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CHEMICAL PROCESSING OF ADVANCED LITHIUM ALUMINOSILICATE CERAMIC SYSTEM

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ABSTRACT:

During the past few decades, new developments in the use of ceramics in more advanced technological applications have drawn considerable attention. It is reported that certain ceramic compositions in the lithium aluminosilicate system have low thermal expansion coefficient and high degree of thermal shock resistance making them useful in specific applications. Being a novel technology for the chemical synthesis of ceramics, the sol-gel method was applied in this work. This process is based on the chemical hydrolysis and condensation reactions starting from molecular or colloidal precursors. Lithium aluminosilicate with molar composition $Li_2O : Al_2O_3 : 3SiO_2$ was selected to be prepared via sol-gel technique. Tetraethoxysilane (TEOS), Lithium chloride [$LiCl_2 . H_2O$] and Aluminum nitrate [$Al(NO_3)_3 . 9H_2O$] were used as precursors in this ceramic synthesis. The effect of CH_3COOH, H_3PO_4 and HNO_3 acid catalysts on the synthesis method was studied. The prepared ceramic was analyzed by TGA, DSC, DTA, XRD, IR and SEM. The results were given, explained and discussed.

KEY WORDS:

LAS, Sol-Gel, Ceramics, Thermal Analysis and Structural Analysis.

INTRODUCTION:

One of the features which characterize materials is that most of the time they are not in themselves final products, nevertheless, every final product has to use materials. Advanced materials are characterized by high purity, high technical performance, increased integration of functions, increased variety and complexity and high value added.

In spite of its extensive use since the earliest civilizations, ceramics have drawn considerable attention in more advanced technological applications to satisfy the increased demands for improvements in specifications and reliability. The engineering properties of polycrystalline ceramics are controlled by the microstructure, which depends on the processing method. Advanced structural ceramics in addition to common properties, have relatively high mechanical strength

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at high temperature , making them useful as components in heat engine, and electronic ceramics. Smart ceramics form intelligent materials and systems that combine sensing and activating functions[1].
The Lithium aluminosilicate system was subjected to some studies. It is reported that the synthesis of the mentioned ceramic is due to the interest in preparing fast-ion conducting glasses and glass-ceramics using sol-gel technology [2]. It is mentioned that one way to improve the ionic conductivity is to produce a silicate network with channels and less dense to facilitate the alkali ion motion specially lithium ion. On the other hand, literatures show that certain ceramic compositions in the lithium aluminosilicate system have very low, zero or even negative expansion coefficient leading them to be applied in specific fields [3]. The crystalline phases of the mentioned ceramic exhibit low thermal expansion coefficient and high degree of thermal shock resistance [4].
The sol-gel process represents a novel method for the synthesis of non-metallic inorganic materials like glasses and ceramics. This process has the advantage of achieving nano-powder production with good homogeneity and high purity at lower temperature. Starting from molecular or colloidal precursors in the sol form, a macromolecular network is obtained through hydrolysis and condensation reactions. The formed gel is then dried , calcined and sintered [5,6].

EXPERIMENTAL:

Alcoholic solutions of $LiCl.H_2O$ (Koch-light) and $Al(NO_3)_3.9H_2O$ (Fisher) were mixed and added to TEOS [$Si(OC_2H_5)_4$] (Aldrich). The effect of catalyst (0.1 : 10 TEOS) was studied by introducing H^+ represented by CH_3COOH, H_3PO_4 and HNO_3 a ratio of 0,1. The precursors were refluxed for 1 hour at 85°C. After cooling, the hydrolyzates were added to TEOS along with drying agent. Formamide being Lewis base like ammonium catalizer was added ($HCONH_2$, FA Prolabo) equal to alcohol and to control drying. The TEOS/water/ethanol molar ratio was 1/10/5. Stable gels were obtained at ambient conditions within 3-5 days, aged for one week, then, dried at 120°C till constant weight [7].
Thermal gravimetric analysis TGA (Netzch TG 209) and differential scanning calorimetry DSC (Netzch DSC 200) were adopted at 10°C/min to follow the decomposition of the dried gels. Phase analysis of the gels calcined at 550°C, 650°C, 750°C and 900°C was detected using X-ray diffractometer (Philips, PW 1390) $2\theta = 2°$ / min Cu K_o radiation. Semi quantitative Infrared spectral analysis with KBr disc technique (Philips PU 9712 spectrophotometer) and scanning electron microscope SEM (JEOL JSM.T20) were used .

