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Formation of β-Alumina in $CuO.Al_2O_3.Na_2O$ System

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The effect of doping by varying amounts of sodium ions (as sodium hydroxide) being 2, 5 and 10% on previousiy heated $CuO.Al_2O_3$ mixtures having molar ratios of 0.25 : 1, 0.5 : 1 and 1 : 1 was studied. The nine $CuO.Al_2O_3.Na_2O$ mixtures were calcined at 900°C. Their structural characteristics were assessed through XRD analysis and complemented by IR spectral data. Accompanying morphological changes were followed through scanning electron microscopy.

The calcination of the mixes produced powders with α-alumina, copper aluminate and/or copper oxide, depending on the copper content, beside the formation of abundant β-alumina. Fibrous β-alumina was obtained with the lowest $CuO : Al_2O_3$ molar ratio (0.25 : 1) with the 5% Na^+ doping corresponding to 1 : 10 $Na_2O : Al_2O_3$. With higher sodium content (10%), corresponding to 1 : 3-5 $Na_2O : Al_2O_3$, as well as higher molar ratio of $CuO : Al_2O_3$ (0.5 : 1), (1 : 1) platy β-alumina was obtained. Such changes were correlated with coordination number of aluminium and the number of coordinated water species in the lattice.

INTRODUCTION

Sodium β-alumina is uniquely used as ionic conducting membranes in sodium-sulphur battaries[1], other important applications as thermostable catalyst for high temperature reactions of the petroleum industry[2], steam reforming of n-hexane[3] and conversion of acetic acid[4] were also roported. Na-β-alumina has the symmetry of the hexagonal space group P $6_3/mmc$ (D^4_{6h}) and consists of densely packed layers of aluminum and oxygen ions having a spinel-like structure separated by loosely packed planes which contain the Na^+ ions and bridging O^{--} ions. The lattice parameters of stable Na-β-alumina (1 : 11–1 : 13 $Na_2O : Al_2O_3$) are $a = 5.50–5.59$ Å and $c = 22.53$ Å. Another metastable β″-alumina (1 : 5 — 1 : 7) is structurally rhombohedral with $\alpha = 5.58$ Å and $c = 33.95$ Å. The former is refered to as 2 block β-alumina while the richer soda compound is the three block variety[5]. The formation of stable β-alumina phases was found to be at around 1400°C in mixtures of Na_2CO_3 and Al_2O_3[6,7], with step formation of β″-alumina at 1100°C. Severe precautions should be performed to avoid the decomposition of the formed β-alumina above 1400°C due to its appreciable equilibrium vapour pressure of Na_2O. The V_2O_5 was previously used as a mineralizer for β-alumina formation in soda-alumina mixtures at lower temperature[7], without residual α-alumina or alkali aluminate. B_2O_3 was found to facilitate its formation through liquid phase development[8].

The present study is considered as an extention of our previous report[9] on the effect of sodium ions (2–10%) on the thermal products resulted from the interaction between CuO and Al_2O_3 at about 900°C. The study was devoted to find out the optimum ratios of $Na_2O : CuO : Al_2O_3$ which lead to formation of crystalline β-alumina at a relatively low temperature and following up the morphological changes.

EXPERIMENTAL

Materials and Techniques

Three $CuO : Al_2O_3$ samples of the mol. ratios. 0.25 : 1(I), 0.5 : 1(II) and 1 : 1(III), were prepared by impregnation of γ-Al_2O_3 (preheated at 550°C for 4 hrs.) with copper nitrate solution of the appropriate concentration. The solids obtained were dried and calcined at 400°C for 4 hrs. These samples were treated with 2, 5 and 10% Na^+ (NaOH) solution, dried and thermally treated at 900°C for 4 hrs. The composition of the nine prepared mixtures are given in Table 1,

TABLE 1
THE CHEMICAL COMPOSITION OF THE PREPARED
$Na_2O.CuO.Al_2O_3$ SAMPLES

Sample group	Notation	% Na^+	Oxides (moles)			Mol. ratio Al_2O_3/Na_2O
			CuO	Al_2O_3	Na_2O	
I	I–2	2	0.2	0.804	0.0322	25
	I–5	5	0.194	0.779	0.0806	10
	I–10	10	0.184	0.738	0.1612	4.6
II	II–2	2	0.346	0.6912	0.0322	21.5
	II–5	5	0.335	0.67	0.0806	8.3
	II–10	10	0.317	0.635	0.1612	4
III	III–2	2	0:54	0.54	0.0322	17
	III–5	5	0.523	0.523	0.0806	6.5
	III–10	10	9.496	0.496	0.1612	3

I–0.25 $CuO : 1\ Al_2O_3$,
II–0.5 $CuO : 1\ Al_2O_3$ and
III–1 $CuO : 1\ Al_2O_3$

An X-ray investigation of the thermal products was performed with a Philips diffracometer (type PW 1051). The patterns were obtained using nickel-filtered copper radiation ($\lambda = 1.5405$ Å) at 36 kV and 16 mA. The diffraction angle 2θ was scanned at a rate of 2° min^{-1}.

The micrographs were obtained by scanning electron microscope (JEOL, JSM T-20 resolution 200 Å; accelerating potential 20 kV).

RESULTS AND DISCUSSION

Colour of Samples

The visual inspection of the colour of the thermally treated, at 900°C, samples are given in Table 2.

TABLE 2
COLOUR OF THE PREHEATED $CuO.Al_2O_3.Na_2O$ SAMPLES AT 900°C FOR 4 HRS.

