic concept and correlated with the observed flame temperatures. A “Multi channel thermocouple setup connected to computer interfaced Keithley multi voltmeter 2700” is used to monitor the thermal events during the process. An interpretation based on maximum combustion temperature and the amount of gases produced during reaction for various AN compositions has been proposed for the nature of combustion and its correlation with the characteristics of as synthesized powder. These powders are characterized by XRD, SEM showing that the powders are composed of polycrystalline oxides with crystallite size of 58 nm to 74 nm.

Keywords: Diopside; Adiabatic flame temperature; combustion; ammonium nitrate; Glycine.

1. Introduction

Diopside (DP) is the magnesium rich end member of the solid solution series of the pyroxene group with chemical formula $\text{CaMgSi}_2\text{O}_6$. DP has attracted the attention of materials scientists due to its technological applications in the field of phosphors, biomaterials, coatings, nuclear waste immobilization, sealing materials in solid oxide fuel cells etc. DP shows high biocompatibility, bioactivity and fracture toughness which are very useful in biomaterial field¹ and high luminescent efficiency², high thermal stability, chemical stability, better sinterability, and other unusual properties. Various methods are employed to produce nano crystalline DP powders like solid state³, sol gel method⁴, precipitation⁵ etc, which are time and energy consuming, and have limitation when applied to bulk synthesis. Solution combustion synthesis (SCS) provides simple, low cost attractive rapid production process, with energy and time savings and can be used to produce homogeneous, high purity, uniformly doped, nano crystalline ceramic powders⁶. The powders characteristics such as crystallite size, surface area, are primarily governed by enthalpy or flame temperature of combustion, which depends on characteristics of the fuel and fuel to oxidizer ratio. So far no body reported the synthesis of DP by SCS. This

paper reports the preparation of nano crystalline DP by SCS process using glycine fuel and ammonium nitrate as an extra oxidizer.

2. Experimental

2.1. Solution combustion synthesis

Analytical grade 2.36 gm of Calcium nitrate nonahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), 2.56gm of Magnesium nitrate hexa hydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) oxidizers, 1.2 gm of fumed silica and 1.66, 2.5, 3.33gm glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) fuel, 0, 4, 8, gm of ammonium nitrate (NH_4NO_3) as extra oxidizer were used respectively for 0, 5, 10molAN Diopside compositions for SCS. These reactants are mixed in 15ml of deionized water to obtain transparent aqueous solutions. These solutions, then kept in a furnace pre heated to 500°C . In the beginning thermal dehydration (at 100°C) takes place forming viscous solution, at 200°C the viscous liquids swelled and auto ignited, with the rapid evolution of a large volume of gases to produce voluminous powders. All process took only seven minutes Powders are then calcined at 800°C for 2hrs to study their crystallinity and phase formation. Under the equilibrium conditions the standard reaction equation in this systems can be represented for all Ca, Mg nitrates – glycine combustion with Ψ moles of ammonium nitrate and fumed silica at stoichiometric ratio ($\Phi=1$). Where Φ = fuel to oxidizer equivalence ratio. All combustion calculations are done as per our earlier paper⁷. DP powders are prepared for three compositions of $\Psi=0, 5, 10$.

In reality above **complete combustion** equations does not occur. Residual carbon is obtained with desired product due to incomplete combustion at combustion temperatures of 475°C - 500°C .

2.2. Phase analysis, morphology and Time –Temp study of nitrate glycine system

X-ray diffraction was carried on the SCS powders for phase identification and the crystallite size estimation [by (-221) peak scanned at a rate of $1^\circ/\text{min}$], using Cu-K α radiation on a Brukers D8 diffractometer, Silicon was used as an external standard for instrumental broadening correction. Microstructure studies on the powders were carried out by using QUANTA 200 ESEM Scanning electron microscope.

