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Combustion Synthesis of Fine Particle Rare Earth Orthoaluminates and Yttrium Aluminum Garnet

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Fine particle rare earth orthoaluminates, $Ln\text{AlO}_3$, where Ln = La, Pr, Nd, Sm, Gd, Tb, and Dy, and yttrium aluminum garnet, $Y_3Al_5O_{12}$ (YAG), have been prepared by a novel combustion process using corresponding rare earth nitrate, aluminum nitrate, and urea/carbohydrazide mixtures. A saturated aqueous solution of the mixture when rapidly heated at 500°C foams and ignites to yield voluminous, crystalline single phase rare earth orthoaluminates in less than 5 min. The solid combustion products were characterized by XRD, SEM, TEM, particle size analysis, and surface area measurements. Rare earth orthoaluminates obtained have 3–4 m^2/g surface area, with particle size in the range of 0.1–0.6 μm and an average agglomerate size of 4–5 μm.

1. Introduction

Rare earth orthoaluminates, $Ln\text{AlO}_3$ (where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, and Dy) and $Y_3Al_5O_{12}$, are of technological importance due to their applications as catalysts (*1*), as laser hosts (*2*), and in MHD Generators (*3*). The conventional synthesis of these oxides is by the ceramic method involving the solid state reactions of the component oxides at elevated temperatures >1300°C (e.g., La_2O_3–Al_2O_3 1450°C, 1 hr) (*4*). The ceramic method usually yields oxides with poor reactivity. Among the other methods used in the preparation of fine particle orthoaluminates are calcination of coprecipitated oxalates (*5*), citrates (*6*), metal salts (*7*), and sol–gel process (*8*, *9*). However, many of these methods are involved, requiring high temperatures and long periods of time.

Recently, a novel combustion process has been developed using metal nitrate (oxidizer)–urea/carbohydrazide (fuel) mixtures for the instant synthesis of α-Al_2O_3 (*10*) and related oxides such as $M\text{Al}_2\text{O}_4$ where M = Ca, Mg, Co, Ni, Zn, $CaAl_{12}O_{19}$, $CeMgAl_{11}O_{19}$ (*11*). Presently we report the preparation and properties of fine particle rare earth orthoaluminates, $LnAlO_3$, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, and Dy, and yttrium aluminum garnet, $Y_3Al_5O_{12}$, by this novel combustion process.

2. Experimental

Rare earth orthoaluminates, $Ln\text{AlO}_3$, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, and Dy, were prepared by the combustion

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TABLE I

COMPOSITION OF THE COMBUSTION MIXTURES AND THE PROPERTIES OF RARE EARTH ORTHOALUMINATES (UREA PROCESS)

No.	Composition of the combustion mixtures	Products	Powder density (g/cm^3)	Surface area (BET) (m^2/g)	Particle size (from surface area) (μm)	50% Average agglomerate size (from sedimentation) (μm)
1.	$La(NO_3)_3 \cdot 6H_2O$ (23.08 g) + A + B	$LaAlO_3$	4.27	3.0	0.46	4.5
2.	$Pr(NO_3)_3 \cdot 6H_2O$ (23.18 g) +A + B	$PrAlO_3$	4.30	3.4	0.41	3.8
3.	$Nd(NO_3)_3 \cdot 6H_2O$ (23.37 g) + A + B	$NdAlO_3$	4.50	3.0	0.44	4.2
4.	$Sm(NO_3)_3 \cdot 6H_2O$ (23.69 g) +A + B	$SmAlO_3$	4.60	3.1	0.42	4.0
5.	$Dy(NO_3)_3 \cdot 5H_2O$ (23.38 g) +A + B	$DyAlO_3$	4.75	3.5	0.36	4.5
6.	$Y(NO_3)_3 \cdot 6H_2O$ (12.25 g) + A + B″	$Y_3Al_5O_{12}$	3.86	7.3	0.21	4.5

Note. A = $Al(NO_3)_3 \cdot 9H_2O$ (20 g); B = urea (16 g); B″ = urea (12.8 g).

of corresponding metal nitrate–aluminum nitrate–urea or carbohydrazide mixtures. Yttrium aluminum garnet, $Y_3Al_5O_{12}$, was prepared by both urea and carbohydrazide processes.