RESULTS AND DISCUSSION:

The sol-gel method proved to be a good technique for the synthesis of advanced materials. It is used to prepare ceramics at relatively lower temperature than the traditional methods. In this paper lithium aluminosilicate ceramic was prepared starting with tetraethoxysilane (TEOS), lithium chloride $LiCl.H_2O$ and aluminum nitrate $Al(NO_3)_3.9H_2O$ via the sol-gel technique. The ceramic (LAS) was prepared by the precursor's hydrolysis followed by the condensation to form the gel under acid catalysis. The gel was then dried and calcined. Crack formation during drying is one of the most serious problems in the fabrication of ceramics specially thin films via sol-

gel processing. Capillary forces and local differential stresses cause crack formation. So, in this work formamide was added as a drying-control chemical additive DCCA to the mixed precursors solution. It also aids in lowering the processing temperature. Percent yield of different catalyzed samples in table 1 showed that the highest yield is for the sample prepared with HNO_3 while the lowest one is for the CH_3COOH. This may be due to the difference in dissociation constant and the weak acidity of acetic acid.

Table 1 : % yield for prepared samples

Acid	% Yield
CH_3COOH	80.90
H_3PO_4	88.29
HNO_3	92.77

1- Thermal Analysis:

a- Differential Scanning Analysis (DSC)

Fig. 1 shows the DSC thermal curves of the prepared samples in which an exothermic peak at 273±1 °C is characteristic for all samples. The formed peak may be due to the burn of organic residues chemically bonded to the gel structure. Another peak at 269°C for the CH_3COOH catalyzed sample appear to interfere with the major one and this may be due to the chelating power of the acetate group which is confirmed with the high ΔH value. Table 2 summarizes the DSC results where minimum T_g of 313°C for the HNO_3 sample suggest a lower degree of crosslinking than that of CH_3COOH and H_3PO_4 leading to a more linear molecules while the other acids suggest a slightly branched ones.

Table 2 : Data obtained from DSC

Acid	T_g (°C)	ΔC_p (j/g.°C)	Exo-Peak (°C)	ΔH (J/g)
CH_3COOH	329	2.72	269, 272	710.1
H_3PO_4	329	2.99	273	596.1
HNO_3	313	1.88	274	661.8

b- Thermo gravimetric Analysis (TGA):

Fig. 2 for the TGA thermal curves confirms the results of DSC where the high exothermic peak reported corresponds to the loss in weight in all samples. The percentage weight loss shows that the HNO_3 catalyzed sample has the lowest weight loss indicating high degree of polymerization (hydrolysis and condensation).

c- Differential Thermal Analysis (DTA):

The DTA thermal curve of HNO_3 catalyzed samples shown in fig. 3 gives an idea about the crystallization , where two exothermic peaks appears at higher temperature than that of DSC. First at 763.74°C which may be due to crystallization, while the other on is at 945.06°C and supposed to be the sintering temperature. Peaks

recorded in the DSC analysis does not appear in the fig as they have very low energy compared with those required for crystallization or sintering

2- Structural Analysis:

a- X-ray Diffraction:

XRD of HNO_3 catalyzed sample calcined at 550°, 650°C and 750°C represented in fig. 4 indicate the start of crystallinity at 750°C, and that all for all prepared samples calcined at 900°C shown in fig. 5 confirms the DTA results where complete crystalline powders are obtained.

b- Infrared Analysis (IR):

Fig. 6 shows the IR for samples calcined at 900°C which confirm results from DTA and XRD for the start of crystallinity.
The reported IR studies of LAS ceramics for the β-eucryptite [8] shows a series of very broad bands with a shoulder at $1085cm^{-1}$. At $1050Cm^{-1}$ a medium peak with a shoulder together with an inflection at $1040cm^{-1}$ are observed which are characteristic of Si(AL)-O stretching vibrations.
Four very strong peaks appear at 1015, 980, 960 and $940cm^{-1}$. The IR spectra for the samples in fig 6 shows a series of peaks can be summarized in table 3.

Table 3 : The assigned band and their wavenumber
for different samples calcined at 900°C

Assignment	Wavenumber (cm^{-1})		
	H_3PO_4	CH_3COOH	HNO_3
O-H bridging	3430	3430	3430
$Si\text{-}O\text{-}Al^6$	1160	1160	1140
$Si\text{-}O\text{-}Al^4$	820	820	820
Si-O strech	1000	1020	1020
$Al^6\text{-}O\text{-}Al^4$	1000	1020	1020

3- Morphological Analysis:

SEM for the samples calcined at 900°C appears in fig. 8 where sample prepared with HNO_3 shows high crystallinity and the fused edges indicates partial sintering which confirms the second DTA peak.

