CLAY BASED TOUGH CERAMIC MATERIALS

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By
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Certificate

This is to certify that the thesis entitled **Clay Based Tough Ceramic Materials** is an authentic record of the research work carried out by Miss. Yamuna. A., under our supervision at Regional Research Laboratory (CSIR) in partial fulfilment of the requirement for the Degree of Master of philosophy in physics of the University of Kerala and further that no part thereof has been presented for any other degree.

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Declaration

I, Yamuna, A., hereby declare that this thesis entitled **Clay based tough ceramic materials** is based on the original work done by me in the Regional Research Laboratory, Thiruvananthapuram and that no part thereof has been presented for the award of any other degree.

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(Yamuna, A.)

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Preface

This work is purely based on "refractories" which is an advanced branch of ceramics and deals with the properties of refractory ceramic materials. The quality of refractory matrials is governed by many factors like the composition and purity of raw materials, the processing technology and the firing schedule. The major factor affecting the final properties is the first parameter. For the sake of economy, usually natural raw materials are used wherever possible. In the present work, two different compositions of tough ceramic materials derived from china clay have been compared: one toughened with olivine and the other with lithium carbonate. The sintering studies of these two compositions were carried out at temperatures ranging from 1150–1350°C. The phase changes taking place during sintering have been identified by X-ray analysis. The first composition of china clay and olivine in the ratio 3:1 gives rise to mullite-cordierite composite while 5% addition of lithium carbonate indicated mullite-spodumene composite formation. The samples were tested for crushing strength, flexural strength, firing shrinkage, plasticity and thermal shock resistance. The microstructure studies were carried out with the help of SEM. Both the compositions made from china clay have got excellent thermal shock resistance and hence recommended for applications where low thermal expansion is needed.

Introduction

Ceramic materials are considered to be substances which are composed of compounds of metallic and non-metallic elements [1]. They predate metals. Archeologists found glass and brick to be among the earliest man made materials. Ceramics are better dielectrics and are more stable than metals in both chemical and thermal environments. Both ceramic and organic materials crystallise less easily than metals. Ceramics exhibit more rigidity and less plasticity compared to metallic materials.

Ceramics are materials consisting of phases. Structurally, ceramics are crystals bonded together; crystalline ceramics are either single compounds or mixtures [2]. They have made essential contributions in many other sectors of industrial society as well. The rapid production of textiles made of synthetic fibres has been made possible by the advent of thread guides of alumina and other ceramic raw materials [3]. Now a days, ceramic products influence our lives in many ways, as shown in **Fig. 1**.

Pottery and porcelain vessels, glass and cement are only among the more familiar. Technologically advanced applications include the magnets in television sets, optical fibres for telecommunications, automobile spark plugs, and the insulators for furnaces. They are widely used in electronics, not only as magnets and as insulators, but also as heating elements and substrates for integrated circuits. As engineering ceramics, they appear in ceramic engines and cutting tools. In bioceramics, they are used for artificial teeth and bones. Table I [3] presents a breakdown of ceramic types by their properties and uses.

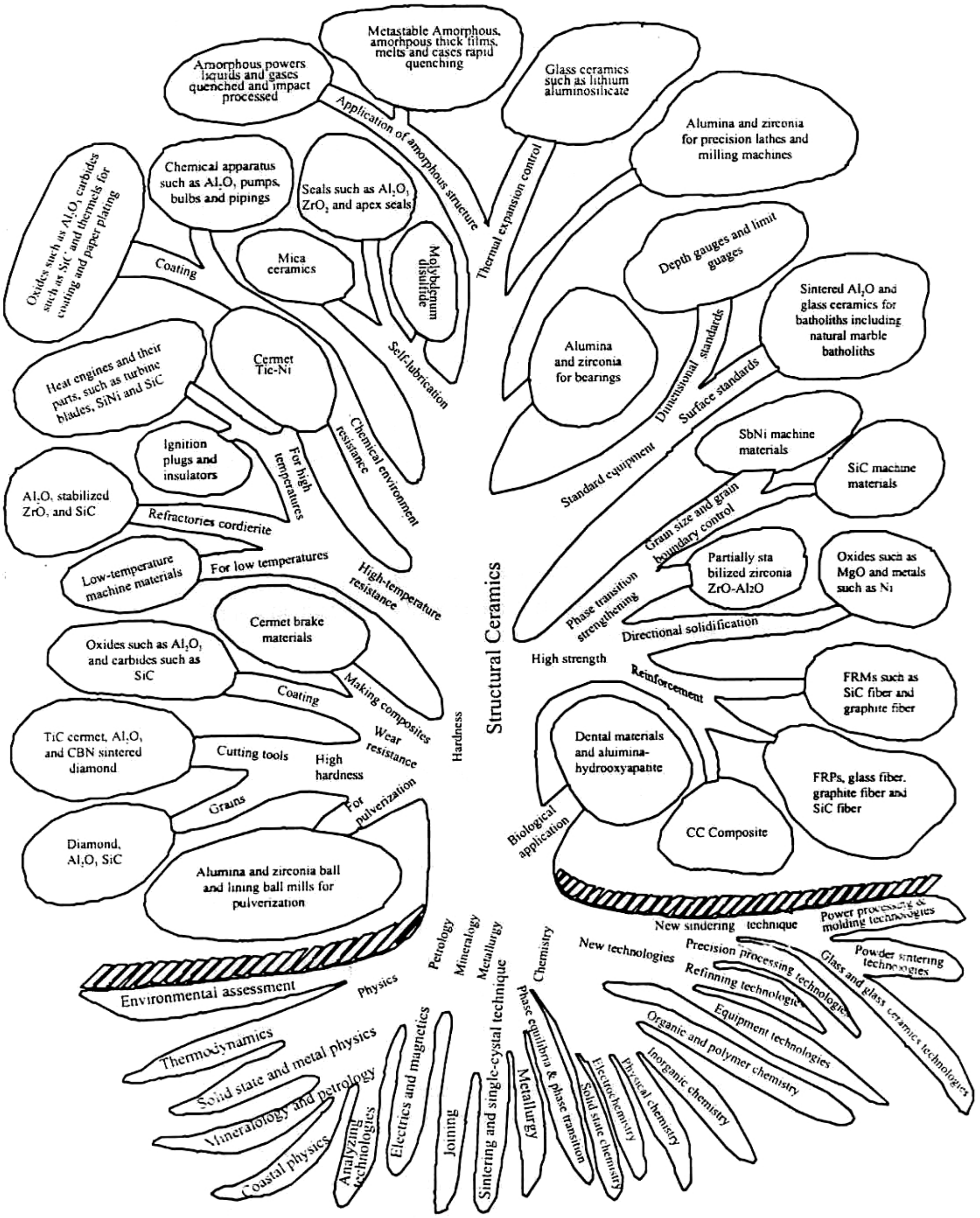


Fig. 1. Structure of basic and applied ceramics

Table 1

Field	Properties	Uses
		Optics, electronics, magnetism
Electroceramics	Good insulating property	Integrated circuit packages, integrated circuit substrates, heat-radiating insulating substrates
	Piezoelectric property	Radiators, ignition components, radio wave filters, piezoelectric transistors, ultrasonic devices electronic lighters, elastic surface wave components, electronic-clocks
	Electronic radiation property	Hot cathodes for the electron gun in television tubes, thermionic devices, electron microspheres, electron-beam welding, heat direct power generators
	Semiconductor sensor properties	Resistance heating elements (high-temperature electronic furnaces), humidity sensors, thermistors (temperature control devices), voltage-dependent resistors (varistors), self-regulating resistance heating elements (in electronic rice cookers, bedding dryers, or hair dryers), gas sensors (gas leak detectors)
	Ionic conduction properties	Oxygen sensors (air/fuel ratio control devices in automobile engines), blast furnace controls
Optoelectro-ceramics	Fluorescence	Fluorophors, materials used in color television tubes
	Polarization	Electrooptical polarization components
Optoceramics	Transparency	Transparency with heat resistance and corrosion resistance (high-voltage sodium lamps), spy holes for kilns, windows for nuclear reactors, transparency to visible light (nonfogging glass)
Magnetic ceramics	Soft magnetism	Memory components for computers, magnetic cores for transformers, magnetic tape, magnetic disks.
	hard magnetism	rubber magnetics, stereo pickups, magnetic heads, magnetic cash cards, magnetic door seals for refrigerators
Thermal properties	Thermal conductivity	Insulating (radiating) substrates for integrated circuits
	Thermal insulating property	Heat-resistant insulators, lightweight insulators, fireproof wall materials, energy-saving furnace materials
	Heat resistance	Heat-resistant structural materials, high-temperature reactor materials, high temperature furnaces, fusion reactor materials, nuclear reactor materials
Mechanical Properties Engineering ceramics	High strength resistance to abrasion, no expansion and contraction	Ultraprecision all-ceramic lathes and machine tools, measuring instruments, and wire drawing dies

	High strength, heat resistance	High performance, highly efficient automobile engines, gas turbine vanes, diesel engines, Stirling engines, heat-resistant tiles for the space shuttle, Automobile parts, manmade satellite parts, rocket fuselages, airplane fuselages
		Biological and chemical
Bioceramics	Bone compatibility (replacement for bone material)	Artificial bones, artificial teeth, artificial joints (surgical knives)
	Corrosion resistance	Physics and chemistry apparatus, chemical engineering apparatus, nuclear power-related materials, linings for chemical apparatus

One of the most widely used ceramic raw materials is clay. This inexpensive material is found in great abundance in nature. Another reason for its popularity lies in the ease with which clay products may be formed. Most of the clay based products fall within two broad classifications: the structural clay products and whitewares [4]. The former include building bricks, refractories, tiles, sewer-pipes etc. *i.e.,* applications in which structural integrity is important. The whiteware ceramics include mainly tableware, and sanitaryware.

According to the functions and properties, ceramics are divided in to pure oxide ceramics, refractories, and cementing materials. Of these, the refractory ceramics are produced and consumed in large tonnages [5]. The salient properties of these materials include the capacity to withstand high temperatures without melting or decomposing, and the capacity to remain unreactive and inert when exposed to severe environments. Also, they have the ability to provide thermal insulation [5]. The performance of a refractory ceramic, to a large degree, depends on its composition. The refractory properties of a product depend on both. the major crystalline phase having high melting point and the presence of small amounts of mineral phases of lower melting points which reduce the refractoriness of the product. It is obvious, that the numerous industrial processes involving different types of furnaces which running under diverse operating conditions require refractories of various compositions and properties [6]. This industry requires specialized refractories to be used as saggers in kilns. Most of the kiln furniture is made of cordierite, mullite or silicon carbide. Basic requirements for kiln furniture are refractoriness, thermal shock resistance, hot strength and long service life [5]. The growing demand for high performance kiln furniture has led to development of special kiln furniture materials. Cordierite and spodumene are the most important among them.

Cordierite does not exist as minable deposits in India. Occurrence of cordierite along with kyanite and sillimanite is present in metamorphic rocks are available in the Edukki District of Kerala. The stable high temperature phase (α) occurs in nature and in ceramic masses, but ceramic cordierite is always a synthetic product. The mineral cordierite ($2MgO2Al_2O_35SiO_2$) is the only three componet compound in the triaxial system $MgO - Al_2O_3 - SiO_2$.

Spodumene is a lithium aluminosilicate having the general formula $Li_2O.Al_2O_3.-4SiO_2$. This is the most important sources of lithium. It is mined by Foote Mineral Company and Lithium Corporation of America, of North Carolina [7]. The discovery that certain bodies in the field $Li_2O - Al_2O_3 - SiO_2$ have respectively, very low, zero or negative expansion coefficient provide a tremendous step forward in producing items of high thermal shock resistance of any desired expansion coefficient [8].

The objective of the work is to prepare toughened ceramics from kaolinite which is a cheap raw material for refractories. Two different compositions with kaolinite were prepared: one with olivine and the other with lithium carbonate. The samples were sintered at a temperature ranging from 1150 to 1350°C and the sintered phases were found to be mullite cordierite composite for the former and mullite-spodumene composite for the latter. The phase changes were studied qualitatively with the help of X-ray diffractogram. The microstructure studies on composites were done by scanning electron microscopy (SEM). The physical, thermal and mechanical properties of both compositions at different temperatures were studied by destructive test methods.

CHAPTER 1

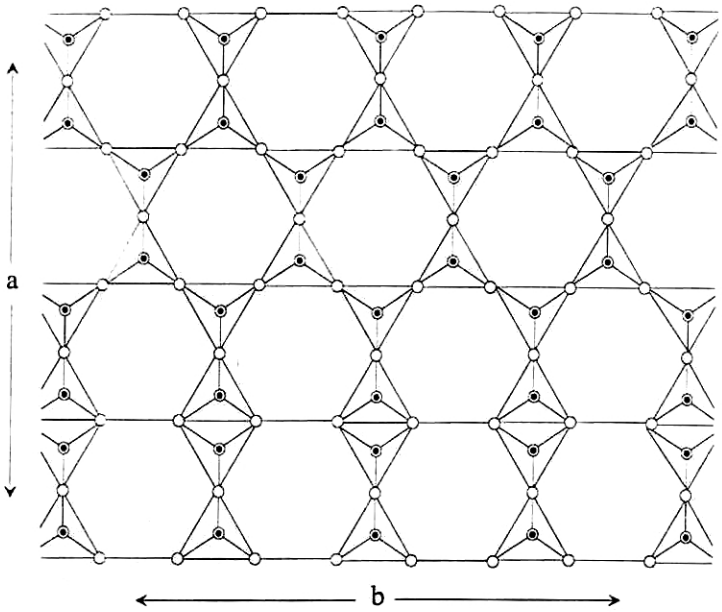
Characterization of Raw Materials

Clays are sedimentary particles on the earth's crust produced by the alteration of feldspatic type of rocks. There are two main groups of clay mineral: the kaolins and montmorillonites. The kaolin group includes kaolinite, nacrite, dickite and halloysite. Of all these, kaolinite is the most important since it is the principal constituent of china clay, ball clay, fire clay and brick clays. It will not be wrong if we say that kaolinite is the backbone of ceramic industry [6].

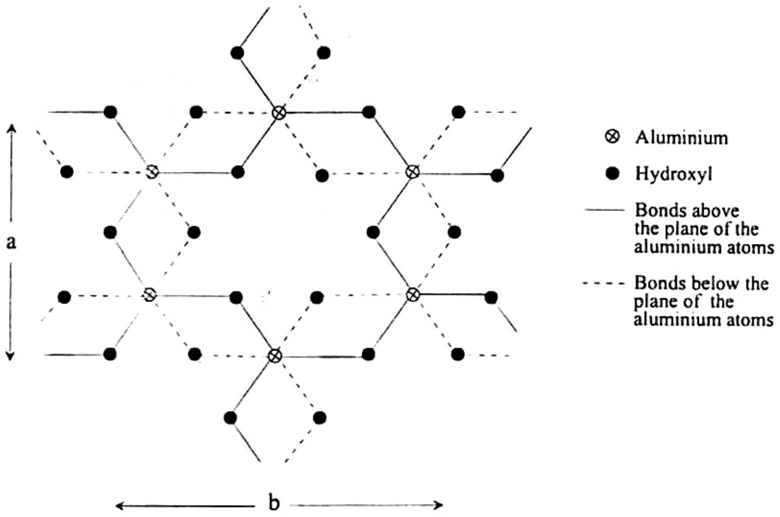
1.1 Kaolinite

Kaolinite is composed of one silica layer and one gibbsite layer in each sheet, resulting in the formula $Al_2[Si_2O_5(OH)_4]$. Due to this combination of layers, kaolinite is termed a one to one (1:1) mineral.

The combination of silica layer and gibbsite layer is electrically neutral and all valencies are satisfied. The link between the kaolinite sheets is achieved by Van der Waals forces, supported by hydrogen bonds between the hydroxyl groups in the gibbsite layer and the oxygen in the silica layer of neighbouring sheet [9]. In ceramic materials, there are two main structural and behavioural consequences of the Van der Waals forces of attraction: (1) they serve as the loci for plastic slip (eg. in clays); and (2) they serve to promote physical adsorption of atoms, ions, or molecules on to solid (and liquid) surfaces [1]. A number of kaolinite sheets are stacked together in this way, forming hexagonal platelets which are typical of kaolinite. The structure of kaolinite is as shown in **Fig. 2**.

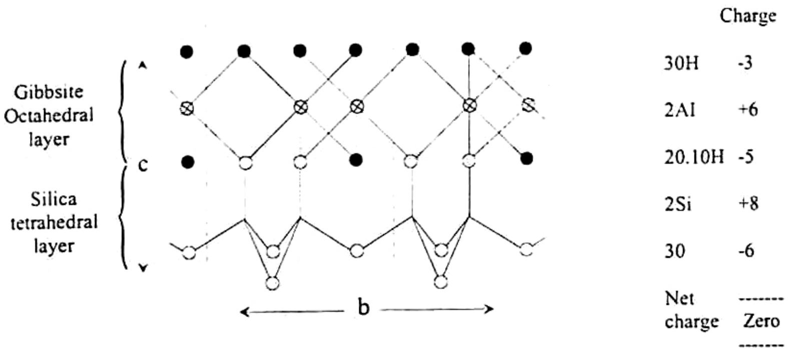


The $[Si_2O_5]_n^{2n-}$ tetrahedral silica layer

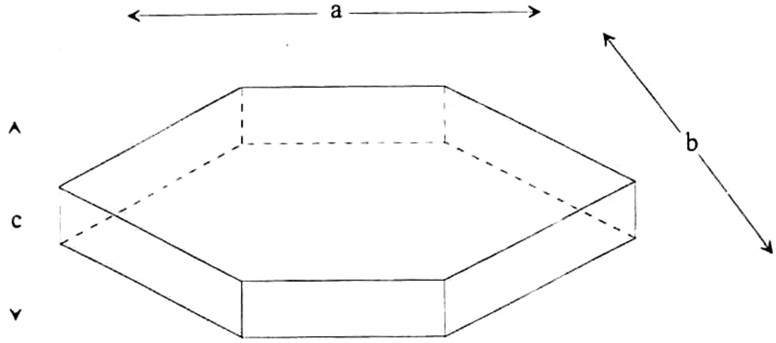


The $n[Al(OH)_3]$ octahedral gibbsite layer

Fig. 2. Structure of kaolinite



The combined tetrahedral and octahedral layers. The structure of the kaolin minerals $Al_2(OH)_4.Si_2O_5$



Hexagonal clay crystallite composed of many stacked layers of kaolin sheets. The crystal is long and wide compared to its thickness

Fig. 2. Structure of kaolinite (contd...)

1.2 Olivine

Olivine belongs to a small group of raw materials which can be used without prior calcination in the manufacture of refractory products. The huge reserves of olivine available in the world, mainly in Norway [10] and its use in natural condition means that it is relatively a low cost refractory material. Olivine consists of about 93% Forsterite (Magnesium orthosilicate) and 7% Fayalite (Iron orthosilicate) [11]. There are large deposits of different quality in Norway, Sweden, Austria, Albania, USA and the former Soviet Union [12]. Because of its relatively high heat capacity and relatively low cost, olivine is one of the most attractive material for refractory ceramics [13].

Olivine ($MgFeSiO_4$) is a natural mineral consisting of a solid solution of approximately

93% Forsterite (Magnesium orthosilicate- Mg_2SiO_4)
6% Fayalite (Iron orthosilicate- Fe_2SiO_4)
0.5% Chromite + Spinel + Magnetite
0.5% Chlorite + Actinolite + Serpentine

It is rhombic in crystal structure and olive-green or greyish green in colour. It is available as a byproduct from magnesite mines [14]. The specific gravity of olivine varies from 3.26–3.40. It has got a hardness of 6.5–7.0 (Mohs' scale). The index of refraction ranges from 1.662 to 1.699. Melting point of olivine is at 1380°C [15].

1.3 Olivine–Physical properties

- High refractoriness
- High heat conductivity
- It has got a good cooling ability
- It has a high resistance to thermal shock which gives durability
- Olivine is basic in nature, and will not react with manganese
- It has a much faster cooling rate than silica.
- Olivine has a lesser thermal expansion rate than quartz
- Low cost refractory material
- Non-hazardous to health

- Free from hydration
- High chemical and mineralogical stability due to strong forsterite binding.
- High resistance to metal penetration.

Typical Chemical composition of Olivine

MgO	-	45–49%
SiO_2	-	37–41%
Fe_2O_3	-	8–12%
Cr_2O_3	-	0.4%
Al_2O_3	-	0.5–2%
NiO	-	0.35%
MnO	-	0.10%
CaO	-	1.34%

1.4 Applications of Olivine

- In the production of manganese and high alloy steels.
- It is used as a refractory mineral in castables and soaking–pit aggregates and tundish liners.
- In refractory incinerators
- It is used as a flux and slag conditioner in blast furnace.
- In foundry, industry, it is used for casting brass, bronze, aluminium, magnesium, titanium and iron.
- Because of its high acid demand value, olivine is best used in systems that used sodium silicate or clay binders.
- In agriculture, it is used to produce magnesium phosphate.
- It is used as a ballast in oil drilling rigs and in the coating of under sea oil and gas pipelines [16].

1.5 Olivine applications–chart diagram

A chart diagram which shows the applications of olivine is as shown in **Fig. 3** [14].

OLIVINE-$(Mg, Fe^{2+})_2SiO_4$ SERPENTINE-ROCK, LARGELY-$Mg_6Si_4O_{10}(OH)_8$

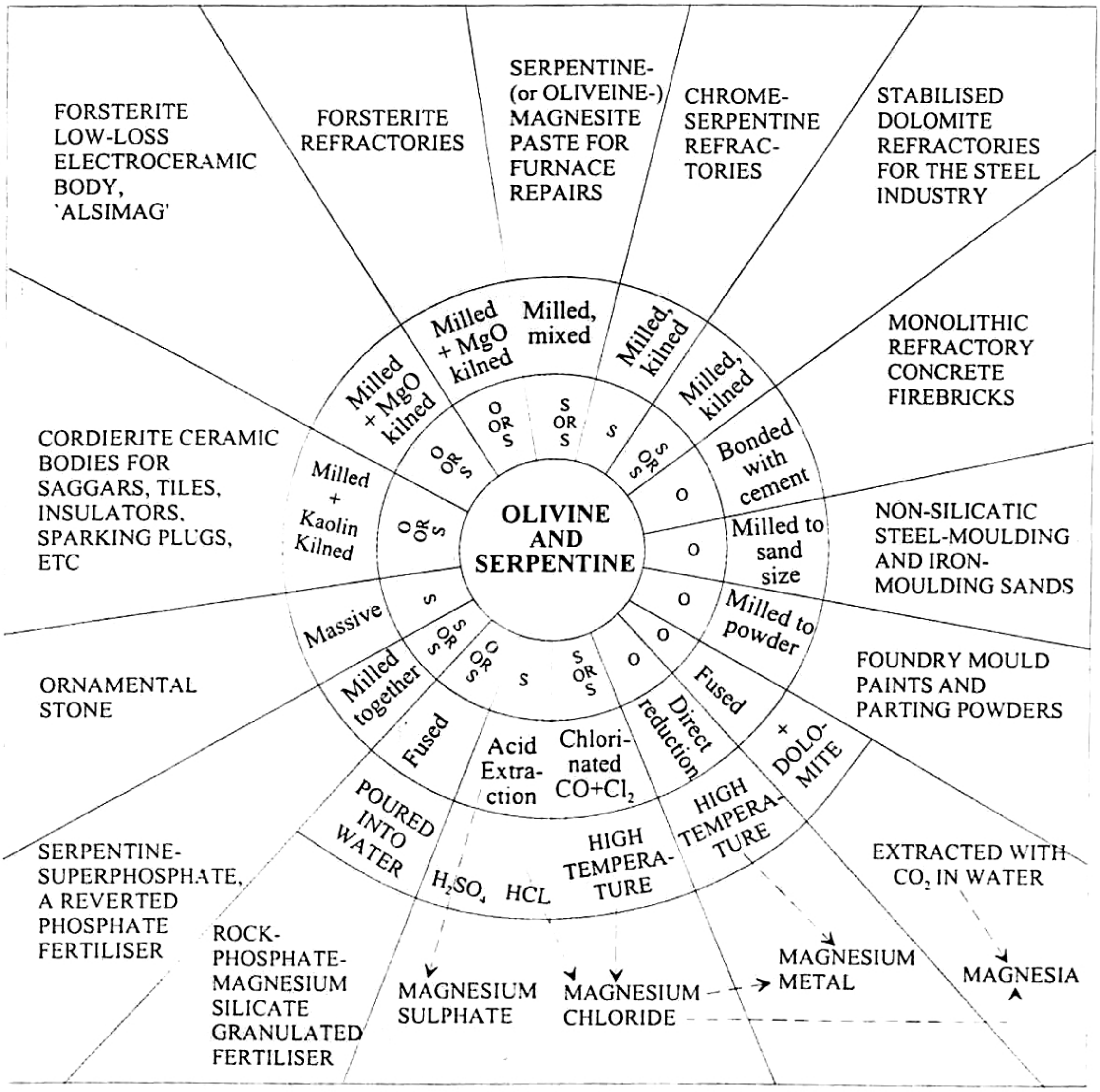


Fig. 3. APPLICATIONS OF OLIVINE

1.6 Cordierite

Cordierite are dense bodies of very low thermal expansion and therefore very high thermal shock resistance [8]. They are difficult to glaze successfully. Suitable for high-frequency and high-tension applications. Cordierite occurs in nature as a rare mineral. It constitutes the phase found in the centre of the triaxial diagram of cordierite as shown in **Fig. 4**.