The temperature-time history of reaction was recorded per half second by a computer interfaced multichannel thermocouple (k type $140\mu\text{m}$) set up connected to Keithley multi voltmeter 2700model data acquisition system using Keithley XLINX Startup software. The vertical cylindrical furnace made of alumina tube of dia 6cm and height 12cm is used. The 50ml beaker of dia 4cm and height 5cm is used for combustion synthesis.

2.3. Thermodynamic modeling

SCS is fast process and completes in few minutes hence the process can be assumed as adiabatic. So temperature generated due to the exothermic reaction is adiabatic temperature. Using the thermodynamic data for the various reactants and products listed in Table 1, the enthalpy of combustion and the theoretical adiabatic flame temperatures as a function of ammonium nitrate (Stoichiometric) were approximately calculated by the following equations using Mathematica software for comparing exothermicity of combustion.

$$\Delta H^{\circ} = \left(\sum n \Delta H^{\circ} \right)_{\text{products}} - \left(\sum n \Delta H^{\circ} \right)_{\text{reactants}} \quad (2) \quad \Delta H^{\circ} = \int_{298}^{T_f} \left(n C_p \right)_{\text{products}} dT \quad (3)$$

Here ΔH° is the enthalpy of combustion reaction, C_p is the heat capacity of products at constant pressure and T_f is the adiabatic flame temperature in Kelvin scale (K).

Table 1. Relevant thermodynamics data⁸⁻¹¹

Compound	Hf (kcal/ mol)	Cp cal/(mol K)a
Ca (NO ₃) ₂ ·4H ₂ O (c)	-509.64	
Mg (NO ₃) ₂ ·6H ₂ O (c)	-624.59	
NH ₄ NO ₃	-87.37	
NH ₂ CH ₂ COOH (c)	-126.22	
CaMgSi ₂ O ₆ (c)	-764.447	52.3+ 0.00774T
CO ₂ (g)	-94.051	10.34 + 0.0027T
N ₂ (g)	0	6.5 + 0.0010T
H ₂ O (g)	-57.796	8.22+0.00015T
O ₂ (g)	0	8.27+0.000258T

Table 2. Characteristics of combustion and powder

Compound DP	0 mol AN	5 mol AN	10 mol
ΔH° kcal/K/mol	-231.75	-603.413	-972.946
Tad(Adiabatic Temp) in °C	1053	1587	1934
Flame Temp by Multi channel Thermocouple in °C	434	718	1096
Normal thermocouple in °C	480,463	637,668	880,902,
Moles of gases evolved	23.11	43.66	64.22
Crystallite size	58nm	59nm	74nm
XRD Peak Intensity	801	822	942

(c) Crystalline; (g) gas; T: absolute temperature ^aCalculated from the discrete value.

3. Results and discussion

3.1. Enthalpies of combustion and adiabatic flame temperature

The theoretical enthalpy of combustion and the adiabatic flame temperature as function of ammonium nitrate are shown in Table. 2. As it can be seen that both the parameters theoretical enthalpy of combustion reaction and adiabatic flame temperatures are directly proportional to the amount of ammonium nitrate and they vary linearly in ascending manner The variation of above both factors with ammonium nitrate can be expressed in linear equation as $\Delta H^{\circ} = -231.75 - 73.906 \Psi$ for enthalpy of reaction and $T_{ad} = 69.4 \Psi + 1326K$ for adiabatic flame temperature .The no moles of gases evolved in each combustion also show same trend of linear variation with moles of ammonium nitrate with general expression $4.112\Psi + 23.11$, where Ψ is no of moles of