Stoichiometric compositions of the metal nitrates (oxidizers) and urea/carbohydrazide (fuels) are calculated using the total oxidizing and reducing valencies of the components which serve as numerical coefficients for stoichiometric balance so that the elemental stoichiometric coefficient (Φ_e) is unity and the energy released by the combustion is at a maximum (*12*). Mole ratios calculated for maximum energy and complete combustion to obtain the rare earth orthoaluminates are $Ln(NO_3)_3 \cdot 6H_2O$: $Al(NO_3)_3 \cdot 9H_2O$: urea/carbohy-

TABLE II

COMPOSITION OF THE COMBUSTION MIXTURES AND THE PROPERTIES OF RARE EARTH ORTHOALUMINATES (CARBOHYDRAZIDE PROCESS)

No.	Composition of the combustion mixtures	Products	Powder density (g/cm^3)	Surface area (BET) (m^2/g)	Particle size (from surface area) (μm)	50% Average agglomerate size (from sedimentation) (μm)
1.	$La(NO_3)_3 \cdot 6H_2O$ (11.54 g) + A + B	$LaAlO_3$	4.89	3.5	0.35	1.22
2.	$Pr(NO_3)_3 \cdot 6H_2O$ (11.59 g) +A + B	$PrAlO_3$	4.91	3.4	0.36	1.50
3.	$Nd(NO_3)_3 \cdot 6H_2O$ (11.68 g) + A + B	$NdAlO_3$	4.93	3.2	0.38	2.00
4.	$Sm(NO_3)_3 \cdot 6H_2O$ (11.84 g) +A + B	$SmAlO_3$	4.92	3.1	0.39	1.70
5.	$Eu(NO_3)_3 \cdot 6H_2O$ (11.89 g) + A + B	$EuAlO_3$	5.01	3.0	0.39	1.25
6.	$Gd(NO_3)_3 \cdot 6H_2O$ (12.03 g) + A + B	$GdAlO_3$	5.19	3.3	0.35	1.40
7.	$Tb(NO_3)_3 \cdot 6H_2O$ (12.07 g) + A + B	$TbAlO_3$	5.25	3.6	0.31	1.37
8.	$Dy(NO_3)_3 \cdot 5H_2O$ (11.69 g) +A + B	$DyAlO_3$	4.82	4.0	0.31	0.80
9.	$Y(NO_3)_3 \cdot 6H_2O$ (6.126 g) + A + B″	$Y_3Al_5O_{12}$	3.81	3.3	0.47	2.20

Note. A = $Al(NO_3)_3 \cdot 9H_2O$ (10 g); B = carbohydrazide (7.2 g); B″ = carbohydrazide (5.76 g).

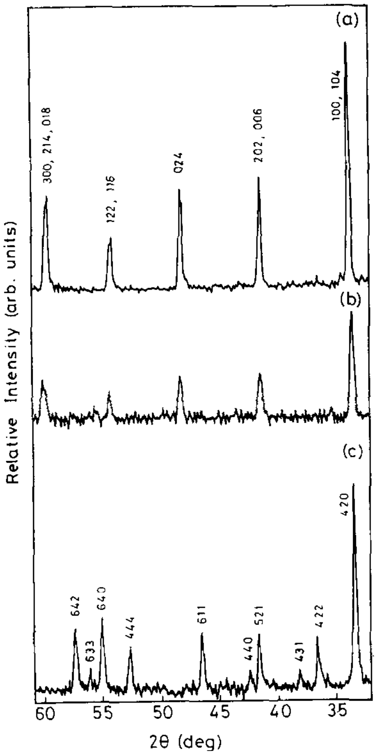

FIG. 1. X-ray powder diffraction patterns of (a) $LaAlO_3$ (urea process), (b) $DyAlO_3$ (carbohydrazide process), and (c) $Y_3Al_5O_{12}$ (urea process).

drazide = 1 : 1 : 5 or 1 : 1 : 3.75. The actual compositions used for the combustion synthesis of rare earth orthoaluminates by urea process and carbohydrazide process are given in Tables I and II, respectively. In the case of the carbohydrazide process the compositions used were in the ratio 1 : 1 : 3.0 instead of 1 : 1 : 3.75 as the reaction was too violent in the latter case. However, this does not affect the stoichiometry and homogeneity of the products as evidenced by the powder XRD patterns and surface area measurements which are comparable with those of urea process.