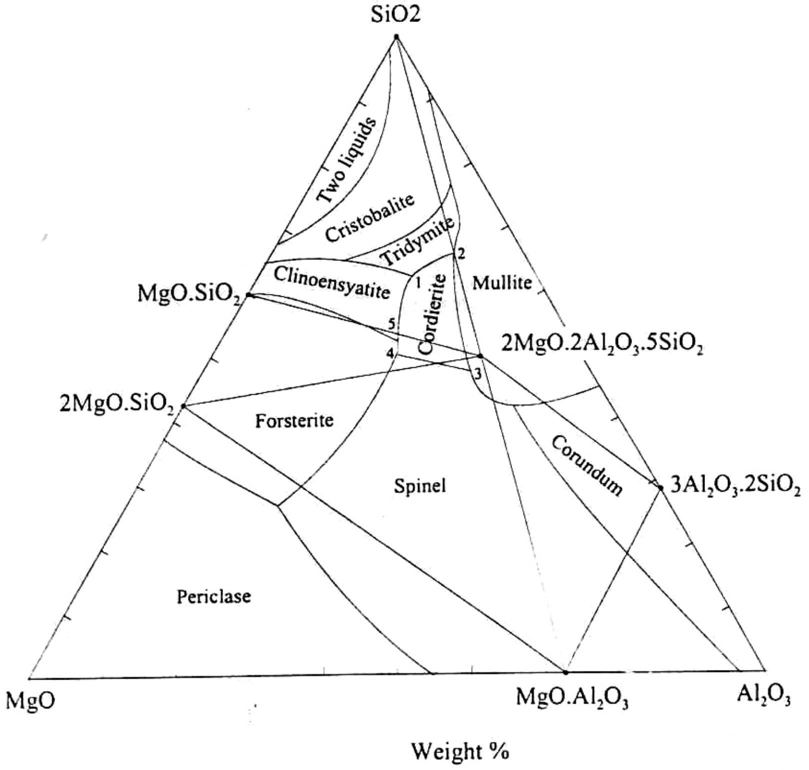


Fig. 4. Phase diagram of cordierite

Cordierite shows polymorphism; three forms having been recognised. Of these, α-form is the stable high temperature form and the only one normally found in nature or obtained in ceramic bodies. β and μ cordierites can only be formed under special conditions. **Fig. 5** shows the variation of expansion coefficient of cordierite with the firing range.

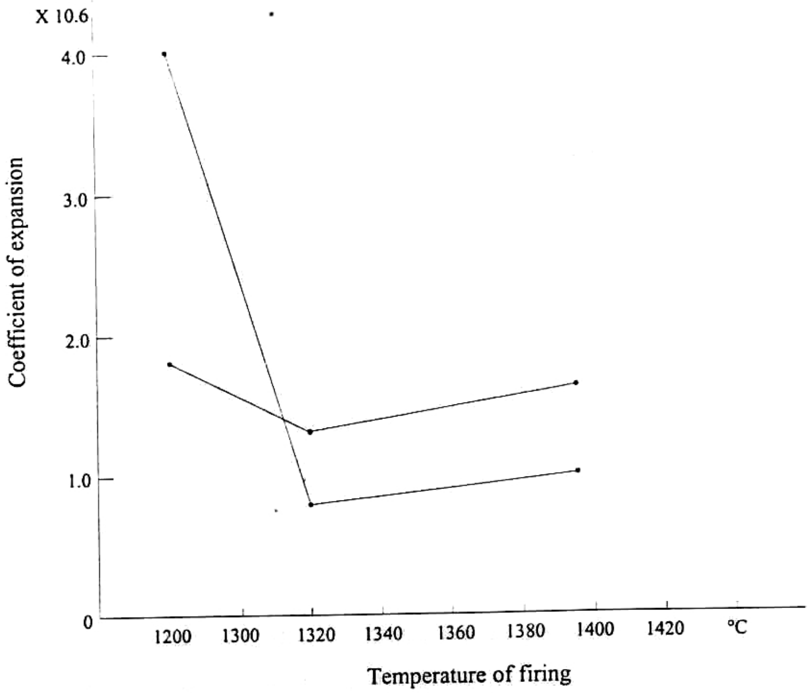


Fig. 5. Expansion coefficient vs. firing range of cordierite

The development of cordierite in a ceramic body cannot be achieved unless equilibrium is rarely reached during ceramic firing [8]. Bodies of high cordierite content inevitably have a short firing range, underfiring (below 1350°C) fails to develop the cordierite and overfiring (above 1450°C) results in deterioration in to foresterite and mullite, both with much higher expansion coefficients. It is easier to produce a porous cordierite body than a vitreous one, both find a number of uses. Some of the uses are mentioned below.

- As kiln furniture
- As resistance wire supports
- To maintain constancy of inductance of the coil
- In electric water-boiler insulators

- In arc chutes, fuse cores etc
- As casings for high currents
- As rheostat blocks and dimmer winding cores
- Resistance bobbing and spools
- Suitable for high-frequency and high tension applications [8]

The most commonly used raw materials for the development of cordierite bond are clay, talc and alumina. Presence of free quartz in the raw materials will adversely affect the thermal expansion property of the body. Lowest thermal expansion is achieved with bodies containing higher cordierite fraction while the more refractory compositions result when mullite content is on its higher side. The fluxing impurities carried over from the stability raw materials play key roles in high temperature performance of the product [8].

Cordierite products show high bending, tensile and compression strength until almost reaching the softening point. They have thermal expansion coefficient of 1.5×10^{-6} per K and excellent thermal shock resistance.

The properties and the structure are considerably dependent upon the material and phase content of the cordierite body as well as upon its production method.

1.7 Specification of Cordierite

Stoichiometric formula	$2MgO$	$2Al_2O_3$	$5SiO_2$ [17].
Composition (mass%)	13.7	34.9	51.4

1.8 Traditional Applications

- Refractory products: Saggers, kiln furniture, gas burners etc.
- Electro ceramics: Resistors, fusibles, flame guard etc.
- Tableware: Flame–proof applications

1.9 Synthetic cordierite from clays

Ceramic products consisting principally of cordierite is always preferred because it has got very low thermal expansion coefficients. The method employing batches comprising a mineral component and a chemical component has been reported by Hickman *et al.* in 1994 (US patent No: 5,332,703) [18]. The mineral component comprising clay and talc and the chemical component consisting essentially of a combination of the powdered oxides, hydroxides or hydrous oxides of magnesium, aluminium and silicon. Ceramics made by extrusion and firing of the batches can exhibit low porosity, high strength and low thermal expansion coefficients. Methods for producing cordierite body having high crystallinity and exhibiting excellent low thermal expansion property in a specific direction at a relatively low firing temperature has been reported by Inoguchi *et al.* in 1983 (US patent No: 4,421, 699) [19]. The method of production was by mixing and kneading a batch raw material containing halloysite particles used as kaolin minerals, and talc particles which are delaminated like particles along the (001) plane, by subjecting the mixed raw material to anisostatic forming such as extrusion forming so as to impart a planar orientation to the platelet shaped talc particles therein and by drying and firing the obtained green body, a cordierite body having high crystallinity was obtained at a relatively low firing temperature.

A modified cordierite ($2MgO.2Al_2O_35SiO_2$) composition in which at least a portion of the silicon dioxide is replaced with germanium oxide has been reported by Bind in 1983 (US patent No: 4, 403, 017) [20]. These compositions have low thermal expansion, excellent formability and thermal shock resistance making them especially suitable for the manufacture of mirror substrates to be used at elevated temperatures. By selecting the proportion of the germanium oxide according to the intended operating temperature, substantially low and even zero thermal expansion can be achieved between room temperature and the selected operating temperature. A low thermal expansion cordiertie ceramic has been reported by Sano in 1985 (US patent No: 4, 495, 300) [21]. It is produced by combining cordierite with zirconium and phosphorous compounds and sintering the resultant mixture thereby giving rise to zircon therein. The cordierite ceramics produced as sintered in the manner described above exhibits thermal expansion totally different from the thermal expansion exhibited by the cordierite ceramics produced by the conventional method. The sintered substance obtained by this method was excellent in dielectric property at a high frequency (1 MHz) and exhibits high dielectric strength at a low frequency (60 Hz).

Cordierite kiln furniture composed of (a) chlorite, china clay and burned clay and (b) chlorite, china clay and sillimanite; or chlorite, clay and burned bauxite were reported by Guner Sumer *et al.* in 1995 [5]. Cordierite thus produced showed an improvement in thermal shock resistance. P. Grosjean *et al.* has been reported that cordierite can be obtained from any raw materials with silica, magnesia and alumina in right proportions [10]. The study of chemical and mineralogical compositions of Egyptian basaltic rocks in order to assess their suitability as an additive for the preparation of cordierite-ceramic bodies has also been reported by Naga *et al.* in 1994 [22]. The research work includes the densification properties and thermal expansion of vitrified cordierite bodies in relation with their phase composition and micro structure.

1.10 Composite from clays

It is often possible to produce a superior material by combining or compounding two or more materials, with properties unattainable in each of them separately. The combination is made up of materials with complementary properties. The materials so produced is termed as composite materials.

Method for producing a polycrystalline body, *i.e.*, a composite ceramic, comprised of a mullite phase and a cordierite phase has been reported by Hodge *et al.* in 1985 (US patent No: 4,528,275) [23]. The body consists of 50% by weight to about 95% by weight of mullite from about 5% by weight to about 50% by weight of cordierite. The production of polycrystalline material comprised of mullite and cordierite is useful as a substrate for silicon with a thermal expansion coefficient identical or close to that of silicon.

Mullite and cordierite are promising materials for electronic packaging due to their dielectric constant and coefficient of thermal expansion being lower than that of alumina. The mullite-cordierite composites prepared using magnesia containing 10–50 wt% of cordierite and another batch prepared using magnesium nitrate were reported by Gopichandran *et al.* in 1995 [24]. The surface area and bulk density of the reported mullite–cordierite composite increased with increase in cordierite content. Cordierite powders can also be obtained by the combustion process. Combustion synthesis of cordierite Cor-I and Cor-II has been reported by K. C. Patil *et al.* in 1993 [25]. Cor-I was prepared by the combustion of an aqueous heterogeneous mixture containing magnesium nitrate, aluminium nitrate. silica fume, ammonium nitrate and urea in the ratio 1:2: 2.5: 9.5: 10 respectively at (525±10°C). The coefficient of combustion derived cordierite were comparable with those of sol-gel derived cordierite.

The ceramic industry normally produces cordierite in situ during firing. This system has several draw backs [17].

- High shrinkage and deformation of the product
- Narrow firing range (under firing/high expansion, overfiring/deformation)
- The reaction temperature is high
- At high temperatures the cordierite bodies colour seriously; this limits non-technical uses

1.11 Lithium in Refractories

Many industrial ceramics must perform under conditions of sudden temperature changes. If, during these temperatute changes, the stress set-up exceeds the strength of the material, failure will occur. For resistance to thermal shock, the thermal expansion coefficient is the most important property of a material. The lower the thermal expansion, the better the thermal shock resistance. The first commercial application of low expansion ceramic parts made from lithium aluminosilicates was the material *stupalith* made by Stupakoff Ceramic and Manufacturing Company in Latrobe, Pennsylvania. The application was proposed for turbine blades, jet turbines, combustion engine parts, nozzle inserts, pouring ladles, electronic insulators, and laboratory combustion boats [7]. Synthesis of lithium aluminosilicates has been preformed by many investigators with a view to determining the refractoriness and thermal expansion of materials possessing various molar ratios of the oxides. For many forming operations, clay is an essential component. Clay can increase the refractorines of lithium aluminosilicates. Low *et al.* in 1996 reported that spodumene can be used as a flux and a filler for cost-effective processing of mullite ceramics [26].

The principal objective of the present work is to produce clay based tough ceramics using different fluxes viz. lithium carbonate and olivine. The sintered materials formed were found to be mullite-spodumene and mullite-cordierite composites by X-ray diffractogram studies. A comparative study on their compressive strengths, modulus of rupture and thermal shock resistance were carried out at temperature varying from 1150 to 1350°C.

CHAPTER 2

Properties and Behaviour of Ceramic Substances

Ceramic materials have many engineering structural applications and hence response of these materials under mechanical and thermal stresses is of vital importance.

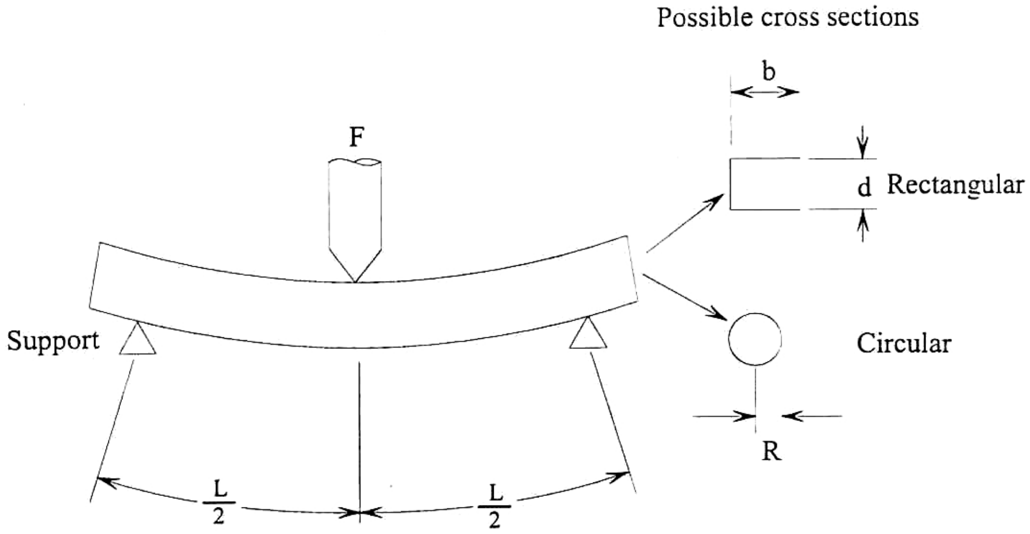
The physical and mechanical properties of ceramics stem from their atomic binding and crystal structure. The mechanical properties are characterised by the lack of plasticity, high hardness and stiffness and good compressive strength [27]. The strength of sintered ceramics is mainly due to the attractive forces between the molecules which is attained by the compactness of the crystals. The strength of various ceramic materials varies on firing depending on the raw materials used, manufacturing process and conditions employed [28].

As many ceramics are used at high temperatures, their ability to withstand thermal shock is of great importance. Thermal stresses arise from several causes. Non-cubic materials may have anisostatic coefficients of thermal expansion; change in temperature will produce thermal stresses between the grains which may lead to fracture [27].

2.1 Mechanical Properties–Theory Behind it

2.1.1 Modulus of Rupture (Flexural strength)

Mechanical characteristics of materials can be ascertained by stress-strain tests. Representative strengths of ceramic materials are determined by performing trans-



$$
\begin{aligned}
\sigma &= \text{Stress} = \frac{M_c}{l} \\
\text{where } M &= \text{Maximum bending moment} \\
c &= \text{Distance from center of specimen to outer fibers} \\
I &= \text{Moment of inrtia of cross section} \\
F &= \text{Applied load}
\end{aligned}
$$

	M	c	I	σ
Rectangular	$\frac{FL}{4}$	$\frac{d}{2}$	$\frac{bd^3}{12}$	$\frac{3FL}{2bd^2}$
Circular	$\frac{FL}{4}$	R	$\frac{\pi R^4}{4}$	$\frac{FL}{\pi R^3}$

Fig. 6. A three-point loading scheme for measuring the stress-strain behaviour of MOR of ceramics

verse bending tests to fracture since there is a significant difference in results obtained from tests conducted in compressive and tensile modes [4].

In this method, a rod specimen having either a circular or rectangular cross-section is bent until fracture using a three-or-four-point loading technique. The three-point loading scheme is illustrated in **Fig. 6**.

At the point of loading, the top surface of the specimen is placed in a state of compression, where as the bottom surface is in tension. Stress is computed from the specimen thickness, the bending moment and moment of inertia of the cross-section. The maximum stress or stress at fracture during bend test is known as the modulus of rupture (flexural-strength) which is an important mechanical parameter for brittle ceramics. For a rectangular cross-section, modulus of rupture

$$\sigma = \frac{3wl}{2bd^2}$$

where w is the load at fracture,

l the span length

b the breadth and

d the thickness of the specimen

When the cross-section is circular,

$$\sigma = \frac{wl}{\pi r^3}$$

r being the radius of the specimen.

During bending, a specimen is subjected to both compressive and tensile stresses, the magnitude of the modulus of rupture is greater than the tensile fracture strength.

The factor which influence the flexural strength of ceramic substances are the shape and size of the test specimen, and the effect of temperature.

2.1.2 Effect of shape and dimension of the test specimen

The specimen cross-section has an effect on the measured values for its strength. In general, test specimens which are thick near the neutral axis have greater flexural strength than do thinner ones. That is, a round rod shows greater strength than a square one, which in turn shows greater strength than an I-shaped rod [29].

For brittle materials such as ceramics, the scale effect has a considerable effect upon the strength of the test specimens. The influence of size upon breakage is a question of the probability of the presence of defects: thus test specimens with large dimension display lower strength than do smaller pieces. Equations (1) and (2) express the relationship between scale and strength using effective volume and effective surface area.

$$\sigma_{f_1} = \left(\frac{V_{E_2}}{V_{E_1}}\right)\frac{1}{m\sigma_{f_2}} \tag{2.1}$$

$$\sigma_{f_1} = \left(\frac{S_{E_2}}{S_{E_1}}\right)\frac{1}{m\sigma_{f_2}} \tag{2.2}$$

where V_{E_2}/V_{E_1}, is the effective volume ratio, S_{E_2}/S_{E_1}, is the effective surface area ratio, and m the Neibull coefficient [4].

The most important problems in measuring compressive strengths are

(i) non-parallel specimen ends or loading heads and

(ii) specimen-interface (end constraint) problems. [30].

2.2 Thermal Properties

Elevated temperatures play an important part in ceramic production. Thermal treatments result in weight and volume changes, promote atom movements and accentuate diffusion rates, reduce porosity and surface areas and change properties.

2.2.1 Drying

Drying is an engineering process. The drying shrinkage of a clay body is an important characteristic because it largely governs the maximum safe rate of drying [31]. During the process of drying, the body will shrink in volume equivalent to the volume of water lost until the particles touch, and thereafter air must enter the pores to take the place of water. As the drying proceeds, more and more of the water is converted inside the structure in to vapour, making it necessary for this to travel out through the nearly empty capillaries to the surface. In **Fig. 7** an attempt

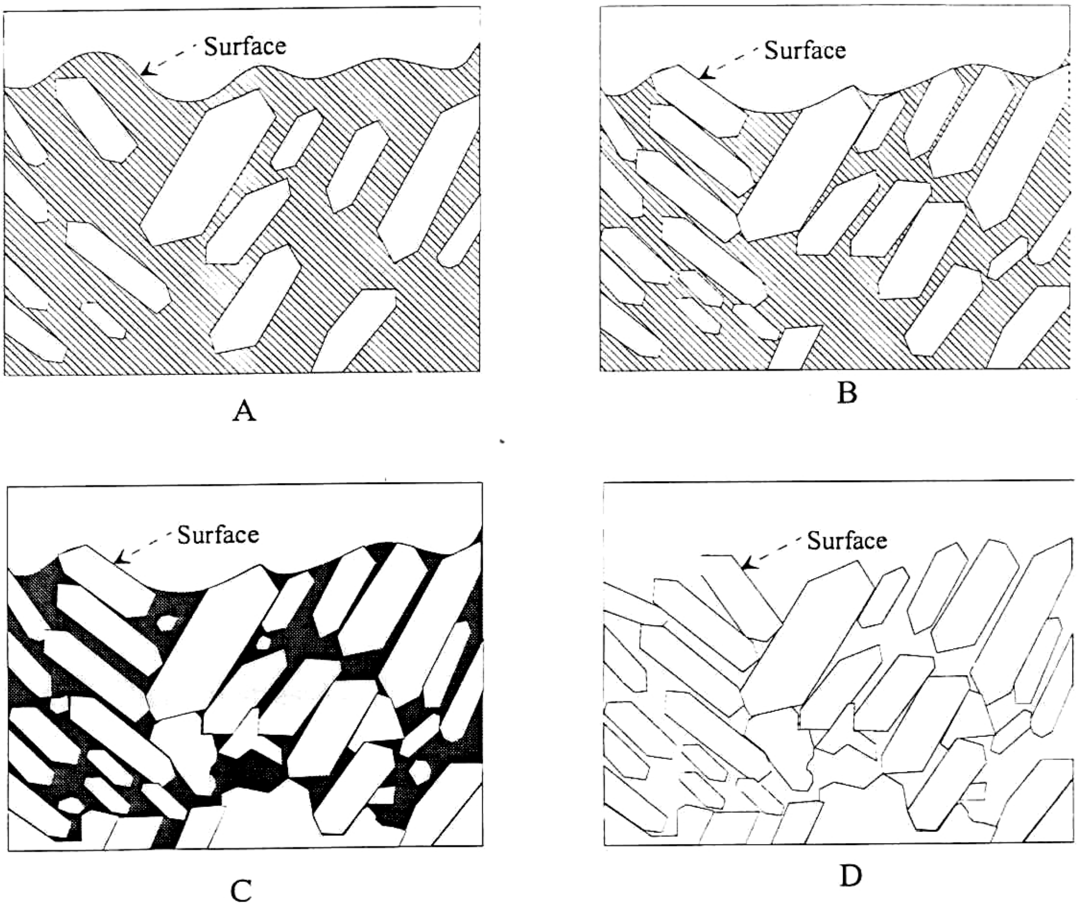


Fig. 7. Enlarged section drawing of clay at various stages of drying

has been made to show how an enlarged section of the clay would look at various stages of the drying process.

In **Fig. 7A**, the clay particles are well separated by a water film, which also run continuously over the surface. In **Fig. 7. B**, the amount of water has decreased until the particles touch one another, but there is still a continuous surface film, In **Fig. 7C**, the water has decreased until the surface layer is broken and the level receeds in to the capillaries with some air in the structure. In **Fig. 7D**, the water is removed and it becomes dry. **Fig. 8** shows typical drying-rate curve for a clay.

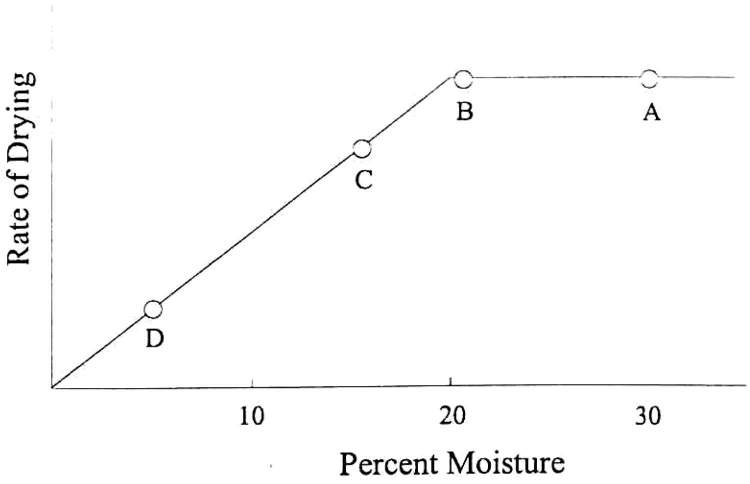


Fig. 8. A typical drying-rate curve for a clay

2.2.2 Thermal stresses

Thermal stresses are those induced in a body as a result of changes in temperature. This may lead to fracture or undesirable plastic deformation. The two prime sources of thermal stresses are restrained thermal expansion (or contraction), and temperature gradients established during heating and cooling [3].

When a solid body is heated or cooled, the internal temperature distribution will depend on its size and shape, the thermal conductivity of material, and the rate of temperature change. Thermal stresses may be established as a result of temperature gradients across a body, which are frequently caused by rapid heating or cooling, in that the outside changes temperature more rapidly than the interior; differential dimensional changes serve to restrain the free expansion or contraction of adjacent volume elements within the piece. Hence, surface stresses being compressive, are induced and are balanced by interior tensile stresses. The interior-exterior stress conditions are reserved for rapid cooling, such that the surface is put in to a state of tension. **Fig. 9** shows, thermal stresses formed in a disk and **Fig. 10** shows thermal stresses in a brick heated at one end [31].

2.2.3 Thermal shock (Spalling) resistance

The resistance to thermal shock of ceramic materials is a highly complicated property [8]. Thermal shock is the fracture of a body resulting from thermal stresses induced by rapid temperature changes. For a ceramic body that is rapidly cooled, the resistance to thermal shock depends not only on the magnitude of the temperature change, but also on the mechanical and thermal properties of the material. The thermal shock resistance is best for ceramics that have high fracture strengths σ_f and high thermal conductivities, as well as low elastic moduli and low coefficients of thermal expansion. The resistance of many materials to this type of material is approximated by a parameter TSR, the thermal shock resistance.

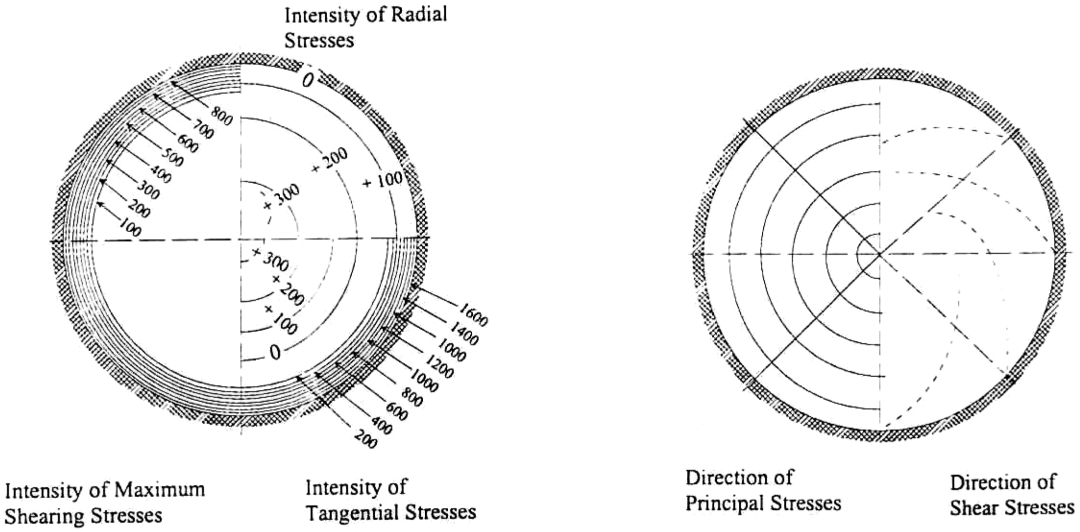
$$TSR = \frac{\sigma_f k}{E\alpha l}$$

E being the elastic modulus, k the thermal conductivity and αl is the linear coefficient of thermal expansion.