CONCLUSION:

The sol-gel method proved to be a good technique for the ceramic synthesis at low temperature. Lithium aluminosilicate was prepared at a temperature of 750°C lower than that used in the traditional which exceed a temperature of 1000°C [3]. The obtained samples have lower crystallization and sintering temperatures. Among used acids HNO_3 stands as the best one for preparing linear highly polymerized gel with a good microstructure and crystallinity.

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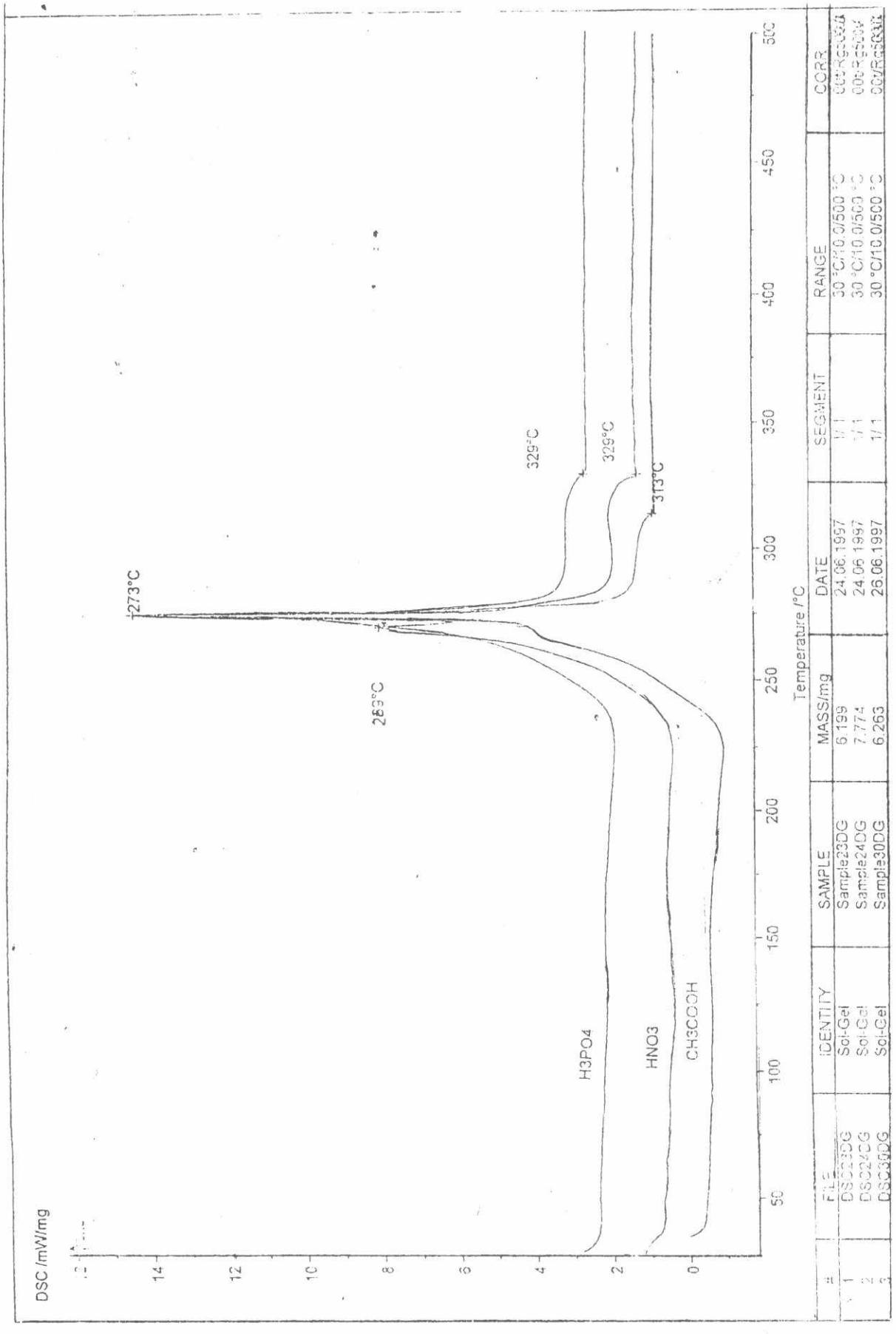

#	FILE	IDENTITY	SAMPLE	MASS/mg	DATE	SEGMENT	RANGE	CORR.
1	DSC23DG	Sol-Gel	Sample23DG	6.199	24.06.1997	1/1	30 °C/10.0/500 °C	
2	DSC24DG	Sol-Gel	Sample24DG	7.774	24.06.1997	1/1	30 °C/10.0/500 °C	
3	DSC30DG	Sol-Gel	Sample30DG	6.263	26.06.1997	1/1	30 °C/10.0/500 °C	