The preparation of $LaAlO_3$ by both urea and carbohydrazide processes and $Y_3Al_5O_{12}$ by the carbohydrazide process are described below.

2.1. Combustion Synthesis of $LaAlO_3$ by the Urea Process

$Al(NO_3)_3 \cdot 9H_2O$ (20 g) and $La(NO_3)_3 \cdot 6H_2O$ (23.086 g) are dissolved in minimum quantity of water along with urea (16 g) in a cylindrical pyrex dish (100 mm diameter × 50 mm height) of approximately 300-ml capacity. The dish containing the solution is introduced into a muffle furnace (l = 28 cm, b = 17 cm, and h = 9 cm) maintained at 500 ± 10°C. The mixture boils, froths, foams, and ignites to burn with a flame temperature 1300°C to yield voluminous and foamy $LaAlO_3$ which occupies the entire volume of the dish (weight 11.4 g, 100% yield).

2.2 Combustion Synthesis of $LaAlO_3$ by the Carbohydrazide Process

$Al(NO_3)_3 \cdot 9H_2O$ (10 g) and $La(NO_3)_3$ $6H_2O$ (11.54 g) are dissolved in a minimum quantity of water along with carbohydrazide (7.20 g) in a cylindrical pyrex dish (100 mm diameter × 50 mm height) of approximately 300-ml capacity. The dish containing the solution is introduced into a muffle furnace (l= 28 cm, b = 17 cm, and h = 9 cm) maintained at 500 ± 10°C. The mixture un-

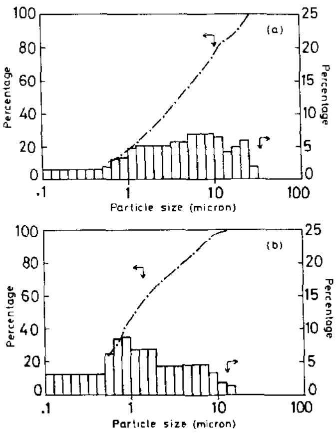

FIG. 2. Particle size distribution of $LaAlO_3$ obtained from (a) urea process and (b) carbohydrazide process.

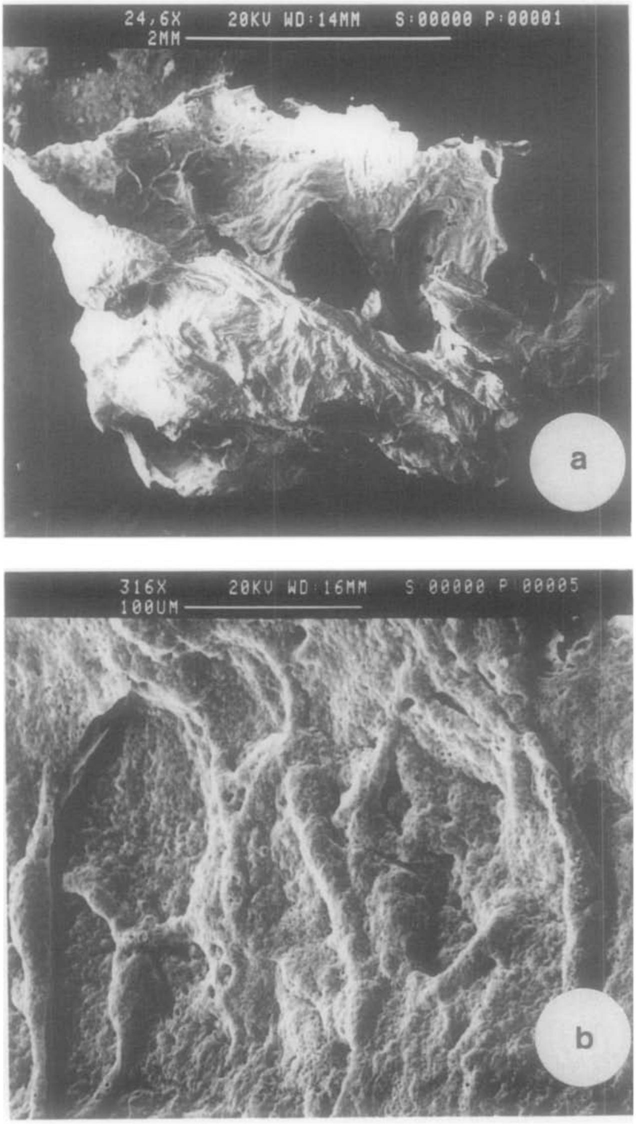

FIG. 3. SEM micrographs showing the foamy macrostructure and the surface of (a and b) $LaAlO_3$ foam (urea process) and (c and d) $LaAlO_3$ (carbohydrazide process).