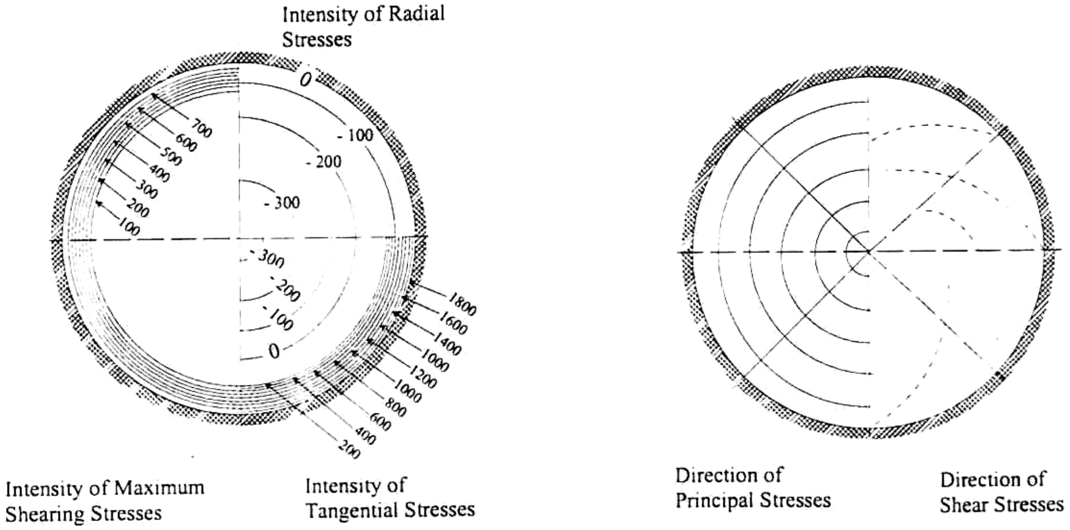
Spalling is due to both shear and tension failures. On sudden heating, spalling is due almost entirely to shear stresses and, on sudden cooling, to tension stresses except at the corners and edges, where shear stresses may still cause failure. The shear values are about equal on heating and cooling, but there are no large tension stresses on rapid heating.

Shear failure occurs suddenly; *i.e.*, complete pieces are split off at each cycle of heating, and they begin to split at the edges and corners, so that the body tends to approach a spherical shape on the end. Tension cracks seldom occur near the corners but usually first appear halfway up the body (eg. brick) where the tensile stresses are maximum. The tension cracks enter the surface at 90°. They do not occur as suddenly as do shear fractures but penetrate deeper and deeper at each cycle until finally the cracks meet at the center. **Fig. 10** shows the cracks developed in a brick due to spalling [31].

Since, the above mentioned important factors-such as mechanical and thermal properties; which measures the toughness of a ceramic body, the experimental work mainly constitute these areas.

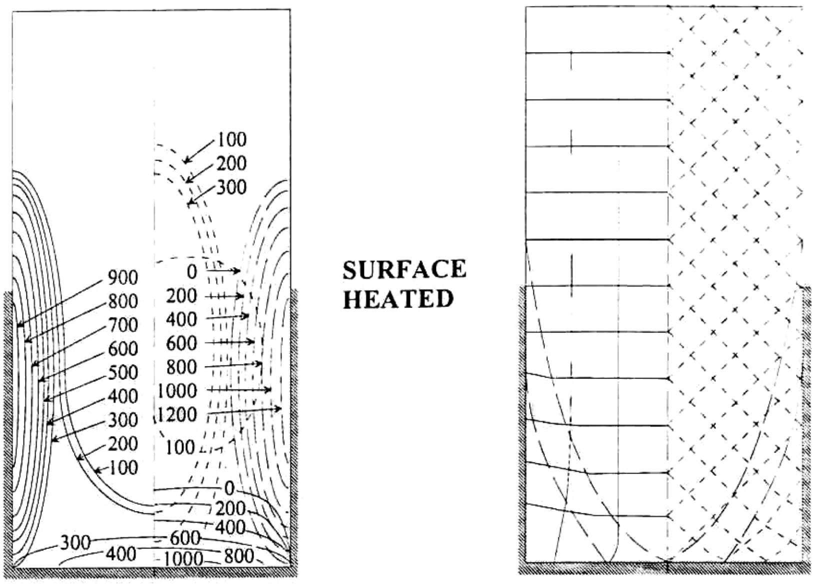


SURFACE COOLED



SURFACE HEATED

Fig. 9. Stresses in a disk

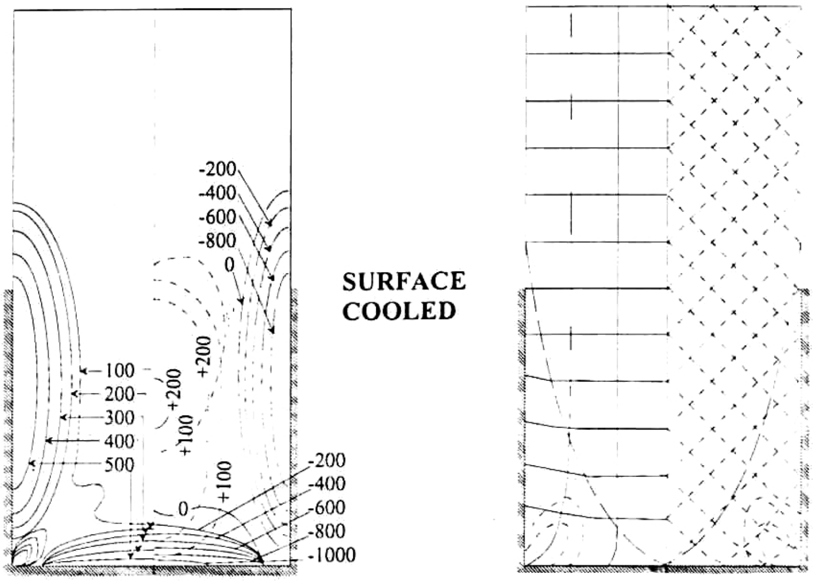


Intensity of Maximum Shearing Stresses

Intensity of Stresses Parallel and Normal to the Center Line

Direction of Principal Stresses

Direction of Shear Stresses



Intensity of Maximum Shearing Stresses

Intensity of Stresses Parallel and Normal to the Center Line

Direction of Principal Stresses

Direction of Shear Stresses

Fig. 10. Thermal stresses in a brick

CHAPTER 3

Experimental: Materials and Methods

3.1 Materials

The major raw materials used for the studies were kaolinite and olivine. Processed (desanded and bleached) kaolinite was supplied by M/s English Indian clays, Kochuveli, Thiruvananthapuram and olivine was supplied by M/s C. G. Gotawat and Co., Bangalore. Olivine was used as the source material for magnesia and clay as the source for alumina and silica. The only one chemical used as the flux material for the studies was lithium carbonate (Li_2CO_3) (AR, 99.5% pure).

Chemical and mineralogical composition of kaolinite is shown in Table 2 and Table 3.

Table 2

Chemical characterization of Kaolinite (wet analysis)

Constituent	% wt
SiO_2	46.00
Al_2O_3	39.00
Fe_2O_3	0.40
TiO_2	0.45
CaO	0.05
MgO	0.05
K_2O	0.03
Na_2O	0.07
LOI	14.00

Table 3

Mineralogical Composition

Constituent	Presence
Kaolinite	Major
Quartz	Minor
Mica	Minor
Graphite	Minor

The wet chemical analysis of olivine sample as shown in Table 3.

Table 4

Chemical Assay of Olivine

Constituent	% wt
MgO	57.2
SiO_2	31.7
Al_2O_3	1.1
FeO	6.4
CaO	2.8
Cr_2O_3	0.1

The mineralogical composition of both kaolinite and olivine were carried out with the help of X-ray diffractogram (Rigaku, Cu k_α radiation, $\lambda = 1.542$ AU). Fig.

11 and Fig. 12 shows XRD patterns of raw kaolinite and raw olivine respectively.

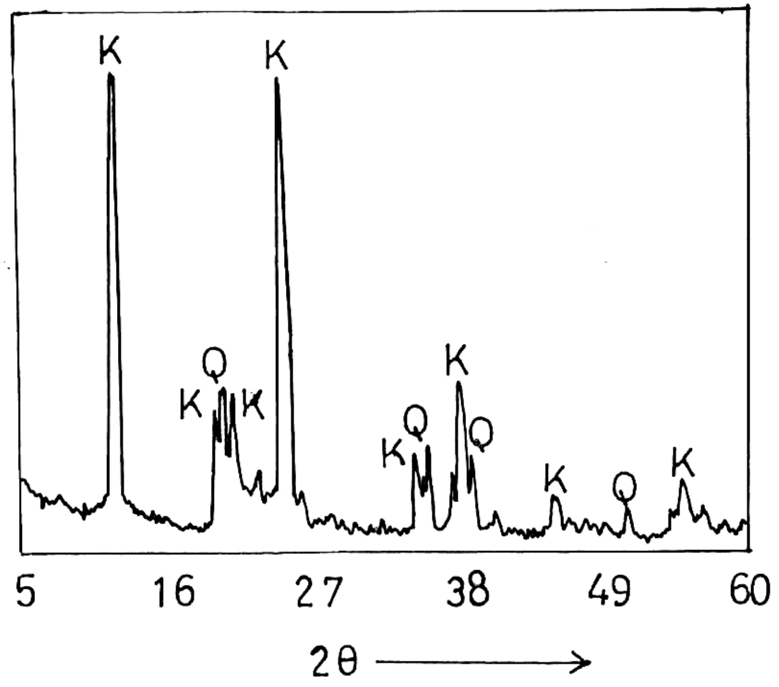
3.2 Batch Formulation

Two different compositions; one from kaolinite and olivine and the other from kaolinite and lithium carbonate, were used for the present study. The flexural strength (MOR) and compression strength were the tests carried out to determine the mechanical strength while thermal shock resistance (spalling resistance) was the test carried out for the thermal efficiency studies. The test specimens for the mechanical and thermal treatments were prepared in the following way.

For first composition, the olivine sand (magnesium alumino silicate) was powdered thoroughly in a ball mill for about 75–90 hours and the minus 350 sieve fraction was collected. A 3:1 combination of kaolinite and olivine K–O (75% kaolinite + 25% olivine) was thoroughly mixed for a period of two hours in a rod mill. The second composition of kaolinite was prepared by the method of wet mixing. A 5% solution of lithium carbonate was prepared and 95% kaolinite was added to it. The mixture was evaporated to dryness and the mix K–L (95% kaolinite + 5% Li_2CO_3) was obtained.

For flexural strength (MOR) measurements of both the compositions of K–O and K–L; the samples were separately made in to hydroplastic mass using distilled water. The quantity of water used during hydroplastic mould preparation was determined by ball-in-hand test for estimating consistency (IS: 110570–1983) [32]. The samples were kept for aging for a period of 48 hours, the mass was extruded through a rectangular mouth piece made of aluminium having dimension (5×10) mm with an approximate length of 100 mm.

Samples for crushing strength measurements were made with great care, in order to avoid shrinkage and distortion that would occur during firing. One of the simplest methods of reducing the firing shrinkage of a refractory body is by introducing a non plastic material such as grog. For this, chamotte of K–O was prepared at 1200°C with a residence time of 1 hour and size separation was carried



FIG·11· XRD PATTERN OF RAW KAOLINITE

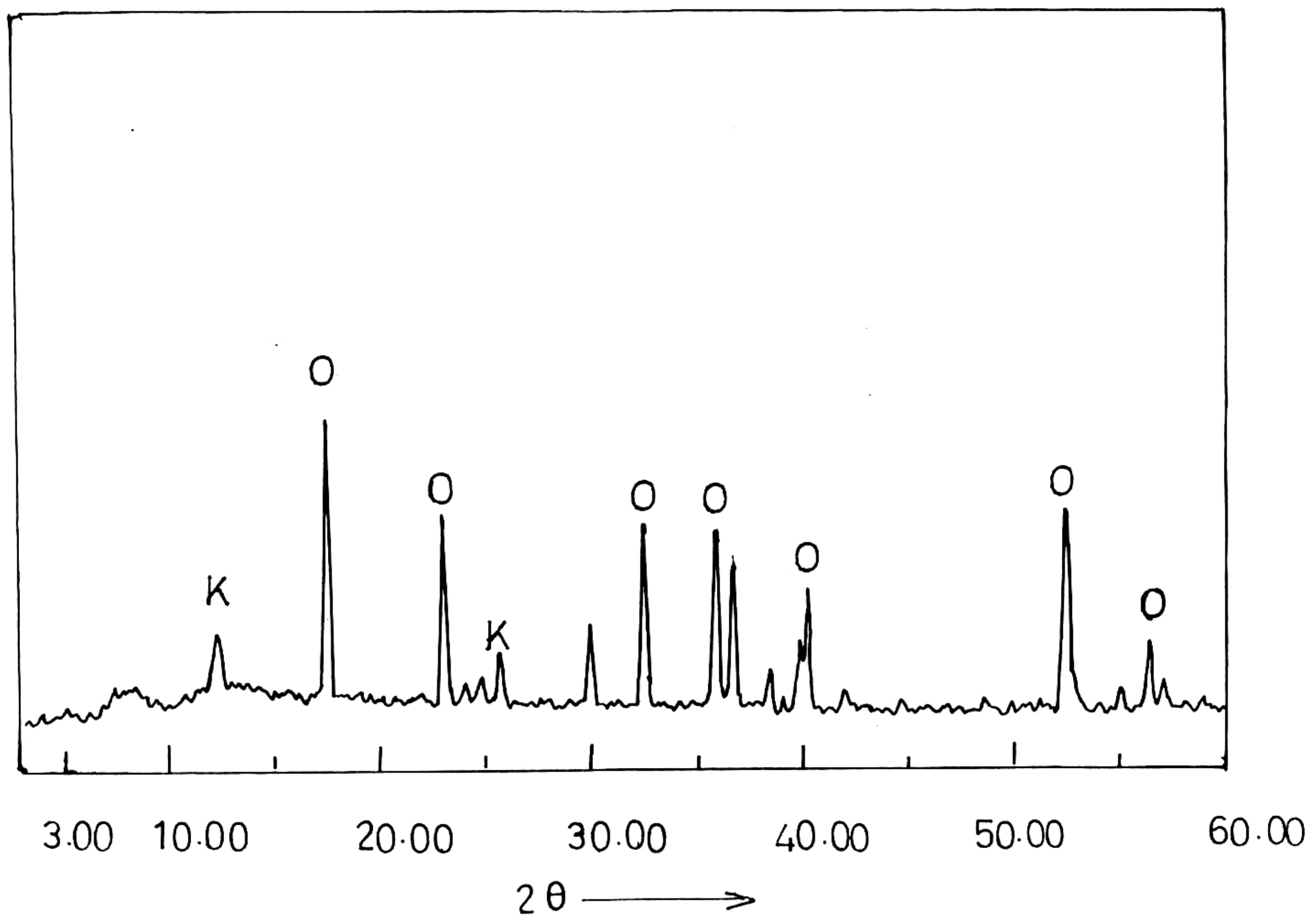


FIG.12. XRD PATTERN OF RAW OLIVINE

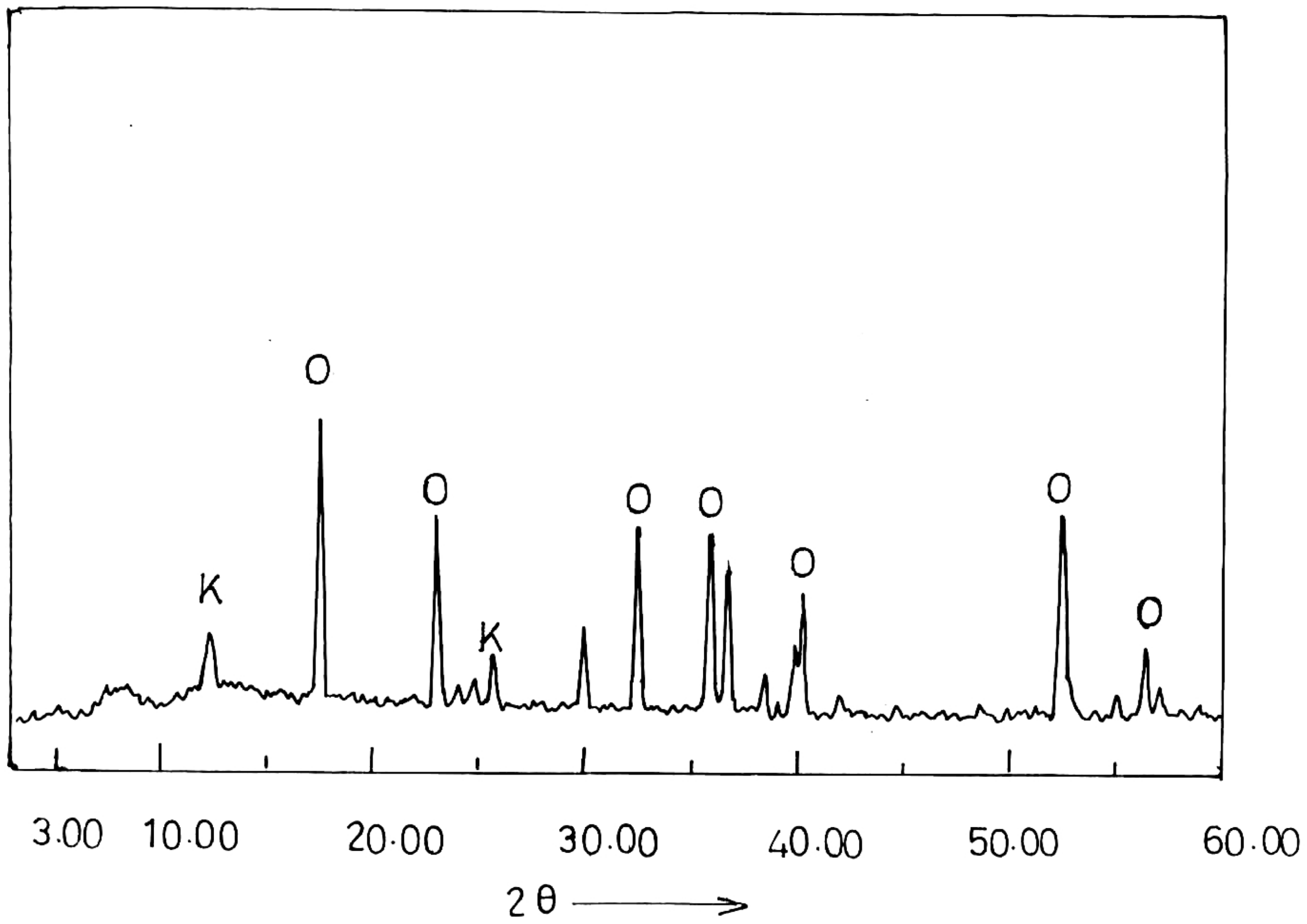


FIG.12. XRD PATTERN OF RAW OLIVINE

out using GF + 4180 Fritset ranging from + 1 mm to 0.069 mm. Fraction between 1- 0.18 mm was added as coarse and that between 0.25–0.063 mm as the fine. The grog was sized for dense packing.

The mix was prepared with K-O, fines and coarse of K-O in the ratio 60: 25: 15 in a steel cylindrical die of radius $\approx$ 1.5 cm. The samples were semi-dry pressed by applying a pressure of 2.5 tons for a period of 60 seconds in a hydraulic press (Carver) whose maximum load capacity is 20 tons.

Samples prepared for both mechanical and thermal measurements were air dried for a period of 48 hours and later oven dried at 110°C for a period of 12 hours. These samples were then fired at temperatures 1150, 1200, 1250, 1300 and 1350°C with a rate of heating of 4°/minute in a silicon carbide furnace whose maximum working temperature is 1450°C.

The phase changes that occurred during firing of both KO and KL at temperatures ranging from 1150–1350°C were studied with the help of X-ray diffractogram (Rigaku, Cu $K\alpha$ radiation, λ = 1.542 AU).

A flow chart which describes the method of preparation of sample K-L as well as K–O is as shown in Fig. 13.

3.3 Experimental Procedures

3.3.1 Modulus of Rupture (MOR)

MOR specifies the flexural strength of the sintered ceramic specimens. The test was carried out by three-point loading as per ASTM standards. The samples of $(5\times 10\times\ 80)$ mm size were used and span length of 60 mm was maintained

$$\text{MOR} = \frac{3wl}{2bd^2}\ \text{kg/cm}^2$$

3.3.2 Crushing strength (CS)

This is the ability of a refractory material to withstand handling and impact at high temperatures. Cylindrical specimens of size (28×20) mm were used for

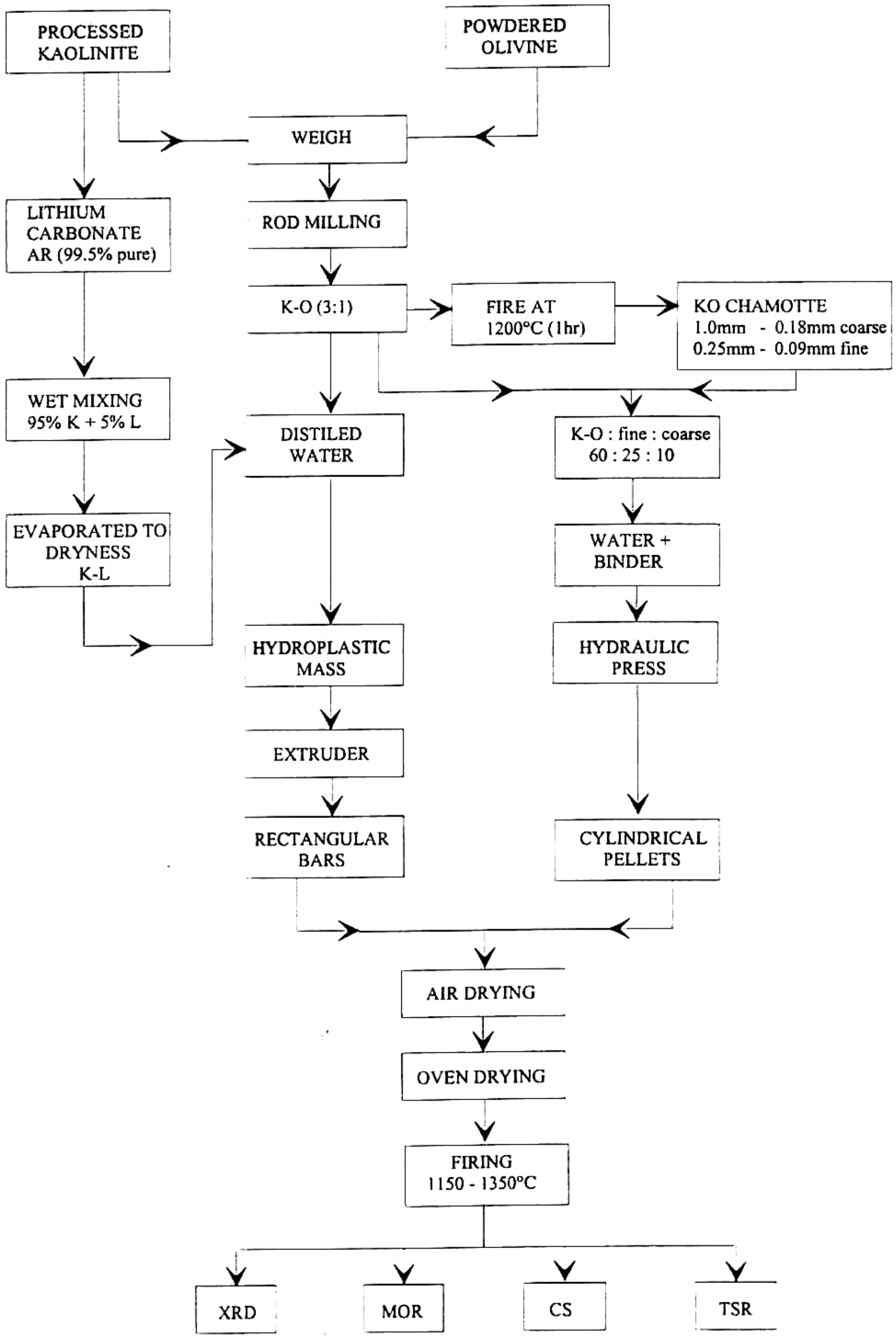


Fig. 13. Method of preparation of K-L and K-O samples

determining CS and the test was carried out as per ASTM standards. Each sample was tested for compressive strength by applying load on its top face.

$$\mathrm{CS} = \frac{\mathrm{Load}}{\mathrm{Area}}\ \mathrm{Kg/cm^2}.$$

The mechanical strength measurements were carried out in a computer controlled universal Testing Machine (UTM) (Model No. 4206; capacity: 150 KN) whose load range can vary from 0.1 N to 150 KN with a scan speed of 5 mm/minute. The INSTRON specifications are as listed in Table 5.

Table 5

Instron Specifications

Machine stiffness	140 KN/nm
Power Requirements voltage	100/120/220/240 volts ± 10% single phase
Frequency	47–63 Hz
Power	2500 V_a max
Environmental-requirements	10° to 30°C -30°C to +50°C 10% to 90% (non condensing)

3.3.3 Thermal Shock Resistance (TSR) or Spalling Resistance

Spalling is defined as the breaking or cracking of a refractory material in service to such an extent that the pieces are separated or fall away. To evaluate the thermal shock resistance of the sintered samples, German standard for water quenching method [33] has been followed and the procedure is as given below.

The cylindrical samples of (28× 20) mm were dried for 2 hours at 110° C in an oven. Then these samples were placed in a muffle furnace whose temperature was maintained at 950± 50°C. The specimens were soaked at this temperature for 30 minutes. Immediately after removing from the furnace, the specimens were plunged in to cold water and quenched for 3 minutes. Again, the samples were dried for 30 minutes at 110°C and placed in the furnace, and the cycle is repeated. This was carried out until the samples were cracked in to two or more large pieces.

The tests were carried out in a muffle furnace whose (coil is made up of kanthal wire and thermocouple is made up of chromel-alumel) maximum operating temperature is 1200°C.

3.4 Results and Discussion

The X-ray analysis of the processed China clay indicated that the major constituent is kaolinite. The presence of quartz as an impurity can be detected. 78% by weight of this material was below 2μ and had a specific surface area of $13 \pm 0.1\text{m}^2\text{g}^{-1}$ (BET N_2 adsorption). The pH of 10% aqueous slurry was 6.0 and the specific gravity was found to be 2.60 which was comparable to that of standard kaolinite.

3.4.1 Physical properties

The compositions made from kaolinite were sintered at temperatures 1150, 1200, 1250, 1300 and 1350°C with rate of heating of 4°C/minute with a temperature interval of 50°C. The most notable appearance of the sintered samples from both the composition was its colour change which ultimately depends on firing temperature. The kaolinite-olivine combination have shown a colour change ranging from light pink to dark brown while kaolinite-Li_2CO_3 combination gave rise to a random orientation of pink spots all over the surface. When the temperature was increased the colour also deepened. The colour change of KO and KL composition are as shown in Fig. 14 and Fig. 15 respectively.