Fig. 1: DSC of different catalyzed samples

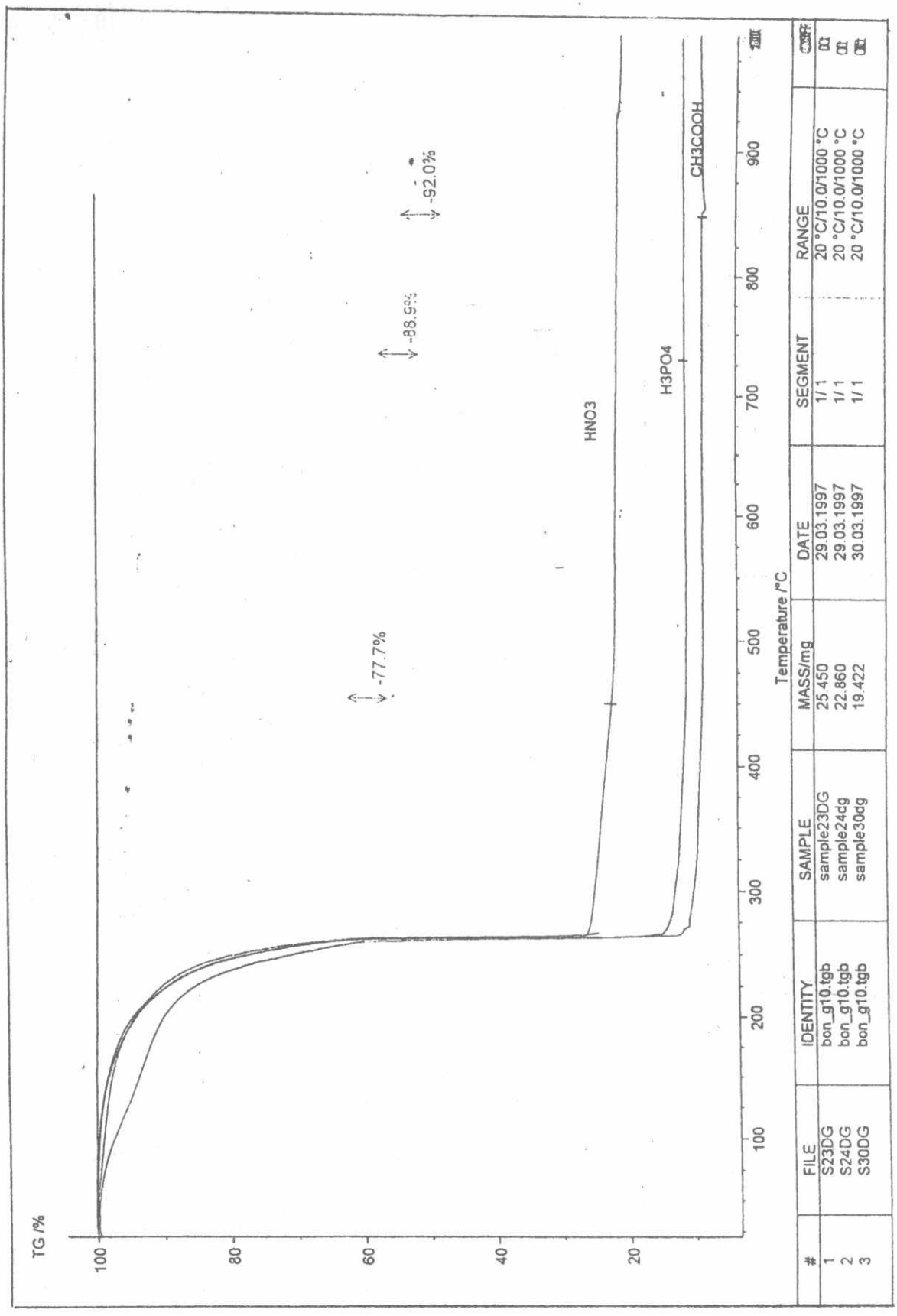

Fig. 2: TGA of different catalyzed samples

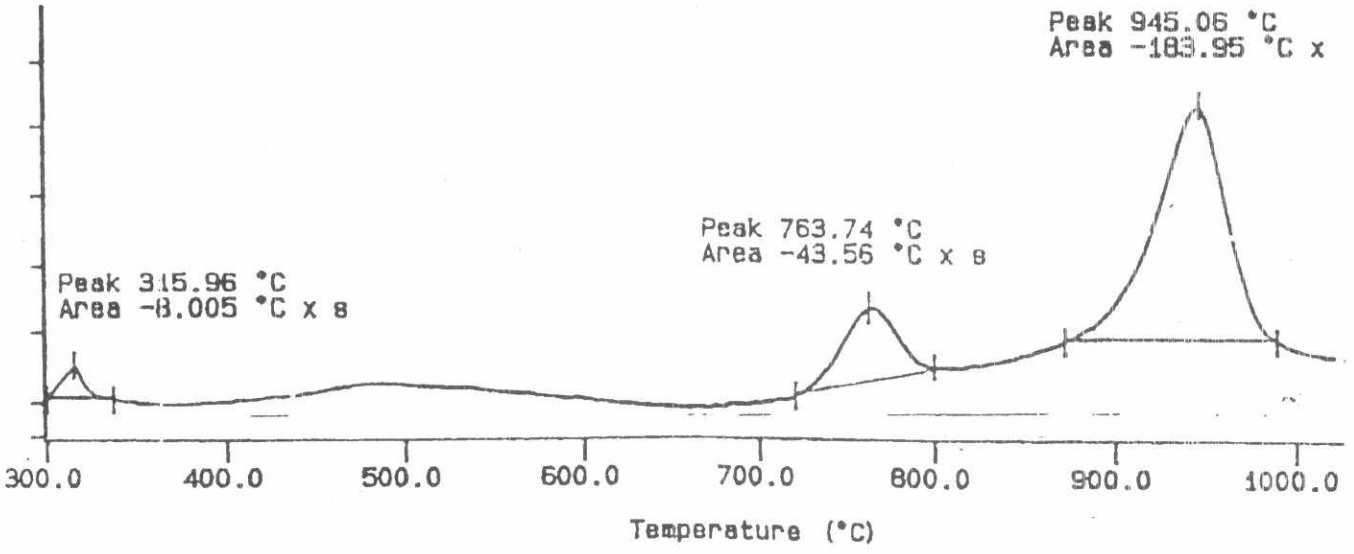