dergoes boiling with dehydration followed by frothing and ignites with an incandescent glow resulting in complete combustion. The product of combustion is again voluminous and foamy $LaAlO_3$ (weight 5.7 g, 100% yield) occupying the entire volume of the container.

2.3. Combustion Synthesis of Yttrium Aluminum Garnet by Carbohydrazide Process

$Al(NO_3)_3 \cdot 9H_2O$ (10 g) and $Y(NO_3)_3$ $6H_2O$ (6.126 g) are dissolved in a minimum quantity of water along with carbohydrazide

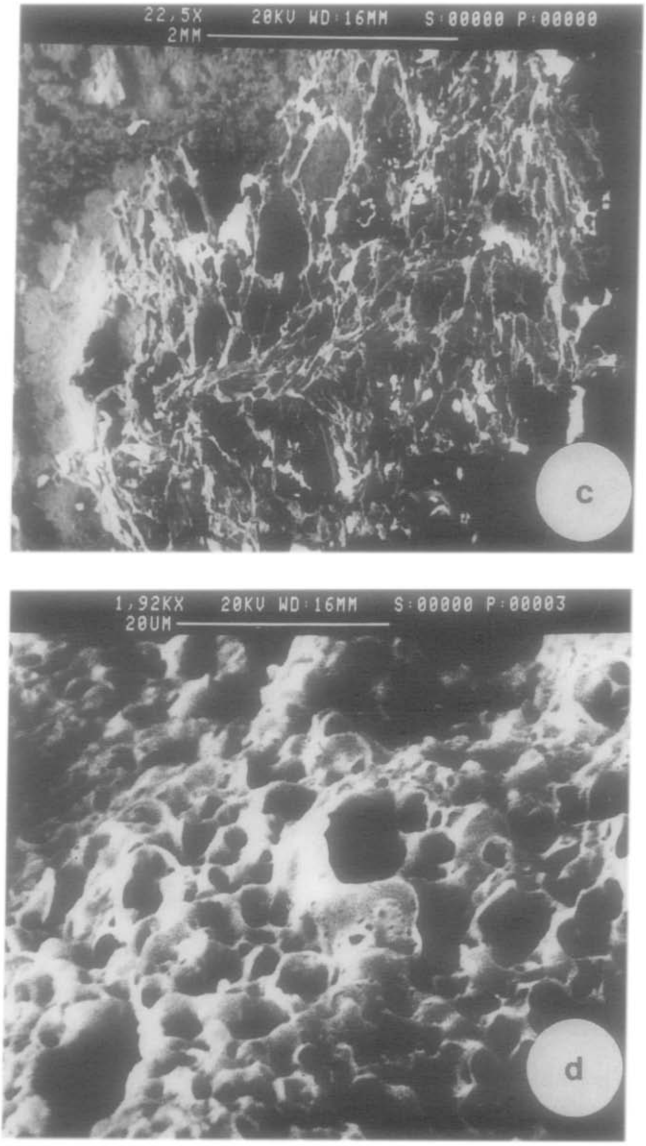

FIG. 3.—*Continued*

(5.76 g) in a cylindrical pyrex dish (100 mm diameter × 50 mm height) of approximately 300-ml capacity and heated rapidly at 500°C in a muffle furnace. The resulting foamy $Y_3Al_5O_{12}$ is voluminous and fibrous.

Yttrium aluminum garnet, $Y_3Al_5O_{12}$, was also obtained by the combustion of a $Y(NO_3)_3 \cdot 6H_2O$ (12.252 g), $Al(NO_3)_3 \cdot 9H_2O$ (20 g), and urea (12.8 g) mixture.