Group	I			II			III		
% Na^+	2	5	10	2	5	10	2	5	10*
Colour	White	Very light buff	Light buff	Buff	Brick buff	Dark grey	Brick buff	Dark grey	Heavy grey

*agglomerated.

From the Table 2, it can be seen, that the colour of the sample may reflect to a certain extent the composition changes. This will be clearly shown through X-ray investigation.

X-ray Diffraction Analysis

Figs. 1, 2 and 3 depict the XRD-patterns of the samples of group I, II and III with different amounts of sodium ions.

The presence of 2% Na^+ in sample 1–2 leads to the formation of both α-Al_2O_3 and $CuAl_2O_4$ (Fig. 1a). The increase of copper content with the same % of Na^+ (2%) produced more $CuAl_2O_4$ on the expense of α-Al_2O_3 (Fig. 2a and 3a).

The introduction of 5% Na^+ or more leads to a marked decrease in the $CuAl_2O_2$ formation with a parallel increase in the amount of CuO-phase [Figs. 1,2,3, (b and c)]. In all cases it can be observed that the introduced Na^+ reacted with alumina forming sodium β-alumina with d-spacing 11.4, 2.8, 2.25, 2.13, 1.58 and 1.407 Å, its predominant formation with higher Na^+ content especially in group I and II is reasonable as the $Na_2O : Al_2O_3$ ratio is around the stoichiometric composition of β-alumina (1 : 11). Increasing the sodium content to 10% in the three groups i.e. mixtures with $Na_2O : Al_2O_3$ ratio will approach 1 : 3–5, which is favourable for richer soda β''-alumina phase. It should be notified that for the

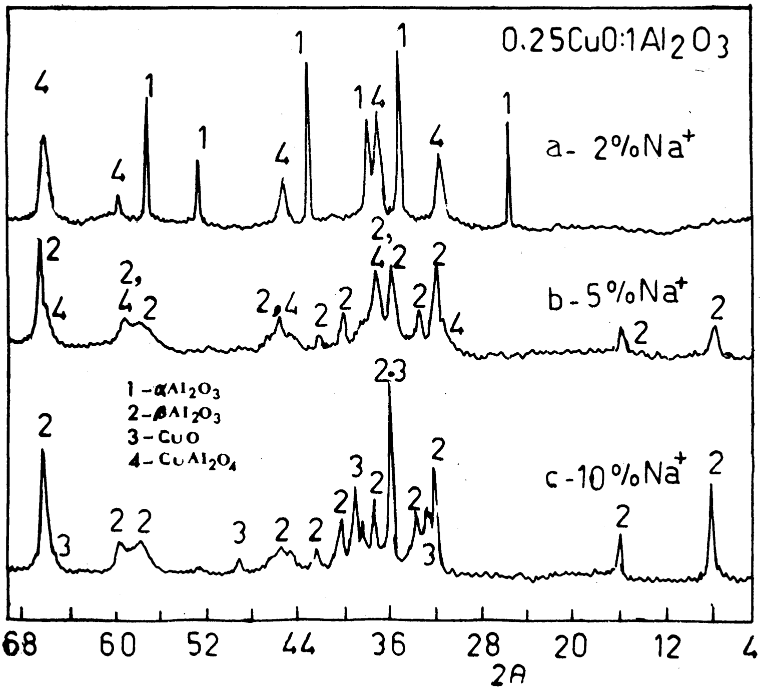

Fig. 1. XRD-patterns of the samples of group I. (0.25 CuO : 1 Al_2O_3).

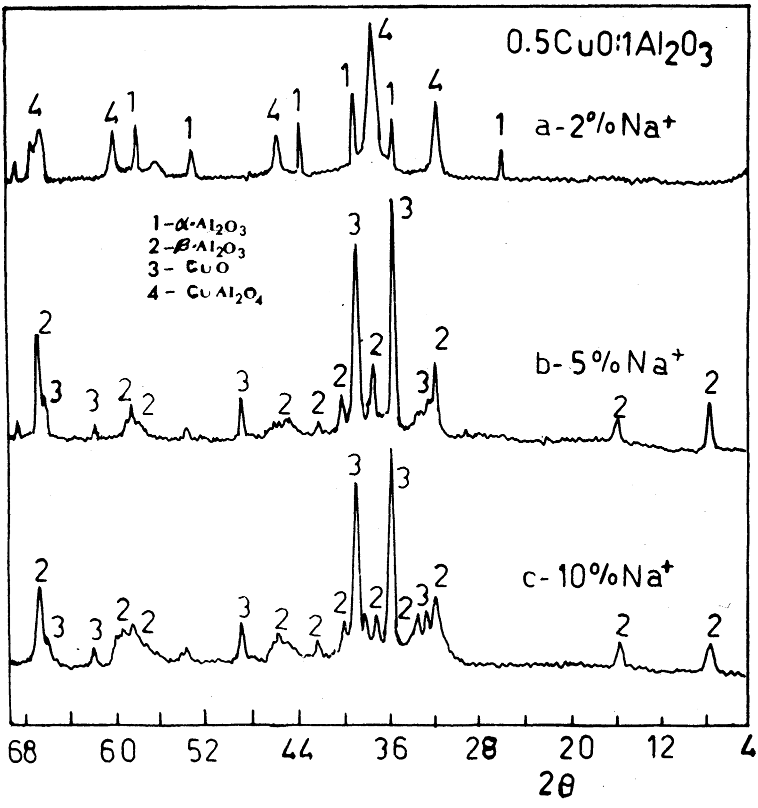

Fig. 2. XRD-patterns of the samples of group II (0.5 CuO : 1 Al_2O_3).