It is interesting to note that the sample KO has got a percentage plasticity of 35 while the percentage plasticity was less than 10 in the case of sample KL.

3.4.2 Mechanical Measurements

The mechanical properties of the samples KO and KL are as shown in Table 6 and Table 7 respectively.

Fig. 14. The colour change of **KO** composition during firing

A. Before firing

B. At 1150° C

C. At 1200° C

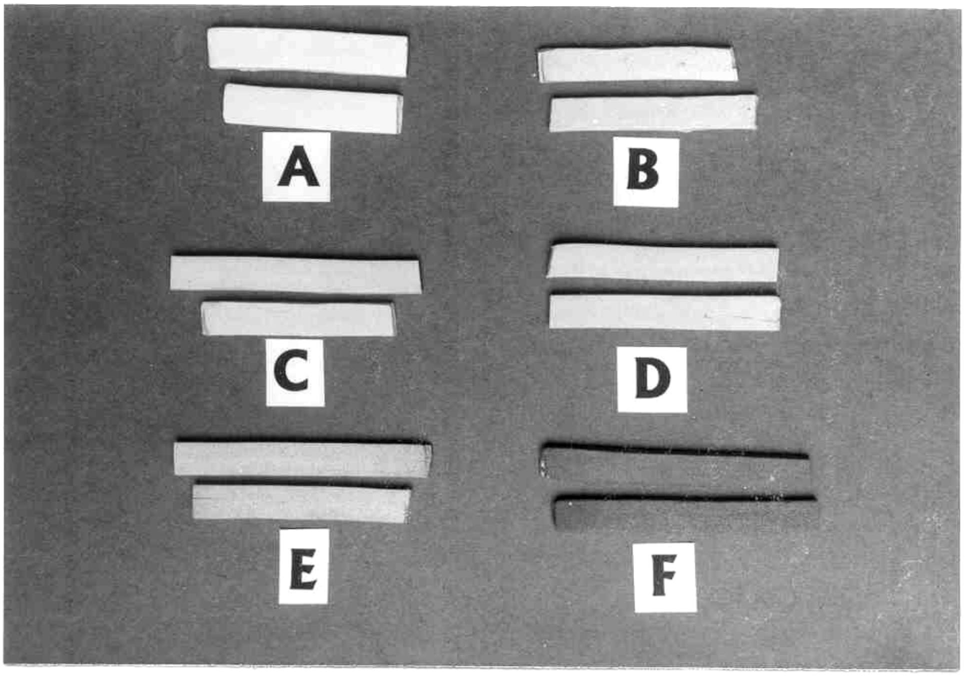
D. At 1250° C

E. At 1300° C

F. At 1350° C

Fig. 15. The colour change of **KL** composition during firing

G. At 1350° C


A
B
C
D
E
F

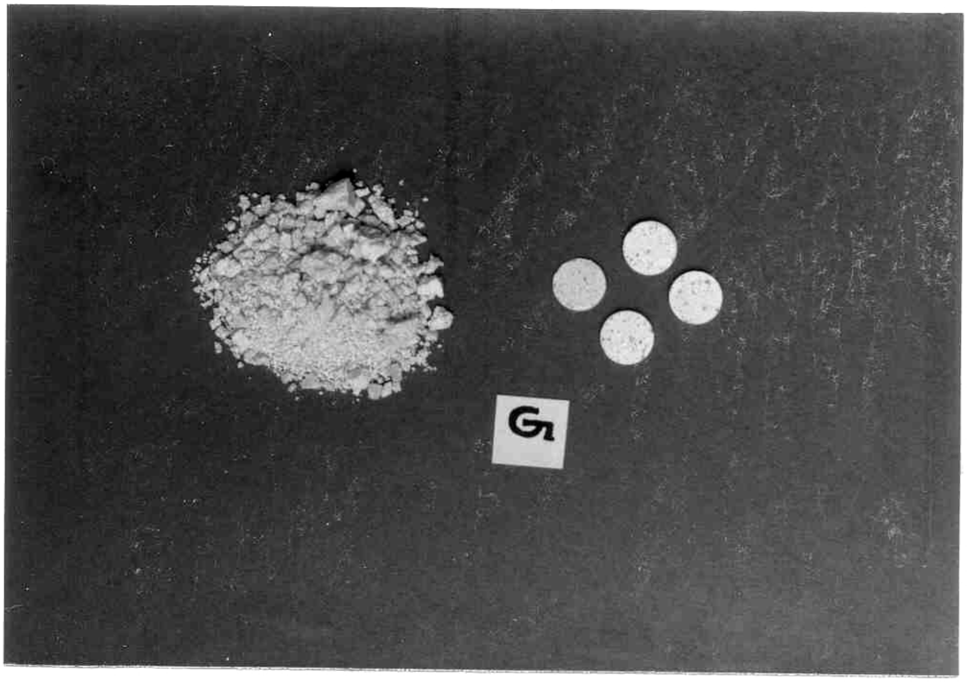

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Table 6

Composition	Temperature (°C)	MOR (MPa)	CS (Mpa)
K-O	1150	34.317	26.08
	1200	31.960	27.99
	1250	35.290	28.07
	1300	32.500	34.29
	1350	35.663	66.16

Table 7

Composition	Temperate (°C	MOR (Mpa)	CS (MPa)
K-L	1150	11.063	42.593
	1200	11.620	31.843
	1250	13.470	27.21
	1300	16.79	23.95
	1350	16.83	21.02

The stress–strain curve for compression strength measurements of KO samples at temp varying from 1150–1350°C are as shown in Fig. 16 (a) to (e) and that of KL samples are as shown in Fig. 17 (a) to (e). It is clear from the figure that the crushing strength is greater for KO composition than KL composition. As the temperature increases, the strength increases linearly in the case of KO samples while there is a linear decrease in the case of KL samples.

The stress-strain curve for flexural strength measurements of KO samples are as shown in Fig. 18 (a) to (e) and that of KL samples are as shown in Fig. 19 (a) to (e). It is interesting to note that the flexural strength values increases with increase in temperature for both KO and KL samples. But the MOR values are higher for KO composition. The mechanical strength measurements clearly reveals that the KO composition is stronger than KL composition.

COMPRESSION STRENGTH (CS) TEST

Stress vs. Strain curves for K-O composition

Fig. 16(a)	At 1150°C
(b)	At 1200°C
(c)	At 1250°C
(d)	At 1300°C
(e)	At 1350°C

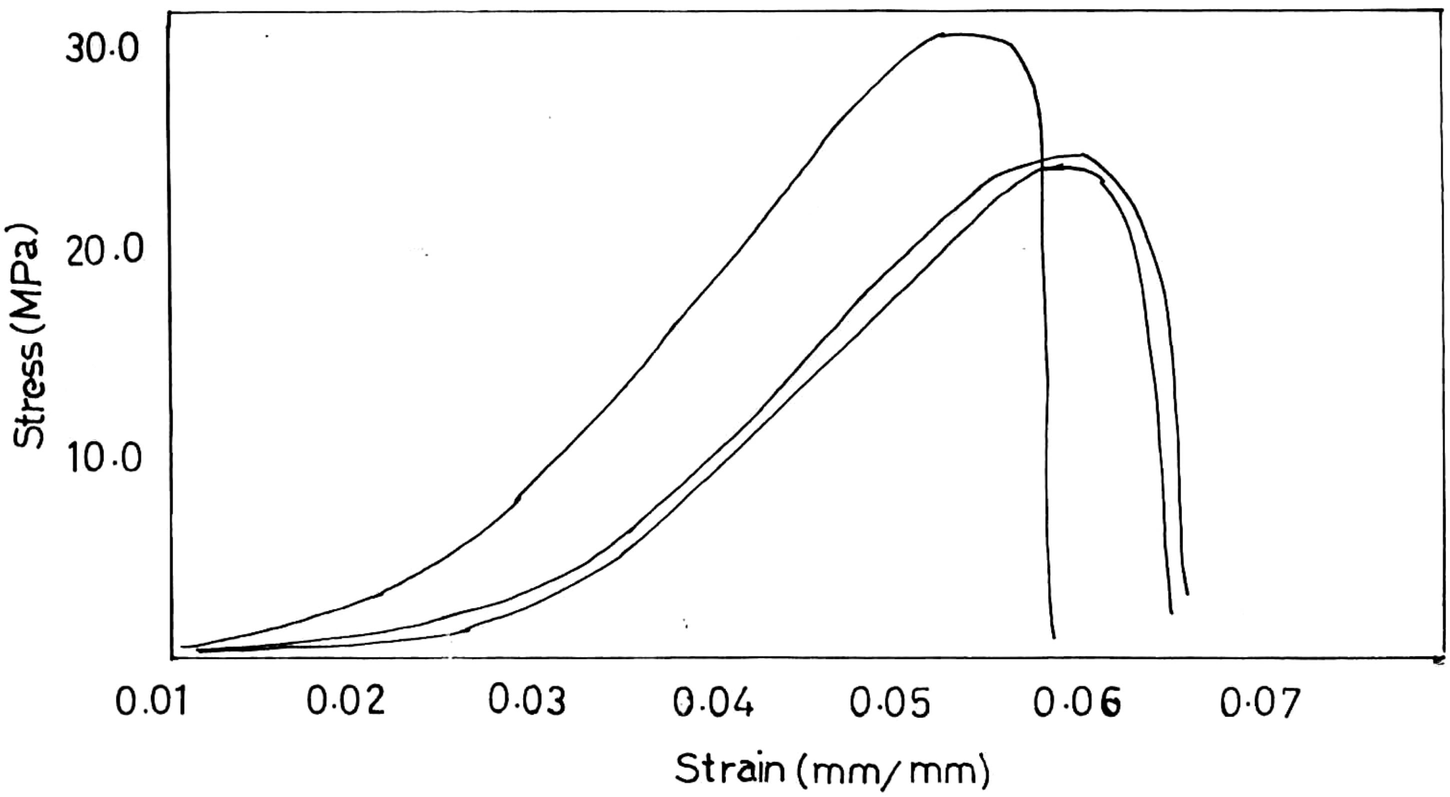


FIG .16(a) KO (1150° C)

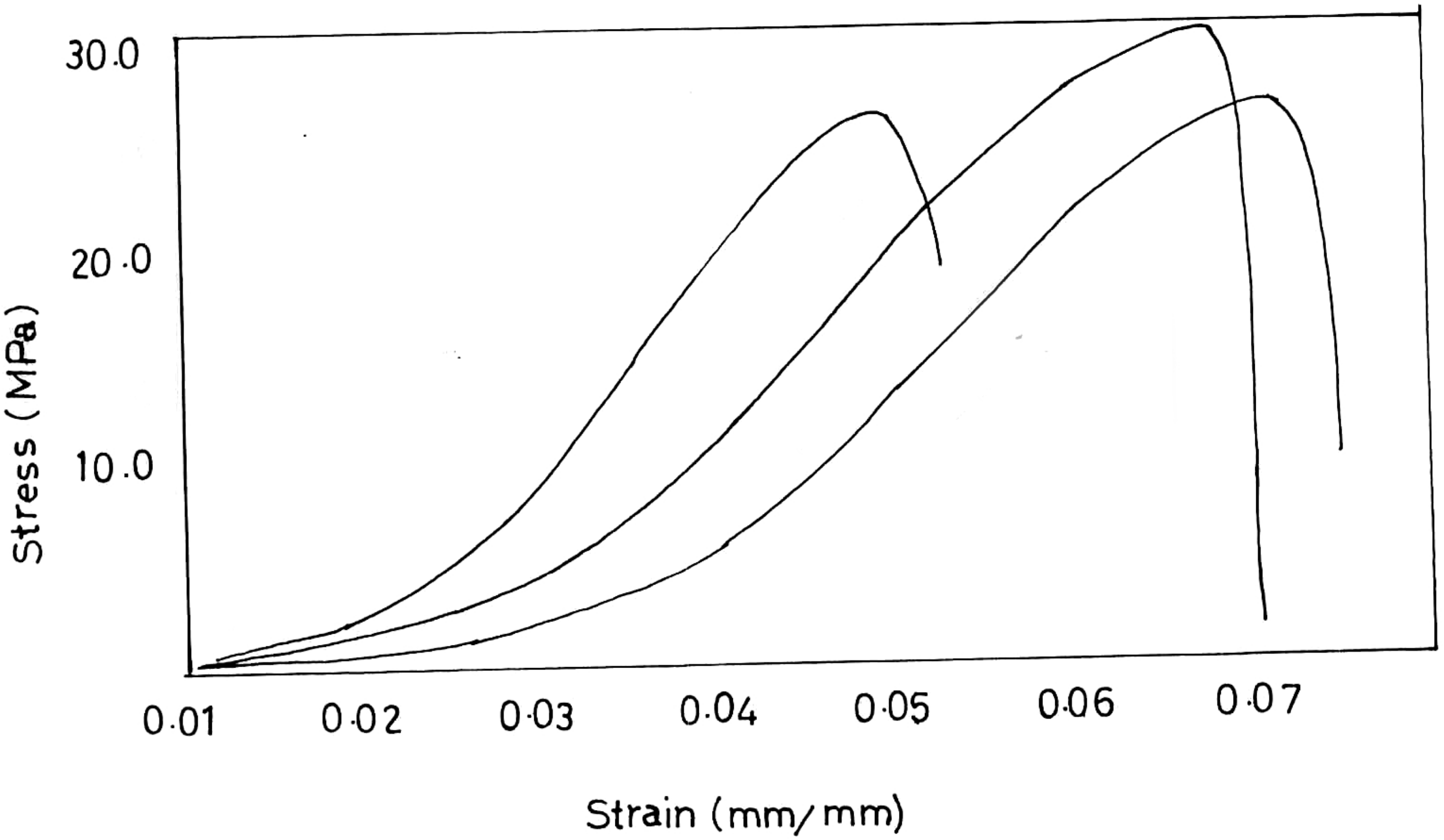


FIG.16(b) KO (1200°C)

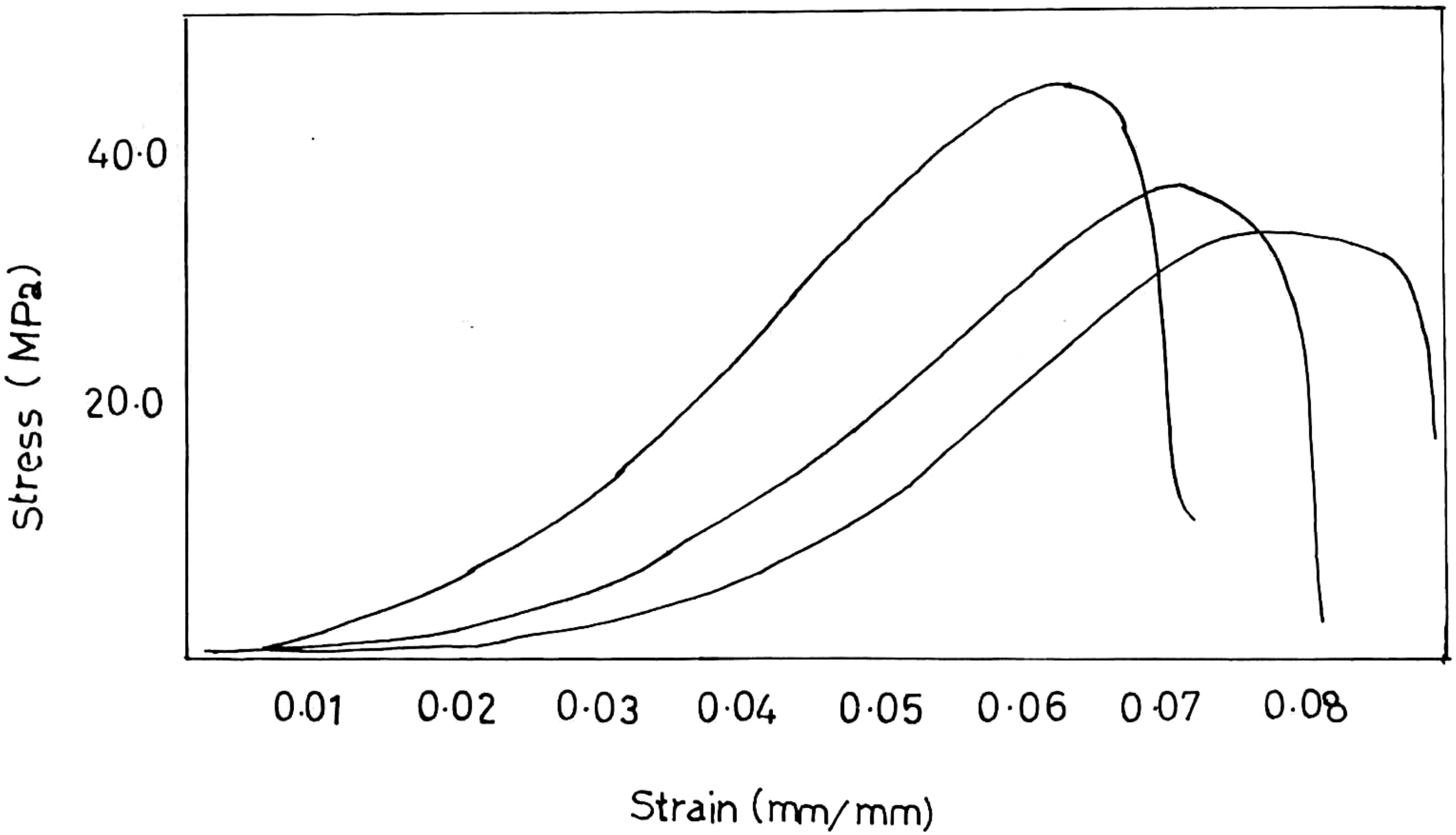


FIG.16(c) KO (1250°C)

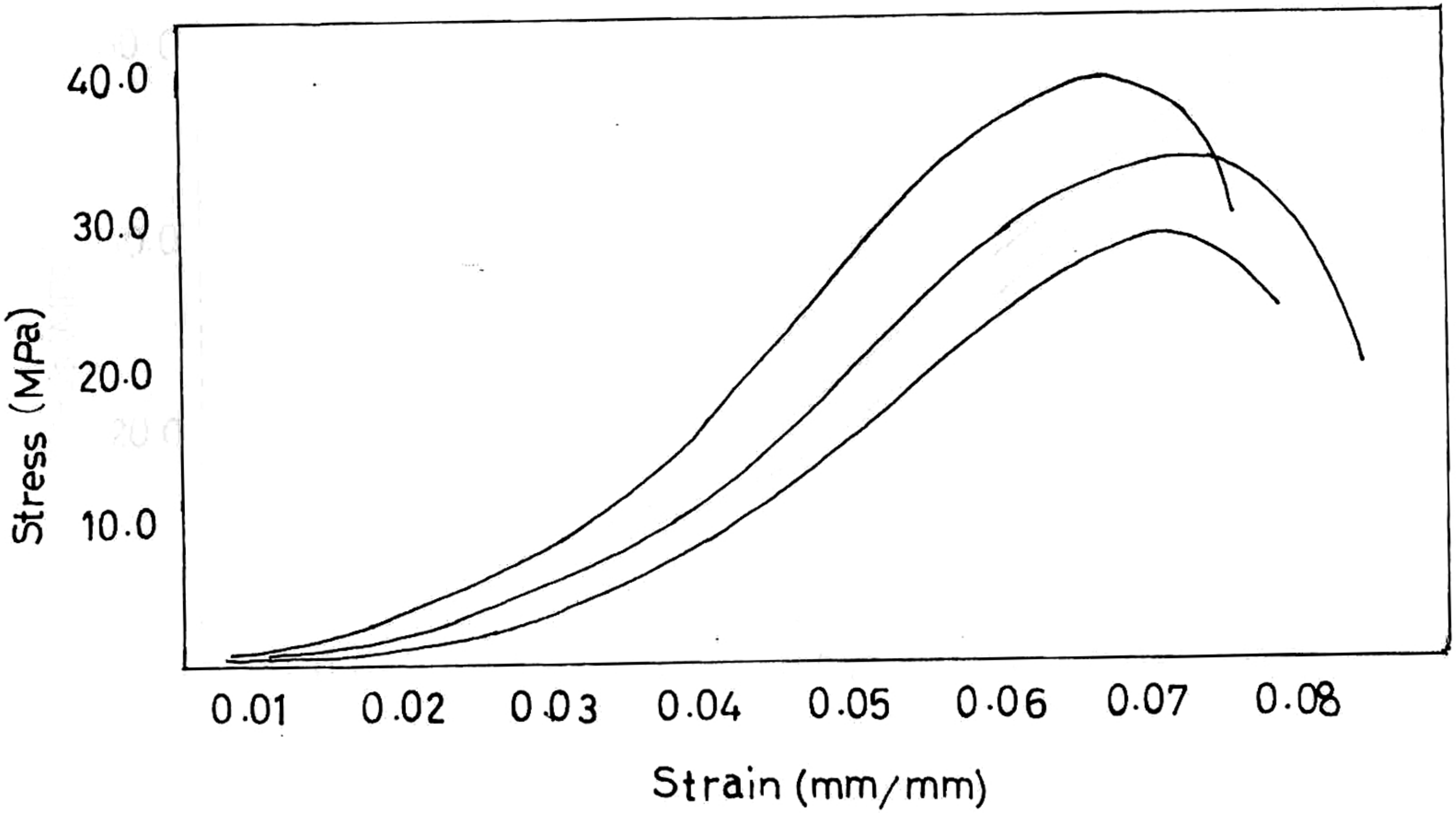


FIG.16(d) KO (1300° C)

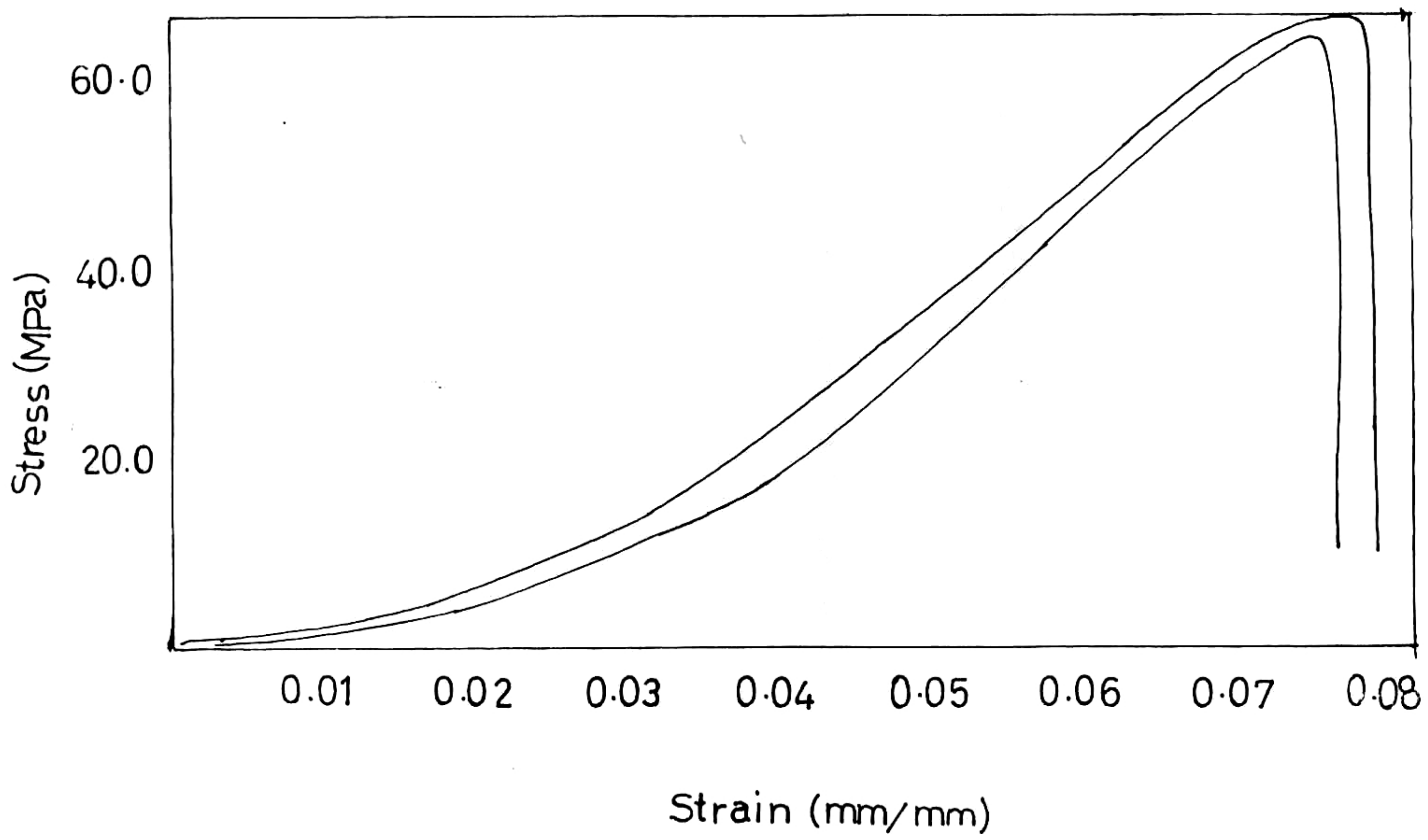


FIG.16(e) KO (1350°C)