ammonium nitrate. The reaction between glycine and calcium, magnesium nitrate at stoichiometric ratio for $\Psi = 10$ mol of ammonium nitrate has highest exothermicity and adiabatic flame temperature of 1934°C . Adiabatic temperatures for $\Psi = 0, 5$ are $1053, 1587^{\circ}\text{C}$, respectively. But measured flame temperatures are very less nearly 50% when compared with calculated temperature which may be due to heat loss, heat capacity & thickness of thermocouple. DP for $\Psi = 10$ shows high flame temp of 1096°C due to the decomposition high concentration of AN. But combustion reaction at $\Psi = 0, 5$ show little exothermicity with flame temp $434, 718^{\circ}\text{C}$ respectively due to low amount of AN generated less heat. The flame temperatures measured with normal thermocouple are even less than the temperatures measured by Multi channel thermocouple (MCT) set up because the diameter of normal thermocouple is bigger than MCT. Due to decrease in thickness, response of thermocouple increases more hence MCT with small diameter thickness show better performance than normal thermocouple. In spite of high reaction enthalpy and combustion flame observed for all cases the crystalline phase has not formed. This may be due to the strong coordination compound formation in between the fuel glycine and nitrate which prevented the release of the cations like calcium and magnesium to form compound. Table 2 also reveals that the enthalpy and the adiabatic flame temperature increase substantially with the amount of AN used during combustion.

3.2. Phase formation and morphology

Fig. 1a shows XRD pattern of the as-synthesized DP powder. Fig1b shows XRD pattern of DP powders calcined at 800°C for 2hrs for all three compositions of different amount of AN. The formation of pure crystalline DP phase is confirmed by comparing the peaks with standard peaks of JCPDS card number 86-0932 for the powders calcined at 800°C for all 0, 5, 10mol of AN compositions with slight variation in their crystallite size and lattice parameters. It can be seen from Fig.1a that in spite of using Ammonium nitrate as extra oxidizer the as prepared Diopside powders show amorphous nature with some

Fig.1. XRD patterns of DP powders synthesized by SCS with varying AN a) as prepared b) at 800°C

peaks of calcium carbonate for 0mol AN composition but it shifts to peak of Diopside at 10mol AN. Even though clear crystallinity is absent. Less crystallinity may be due to formation of strong coordination compound bond between glycine and nitrates. But somehow ammonium nitrate content increased the yield of the powder by increasing the foamy nature as the content increases which can be seen in 10molDP a white big foam formation occurred with surrounding grey colored powder where as for both $\Psi=0,5$ composition only powder is obtained and no foaminess and yield is also less. Color of as prepared powders are yellowish cream, grey, whitish grey for the 0, 5, 10mol AN composition respectively. This grey color is due to incomplete glycine nitrate combustion with unavailability of oxygen for high no of carbon atoms in glycine fuel. The presence of carbon with zero value of enthalpy reduces the total enthalpy of reaction and adiabatic temperature.

Table 1 also shows the variation of intensity of the XRD peak of DP at 800°C and their crystallite size with Ψ . The both intensity and crystallite size increase from $\Psi=0, 5, 10$ attaining highest at $\Psi=10$. It may be due to the low temperature generated due to low enthalpy of the reaction for $\Psi=0, 5$. This might have prevented the local sintering of particles hence resulting in small crystallites. For oxidizer rich DP $\Psi=10$ precalcined powder might have developed high crystallite size due to high enthalpy and high local temperature generated might have helped sintering of particles and further lead to grain coarsening with increasing their size. Even though the enthalpies of reactions are higher in 10mol AN case but the amount of gases produced in the reaction are more than the $\Psi=0, 5$ composition. So these gases absorb the more amount energy and hence reduce the flame temperature and heat supplied to the powder may be very less than that needed to convert into crystalline state and forms weak crystalline form in opposite to anticipated highly crystalline form by the ammonium nitrate. The formation of carbon residue of zero enthalpy reduces the enthalpy of reaction and adiabatic temperature so form amorphous with little crystallinity peak at $\theta=29.9$. Impurity phase calcium carbonate arising for low oxidizer case (formed due to sorption of lot of carbon dioxide produced during combustion by free CaO) merges into main structure of silicate which can be seen in XRD pattern of Fig. 1a. The formation of crystalline DP at 800°C shows that temperature given was enough to promote crystallization. Associated gas evolution results in highly porous structure as the amount of gas increases agglomerates are more likely to break.