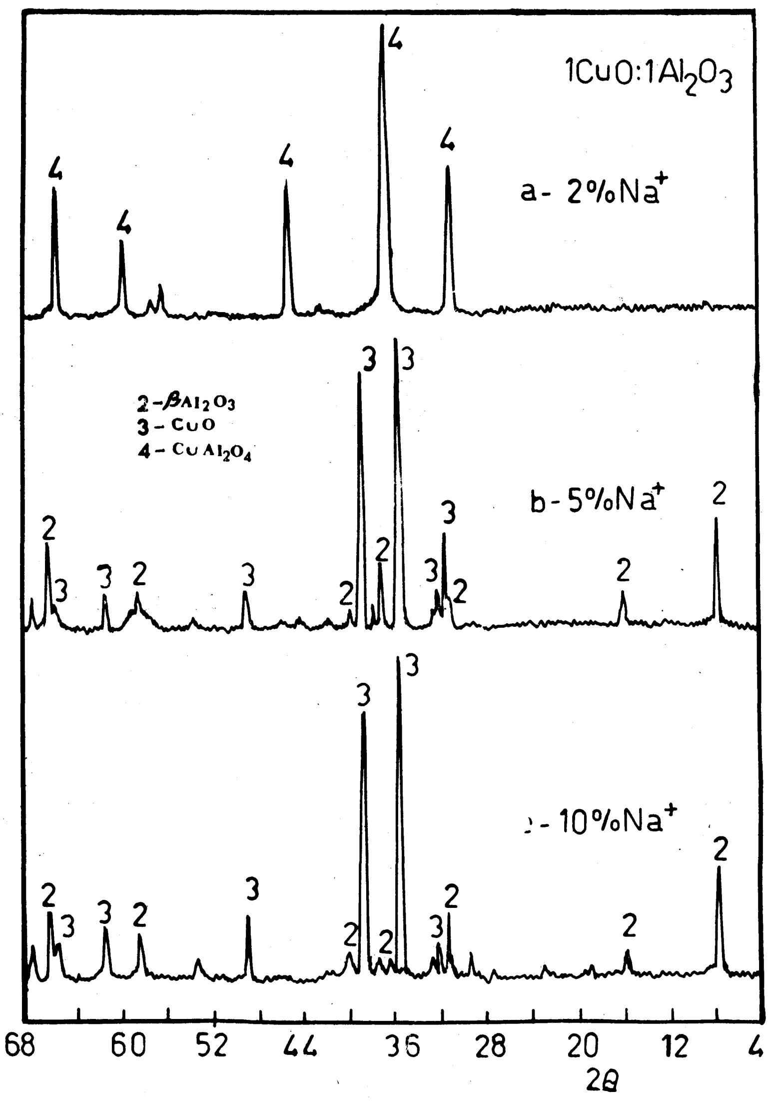

Fig. 3. XRD-patterns of the samples of group III. (1 CuO : 1 Al_2O_3).

highest $CuO : Al_2O_3$ ratio (1 : 1) β''-alumina content was abundant even at level of 5% Na^+. This proves the mineralizing effect of CuO beside the appropriate $Na_2O : Al_2O_3$ ratio at such low temperature. A parallel enrichment in the CuO content at the expense of $CuAl_2O_4$ denotes the deficiency of the system in Al_2O_3, which was preferentially consumed in the β or β''-alumina. The latter formation in the mean time stabilized the copper ions in their divalent state either in the form of $CuAl_2O_4$ or as CuO.

The increased CuO content in the system can be inferred to the higher affinity of sodium ions to react with alumina to form aluminate preventing the inward migration of Cu^{2+} to react with alumina to yield $CuAl_2O_4$.

Scanning Electron Microscopic Investigations

The scanning electron micrographs are given in Figs. 4,5 and 6 for groups I, II and III respectively. The presence of Na^+ at the level of 2% in the three groups affected the grain growth of alumina. The sharp edged hexagons in Fig. 4-a for sample 1–2 become less defined in sample 11–2 (Fig. 5-a) with some silvery scales. At higher CuO : Al_2O_3 molar ratio as