2.4. Physical Methods

The solid combustion products, LnAlO$_3$ and $Y_3Al_5O_{12}$, were identified by X-ray powder diffraction patterns and their fine particle nature was studied using SEM, TEM, particle size analysis, and surface area measurement.

The X-ray powder diffraction patterns

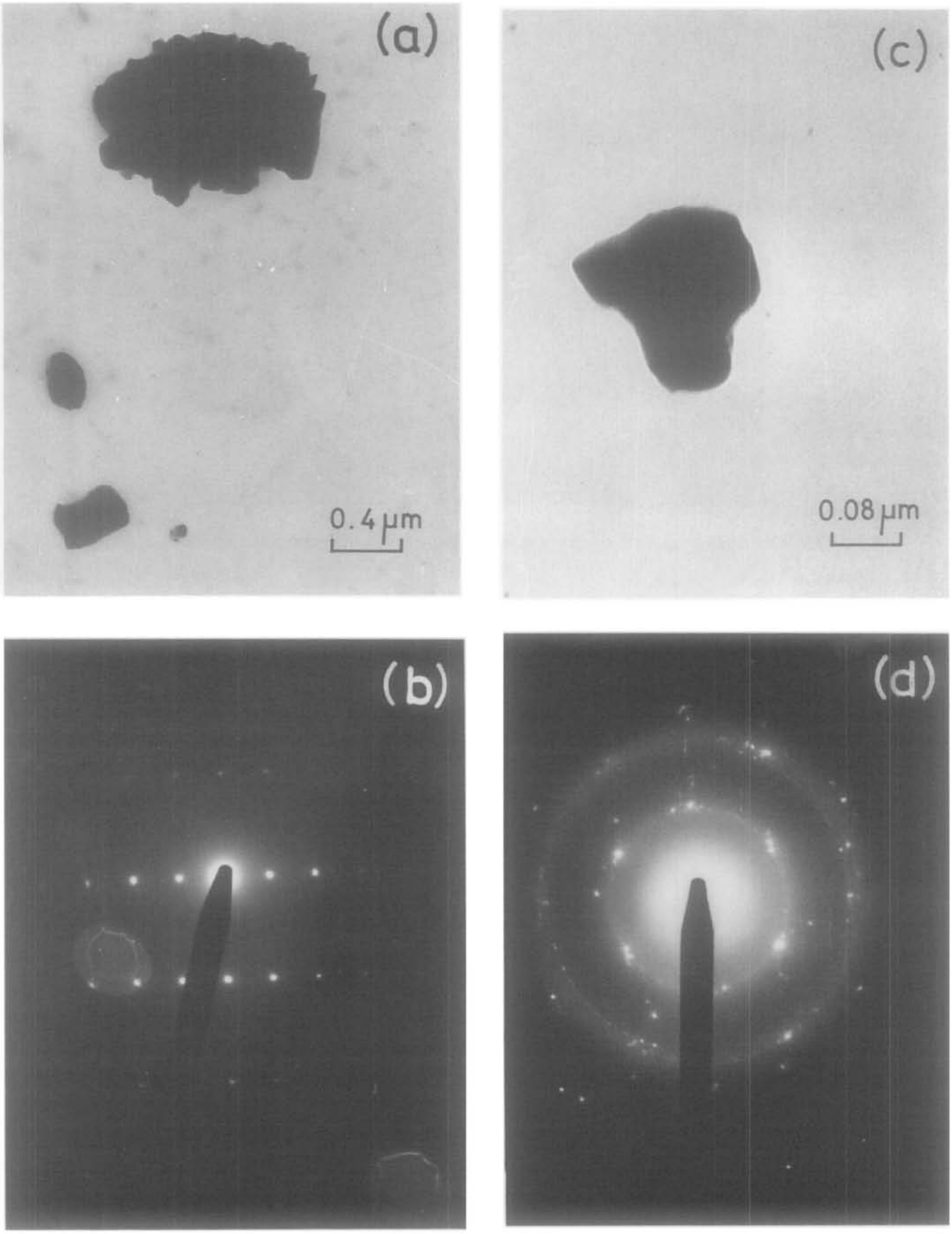

FIG. 4. TEM micrographs showing the particles and the electron diffraction patterns of (a and b) $LaAlO_3$ (urea process) and (c and d) $DyAlO_3$ (carbohydrazide process).