COMPRESSION STRENGTH (CS) TEST

Stress vs. Strain curves for K-L composition

Fig. 17(a)	At 1150°C
(b)	At 1200°C
(c)	At 1250°C
(d)	At 1300°C
(e)	At 1350°C

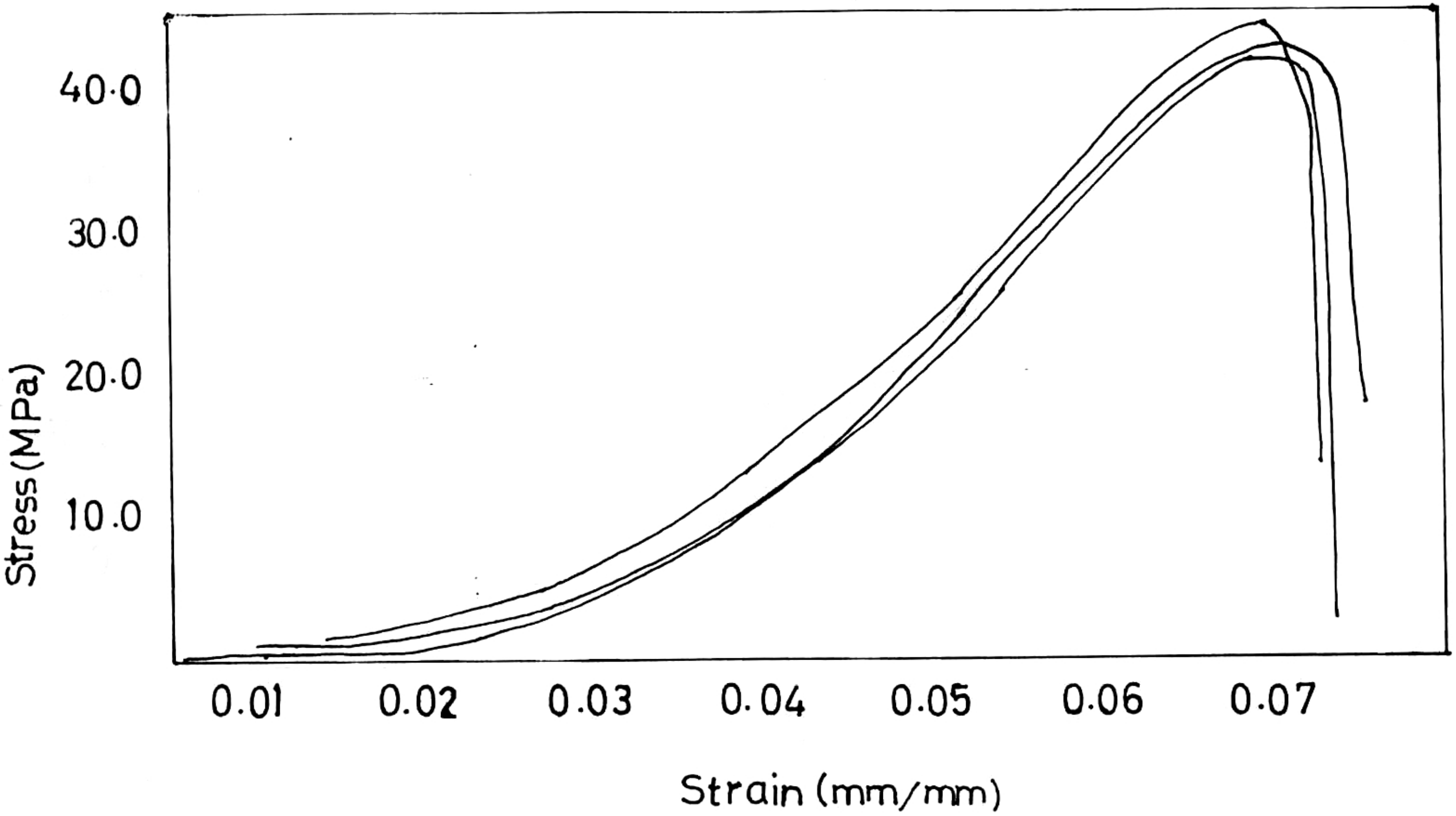


FIG.17 (a) KL (1150°C)

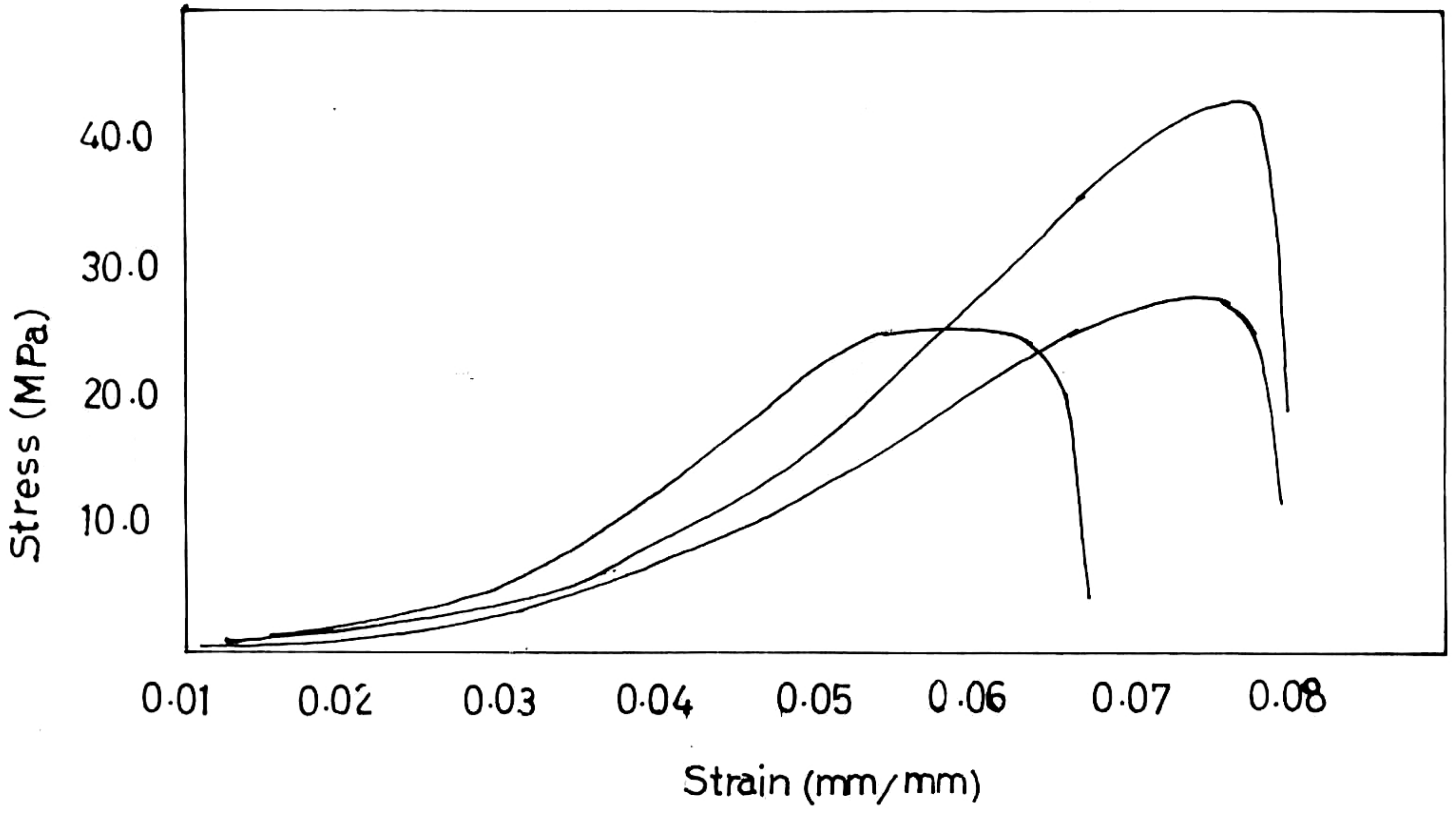


FIG.17 (b) KL (1200°C)

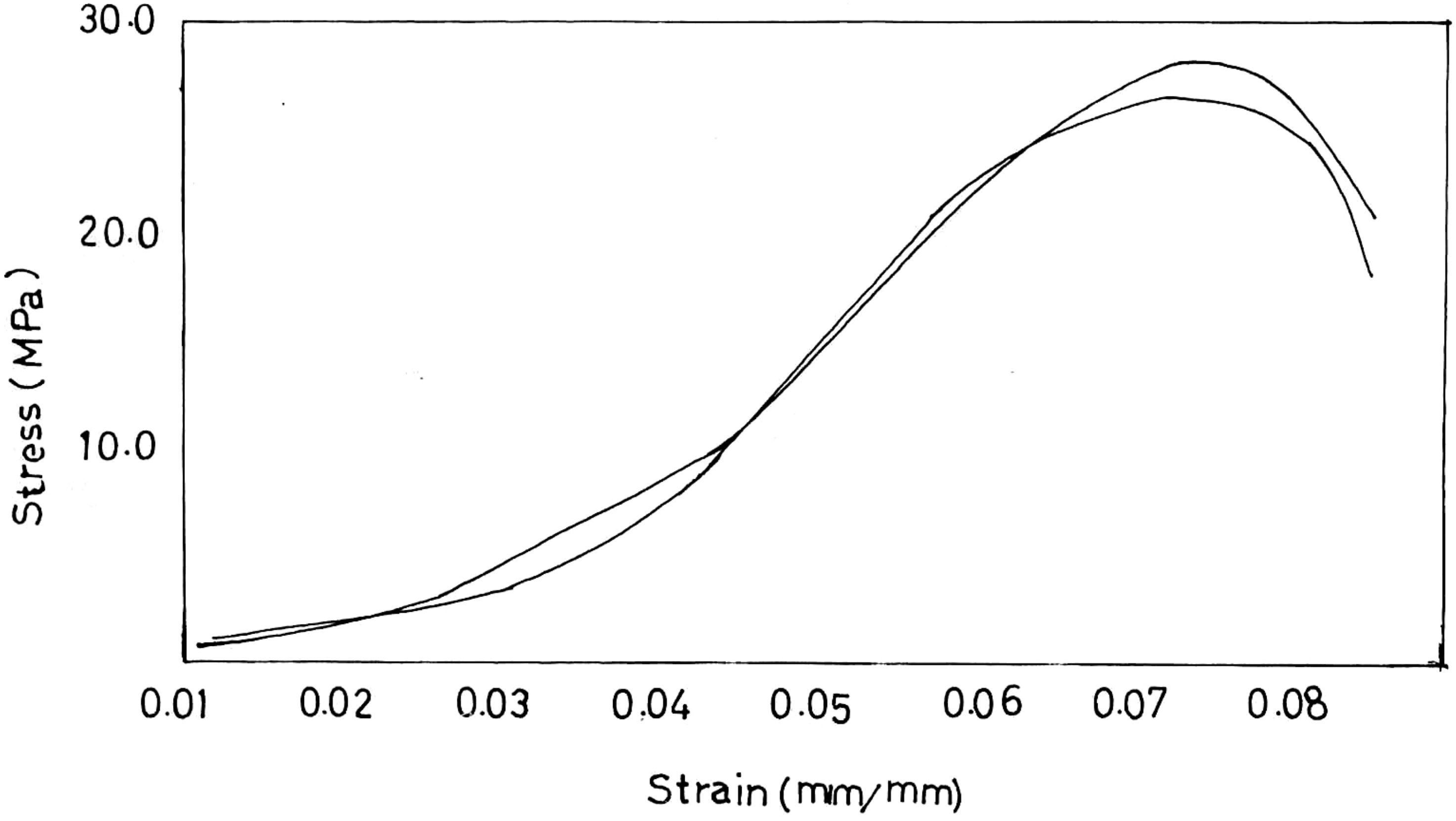


FIG.17 (c) KL (1250°C)

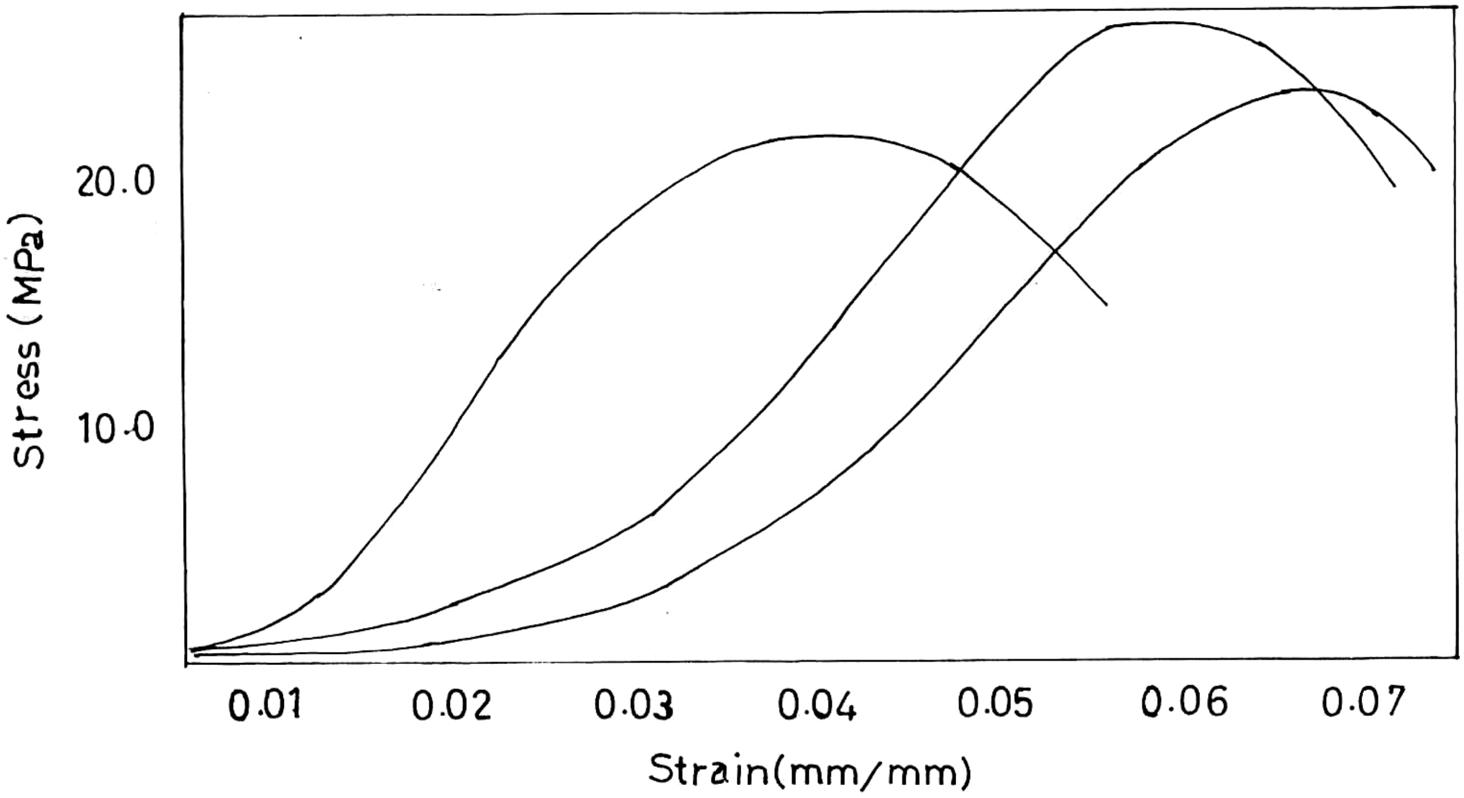


FIG.17(d)KL (1300°C)

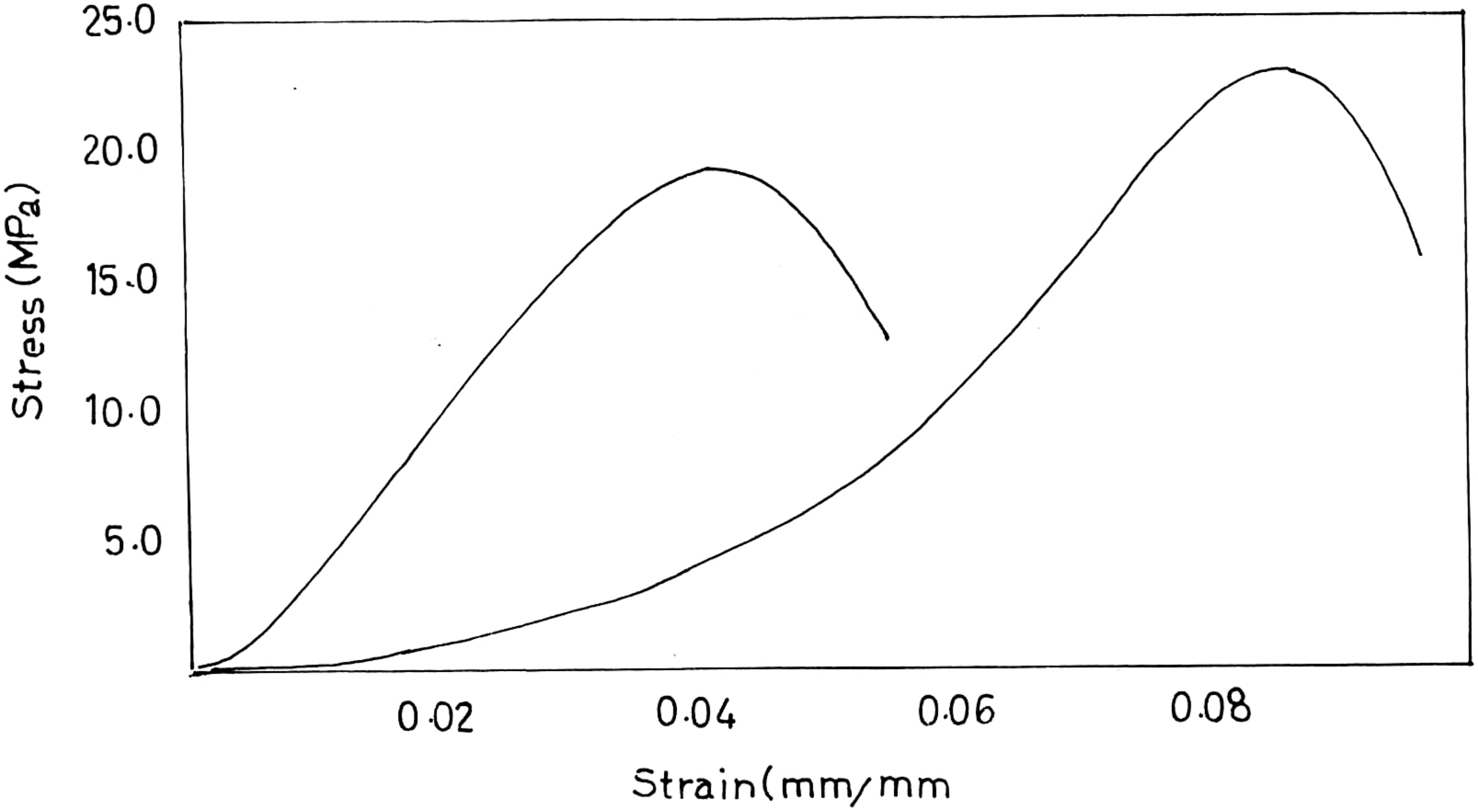


FIG.17(e) KL (1350° C)

FLEXURAL STRENGTH (MOR) TEST

Stress vs. Strain curves for K-O composition

Fig. 18(a)	At 1150°C
(b)	At 1200°C
(c)	At 1250°C
(d)	At 1300°C
(e)	At 1350°C

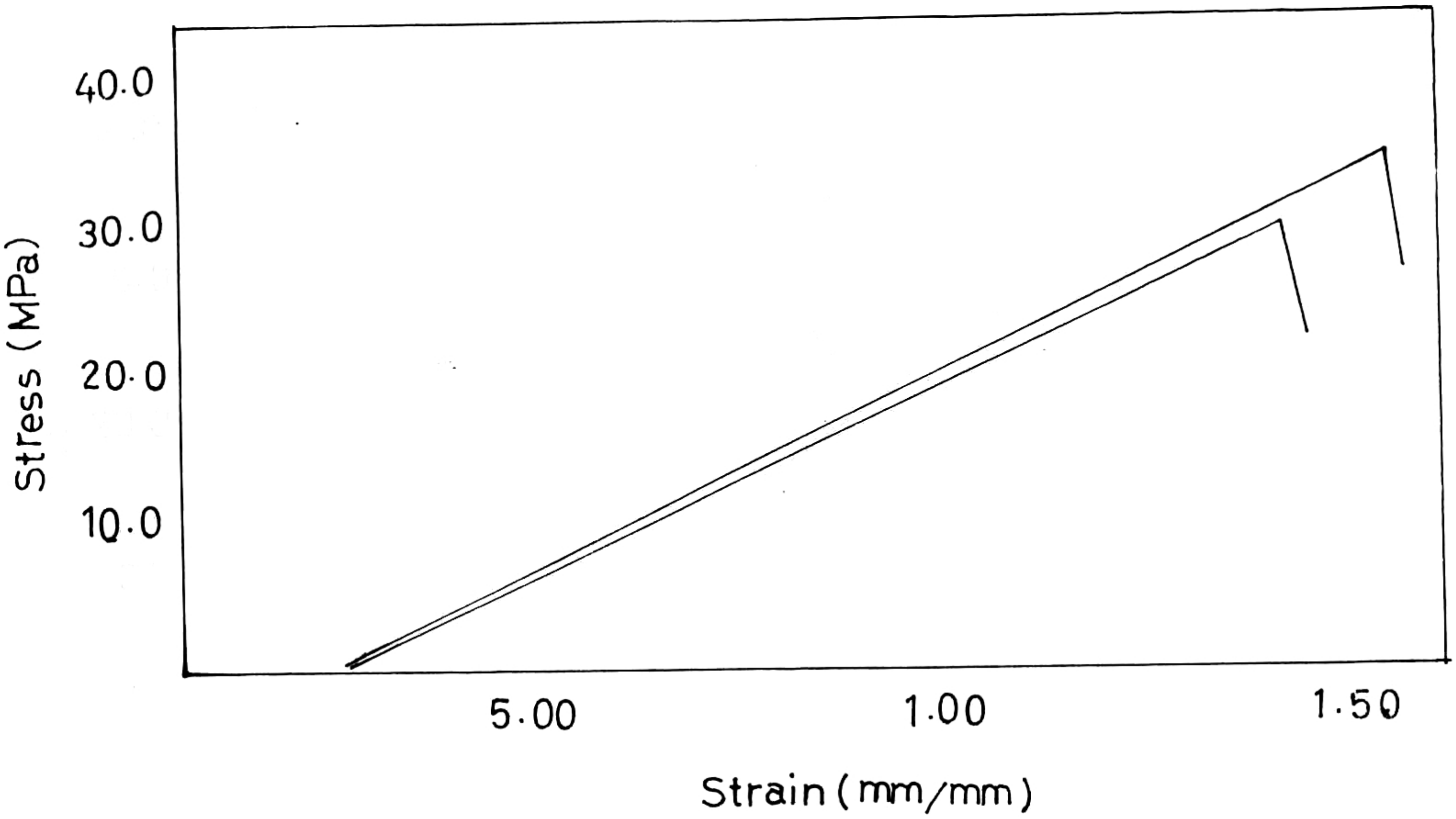


FIG.18 (a) KO (1150°C)

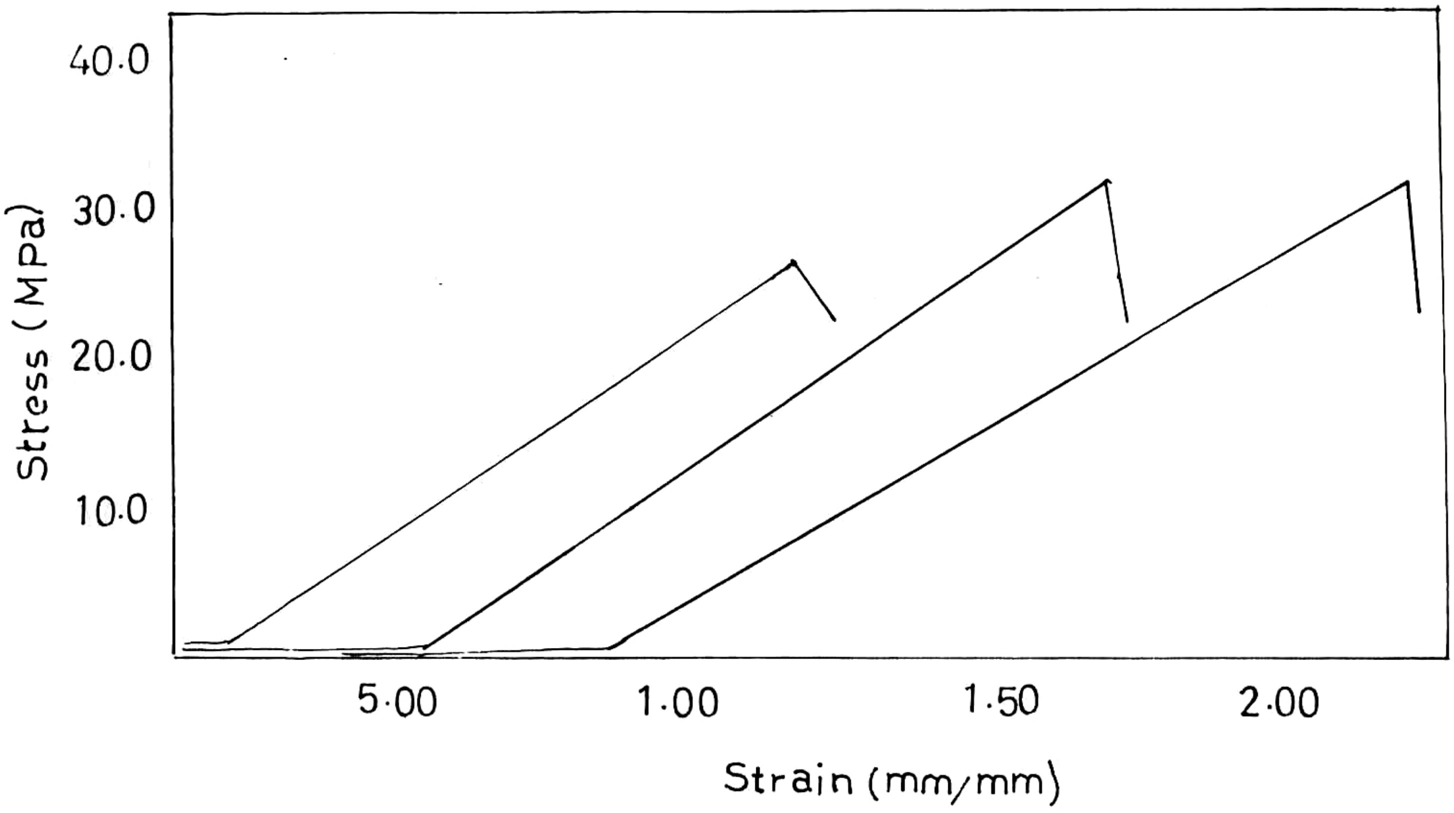


FIG.18 (b) KO (1200° C)