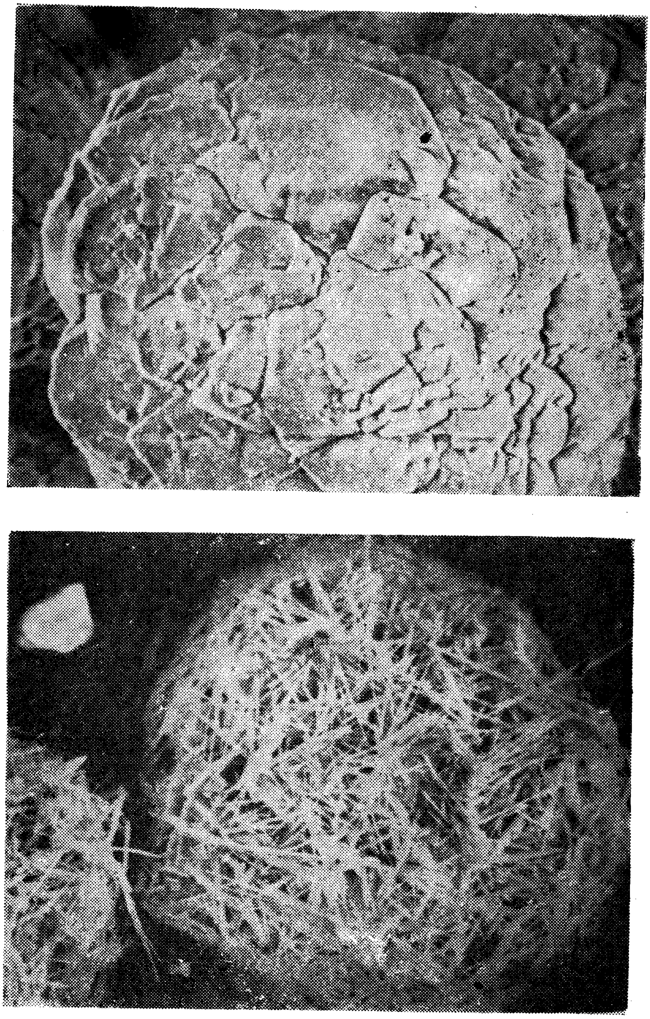

Fig. 4-a-b. Scanning electron micrographs of the samples of group I (0.25 CuO : 1 Al_2O_3).

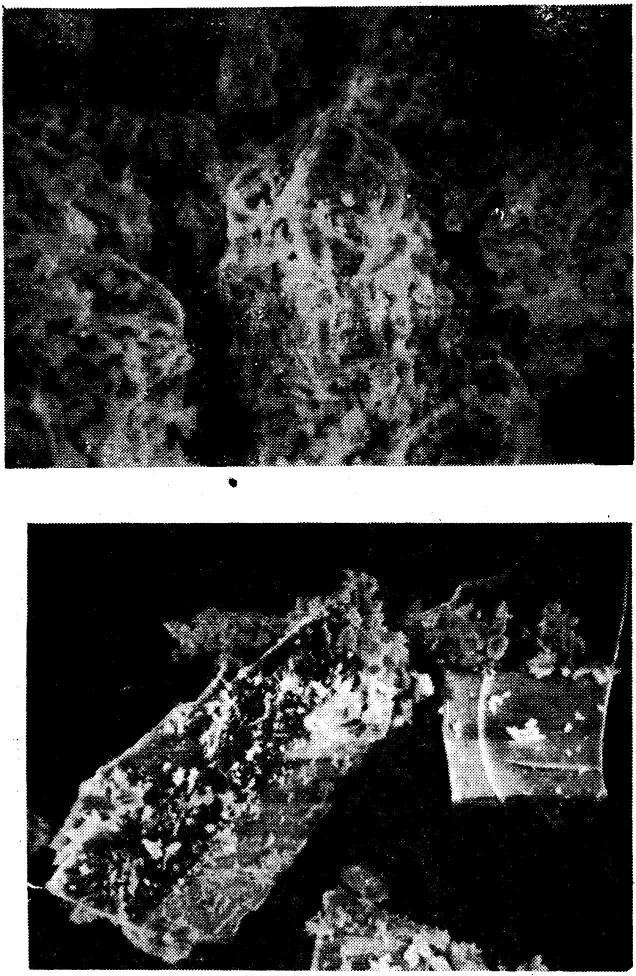

Fig. 4-c-d. Scanning electron micrographs of the samples of group I (0.25 CuO : 1 Al_2O_3).

group III, sample III-2, most of the small grains lost their contact boundries beside an exaggerated grain growth of the $CuAl_2O_4$ spinel (larger ones) (Fig. 6-a). A possible presence of a second phase is evidenced from the scattered scales perhaps β-alumina.

Increasing the percentage of sodium to 5% promoted the intensive and bulk development of fibrous structure. These fibres are aligned at the grain boundries as well as in the bulk of the grains (Fig. 4-b). This is a typical morphology of β-alumina as previously reported elongated crystals having width ratio of 50 : 1 were obtained but at temperatures above 1400°C[6,10,11,12]. The chemical composition here is 1 : 10 Na_2O : Al_2O_3 i.e. within the favourable composition for β-alumina with 1 : 11 ratio. This