Fig. 3: DTA of sample prepared using HNO_3 catalyst

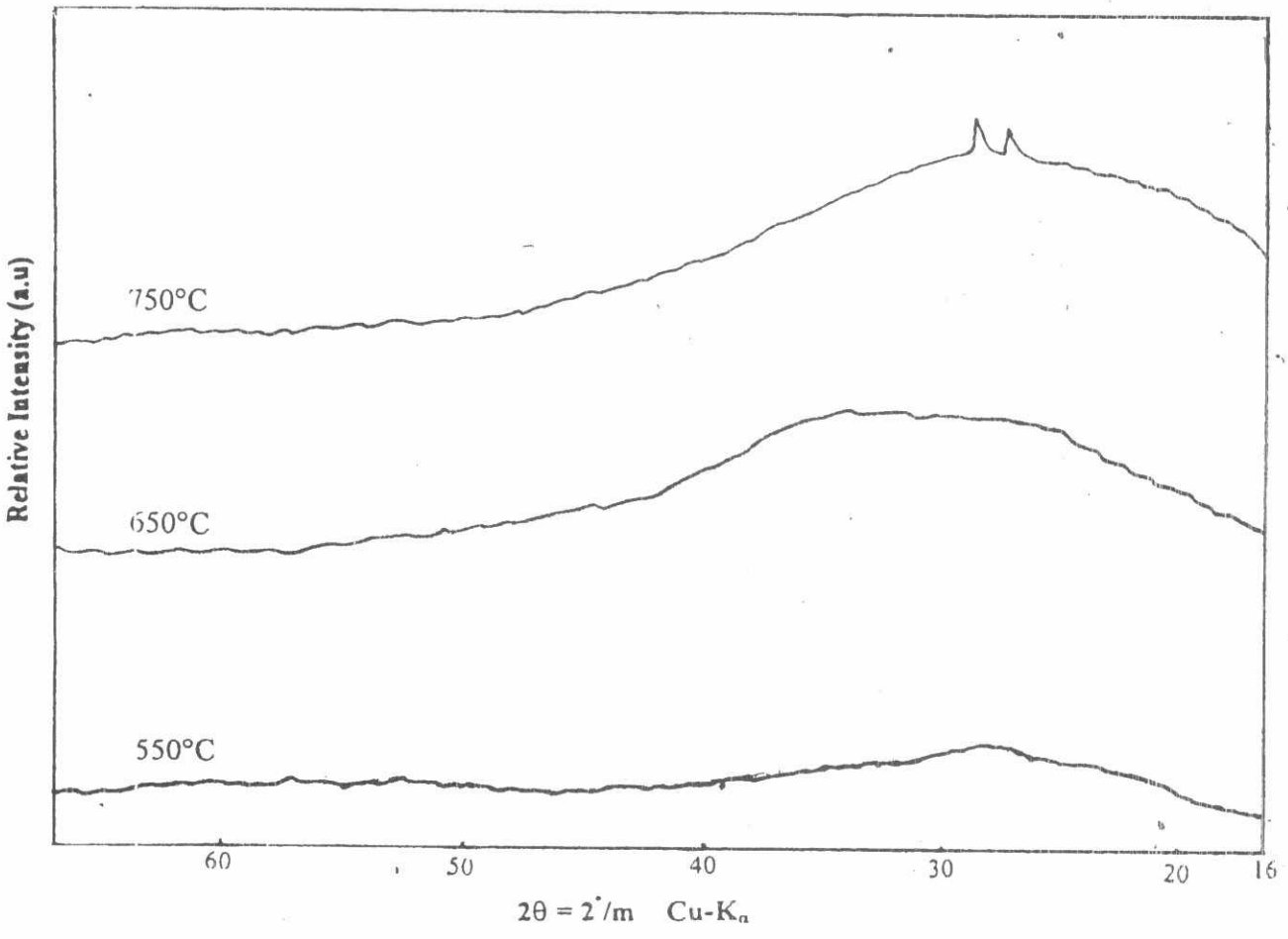

Fig. 4: XRD of sample prepared using HNO_3 catalyst calcined at different temperatures