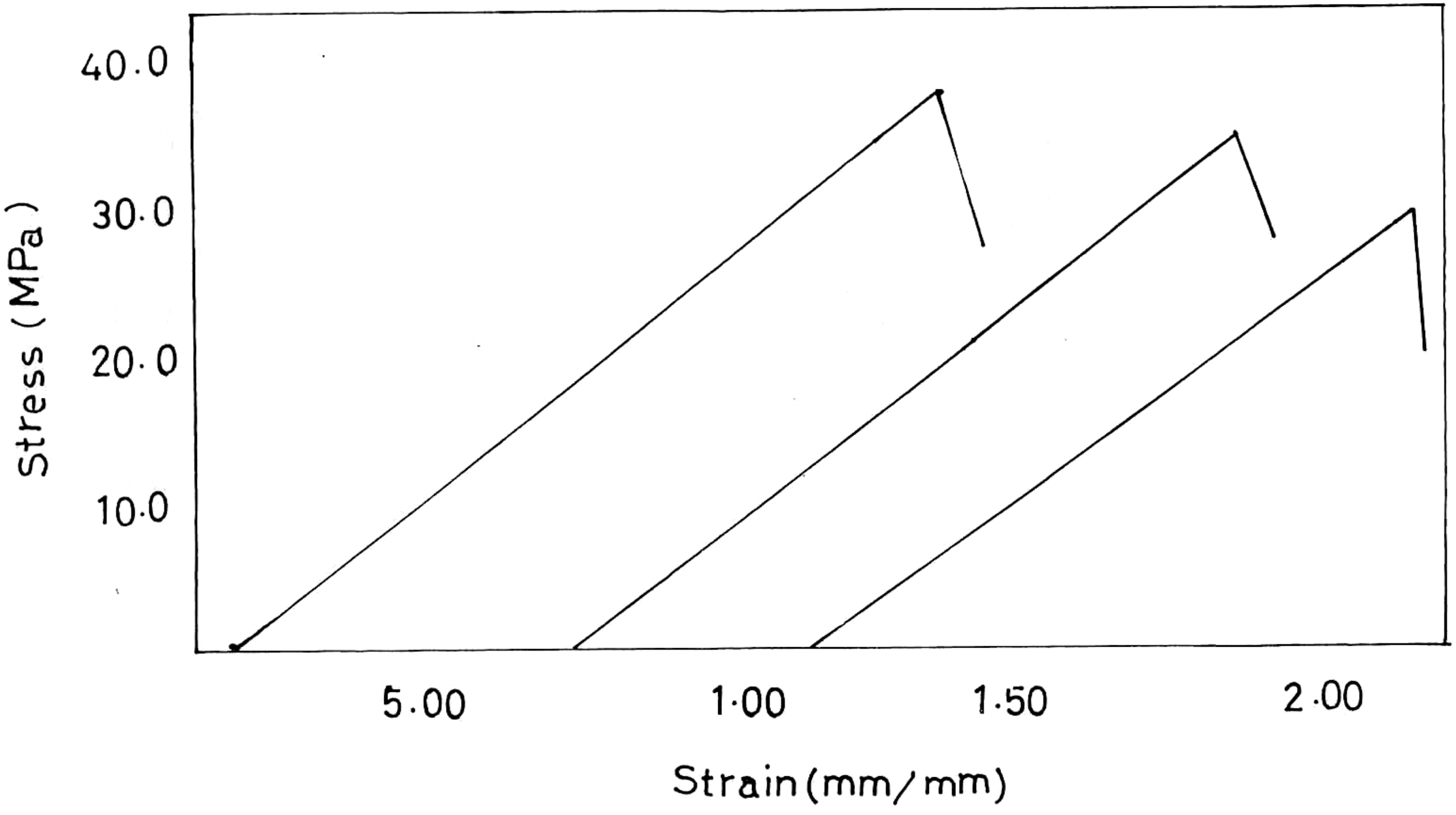


FIG.18 (c) KO (1250° C)

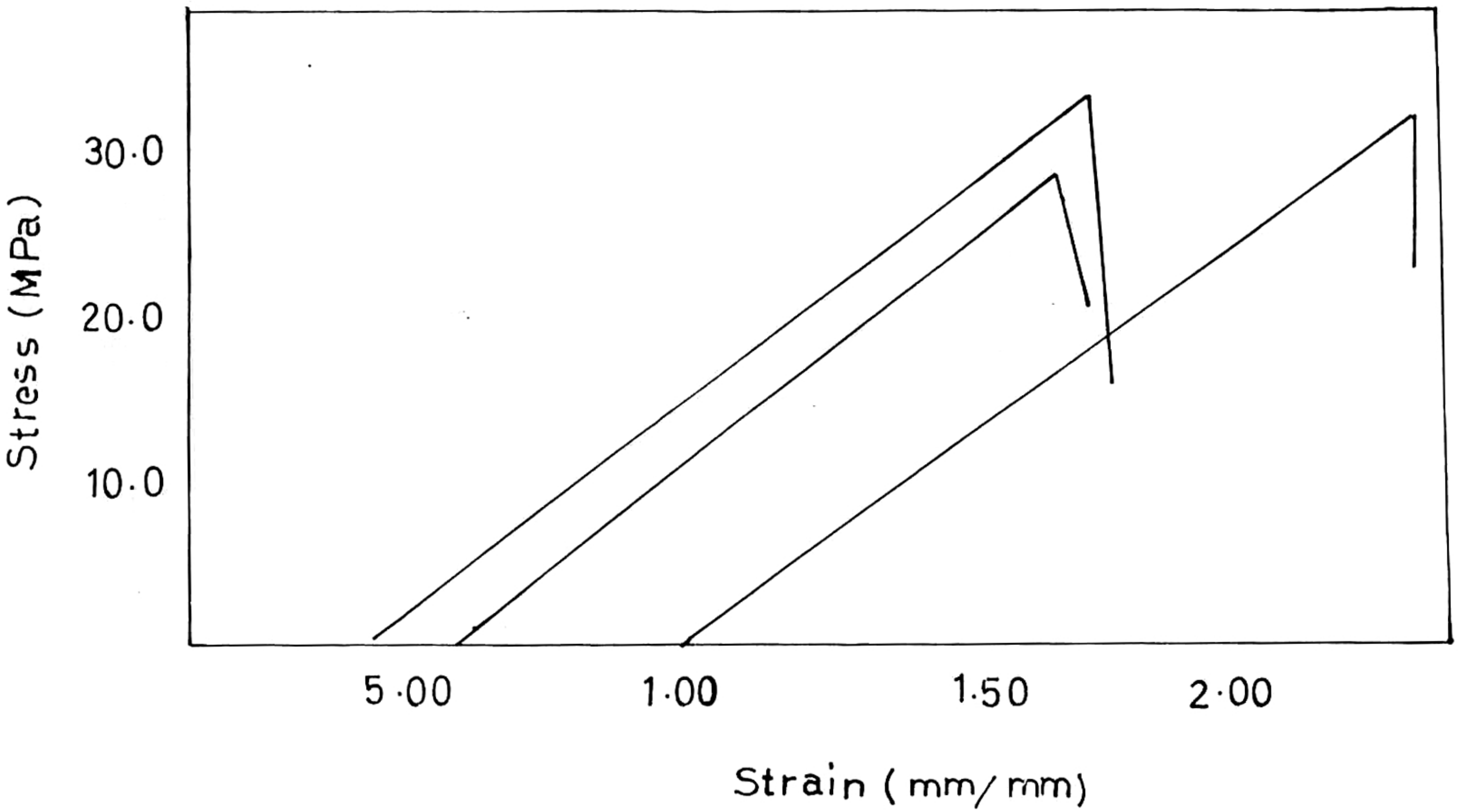


FIG.18(d) KO (1300°C)

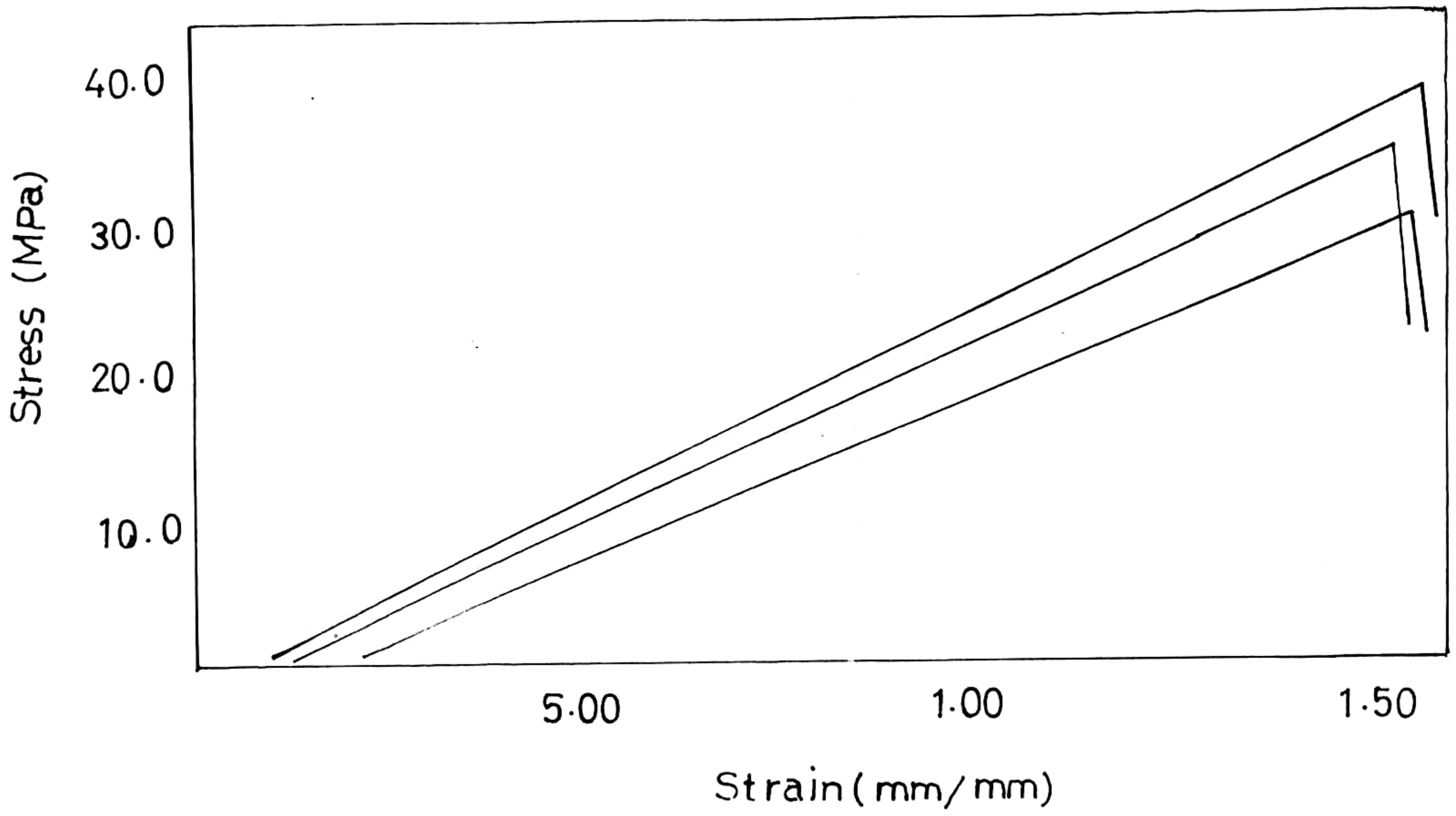


FIG.18(e) KO (1350°C)

FLEXURAL STRENGTH (MOR) TEST

Stress vs. Strain curves for K-L composition

Fig. 19(a)	At 1150°C
(b)	At 1200°C
(c)	At 1250°C
(d)	At 1300°C
(e)	At 1350°C

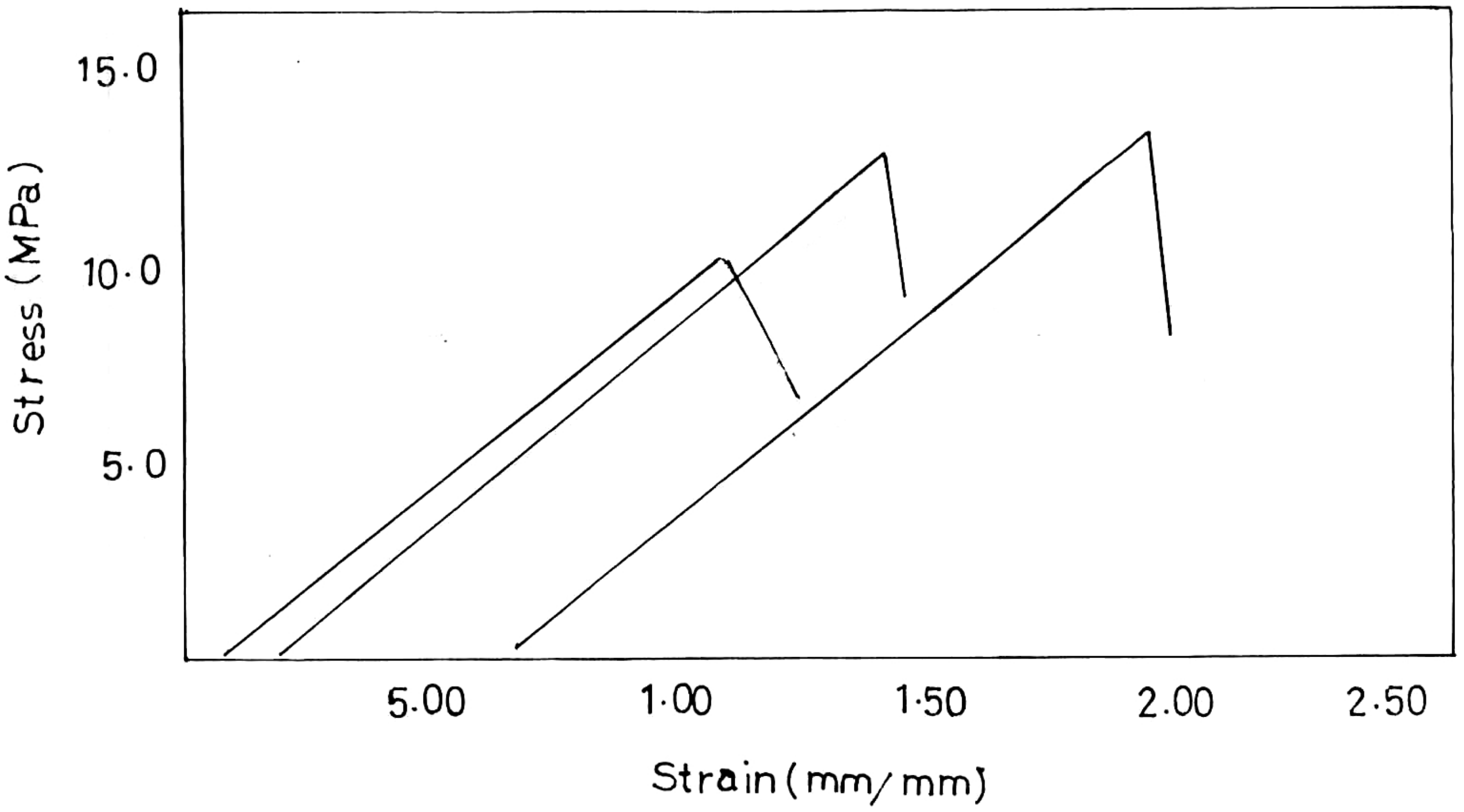


FIG.19(a) KL (1150°C)

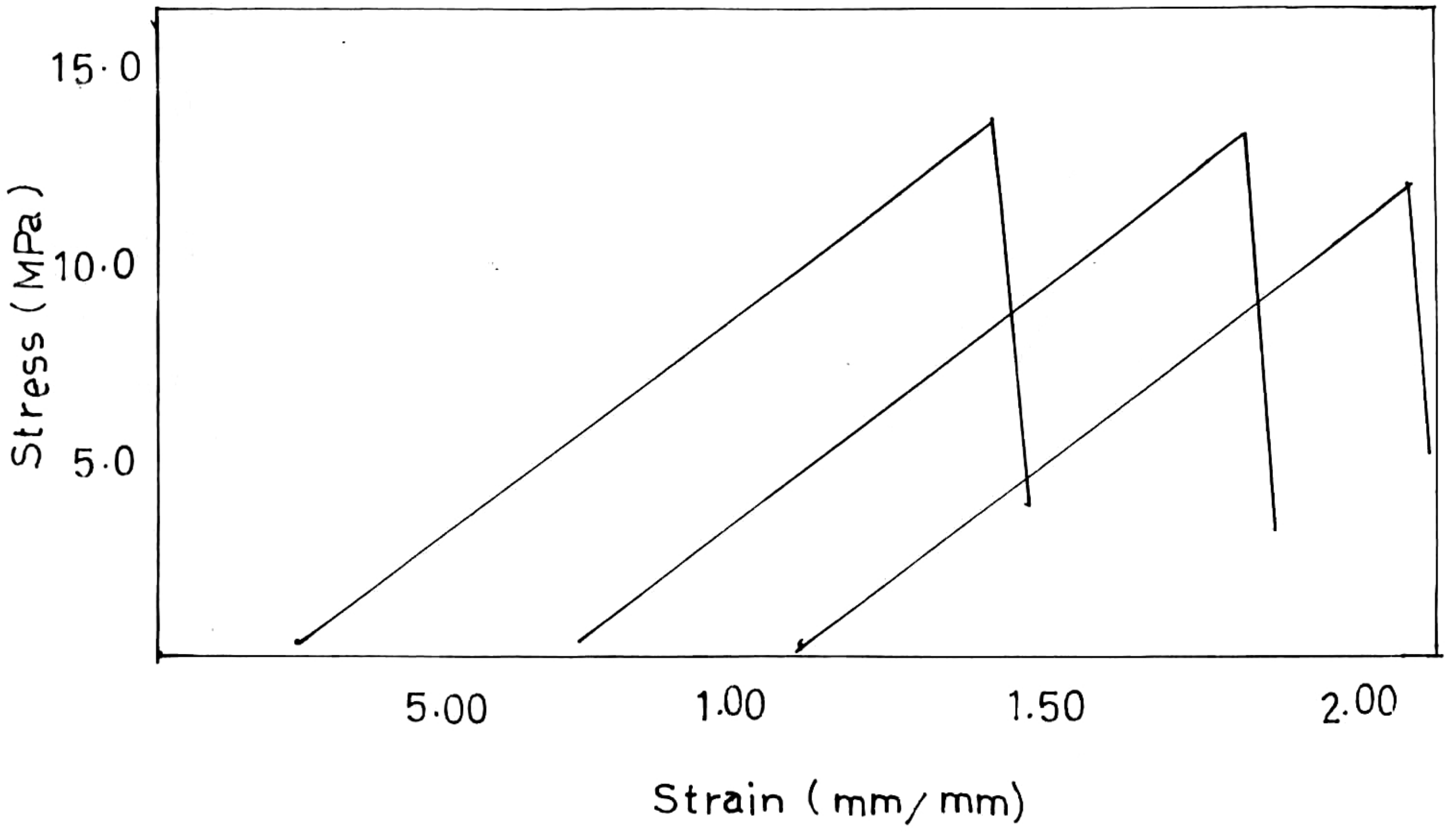


FIG.19 (b) KL (1200° C)

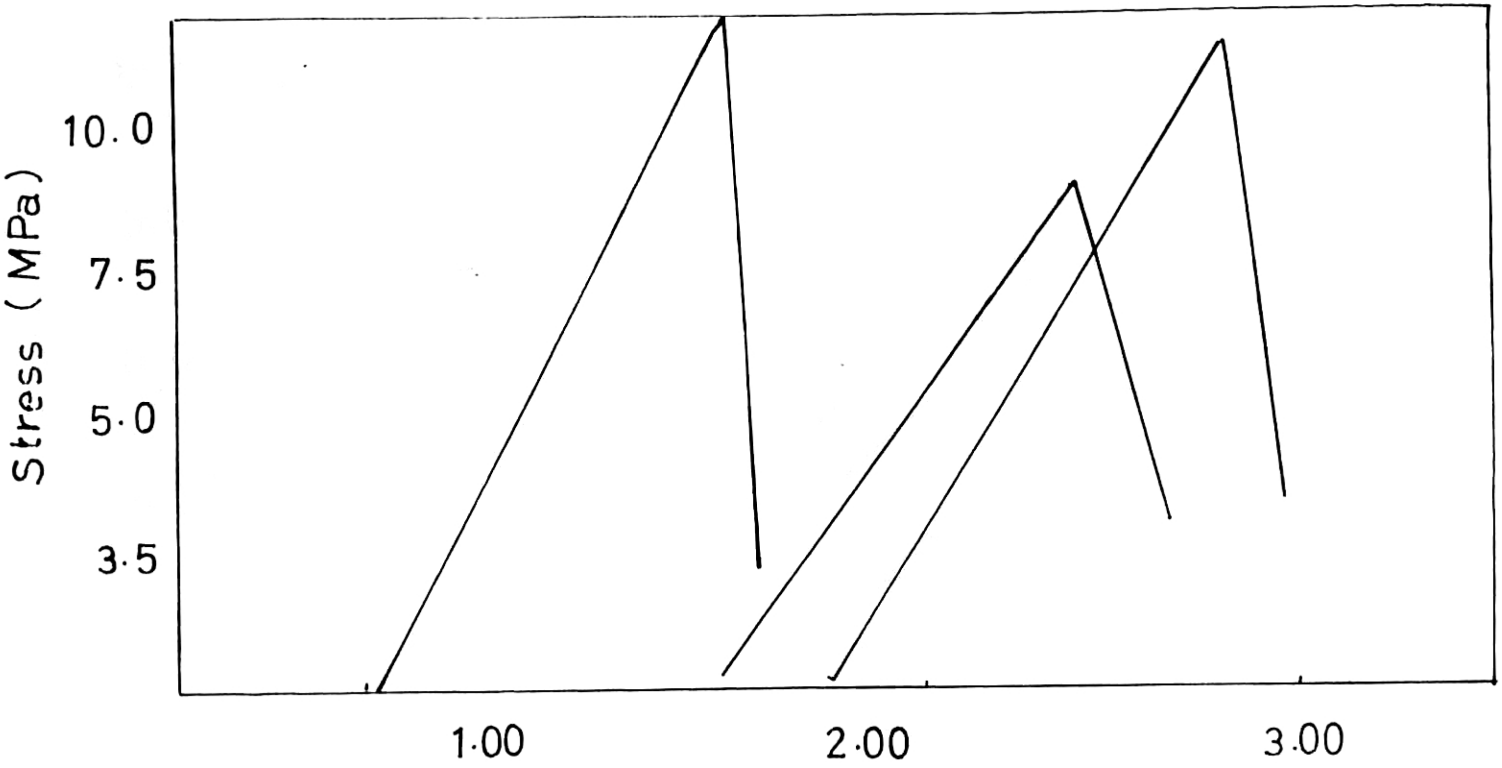


FIG.19(c) KL (1250°C)

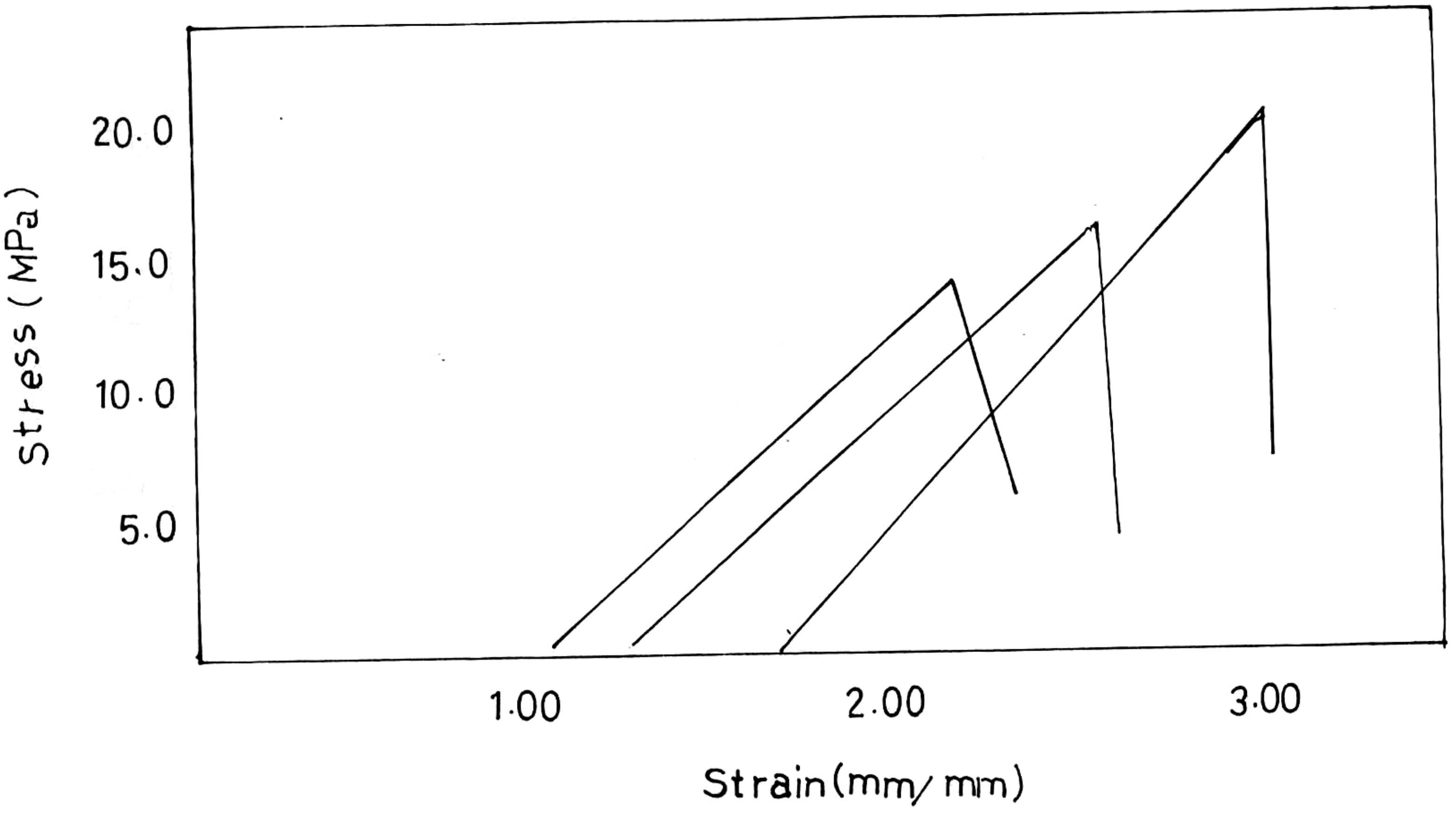


FIG.19 (d) KL (1300 °C)

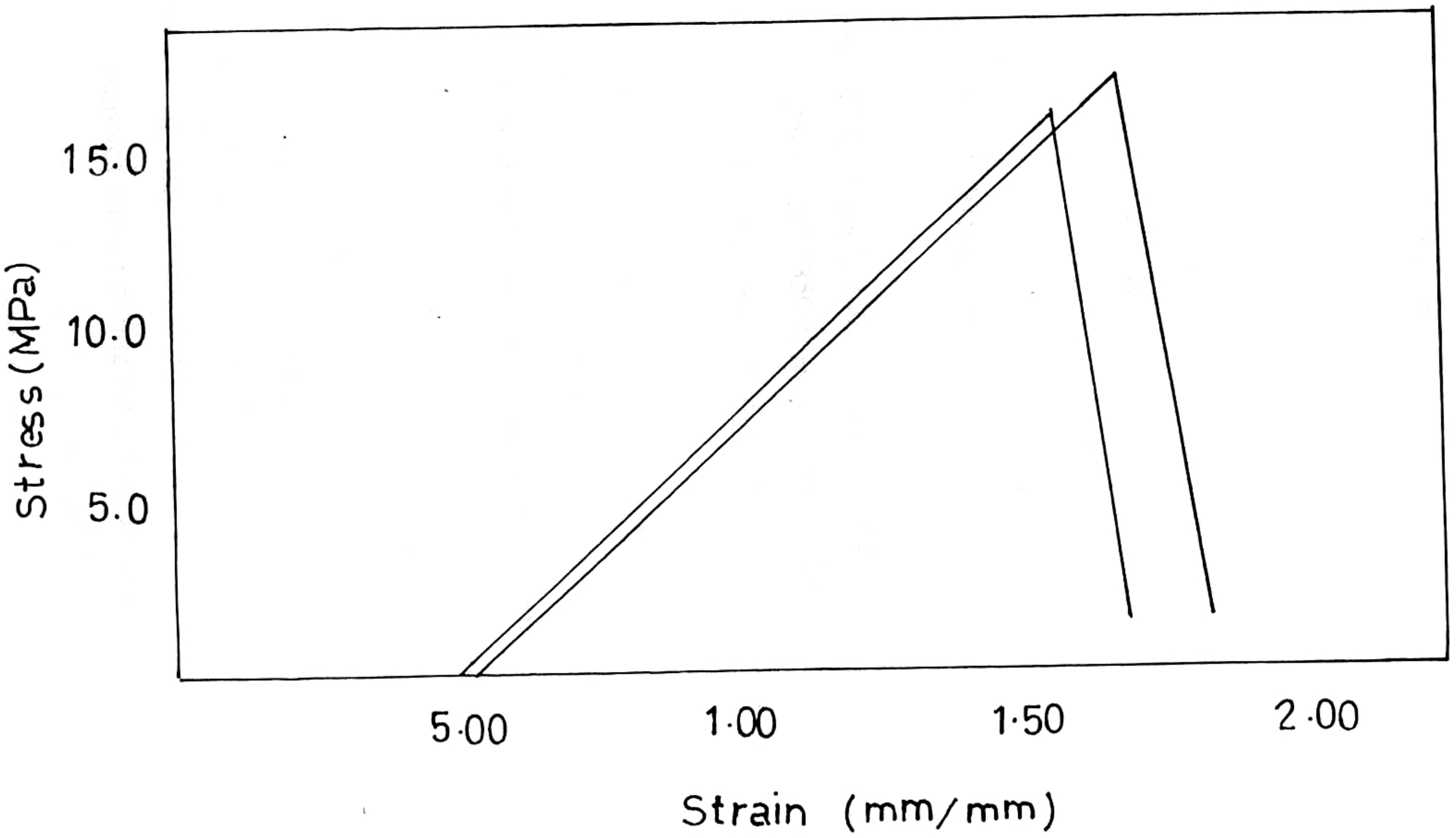


FIG.19 (e) KL (1350° C)

3.4.3 Identification of sintered phases by XRD

The colour change of KO samples are due to the presence of olivine. It is known that the oxidation processes are the prime causes of high temperature alteration of the olivine solid solution. The natural olivine experienced decreasing density after firing at 1500°C for varying lengths of time.

