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Synthesis of Lanthanum Aluminate by Thermal Decomposition of Hydrated Nitrates

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Abstract: Ultrafine lanthanum aluminate has been prepared by the thermal decomposition process. Corresponding metal nitrates were comelted and quenched at room temperature. The resulting mass was dehydrated and calcined at different temperatures. X-ray diffraction, scanning electron microscope, thermogravimetric and differential thermal analysis, and particle size measurements were carried out. The powders, when pelletized and sintered at 1500 °C for 15 h, achieved 92% theoretical density. Dielectric constant and loss factor of this material, studied in the frequency range 30 Hz to 13 MHz, were found to be 22 and 8×10^{-4} at 10 kHz, respectively. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Lanthanum aluminate belongs to the perovskite type oxide materials and has attracted much attention for various applications in high frequency capacitors,[1] as gas sensors,[2] and is considered as an electrically insulating buffer layer in the form of thin films on substrate for the deposit of ferroelectric materials.[3,4]

Single crystal lanthanum aluminate ($LaAlO_3$) is a promising substrate material for deposition of thin films of the high temperature superconductors because of its good lattice match and dielectric properties.[5,6] For practical applications, high T_c superconducting thin films on silicon or sapphire substrates with a $LaAlO_3$ buffer layer would be more desirable than thin films on single crystal substrate.[7]

The direct formation of $LaAlO_3$ from aluminium oxide (Al_2O_3) and lanthanum oxide (La_2O_3) occurs typically in the range of 1500–1700 °C, with melting occurring at about 1830 °C.[8] This conventional ceramic method by the direct combination of corresponding oxides by calcining at high temperatures and ball-milling are not adequate for many advanced applications and suffers from many inherent shortcomings. Problems have arisen with poor sintering behaviour and nonhomogeneity, which have a detrimental effect on the electrical and mechanical properties. Several wet-chemical methods[9–11] have been used to obtain better homogeneity and control of stoichiometry by several other researchers. Among these, coprecipitation and sol gel are the most widely investigated for ceramic powder preparations. The powder obtained from the coprecipitation technique is highly agglomerated in nature and further ball-milling is necessary to obtain fine powders with small particle size.

The success of sol–gel process in the synthesis of ceramic powders is due, in particular, to the possibility of working at low temperature and attaining good homogeneity in the solution phase. Nevertheless, for complex compositions the sol–gel process is delicate to use because, in certain cases, it requires very specific control of pH concentration or sequence of addition. The all-alkoxide sol–gel route requires either synthesizing bi- or tri-metallic alkoxides, a process that may be complicated and costly, or using alkoxide mixtures with inherent difficulties caused by the marked differences in reactivity of those

compounds. Since for commercial large scale production the synthesizing method has to be relatively simple and cheap, a cost-effective technique using readily available starting materials has to be developed. The main purposes of the present work were to synthesise fine particle $LaAlO_3$ powder by the thermal decomposition of hydrated metal nitrates and to study the dielectric and the sintering behaviour of these powders.

2 EXPERIMENTAL

2.1 Powder preparation

Figure 1 shows the flow diagram of the experimental processing route for $LaAlO_3$ powder. The starting materials $Al(NO_3)_3.9H_2O$ and $La(NO_3)_3.6H_2O$ were all analytical reagent grade supplied by BDH, Bombay, India. Stoichiometric amounts of aluminium nitrate and lanthanum nitrate were allowed to dissolve in its crystallization water by gradually heating it up to 120 °C, until a clear solution is obtained. This solution was quenched at room temperature to avoid phase separation. The resulting solid mass was broken into coarse lumps and dehydrated for 24 h at a temperature of 80–90 °C and was transferred into a pyrex beaker and heated at a temperature of 400 °C. The coarse mass decomposes to form the corresponding mixed oxides. The products were hand ground and calcined for 4 h at different temperatures (600, 650, 800, 900 and 1000 °C).

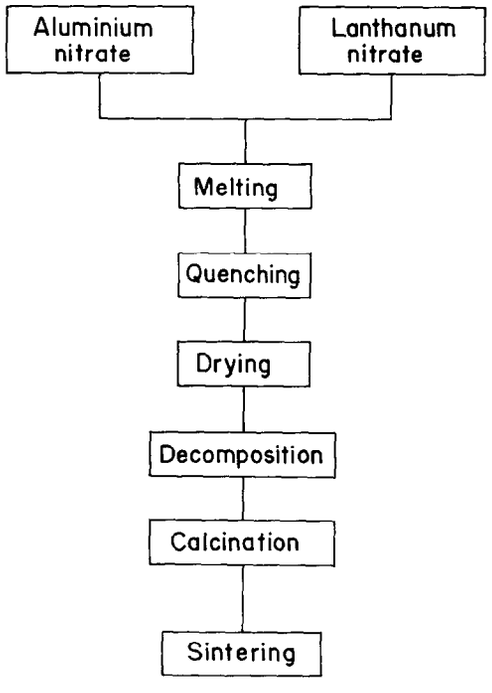

Fig. 1. Flow diagram showing the processing route for $LaAlO_3$ powder.