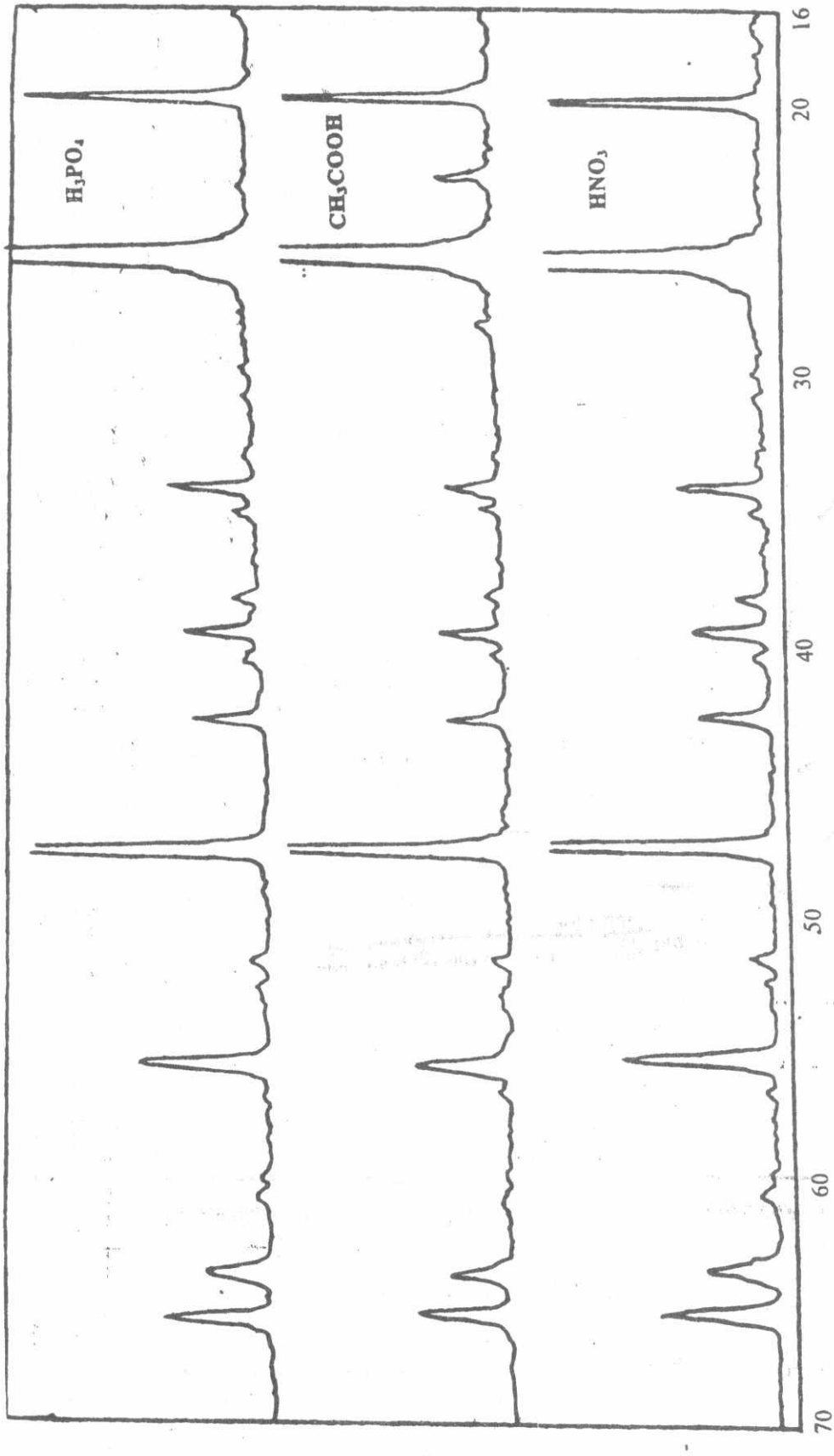

Fig. 5: XRD of different catalyzed samples calcined at 900°C