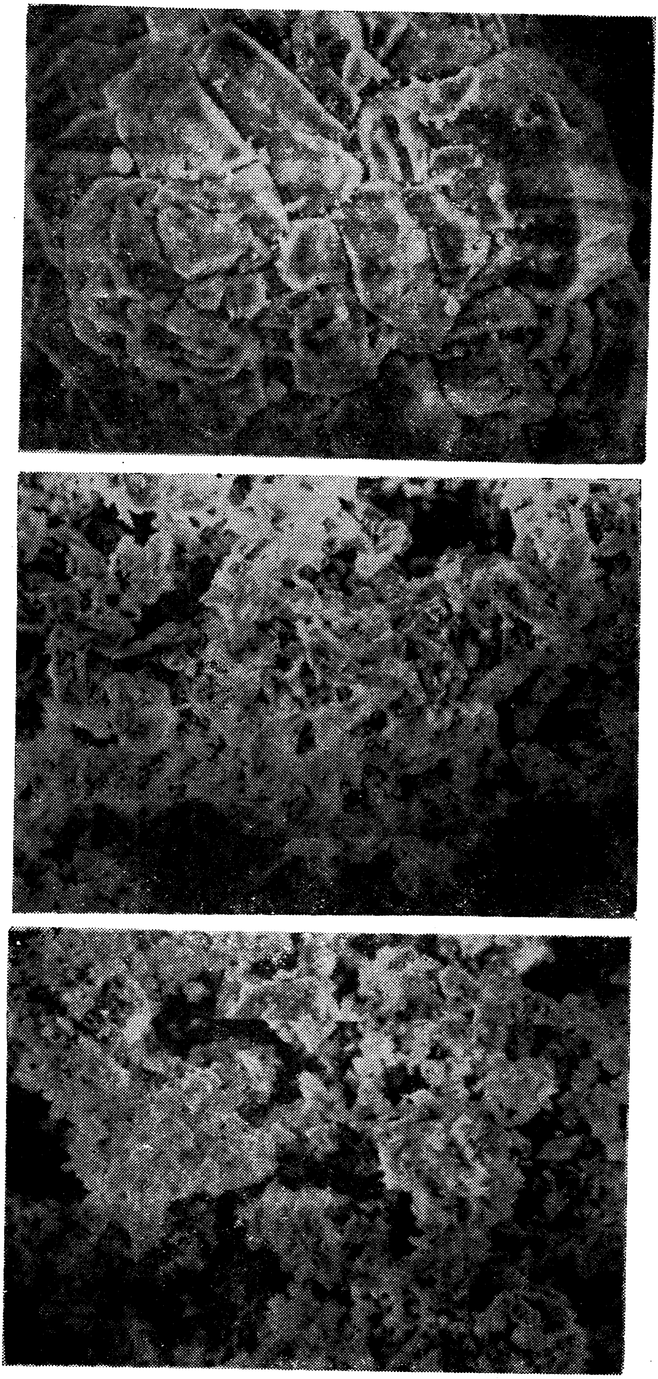

Fig. 5. Scanning electron micrographs of the samples of group II (0.5 CuO : 1 A_2O_3).

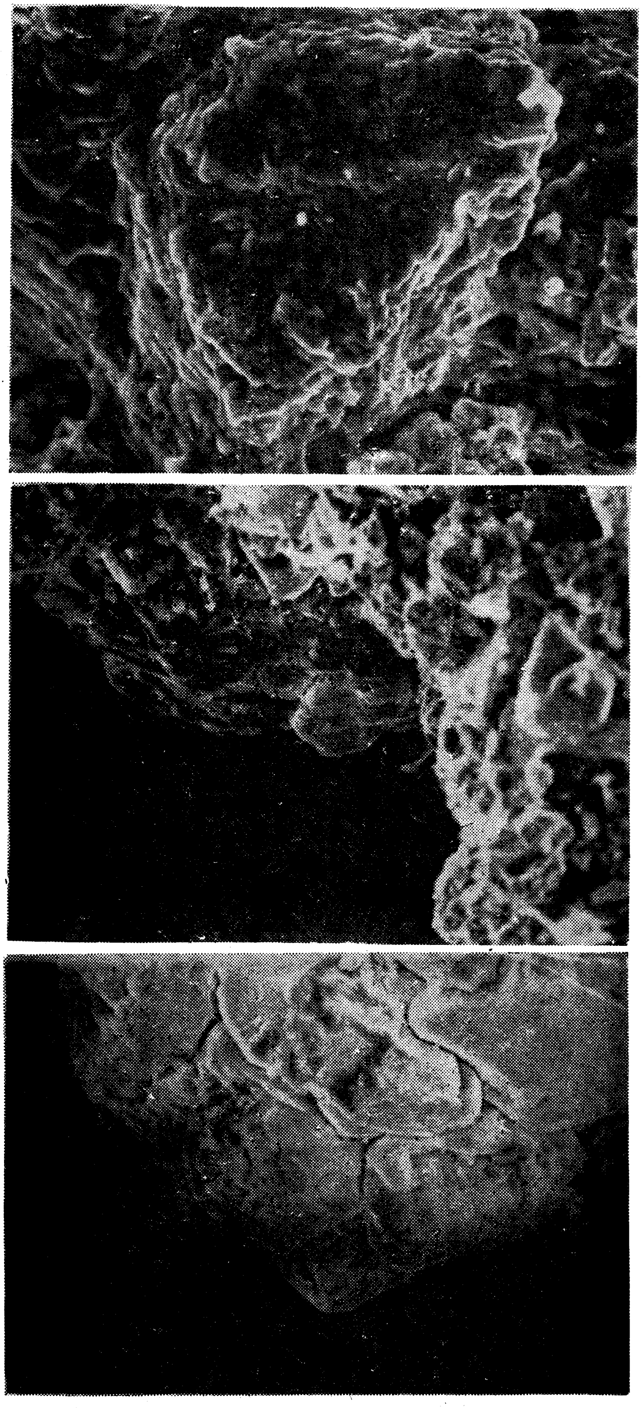

Fig. 6. Scanning electron micrographs of the samples of group III ($1\ CuO : 1\ Al_2O_3$).

unique structure turned to be elongated laths and scattered in a semi-continuous platy matrix probably β''-with higher CuO : Al_2O_3 ratio as in Fig. 5 for specimen II-5. Similar platy and scaly structure of standard fused β-alumina supplied by the Institute of Steine and Erden. Clausthal-BRD are shown in Fig. 4-d. At still higher Na^+ content as in Fig. 4-c for sample I-10, the scales dominate as the ratio of Na_2O : Al_2O_3 reaches 1 : 4.6 which is more favourable for the β''-formation. These features show considerable grain growth with high CuO : Al_2O_3 ratio (0.5 : 1) (Fig. 5-c for sample II-10). As the level of CuO : Al_2O_3 molar ratio increased to 1 : 1 whether, in presence of 5% or 10% Na^+, the sharp original borders are fused and the development of silvery plates which have larger size than their parents are observed. Well defined cleavage lines are also shown at crystal sides. This complete change of the microstructures is probably due to the formation of a liquid phase.