2.2 Characterization methods

Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out, using a Seiko TGA/DTA model 242 thermal analyser, for the quenched product before decomposition from room temperature to 1000 °C at a heating rate of 10 °C min^{-1}, in nitrogen atmosphere. X-ray diffraction (XRD) patterns were recorded using a Rigaku X-ray diffractometer with Ni filtered CuK_α radiation (1.5418 Å) to determine the phases present in the calcined powders and to estimate crystallite size. The crystallite size was estimated from the X-ray line broadening of the (110) diffraction peak using the Scherrer formula:[12]

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where D is the crystallite size in nm, λ is the radiation wavelength, θ is the diffraction peak angle and ισ τηε ψωρρεψτεδ λινε χιδτη ατ ηαλφπεακ ιντενσιτθ• ηε ψωρρεψτιων φωρ ινστρυμενταλ πεακ βρωαδενινγ χασ μαδε υσινγ τηε θαρρεν φωρμυλα≡ $\beta = (b^2_{obs} - b^2)^{1/2}$ ∴ χηερε b_{obs} is the line width at half-peak intensity related to $LaAlO_3$ and b is the line width of the diffraction peak (004) of the metallic silicon which is used as the standard.

The surface morphology of the synthesized powder was studied using a Hitachi S2400 model scanning electron microscope (SEM). The specific surface area of the powder was measured by the conventional BET technique with nitrogen adsorption. The particle size measurements were done using a Malvern Master sizer particle size analyser employing the laser diffraction technique. For sintering studies, the powders were uniaxially cold pressed at a compaction pressure of 200 MPa using 3% polyvinyl alcohol (PVA) solution as a binder. These pellets were sintered at various

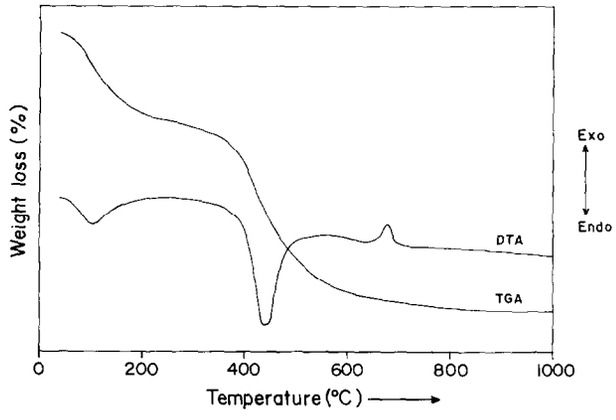

Fig. 2. TGA–DTA curve for the quenched solid mass.

temperatures for sintering studies. The green densities of the compacts were calculated from the dimensions of the samples and their weight and the sintered density was determined by Archimedes principle.

The sintered pellets were well polished and both the faces were coated with conducting silver paste. Dielectric constant and loss factor of $LaAlO_3$ were measured, using a HP 4192A complex impedance analyser, in the frequency range from 30 Hz to 13 MHz at room temperature.

3 RESULTS AND DISCUSSION

3.1 Thermal analysis

Figure 2 shows the TGA and DTA curves for the solid mass before decomposition from room temperature to 1000 °C. It has been observed that there are two major weight losses. The first weight loss in the TGA correlating with the small endothermic peak in the DTA is because of the dehydration of water. The second major weight loss at about 400 °C, which corresponds to the large endothermic DTA peak, is caused by the nitrate decomposition. The DTA analysis also revealed a small exothermic peak at 650 °C, which was exactly the temperature of crystalline $LaAlO_3$ formation as indicated by X-ray analysis. The TGA analysis did not show any weight change in this temperature range.