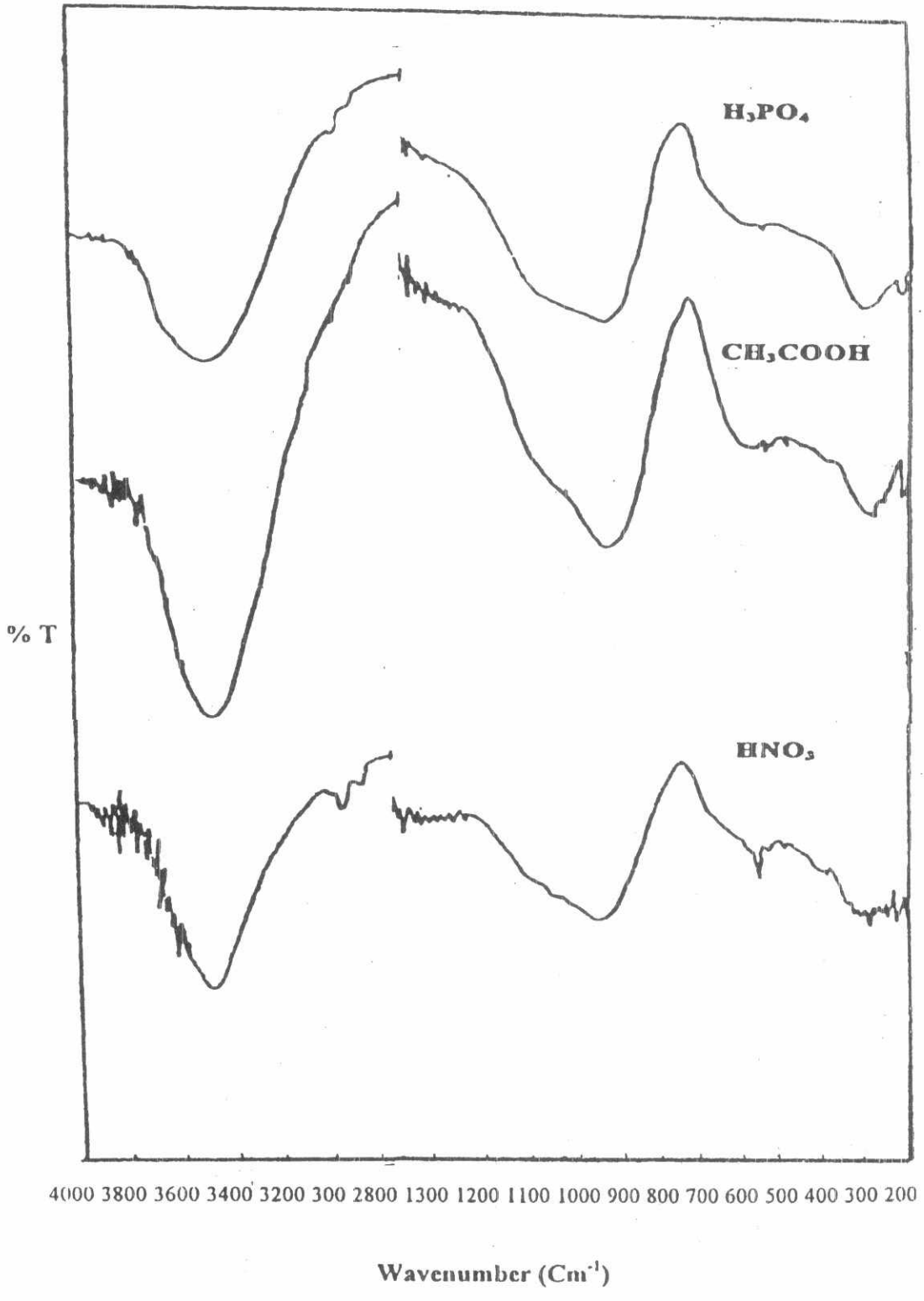

Fig. 6: IR of different catalyzed samples calcined at 900°C