I.R. Investigations

The IR—spectra for investigated samples of group (I, II and III) are represented in Figs. (7, 8 and 9) respectively. The spectrum corresponding to the standard β-alumina is included with those of group I for the sake of comparison.

In the group frequency region up to 1300 cm^{-1}, (Table 3), multiple bands and shoulders are assigned to various water species. The band above 3400 cm^{-1} is due to (OH^-) ions formed by dissociation of water molecules in the conduction layer of β-alumina[13]. The O-H bending frequency occurs between 1200 and 1600 cm^{-1} region where it is "free" hydroxyl while it is recorded near 1650 cm^{-1}, in case of both adsorbed water and water of hydration[14]. Its higher intensity only in sample 1–5. (Fig. 7) compared with others means that hydrogen bending grows stronger with the concentration. This is coinciding with XRD findings as well as S.E.M. observations denoting higher β-alumina content. This assumption holds true also for its analogue in group II sample II-5 (Fig. 8). These species could also be detected in the standard β-alumina prepared by arc fusion as well as all samples of the III-group containing equimolecular CuO and Al_2O_3 along with Na_2O. This denotes the persistance of water species in the lattice.

In the finger print region the stretching frequency of the Al–0 in O_d and T_d of alumina groups denote the spinel structure of β-alumina. The Al-O stretching of AlO_6 octahedron are only detected in the lowest concentration of Na^+ with the smallest ratio 0.25 CuO : 1 Al_2O_3 (1) sample 1–2. The T_d coordination is observed in samples with lower ratio of CuO: Al_2O_3 with 2 and 5% Na^+ or higher ratio of CuO : Al_2O_3 but with only 2% Na^+. Bands could hardly be detected in group III containing equimolecular ratios of CuO and Al_2O_3 in this region.

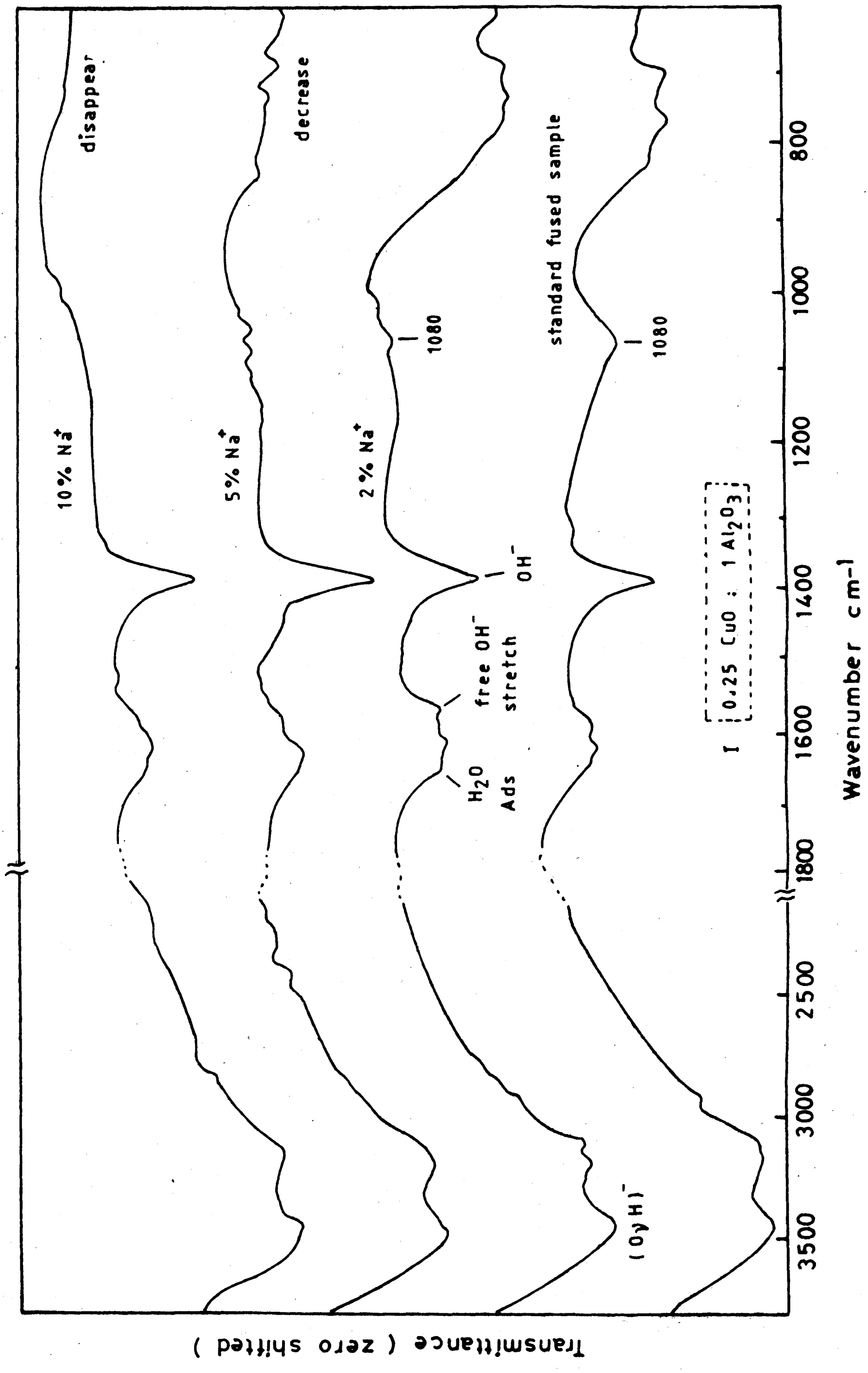

Fig. 7. IR spectra of the samples of group I (0.25 CuO : 1 Al_2O_3) with the spectrum of standard β-alumina.