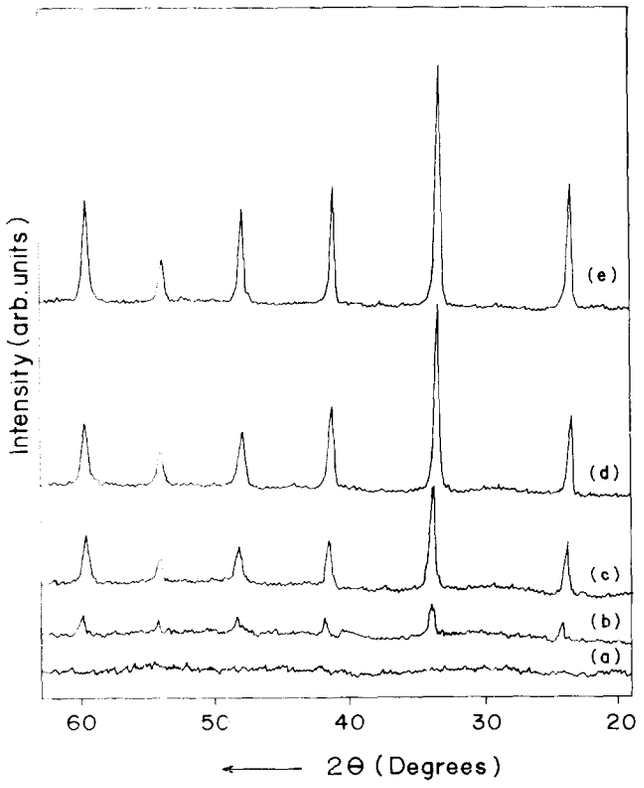

Fig. 3. XRD patterns of the $LaAlO_3$ powder calcined at various temperatures for 4 h (a) 600; (b) 650; (c) 800; (d) 900; and (e) 1000 °C.

3.2 X-ray diffraction analysis

The XRD patterns of the reaction product presented in Fig. 3 show how progressively the $LaAlO_3$ phase was formed with an increase in calcination temperature from 600 °C to 1000 °C. The as-prepared powder was X-ray amorphous. At 650 °C the powder became feebly crystalline and further heating increased the intensity of the X-ray peaks without any phase change. Powders calcined at 1000 °C showed the fully crystalline structure of $LaAlO_3$. The lattice constants calculated were in good agreement with those reported in the literature.[13]

3.3 Surface area measurement

Specific surface area (S_{BET}) of the $LaAlO_3$ powders calcined at different temperatures were in the range 8–23 $m^2 g^{-1}$. Table 1 shows the variation of surface area with calcination temperature. It was observed that the surface area decreases as the calcination temperature increases, since the crystallite size increases with temperature.

3.4 Particle size distribution

The crystallite sizes calculated from XRD line broadening are below 150 nm. The mean particle size (D_{BET}) obtained from surface area was calculated based on the equation,

$$D_{BET} = \frac{6}{\rho S_{BET}}$$

where ρ is the theoretical density of the powder (5860 k gm $^{-3}$).[14] Particle sizes calculated from the surface area are in the range of 40–120 nm. Variations of the particle size with calcinating temperature are listed in Table 1. The particle sizes calculated from surface area are comparable with the crystallite sizes calculated from XRD line

Table 1. Variation of surface area and particle size with temperature

Annealing (T, °C)	S_{BET} ($m^2 g^{-1}$)	D_{BET} (nm)
600	23	45
650	16	64
800	13	79
900	10	102
1000	8	128

broadening. The particle size distribution of as-prepared $LaAlO_3$ (Fig. 4) shows that the average agglomerate particle size is less than 3 μm.

3.5 Microstructure and densification

Figure 5 shows the SEM image of the as-prepared powder which reflects the agglomerate nature of the powder and shows irregular morphology. The green density was calculated to be about 30% of the theoretical density. The sintering density of the pellets heated at 1500 °C for 15 h was determined to be 5390 kg m^{-3}, which was about 92% of the theoretical density. The low sintered density may be caused by the agglomerative nature of the powders. Figure 6 shows the variation of sintering density with temperature. It was observed that the sintering density increases due to the breakdown of agglomerates by grinding. The powders ground for 10 h could be sintered to 96% of theoretical density.

3.6 Dielectric studies

Dielectric properties of $LaAlO_3$ were studied in the frequency range 30 Hz to 13 MHz at room temperature. The variations of the dielectric constant (ε') and loss factor (tanδ) with frequency (log f) are shown in Figs 7 and 8. Both the dielectric constant and loss tangent decrease with increasing frequency and were measured to be 22 and 8×10^{-4} at 10 kHz, respectively. These results were comparable with the reported values for the $LaAlO_3$ single crystals.[15] This relatively low dielectric constant and low loss tangent, makes lanthanum aluminate

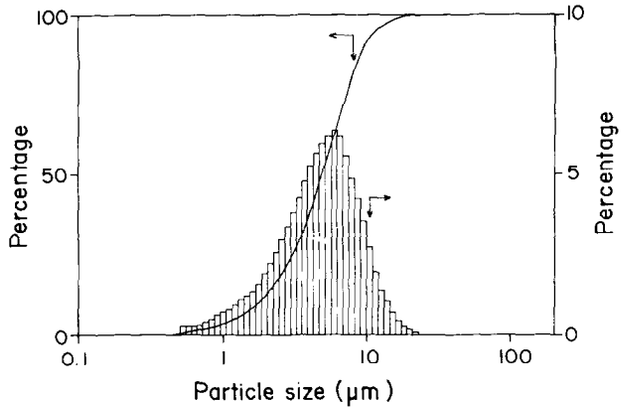

Fig. 4. Particle size distribution of the $LaAlO_3$ powder calcined at 1000 °C for 4 h.