The X-ray diffraction studies have shown that the sintering has brought in very interesting phase changes. When KO was fired at 1150°C, the peaks formed were that of primary mullite, olivine, magnesium and cordierite. At 1200°C, the major peaks were that of cordierite and secondary mullite. These peaks were reported at 1250, 1300 and 1350°C. When K-L was fired at 1150°C, along with the peaks of cristobalite and mullite, a new phase appeared which was identified to be spodumene [LiAl (Si_2O_6)] (Lithium Aluminium Silicate). The same behaviour was observed at 1250°C and 1350°C as well. To confirm the formation of spodumene, sintering processes were repeated using 15% Li_2CO_3. The X-ray diffractogram proved the presence of spodumene beyond doubt. Fig. 20(a) to (e) shows XRD pattern for K-O and Fig. 21 that of K-L sample.

Cordierite compounds are well known for their hardness. They exhibit a very low thermal expansion coefficient and have excellent thermal shocks exerted by abrupt temperature changes. Lithium compounds are noted for their mineralising action. Carbonates, fluorides and chlorides are commonly used. Lithium salts helped in mullite formation at very low temperatures $\approx$ 550°C. Interestingly, the sintering process resulted in the formation of an additional phase *i.e.,* spodumene indicated by pink spots. In spite of uniform mixing, the third phase has appeared as specs. This may be due to the diffusion of the highly mobile lithium ions in to the mesopores formed during the dehydroxylation of kaolinite during sintering. It is also proved that the Li ion fits in to the lattice during slow dehydroxylation and this intimate contact with Al and Si results in the formation of spodumene.

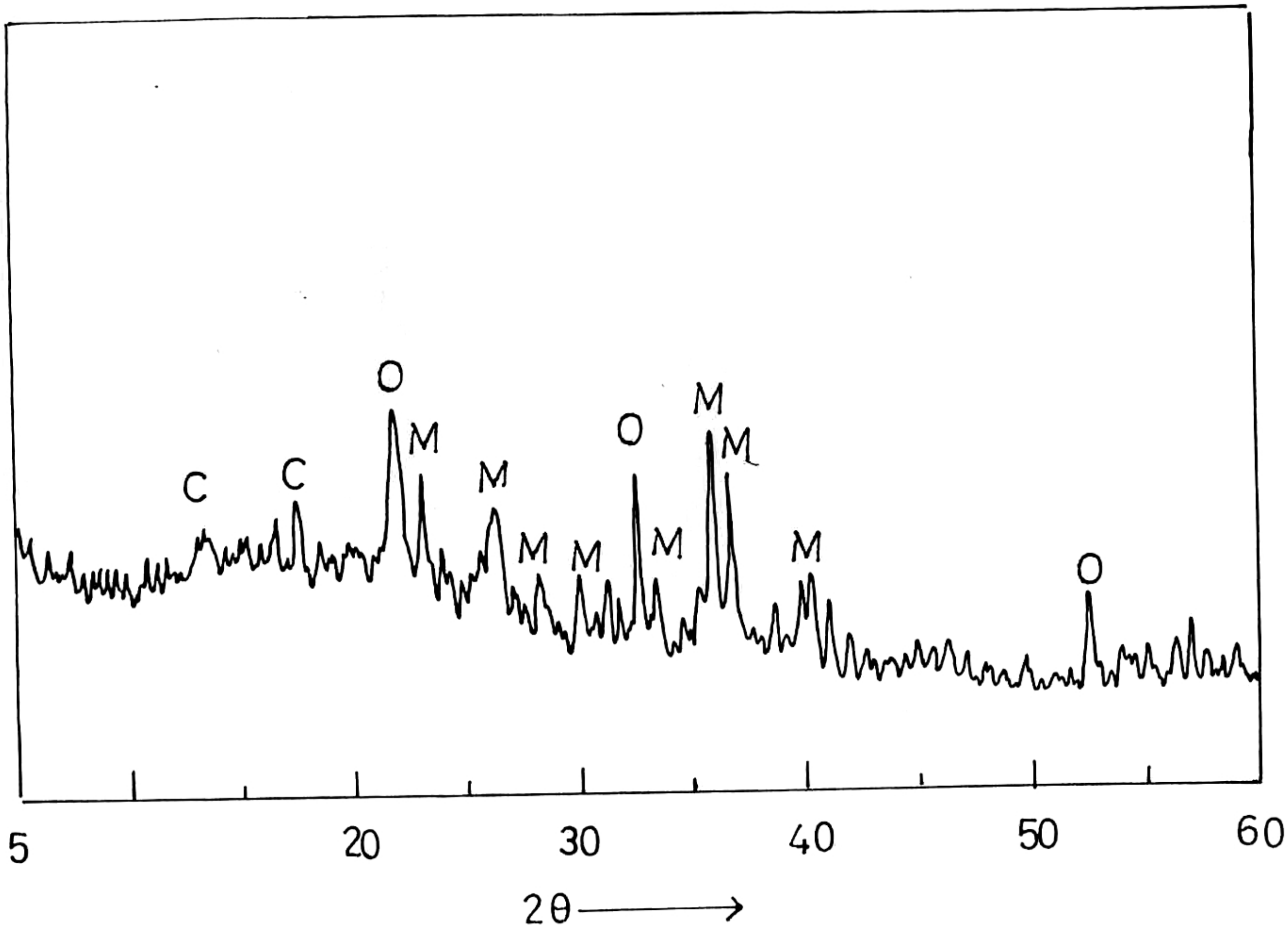


FIG. 20 (a) KO (1150° C)

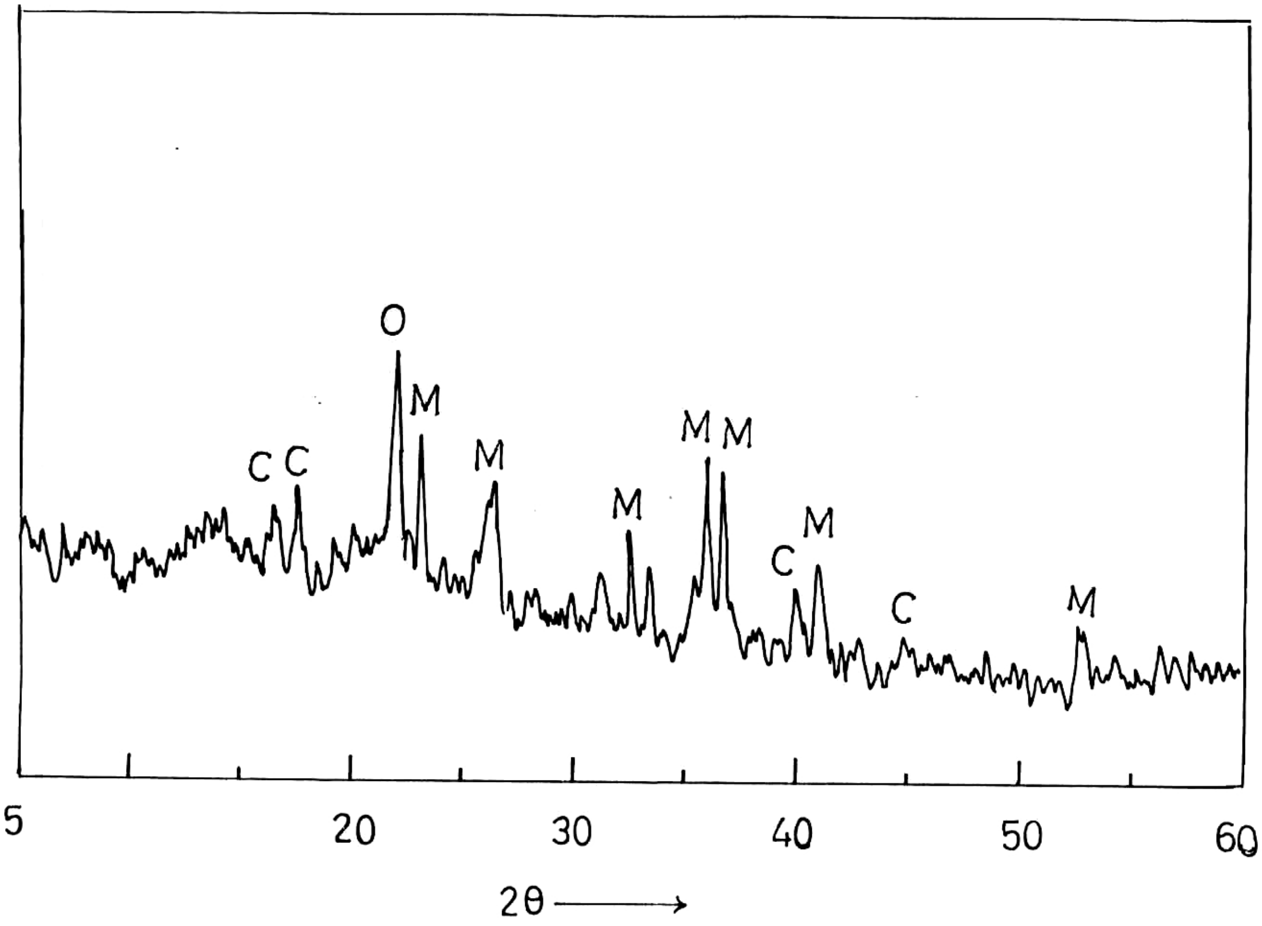


FIG. 20 (b)   KO (1200° C)

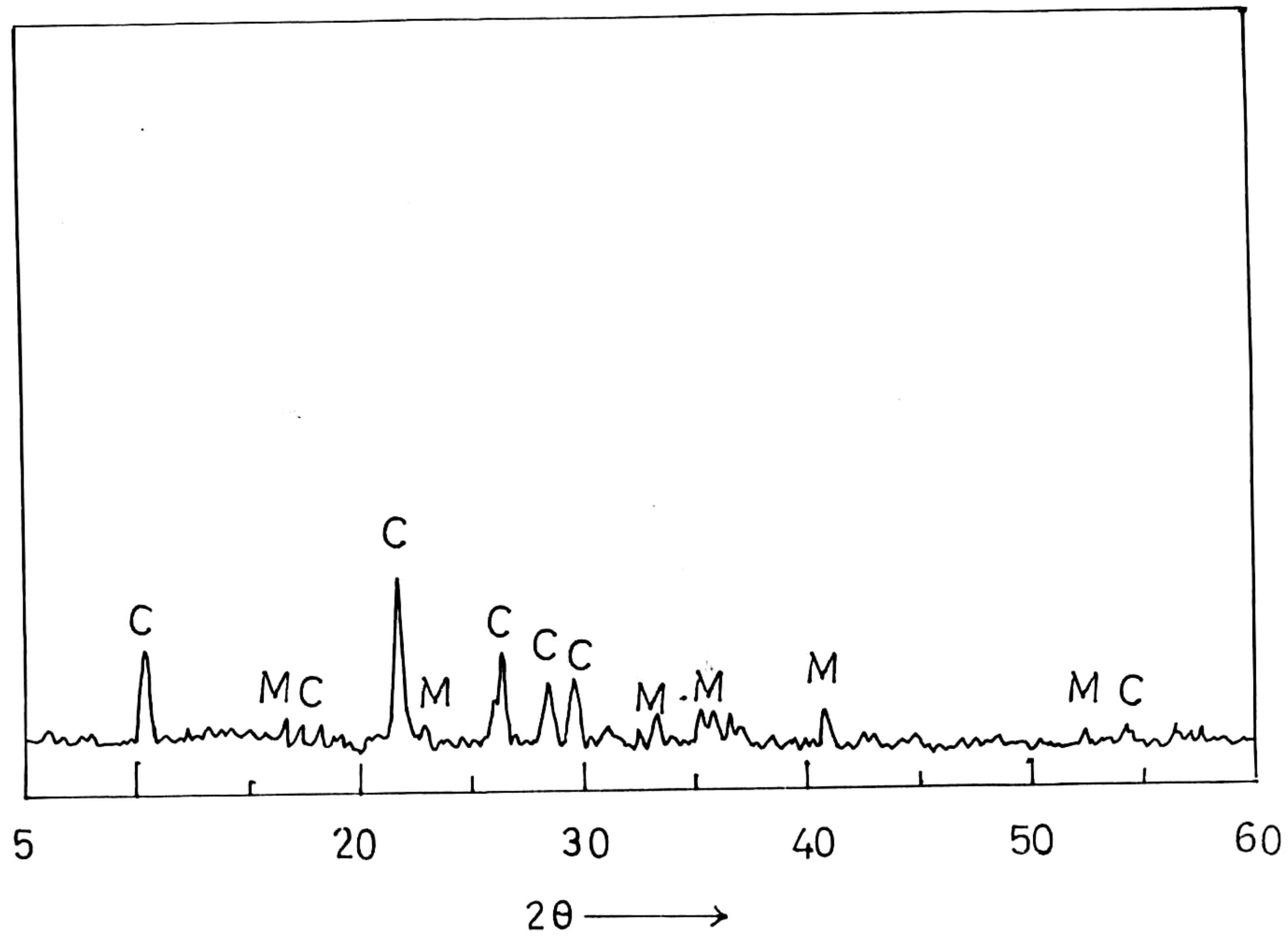


FIG. 20 (c) KO (1250°C)

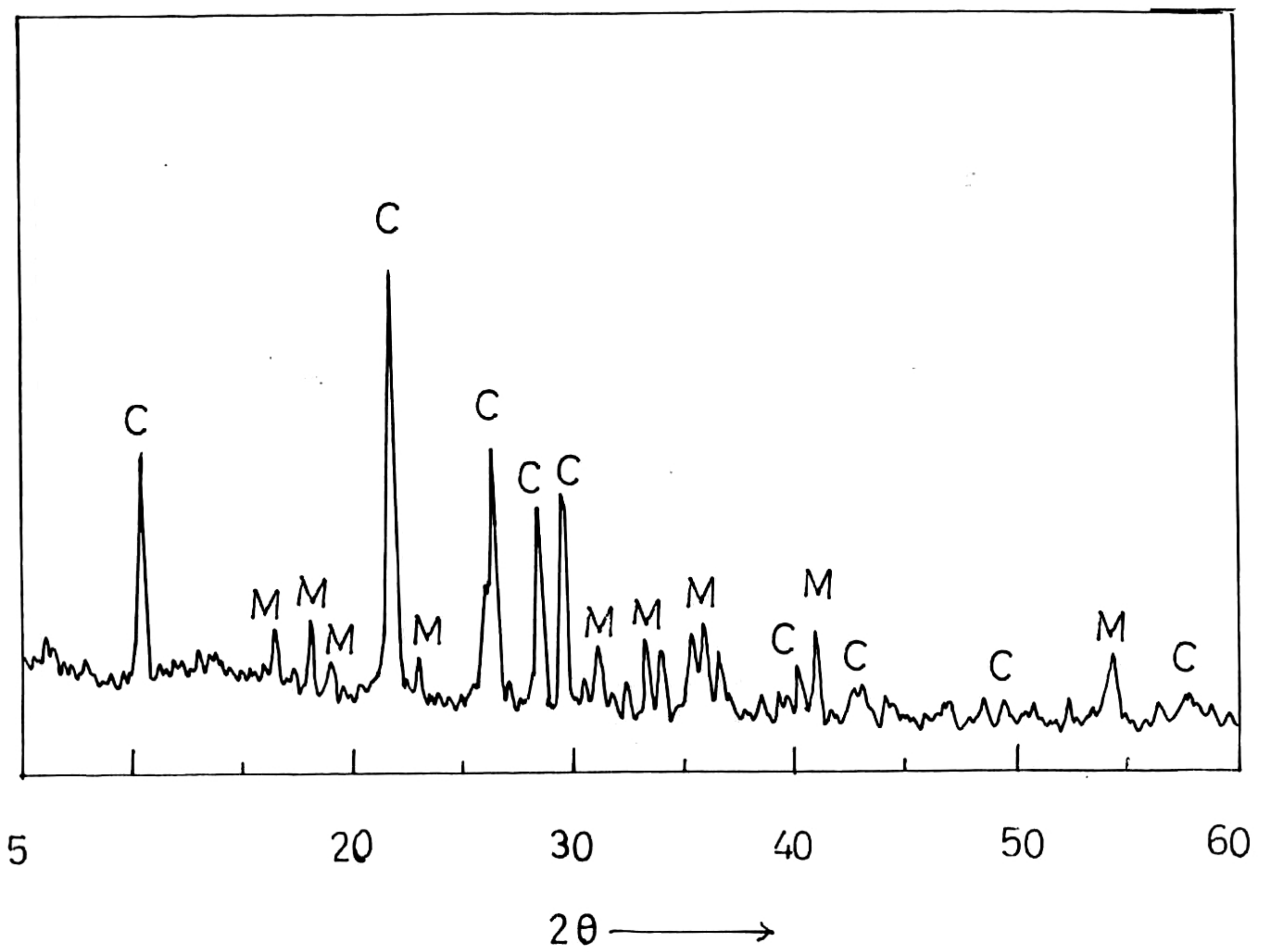


FIG. 20 (d) KO (1300°C)

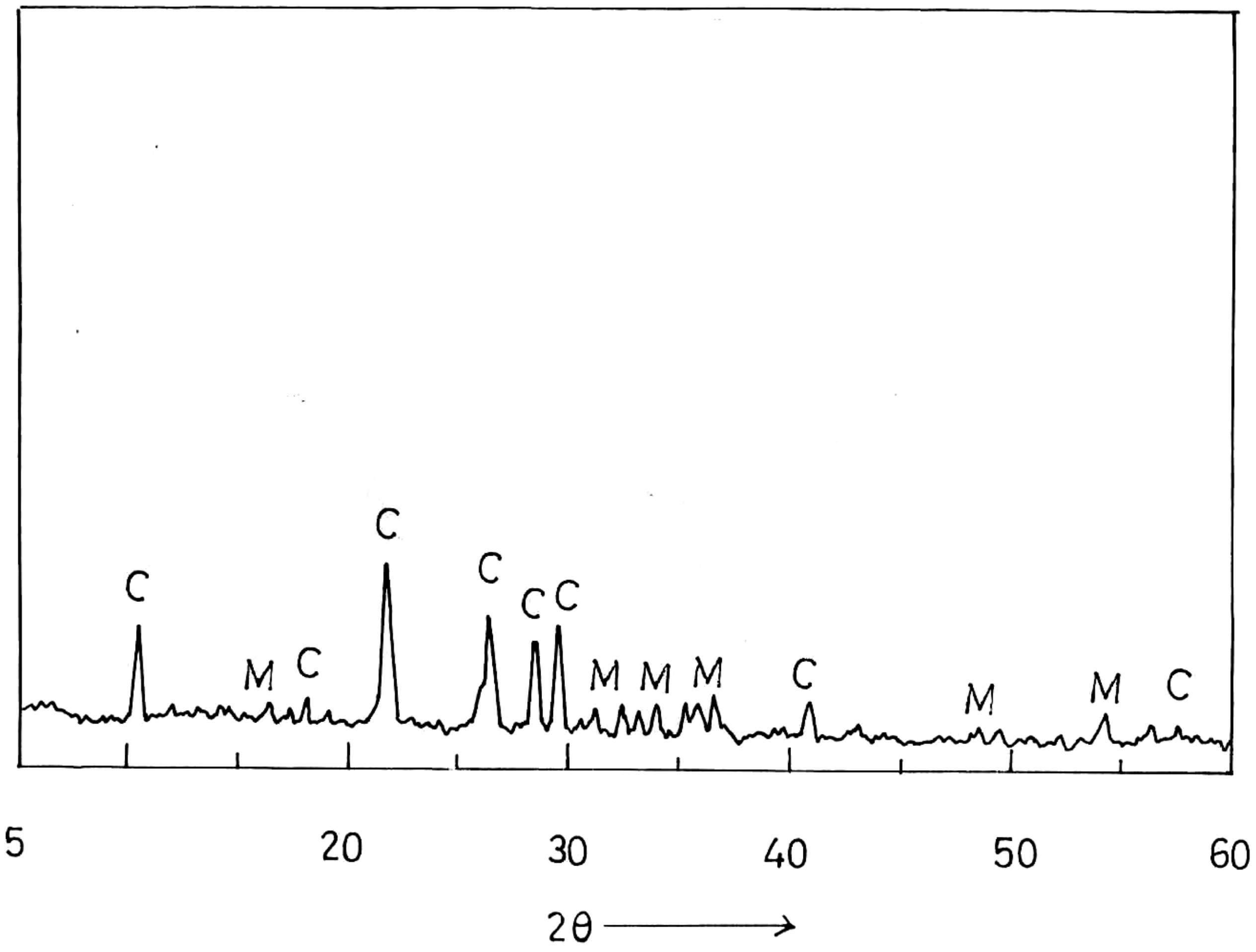


FIG. 20(e) KO (1350° C)

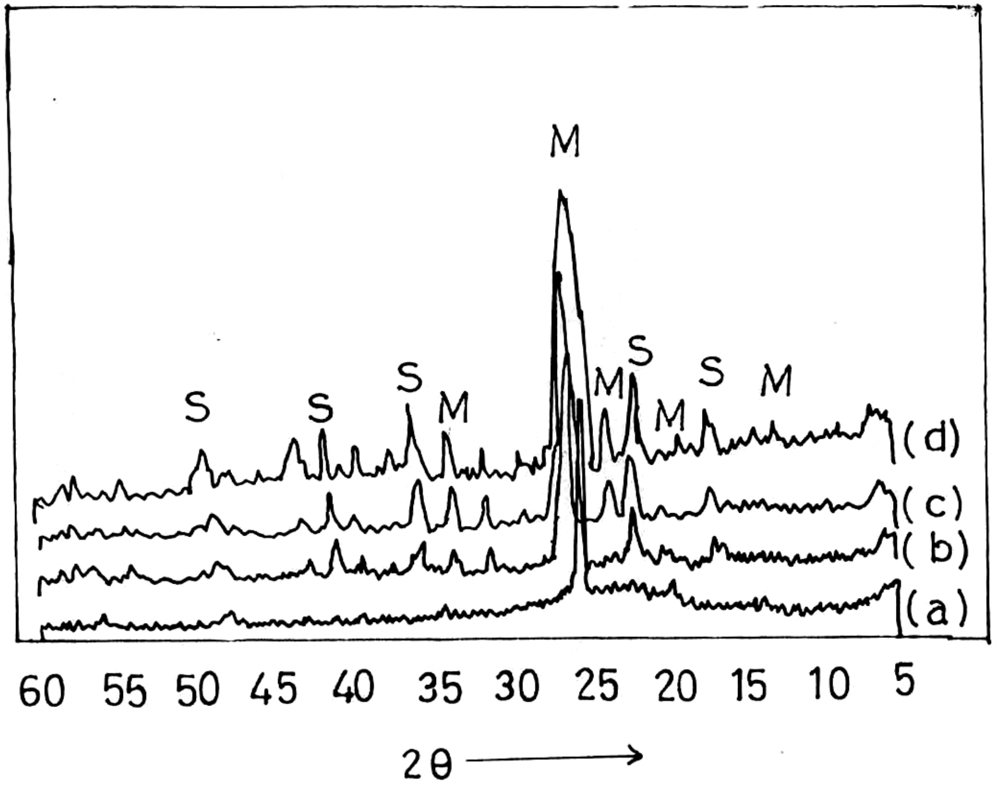


FIG.21. XRD PATTERNS OF KL SAMPLES
(a).1200°C (b)1250°C (c)1300°C (d)1350°C

3.4.4 Shrinkage properties

The percentage of volume shrinkage as well as apparent porosity obtained for K-O and K-L composition are as given in Table 8 and Table 9 respectively.