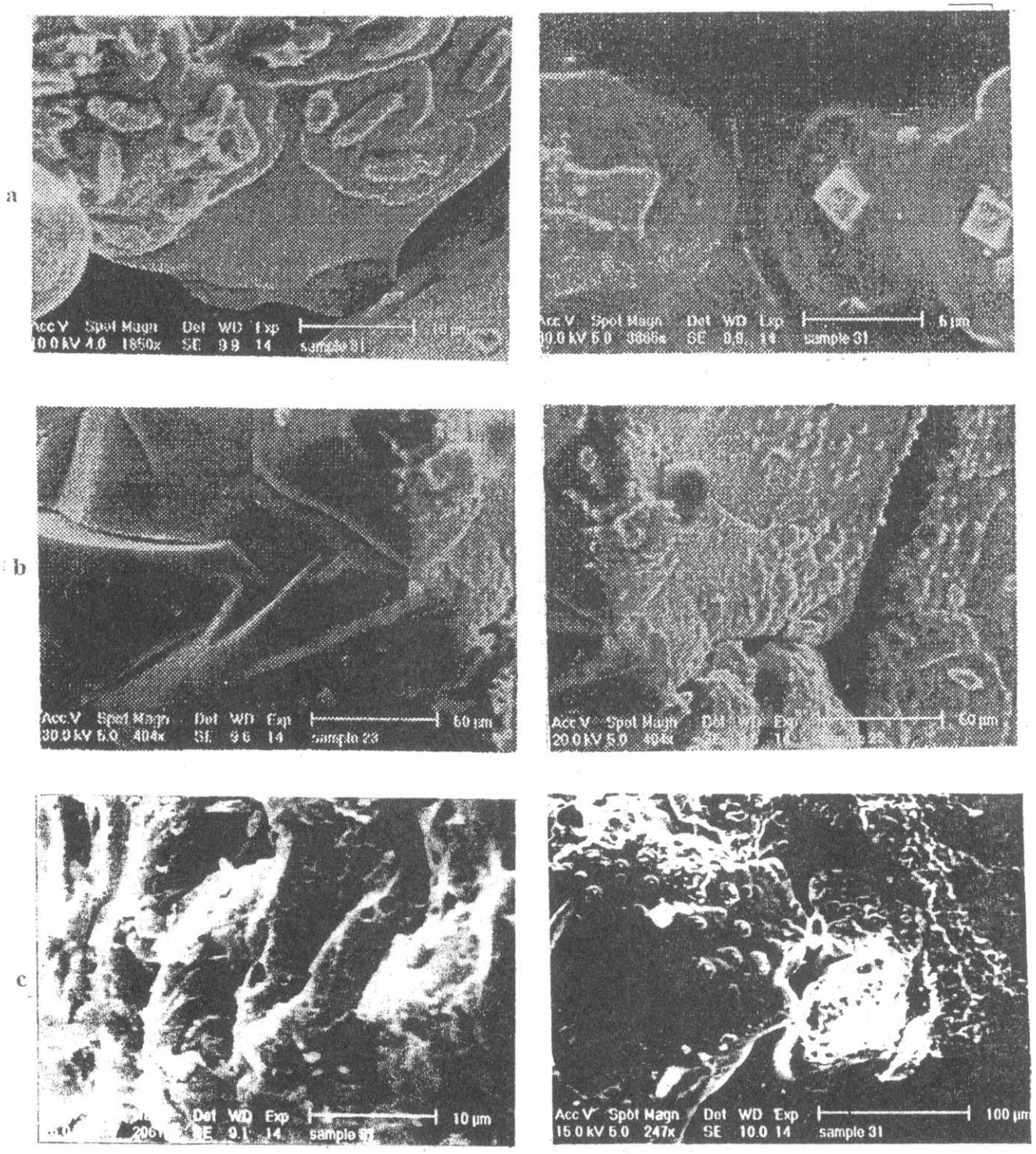

Fig. 7: SEM of different catalyzed samples calcined at 900°C

a - HNO3 b - H3PO4 c - CH3COOH