SEM shows the formation of porous morphology with sphere like agglomerates ranging from 4 to 100 μm . Fig. 2a shows microstructure of as prepared DP 10molAN powder with big agglomerates of 2 μm formed by 80-90nm particles. The agglomerates are porous due to high moles of gases released in 10moleDP case. Some particles are sintered to form big hard aggregates of 0.8-1 μm . But in case of calcined powder same powders are sintered to form big hard aggregates of 2 microns without the grain boundaries. Some isolated 100nm sized particles are also seen in calcined DP powder.

Fig.2. SEM graphs of DP powders synthesized by SCS with 10 mol AN a) as prepared b) at 800°C

3.3. Time-temperature study

Typical time–temperature profile of Calcium- Magnesium - Ammonium nitrate- glycine combustion reaction for stoichiometric 10 mol of ammonium nitrate is presented in Fig. 3b. It shows series of alternate peaks of temperature ranging from 300 to 1100 °C. This shows step wise linear layer by layer combustion as opposite to trend shown in case of alumina combustion⁶ where a single peak was observed showing the signature of volume combustion. Initially the temperature rises to 100 °C maintain constant at that temperature until all water evaporates. At a temperature, specific to a system where the heat evolution exceeds the heat lost to the surroundings, is called the ignition point (T_{ig}) with associated sharp rise in temperature. Here in this case the factors important are Ignition temperature (T_{ig}) is 141°C, maximum combustion temperature (T_{cmax}) is 1096°C, flame residing time for all peaks and even for main peak is 2 to 3 seconds.

Fig.3a. Multi Channel Thermocouple Setup b) Time –Temp graph of 10AN Glycine –Nitrate combustion

4. Conclusions

Phase pure crystalline DP powders of 58 to 74 nm size with porous agglomerates are successfully prepared first time by SCS process using glycine fuel by calcining at 800°C. The properties like microstructure, crystallite size, phase purity, etc of DP powders vary with the Ammonium nitrate content. The adiabatic flame temperature cannot explain the formation of amorphous phase. Phase formation and crystallinity may depend on complexing agents and ligands of fuels. Adiabatic flame temperatures were calculated theoretically according to the thermodynamic concept by thermodynamic data and compared with the measured data. It is found that the theoretical adiabatic temperature increases with increasing the value of Ammonium nitrate to a maximum of 1934°C (at $\Psi = 10$) but measured temperature for the same is 1091°C due to more moles of gases formed during combustion take away the heat generated and also due to incomplete combustion. Time temperature study shows that the Ca-Mg nitrate-glycine combustion is linear combustion with stepwise layer by layer combustion.

References

1. C.Wo, J. Chang, J. Biomed. Mater. Res., Part B **83B** (1), 153 (2007).
2. T. Kida, M. M. Rahman, and M. Nagano, *J. Am. Ceram. Soc.*, **89** [5] 1492 (2006).
3. S. Yamamoto, T. Nonami, Hiroko hase, and N. Kawamura *J. Aus Ceram .Soc.* **48**, 180 (2012).
4. N. Y. Iwata, G.H.Lee and N.Kawashima *Colloid Surf.,B* **33**,1 (2004).
5. A.U. Pawar, A.P.Jadhav and Y.S.Kang *J. Lumin* **132**,659 (2012).
6. K C, Patil, M.S Hegde, Tanu Rattan, S.T.Aruna *Chemistry of nanocrystalline oxide materials; combustion synthesis, properties and applications* (Sinapore;World Scientific;2008.)
7. B.N Sherikar. A.M.Umarji, *Tran.Ind.Ceram.Soc* **70**(3), 167(2011).
8. R.H. Perry, C.H. Chilton, *Chemical Engineering Handbook*, 7th edn.(McGraw-Hill, New York, 1997).
9. D. R.Lide, *CRC Handbook of Chemistry and Physics* 72nd edn.(CRC Press, Boston 1991-1992).
10. K. M. Krupka, D. M. Kerrick, *Am. Mineral*, **70**, 261(1985).
11. C. H. Yoder and N. J. Flora, *Am Mineral*, **90**, 488 (2005).