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Photoacoustic study of the effect of hydroxyl ion on thermal diffusivity of γ alumina

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The effect of the chemisorbed hydroxyl groups on the thermal diffusivity of γ alumina is determined by evaluating the thermal diffusivity at various degassing temperatures and by doping it with rare earth oxide using photoacoustic technique. The thermal diffusivity is found to decrease with the increase in degassing temperature as well as with the increase in the doping concentration of rare earth oxide. This decrease has been attributed to the loss of hydroxyl ion from the γ - Al_2O_3 .
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Alumina (Al_2O_3) is an important material in adsorption and catalysis. It is widely used as substrate material in evolving technologies such as microelectronics, magnetic, and optical devices, and protective coatings. Among the several crystallographic modifications,¹ the transition phases η and γ - Al_2O_3 are of special interest since they can provide high specific surface areas ($\cong 200 \text{ m}^2/\text{g}$). These modifications have a defect lattice of the spinel type.^{1,2}

When exposed to moist air the alumina surfaces are terminated by a monolayer of hydroxyl (OH) groups.^{3–7} When degassed at higher temperatures, these surface OH groups get progressively removed.⁴ At about 900–1000 °C these OH groups get completely expelled, leaving coordinated O^{2-} on the outer surface layer. The removal of OH ions by condensation results in defect lattice as the sample is heated beyond 500 °C.^{3,4}

The performance of the pure oxides can be considerably changed by supporting and/or mixing oxide systems. For example, adding rare earth oxides promotes the effectiveness of alumina due to the formation of R–O–Al bond [RAIO₃ phase].⁸ On the basis of transmission electron microscopy (TEM) data, it is found that the presence of rare earth cations modify the crystal growth characteristics of Al_2O_3 and that the lanthanides hinder the reactivity of strong Lewis acid sites at the Al_2O_3 surfaces. Thus, the OH content of alumina decreases on rare earth doping.⁹

Apart from the catalysis and adsorption studies, evaluation of thermal parameters of Al_2O_3 , like thermal diffusivity, are important means of thermal characterization. It has been well recognized that the photoacoustic (PA) effect is an effective technique for evaluating the thermal diffusivity of samples.^{10–17} The basic principle behind the PA effect is that when a sample is illuminated by an intensity modulated (chopped) light, the resulting periodic optical absorption generates stress and thermal waves in the sample. The PA signal can be detected either directly by using a transducer in contact with the sample or indirectly by keeping the sample in a cell and measuring the acoustic wave generated in the

coupling gas with a sensitive microphone.¹⁷ By studying the chopping frequency dependence of the acoustic signal generated in the coupling gas at a fixed optical wavelength, the thermal diffusivity of the sample can be evaluated.¹⁵

This communication deals with the study of the effect of OH ions on thermal diffusivity of alumina, by evaluating its thermal diffusivity after heating to various degassing temperatures and doping it with rare earth oxide. In the single beam PA spectrometer¹⁷ assembled for the present investigation, the 488 nm line of an argon ion laser (LiCONiX 5300) has been used as the pump source. To generate acoustic signal in the PA cell, the pump beam is modulated using an electromechanical chopper. The acoustic signal generated in the coupling medium is detected by a small, highly sensitive ($100 \mu\text{V}/\text{Pa}$) microphone is kept close to the sample compartment and its output is processed by means of a lock-in amplifier (EG & G Model 5208).

Thermal diffusivity can be evaluated from the chopping frequency dependence of the PA signal.¹⁴ For a given sample thickness (l_s), one can have a transition from a thermally thin regime to thermally thick regime by increasing the chopping frequency. The transition appears as a slope change at the characteristic frequency (f_c) in the log (amplitude) versus log (frequency) plot. Knowing the actual thickness of the sample (l_s), the thermal diffusivity (α) can be calculated using the relation, $\alpha = l_s^2 f_c$.

In our experiment, γ - Al_2O_3 is prepared by the dehydroxylation of hydrous oxides at low temperature (~ 350 °C).¹⁷ The mixed oxide is prepared by coprecipitation from a nitrate solution. Aqueous ammonia solution is added to a mixed aqueous solution containing rare earth nitrate and aluminium nitrate. It is then dried overnight at 110 °C and then calcined at 400 °C for 3 h to form the mixed oxide.