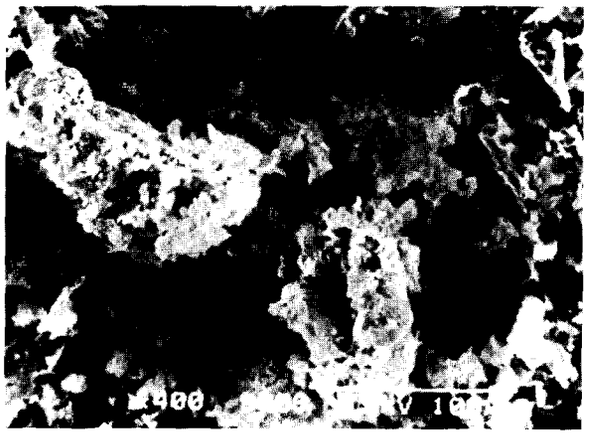

Fig. 5. SEM image of the as-prepared $LaAlO_3$ powder.

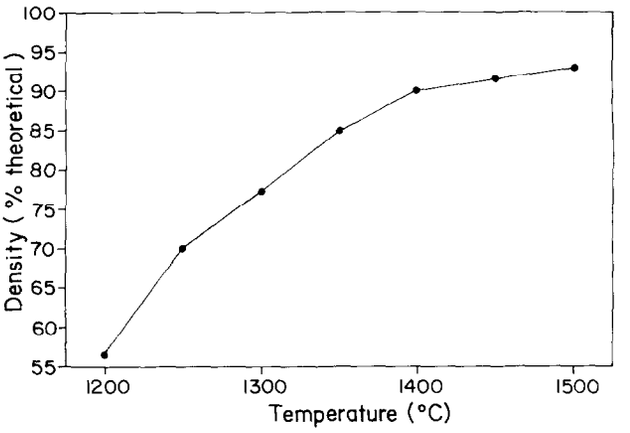

Fig. 6. Variation of the sintered bulk density for $LaAlO_3$ powder with temperature.

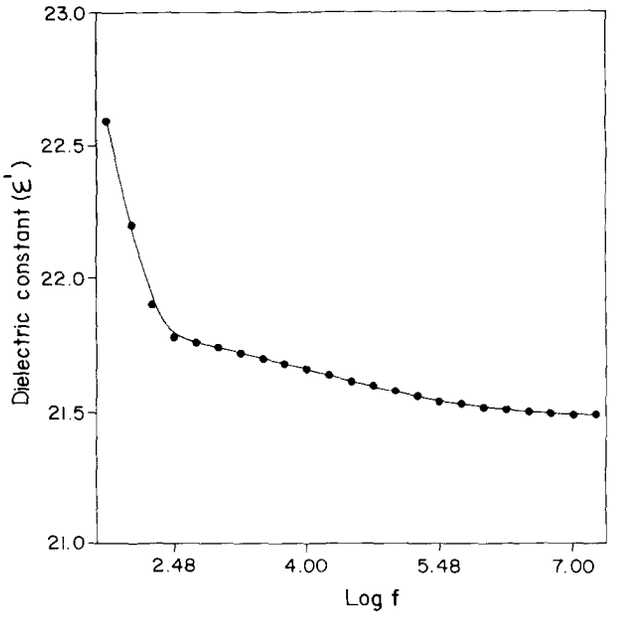

Fig. 7. Variation of dielectric constant (ε') with frequency.

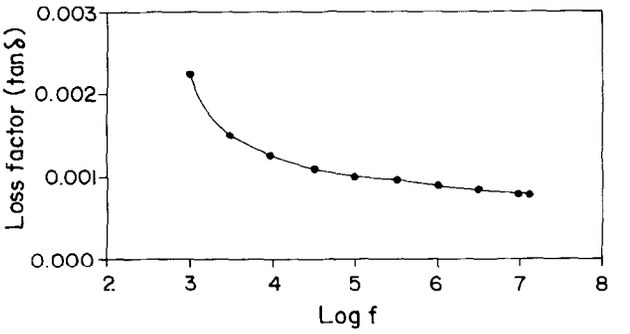

Fig. 8. Variation of loss tangent (tanδ) with frequency.

one of the most desirable substrate materials for thin film high T_c superconductors.

4 CONCLUSION

Lanthanum aluminate has been successfully synthesized by a thermal decomposition of mixed hydrated metal nitrates. This method is simple and is useful for the large scale production of fine particle, homogeneous oxide powders with readily available starting materials.

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