were recorded using a Phillips Model PW 1050/70 X-ray diffractometer using Cu$K\alpha$ radiation with a Ni Filter. SEM micrographs were taken using a Cambridge Stereoscan Model S-150 scanning electron microscope. TEM studies were done using a Philips EM 301 transmission electron microscope operated at 100 kV. Particle size measurements were done using a Model SKC 2000 Micron Photo Sizer employing the sedimentation principle. The surface areas of all the oxides were measured by nitrogen adsorption employing a Micro Meritics AccuSorb 2100E instrument.

3. Results and Discussion

Redox mixtures containing stoichiometric amounts of rare earth metal nitrates and aluminum nitrate (oxidizer)–urea/carbohydrazide (fuel) when rapidly heated with a heating rate >100°C/min spontaneously ignite and burn to yield corresponding rare earth orthoaluminates and YAG. The combustion appears to be controlled due to formation of aluminum hydroxide gel which is a well-known fire retardant (*13*, *14*). This phenomenon is used in the preparation of fine particle α-alumina (*10*) and transition metal aluminates (*11*). Unlike transition metal aluminates, $M\mathrm{Al_2O_4}$, where M = Mn, Co, Ni, and Cu, which could only be prepared by the carbohydrazide process (*11*), rare earth orthoaluminates have been obtained by the use of both urea and carbohydrazide fuels. Rare earth orthoaluminates prepared using the carbohydrazide process are finer than those prepared with the urea process. The carbohydrazide process has the advantage of no restriction of critical mass/volume ratio of the mixture to the volume of the container for initiation of combustion (*10*). This may be due to their difference in combustion behavior. That is, the urea process affords combustion through gas phase reactions whereas the carbohydrazide process is deflagrating in its exothermic decomposition of carbohydrazide.

3.1. Rare Earth Orthoaluminates and YAG

The formation of single phase products was confirmed by the characteristic X-ray diffraction patterns of $Ln\mathrm{AlO_3}$ and $Y_3Al_5O_{12}$. Typical X-ray powder diffraction patterns of $LaAlO_3$ (urea process), $DyAlO_3$, and $Y_3Al_5O_{12}$ (carbohydrazide process) are given in Fig. 1. The lattice constants calculated from the XRD patterns are in good agreement with the literature (*15*), e.g., $LaAlO_3$; $a = b = 5.362 \pm 0.014$ Å; $c = 2.428 \pm 0.008$ Å, YAG; $a = b = c = 11.98 + 0.017$ Å.

The properties of rare earth orthoaluminates prepared by both urea and carbohydrazide processes are summarized in Tables 1 and 2, respectively. The as-prepared $LaAlO_3$ (carbohydrazide process) has foam and tap density values of 0.02 and 0.1 g/cm^3 respectively as opposed to 0.05 and 0.02 g/cm^3 for the urea process. The powder density of the as-prepared $Ln\mathrm{AlO_3}$ and YAG by both urea and carbohydrazide processes are in the range 70–80% of the theoretical density. Particle size distribution of $LaAlO_3$ obtained by both processes are shown in Figs. 2a and 2b for comparison. It can be seen that the average agglomerate size of rare earth orthoaluminates obtained by the carbohydrazide process are smaller and are in the range 0.8–2.0 μm compared to those obtained from the urea process (4–5 μm). The BET surface area of the orthoaluminates obtained by both the processes are in the range 3–5 m^2/g. Scanning electron micrographs of a portion of $LaAlO_3$ foam obtained by both urea and carbohydrazide processes are shown in Figs. 3a and 3b and 3c and 3d, respectively. The surface of $LaAlO_3$ obtained by the carbohydrazide process has a more open structure than does the one obtained from the urea process.

The TEM micrographs of particles of $LaAlO_3$ (urea process) and $DyAlO_3$ (carbohydrazide process) are given in Figs. 4a and 4c. These combustion-synthesized products have platelet particles of sizes 0.8 and 0.2 μm, respectively. The electron diffraction patterns of $LaAlO_3$ and $DyAlO_3$ shown in Figs. 4b and 4d respectively indicate the crystalline nature of the products.

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