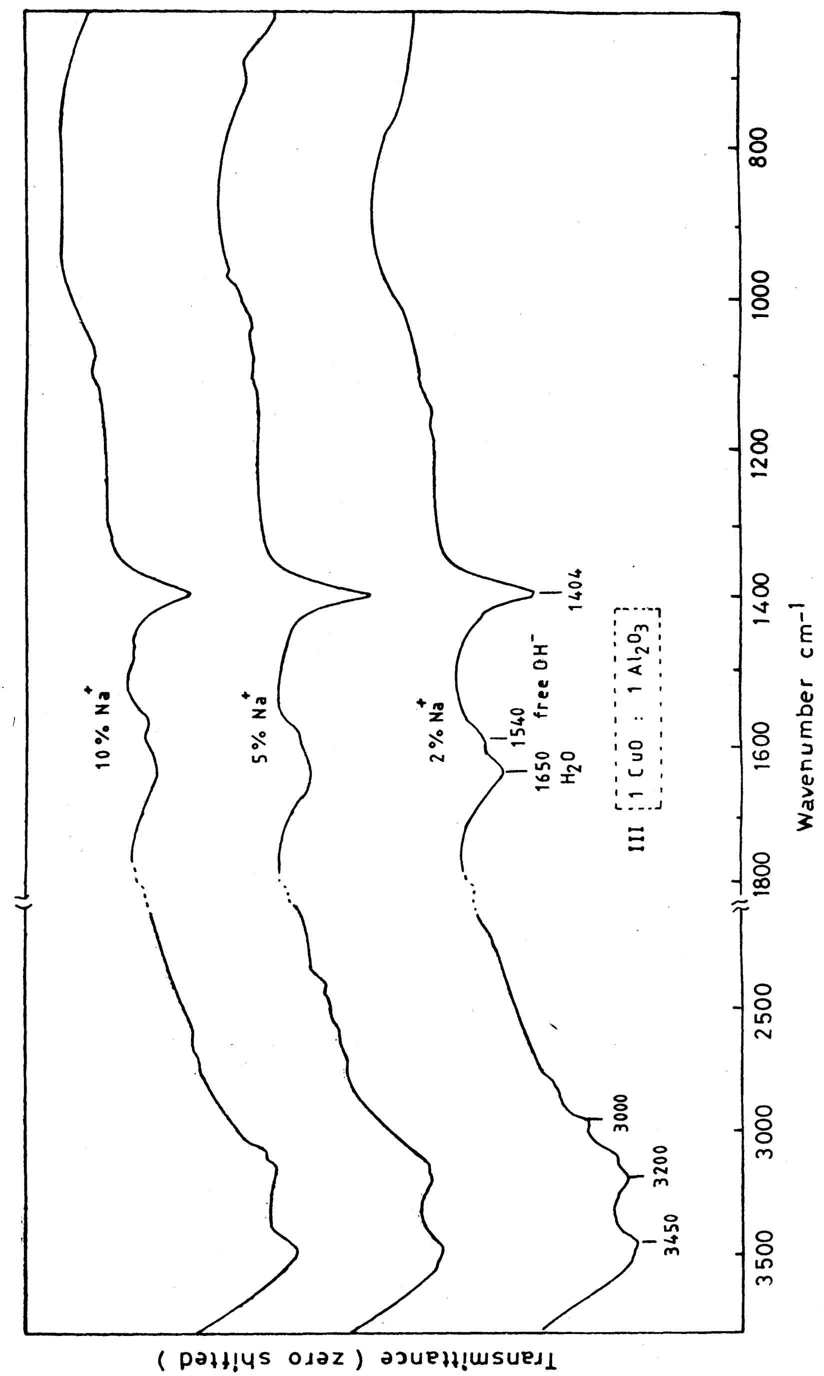

Fig. 8. IR spectra of the samples of group II (0.5 CuO : 1 Al_2O_3).