Table 8

Sample name	Temp °C	% firing shrinkage (volume)	% apparent porosity
K-O	1150	1.12	28.68
	1200	3.44	27.94
	1250	5.31	22.66
	1300	10.43	21.64
	1350	10.98	4.76

Table 9

Sample name	Temp °C	% firing shrinkage (volume)	% apparent porosity
K-L	1150	12.25	56.72
	1200	14.16	47.30
	1250	17.57	42.96
	1300	19.03	38.66
	1350	21.72	27.96

The results obtained show that the shrinkage rate is higher for KL composition than KO composition and this increases linearly with temperature. This may be due to the reason that the carbonate in the K-L composition escapes as CO_2 and other oxides. But in the case of K-O composition firing shrinkage occurs in a lesser rate than K-L composition.

The percentage of apparent porosity decreases with increase in temperature for both compositions. The values obtained show that the percentage water absorption is higher in the case of K-L than KO composition. The pore volume is higher in the case of sintered KL samples than K-O. This may be the reason for the higher apparent porosity which is approximately twice that of the amount of water absorbed.

3.4.5 Spalling resistance

The thermal shock resistance test by water quenching method has been carried out for cylindrical samples of both K-O and K-L compositions. It is observed that the minor cracks are developed after 7 cycles and the major cracks are developed after 9 cycles. Samples remain unbroken in to two pieces till 11–12 cycles.

Thermal shock proof ceramic material is based on magnesium aluminium silicate (Cordierite) and lithium aluminium silicate (spodumene). The most effective way to improve thermal shock resistance of ceramic materials is to reduce their thermal expansion. The thermal expansion properties of lithium alumino silicates can reach zero or even negative values so that the thermal resistance exceeds that of cordierite ceramics.

During firing at a temperature of 1450°C, K-O mix melts in to olive-green liquid which on cooling became a harder melt while K-L mix remained without any dimensional change.

3.4.6 Microstructure

The microstructure studies of polished K-O as well as K-L samples were carried out with the help of Scanning Electron Microscope (Jeol). Fig. 22 represents the magnified form of K-O structure and Fig. 23 shows magnified form of K-L structure.

The overall microstructure of K-O and K-L samples are as shown above. It is clear that the samples are composed mainly of fine cordierite crystals embedded in finer crystals of mullite and quartz. Fig. 22 shows the prismatic forms having pseudo-hexagonal shapes, which are characteristic of cordierite crystals.

Fig. 22. SEM photograph of *KO* sample which shows prismatic forms having Pseudo - hexagonal shapes. A. (magnification X 3000)

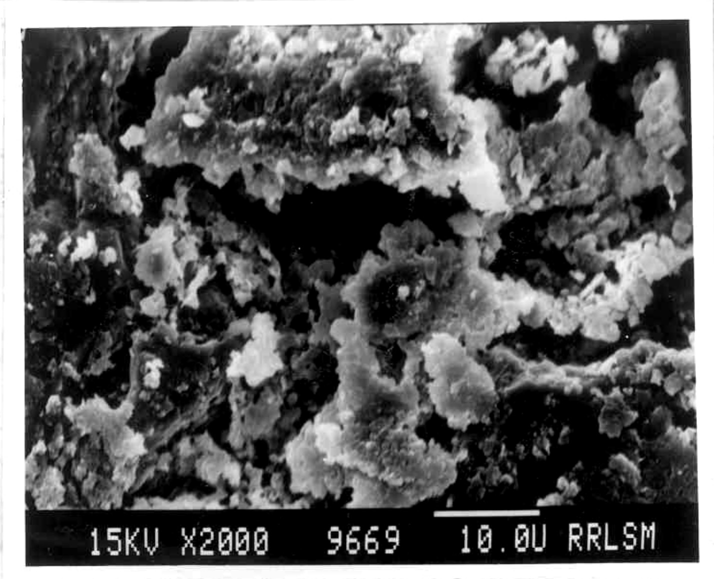
Fig. 23. SEM photograph of **KL** sample (Fine grained microstructure of mullite - spodumene composite)

B. (magnification X 2000)

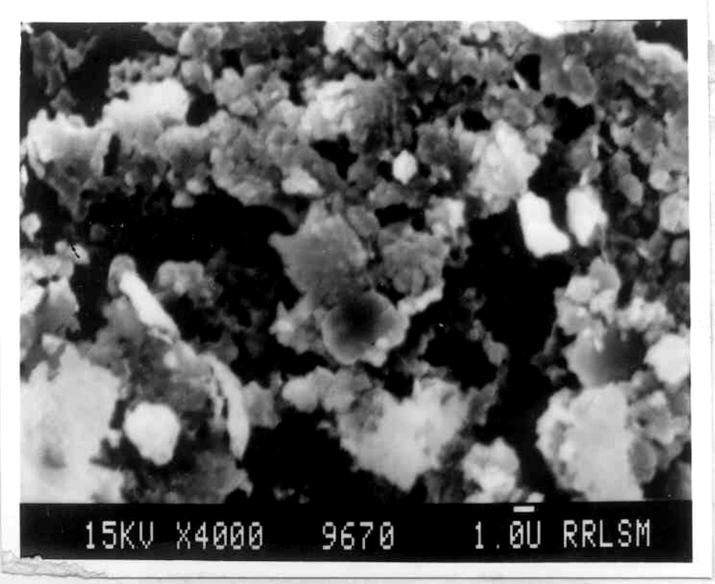
C. (magnification X 4000)


15KV X3000 9668 10.0U RRLSM

A


15KV X2000 9669 10.0U RRLSM

B


15KV X4000 9670 1.0U RRLSM

C

3.5 Conclusion

clay based high yield tough ceramic materials have been produced by two different compositions (a) kaolinite-olivine and (b) kaolinite-lithium carbonate. Sintering studies of both compositions at higher temperatures were carried out and the former composition gave rise to cordierite-mullite composite and the latter composition gave rise to spodumene-mullite composite. The physical, mechanical and thermal properties show better values compared to kaolinite samples. Both the compositions, gave excellent thermal shock resistance. 5% Lithium carbonate based materials showed a higher operating temperature than that of cordierite ceramics. But lithium being one of the less abundant elements, olivine can be recommended as the fluxing substance in order to produce thermal shock proof materials. The resulting composite can be used for making catalytic converters, spark plugs and exhaust pipes of automobiles and also can be used as saggers in ceramic industry.

3.6 Suggestions

Toughened ceramic bodies can be prepared from kaolinite and olivine; (cheap raw materials) without much expenditure and should be tested for catalytic converters in automobiles which will reduce air pollution to a considerable amount.

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PAPERS PRESENTED

PROCEEDINGS

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SINTERING OF KAOLINITE BY CONVENTIONAL AND FLASH CALCINATION TECHNIQUES

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ABSTRACT

Sintering studies of kaolinite (processed China clay from M/S.English Indian Clays Limited, Kochuveli, Thiruvananthapuram) have been carried out using conventional and flash calcination techniques. In both these techniques, dehydroxylation patterns as well as the formation of new phases have been monitored by X-ray diffraction studies. Effect of addition of fluxes viz. $CaCO_3$, K_2CO_3, Li_2CO_3 and Na_2CO_3 has been investigated in conventional and flash calcination techniques. It was observed that when 5 % K_2CO_3 was used as flux the cristobalite phase did not appear at all in the sintered matrix where as in the case of the latter, this phase was very prominent. As cristobalite undergoes phase change during heating (α to β) resulting in volume change this phase is undesirable in applications where the material is subjected to heating and cooling cycles. Hence this observation is of significance in ceramic processing.

INTRODUCTION

Kaolinite [$Al_2Si_2O_5(OH)_4$ (1:1 dioctahedral alumino silicate) is a mineral of considerable industrial significance. The heat treatment (calcination) of clays is a common industrial process with the principal objective of stabilization of materials by dehydroxylation. The dimensional changes which occur during firing have much importance because, shrinkage takes place in almost all materials during this process. In the present work, the sintering of kaolinite has been carried out by many authors [1-4]. Induced mulletization of kaolinite in presence of mineralizers has also been reported where oxides, carbonates, oxalates, sulphates, borates, tungstates etc. have been used to accelerate the conversion of kaolinite to mullite. Sintering processes were carried out at different temperatures in presence of metal carbonates as fluxes or mineralizers viz. $CaCO_3$, K_2CO_3, Li_2CO_3 and Na_2CO_3 using two different sintering techniques: conventional and flash calcination. The physico-chemical changes involved have been monitored at different calcination conditions.

Materials and Methods.

Processed (desanded and bleached) kaolinite used in this study was supplied by M/S. English Indian Clays Limited (EICL), Kochuveli, Thiruvananthapuram, Kerala. Kaolin sample was heat- treated by conventional and flash calcination techniques. The kaolinite samples were mixed with each fluxes viz. K_2CO_3, Li_2CO_3 and Na_2CO_3 (AR grade) in a 5 % aqueous slurry which was evaporated to dryness to get a perfect mix. $CaCO_3$ being insoluble in water was dry mixed using an agate mortar. The samples thus prepared have been designated as K-Ca(95% kaolin + 5% $CaCO_3$),K-K(95% kaolin + 5% K_2CO_3),K-Li(95% kaolin + 5% Li_2CO_3) and K-Na(95% kaolin + 5% Na_2CO_3) respectively. The dried powders were pelletised at a pressure of 475 kg/cm^2 and was used for conventional sintering studies. For flash calcination, [5-6], the samples were mixed with 2.5 gm of urea (AR grade), which was made into a paste with 2-3 drops of conc.HNO_3. Both types of sintering were carried out in a muffle furnace. The process were carried out from 600-1350 °C at a heating rate of 4°C/min and with a residence time of 1 hour at the soak temperature. For flash calcination, the sample in a platinum dish was introduced into the furnace which was previously heated to the desired temperature. A flash is produced within seconds. The sample was allowed to remain in the furnace for 1 minute. The same sintering processes were adopted for the kaolinite samples with mineralizers as well. All these sintered samples were characterized by X-ray analysis.

RESULTS AND DISCUSSION

The X-ray analysis of the raw material indicated that the major constituent is kaolinite (Fig.1). The presence of quartz as an impurity can be detected. 78 % by weight of this material was below 2 u and had a specific surface area of $13 \pm 0.1\ m^2g^{-1}$ (BET N_2 adsorption). The pH of 10 % aqueous slurry was 6.0 and the specific gravity was found to be 2.60 which was comparable to that of a standard kaolinite. The chemical assay carried out by classical wet chemical analysis is given in Table -1.

TABLE -1
CHEMICAL ASSAY OF KAOLINITE SAMPLE

Constituent	% (wt)
SiO_2	46.00
Al_2O_3	39.00
Fe_2O_3	00.40
TiO_2	00.45
CaO	00.05
MgO	00.05
K_2O	00.03
Na_2O	00.07
LOI	14.00

Identification of sintered phases by XRD

The X-ray diffraction studies have shown that the sintering has brought in very interesting phase changes. In conventional calcination process, heating of kaolinite above 650°C will result in metakaolinisation and the process gets completed at 900°C. Around 1100 °C, primary mullite phase appears. Conventional sintering with fluxed kaolinite were carried out at temperatures ranging from 600-1350°C. All samples gave only metakaolin at 600 and 900°C. At 1100°C, cristobalite and mullite phases were observed for K-Ca. These were the prominent phases upto 1350oC.Meanwhile when the same procedure were repeated using **K-K**, mullite phase alone was prominent at 1100, 1250 and 1350°C. No peaks of cristobalite was identified. when K-Li was sintered at 1100°C, along with the peaks of cristobalite and mullite, a new phase appeared which was identified to be spodumene $[LiAl(si_2O_6)]$ (Lithium aluminium silicate). The same behaviour was observed at 1250°C and 1350°C as well. To confirm the formation of spodumene, sintering processe were repeated using 15 % Li_2CO_3. The X-ray diffractogram proved the presence of spodumene beyond doubt. when **K-Na** was sintered, the phases observed were mullite, cristobalite and tridymite. These characteristic peaks were observed both at 1250 and 1350°C.

During flash calcination process, metakaolin was formed upto 900°C for **K-Ca, K-K, K-Li** and **K-Na** combinations. But at 1100°C **K-K** gave mullite phase alone. The sintering of **K-Ca, K-Li** and **K-Na** gave detectable peaks of cristobalite and mullite.

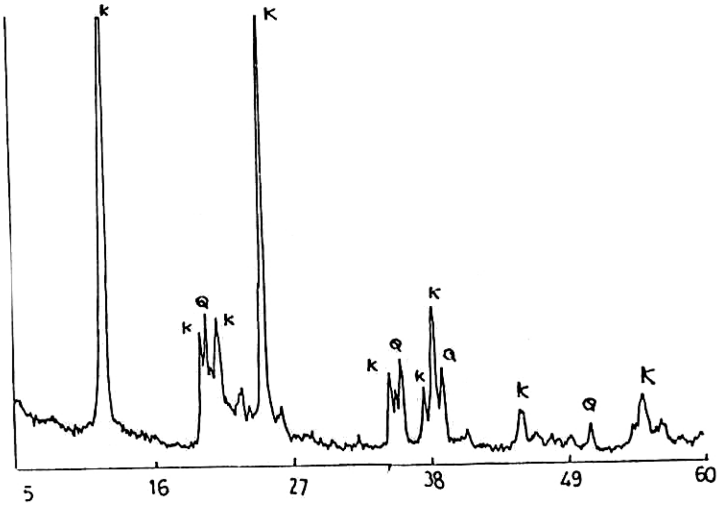
Table-2 indicates the conditions and the phases formed during sintering. The x-ray patterns of the sintered phases are given in Fig.2 (a-f).

TABLE-2

Clay used	Temperature	Time (in min.)	Phase/s formed
K-Ca	600	150	MK
	900	225	MK
	1100	275	C,M
	1250	312	C,M
	1350	337	C,M
K-K	600	150	MK
	900	225	MK
	1100	275	M
	1250	312	M
	1350	337	M
K-Li	600	150	MK
	900	225	MK
	1100	275	C,M,S
	1250	312	C,M,S
	1350	337	C,M,S
K-Na	600	150	MK
	900	225	MK
	1100	275	C,M,T
	1250	312	C,M,T
	1350	337	C,M,T

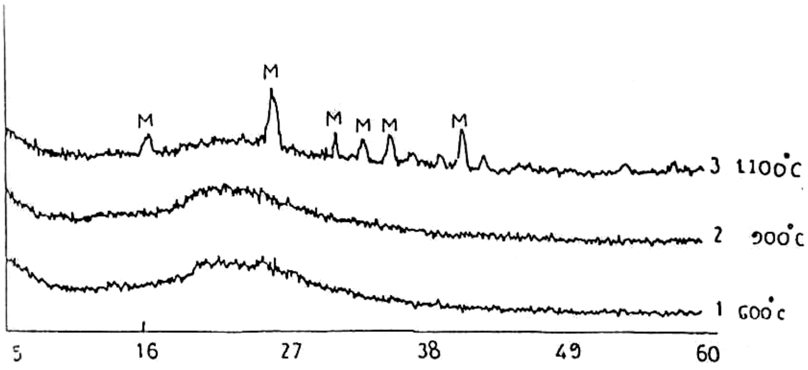
MK-Metakaolin, C-Crisyobalite, M-Mullite, S-Spodumene,T-Tridymite

A comparison of the sintered phases indicate that the presence of calcium and sodium as mineralizers have resulted in cristobalite formation along with mullite where as

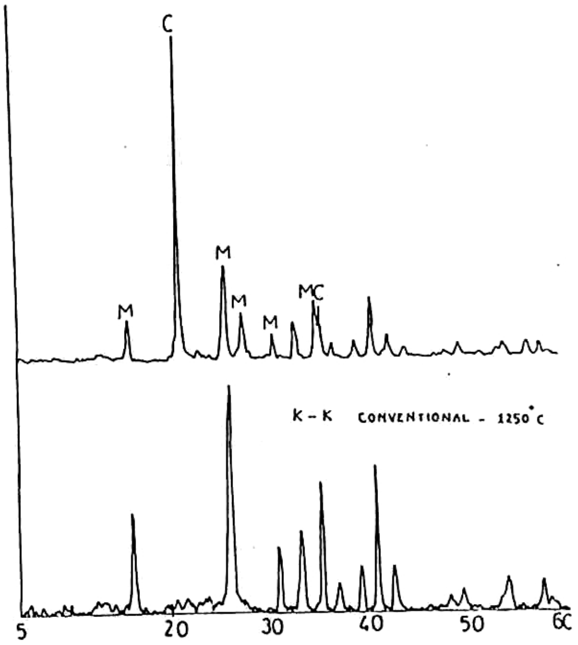


2θ ------>
FIG.1 KAOLINITE - RAW

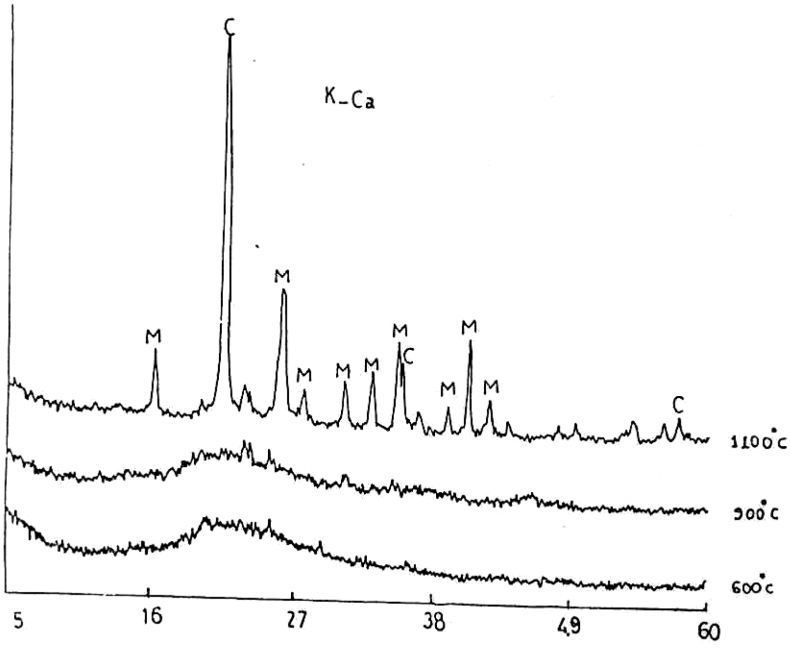
FIG.2 X-RAY PATTERNS OF SINTERED SAMPLES (a-f)



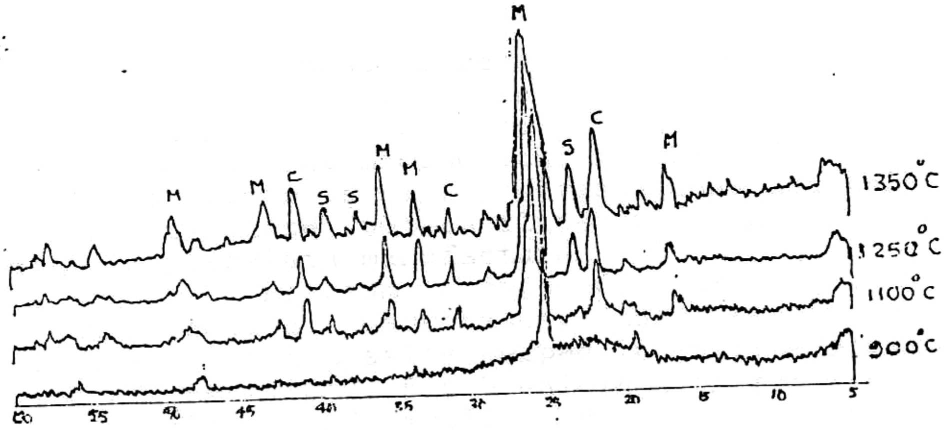
2θ ------------>
(a) X-RAY PATTERNS OF SINTERED SAMPLES (K-K)



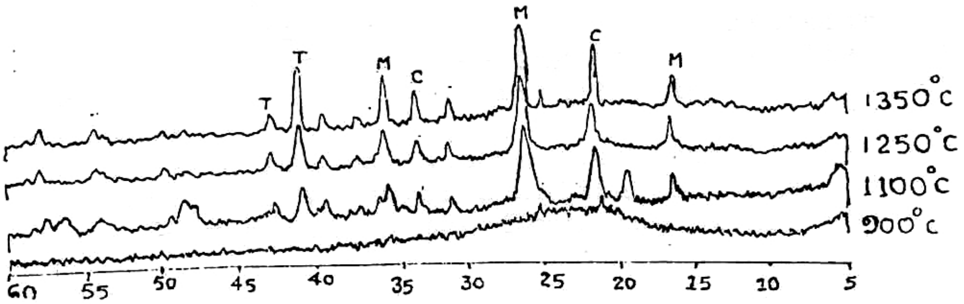
2θ ----------->
(c) A COMPARISON OF X-RAY PATTERNS OF K-Ca & K-K (1250°C)



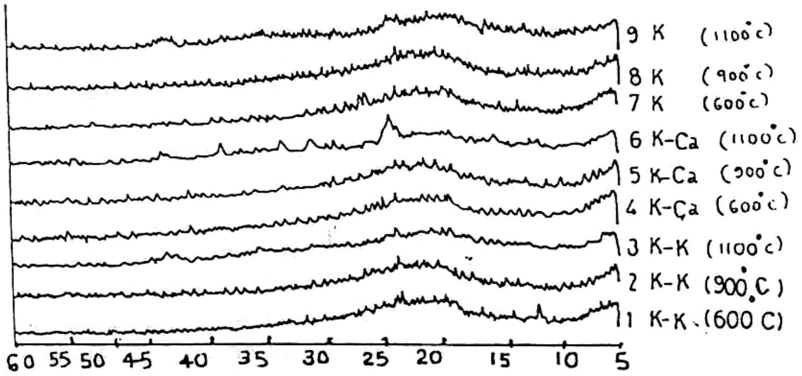
2θ ------------>
(b) X-RAY PATTERNS OF SINTERED SAMPLES (K-Ca)



2θ ------------>
(d) X-RAY PATTERNS OF SINTERED SAMPLES (K-Li)



2θ ------------>
(e) X-RAY PATTERNS OF SINTERED SAMPLES (K-Na)



2θ ----------->
(f) X-RAY PATTERNS OF FLASH CALCINED SAMPLES

the presence of potassium resulted in the elimination of this phase totally. Cristobalite in ceramics generally introduces thermal instability as the to change at 220°C results in a volume change causing microcracks in the body. Hence the use of K_2CO_3 as mineralizer is highly advantageous and this could be the reason why orthoclase (potash fledspar) is added as an essential ingradiet in porcelain manufacture.

Lithium compounds are noted for their mineralizing action. Carbonates, fluorides and chlorides are commonly used. Lithium salts helped in mullite formation at very low temperatures 550°C. Flash calcination for 1 minute indicated that cristobalite and mullite phases are formed during this process. Interestingly, the conventional calcination resulted in the formation of an additional phase ie. spodumene indicated by pink spots. Inspite of uniform wet mixing, the third phase has appeared as specs. This may be due to the diffusion of these highly mobile lithium ions in the mesopores formed during the dehydroxylation of kaolinite during sintering. In flash cacination, the rate of heating is faster than the rate of diffusion and this might have resulted in instantaneous reaction with kaolinite.

It is also proved that Li ion fits into the lattice during slow dehydroxylation and this intimate contact with Al and Si results in the formation of spodumene.

CONCLUSION

The transformation of kaolinite to mullite is thermodynamically feasible above 1100°C by conventional sintering and flash calcination. The mineralizers under investigation helped mullite formation at lower temperatures along with cristobalite with an exception of K_2CO_3. Lithium as a mineralizer indicated an interesting phenomenon of formation of spodumene specs in slow sintering. Flash calcination does not indicate this phase formation.

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TOUGHENED CERAMICS FROM KAOLINITE

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Trivandrum

Abstract

In the present work, two different compositions of tough ceramic materials derived from china clay have been compared : one toughened with olivine and the other with lithium carbonate. The sintering studies of these two compositions were carried out at temperatures ranging from 1150-1350°C. The phase changes taking place during sintering have been identified by x-ray analysis. The composition of china clay and olivine in the ratio 3:1 give rise to cordierite while 5% addition of lithium carbonate leads to mullite and spodumene phase formation. Samples were tested for crushing strength, flexural strength, bulk density, apparent porosity and thermal shock resistance. The results obtained were compared with that of natural cordierite. Both the compositions made from china clay have got excellent thermal chock resistance and hence recommended for applications where low thermal expansion is preferred.

THE INDIAN CERAMIC SOCIETY
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Executive Secretary

Ref. No. ICS:60AS: I
September 13, 1996

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Dear Author(s),

Kindly refer to your following paper(s)* sent to us for presentation at the 60th Annual Session of the Indian Ceramic Society scheduled to be held at Ranchi during December 12-13, 1996.

Your ~~paper~~/paper ~~has~~/have been selected for presentation in the Poster Session. **The size of the Poster should be 85 cm x 60 cm.** The Poster should be clearly readable from a distance of 2 metres. Kindly arrange to prepare the Poster accordingly and bring it along with you at the Session venue.

An abstract of the paper, however, will be included in the preprint volume to be published on the occasion and distributed among the delegates on the eve of the Session. **The abstract should be restricted to only one page (A4 size), printing area being 24 cm x 16 cm..**

Kindly, therefore, send us **the camera-ready copy of the abstract using an electronic typewriter or a laser printer (please avoid dot matrix printer)** which should not exceed one page in any case. **The copy should reach this office latest by October 20, 1996.**

Looking forward to your kind co-operation and expeditious action.

Thanking you,

Yours faithfully,

(A. K. Banerjee)

20. Toughened Ceramics from Kaolinite - A. Yamuna and M. Lalithambika (RRL, Trivandrum)