To determine the thermal diffusivity, 0.4–0.7 g of the sample is pelletized under high pressure. Keeping the sample (in the form of a pellet) in the PA cell, the frequency dependence of the acoustic signal amplitude is studied. Determining the sample thickness (l_s) and the characteristic frequency

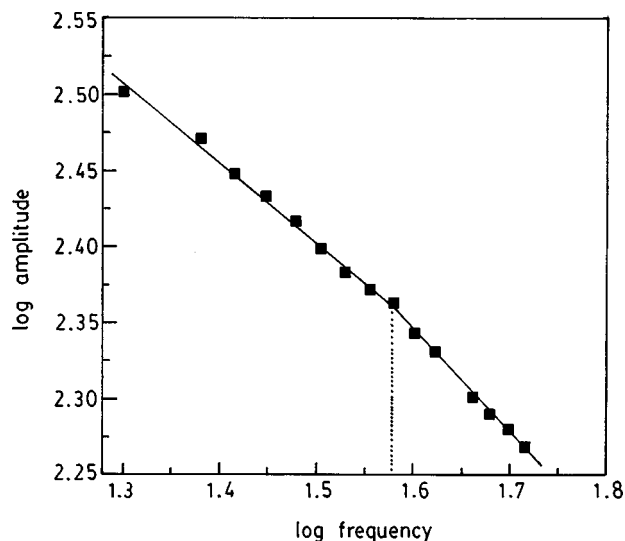


FIG. 1. The log–log plot of the variation of signal amplitude with frequency at room temperature. ($\text{Al}_2\text{O}_3=100\%$ and $\text{Nd}_2\text{O}_3=0\%$).

(f_c) from the log–log plot (Fig. 1), the thermal diffusivity can be calculated. Then the Al_2O_3 sample is kept in an oven at a set temperature (500 and 1000 °C) for about 3 h in order to degas it so as to eliminate the OH ions. The thermal diffusivity (α) of Al_2O_3 at each set temperature is determined.¹⁷ The thermal diffusivities of copper and aluminium were also determined to calibrate the present experimental setup. The values obtained in the case of copper (1.177 cm^2/s) and aluminium (0.979 cm^2/s) agree well with the reported values (1.16 and 0.98 cm^2/s , respectively). The accuracy of the measurements depends on the determination of sample thickness (l_s) and characteristic frequency (f_c). The values of thermal diffusivity are correct up to the third digit.

It has been found that¹⁷ when Al_2O_3 is degassed at 500 °C, α falls by 8.2% and at 1000 °C α falls by 12.4% of the value before degassing, when it had a monolayer of OH ions at various sites.³ The observed decrease in α is, therefore, attributed to the loss of OH ions from Al_2O_3 .¹⁷

The experiment is repeated after doping Al_2O_3 with Nd_2O_3 . It is seen that the doping causes a decrease in the thermal diffusivity of Al_2O_3 . The doped samples are then degassed at 500 °C and the thermal diffusivity is found to decrease further. Results are given in Table I(a).

It has been found from the IR spectrum that the doping of Al_2O_3 with Nd_2O_3 also decreases the OH content.^{8,9} This implies that Nd has interacted extensively with the OH groups on the surface. The calcination of these doped samples further reduces the OH content.⁹ The thermal diffusivity of Al_2O_3 is also found to decrease with the increase of Nd_2O_3 (Table I). From Table I(b) it is evident that α decreases further on calcination, as expected. These results further suggest that the observed variation of thermal diffusivity is due to the loss of OH ions.

Due to the larger surface area, Al_2O_3 has more adsorbed OH ions than Nd_2O_3 . If we compare the thermal diffusivity of Al_2O_3 and Nd_2O_3 before and after degassing, it can be

TABLE I. Thermal diffusivity of Al_2O_3 doped with Nd_2O_3 .

l_s $\times 10^{-3}$ m	f_c (Hz)	Al_2O_3 (%)	Nd_2O_3 (%)	Thermal diffusivity $\times 10^{-4}$ m^2/s
(a) At room temperature (30 °C).				
1.15	37.9	100	0	0.502 ± 0.001
0.89	45.6	95	5	0.361 ± 0.001
0.93	30.5	90	10	0.264 ± 0.001
0.87	33.9	80	20	0.257 ± 0.001
0.86	33.3	40	60	0.246 ± 0.001
0.82	33.9	20	80	0.228 ± 0.001
0.54	33.9	0	100	0.099 ± 0.001
(b) At 500 °C.				
l_s $\times 10^{-3}$ m	f_c (Hz)	Al_2O_3 (%)	Nd_2O_3 (%)	Thermal diffusivity $\times 10^{-4}$ m^2/s
1.15	34.8	100	0	0.461 ± 0.001
0.89	38.9	95	5	0.262 ± 0.001
0.93	34.5	90	10	0.243 ± 0.001
0.87	30.6	80	20	0.211 ± 0.001
0.86	29.6	40	60	0.209 ± 0.001
0.82	28.1	20	80	0.189 ± 0.001
0.54	32.5	0	100	0.095 ± 0.001

seen that the decrease in the thermal diffusivity of Nd_2O_3 is much less than that of Al_2O_3 . This further confirms the role of OH ions on the thermal properties of Al_2O_3 .

With this supporting evidence, we can conclude that the OH ions have significant effect on the thermal diffusivity of alumina.

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