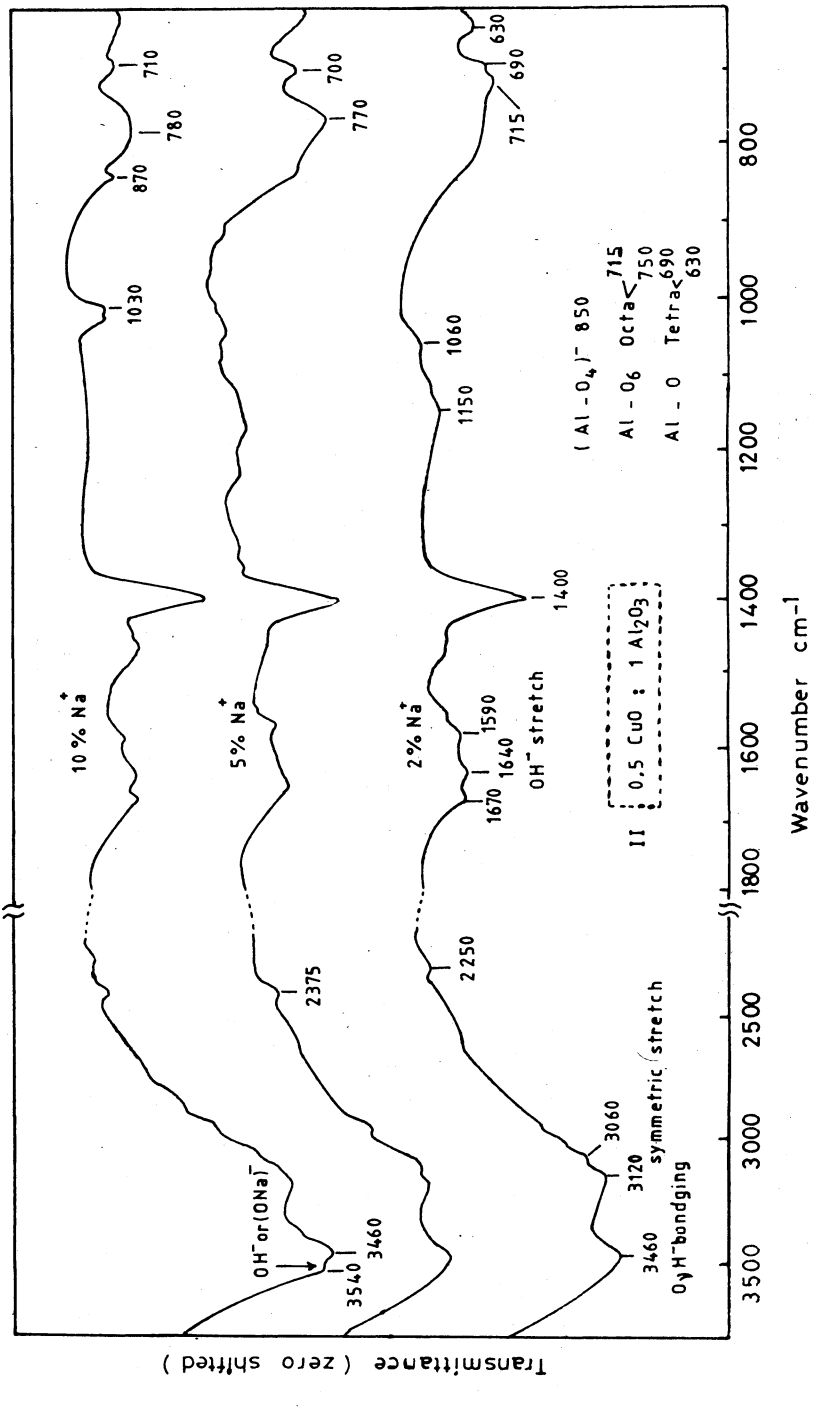

Fig. 9. IR spectra of te samples of group III (1 CuO : 1 Al_2O_3).

TABLE 3

I.R. BANDS RECORDED IN SAMPLES WITH 0.25 CuO : 1 Al_2O_3 AND 0.5 CuO : 1 Al_2O_3 WITHIN 1300-600 cm^{-1} RANGE

Band Assignment	Specimen notation					
	1–2	1–5	1–10	II–2	II–5	II–10
	—	—	—	1150	1150	—
	1080	1080	—	1060	1050	1030
Td(AlO_4)*	—	850	850	—	845	850
Al-O st.	750	750	—	—	770	780
Od(AlO_6)**	705	705	—	715	700	700
Td(AlO_4)	—	—	—	690	—	—
Td(AlO_4)	630	630	—	630	—	—

*Ref. 15, **Ref. 16.

The present low temperature formation of Na-β-alumina at 900°C is attributed to the mineralizing action of CuO especially at its lowest content which catalyzed the process. In this respects its effect over rides that of V_2O_5 which was previously denoted to enhance β-phase formation at 1200°C[6]. Proposed mechanism was the formation of $NaAlO_2$ at lower temperature than 1000°C. Above 1200°C the dissociation of sodium venadate and accompanying aluminate yield β-alumina. Further the parallel replacement of 5 Al^{3+} by 3 V^{5+} in the formed β-phase enriched the media with Al^{3+} which is more favourable for β- and non β''-phase. The present reaction courses could be summarized as follows: β-alumina phase was formed at low calcination of mixtures with CuO : Al_2O_3 ratios 0.25 : 1 having 2% Na^+ along with α-alumina and $CuAl_2O_4$ spinel. Higher Na^+ content increased the yield of fibrous β-alumina at the expense of both other two phases α-alumina and $CuAl_2O_4$. A still higher soda 5% and/or CuO : Al_2O_3, ratio (0.5 : 1) platy β-alumina was enriched.

At the highest CuO : Al_2O_3 ratio and Na^+ content 10%, all the soda was consumed in the β''-phase and CuO was formed. The enriched tetrahedral and octahedral coordination of Al-O as well as coordinated water species at these levels confirm open structure of β-phase.

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Indian Thermal Analysis Society, with the cooperation of M/s. Stanton Redcroft Ltd., England has instituted the Stanton Redcroft-ITAS Award to be presented to a scientist, below the age of 40 years (as on 31. 12. 1989), who has made effective contribution in thermal analysis in the academic and/or industrial fields. The award carries Rs. 2001/-, a medal and a citation. Further, the awarded will receive assistance towards travel and stay at Srinagar where the VII National Symposium on Thermal Analysis will be held during October 23–25, 1989. The award will be presented during the Symposium. Only members of the Society are entitled to nominate candidates for the award,. 3 copies of the nomination should be forwarded to the Convener to reach him on or before July 31, 1989.

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