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GLASS FORMATION AND PROPERTIES OF GLASS AND GLASS-CERAMICS
IN $\text{SrO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ & $\text{BaO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ SYSTEMS

A Thesis

Submitted to the Faculty of Graduate Studies Through the
Department of Engineering Materials in Partial Fulfilment
of the Requirements for the Degree
of Master of Applied Science at the
University of Windsor

by

Naweed-ul-Islam

Windsor, Ontario

1970

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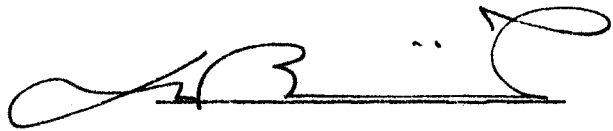
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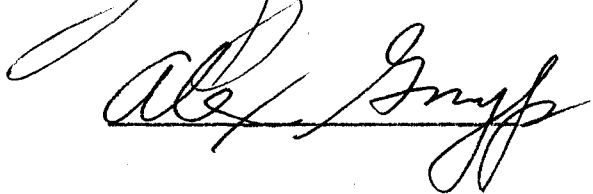
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ABSTRACT

Regions of glass formation along with density, refractive-index and thermal expansion properties of glass have been determined in the systems SrO-La₂O₃-B₂O₃ and BaO-La₂O₃-B₂O₃. A study of the variation of molecular refractivity with the addition of La₂O₃ to a SrO-B₂O₃ glass has also been presented. Glass of composition (mole%) 15 BaO, 20 SrO, 20 La₂O₃ and 45 B₂O₃ containing a small quantity of P₂O₅ as a catalyst was subjected to suitable heat-treatment, guided by DTA diagram of the glass. Crystallization of lanthanum meta-and orthoborates as a result of heat-treatment in specific ranges of temperature was detected by means of X-ray diffraction analysis. Refractive index, thermal expansion, microhardness and chemical durability properties of glass improved as a result of catalyzed crystallization in specific temperature ranges.

ACKNOWLEDGEMENTS

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I INTRODUCTION

At the beginning of this century progress in glass technology was based on further developments of silicate and to a lesser extent borate and phosphate glasses. It is, however, now being considered that borate glasses, due to their superior optical as well as high strength properties, also deserve attention.

Recently a number of publications have appeared in the literature showing the influence of rare earth elements on various properties of engineering materials, including glasses. Compositions of borate glasses having lanthanum oxide (La_2O_3) as a major modifying constituent have been patented (1). Since most of the scientific information in this area is covered by trade secrets and patent rights, a systematic study is highly desirable.

Boundaries of glass formation have already been established in the system, $\text{CdO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ and optical properties as well as densities reported (2). No such work for the systems $\text{SrO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ and $\text{BaO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ has, so far, appeared in the literature. Cadmium belongs to Group II-B whereas strontium and barium belong to Group II-A of the periodic chart. The present study is initially concerned with the determination of regions

of glass formation and testing for the properties of glass in the systems $\text{SrO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ and $\text{BaO-La}_2\text{O}_3\text{-B}_2\text{O}_3$.

Crystallization of glasses from the system, $\text{CdO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ has been reported recently (2). This possibility has also been attempted in the present work for a glass whose composition is based on the constituents of the systems, under investigation. Controlled crystallization of glass which itself is non-crystalline produces polycrystalline solids known as glass-ceramics. In glass-ceramics the crystalline phases are entirely produced by crystal growth from a homogeneous glass phase and this distinguishes these materials from traditional ceramics, where most of the crystalline material is introduced when the ceramic composition is prepared although some crystallization may occur or new crystal types may arise due to solid state reactions.

Since molten glass can be obtained in a homogeneous condition, uniformity of chemical composition can easily be achieved for glass-ceramics. The homogeneity of the parent glass together with the controlled manner in which crystals are developed results in ceramic materials possessing a very fine-grained uniform structure free from porosity. This is beneficial in a number of ways since it favours the development of high mechanical strength and also results in improved

electrical insulating characteristics. A pertinent feature of the production of glass-ceramics is that through the variations which can be applied in the heat-treatment process, various types of crystals can be developed in controlled proportions. As a result, the physical characteristics of glass-ceramics can be varied in a controlled manner and this factor has an important bearing upon the practical applications of glass-ceramics.

Glass is a very convenient medium for fundamental studies of this type because glass-like liquids have such high viscosities that the diffusion processes and atomic rearrangements which control nucleation and crystal growth occur relatively slowly. Because of the rapid increase of viscosity which occurs when the temperature falls, it is possible to arrest the crystallization process by rapid cooling. Thus various stages in crystal growth and development can be frozen for examination by convenient methods. While glasses having compositions corresponding to simple compounds can be made, glasses of great complexity are also possible.

In the general field of materials technology glass-ceramics are of great importance since these

offer combinations of physical properties which were hitherto unattainable. As will be seen in the present work, a considerable improvement of properties has been achieved during conversion of a borate glass to glass-ceramics.

II THEORETICAL BACKGROUND AND LITERATURE REVIEW

Glass possesses a number of properties which are characteristics of the liquid state thus the classification of glass as a liquid of very high viscosity will be in accordance with modern views. A widely accepted definition of glass as proposed by A.S.T.M. (3) is, that glass is an inorganic product which has cooled to a rigid condition without crystallization.

The relationship between glassy state, the normal solid and the liquid states can be understood from what happens during the cooling of the melts. For a substance which crystallizes, it is observed that there is a closely defined temperature at which solidification occurs and at this temperature a discontinuous volume change (often a contraction) occurs. In addition heat is evolved when solidification takes place. For a substance which can be cooled to the glassy state, on the other hand, no discontinuous volume change is found and there is no exothermic effect corresponding to the change from the liquid to the solid state. Instead, the viscosity of the melt increases as the temperature falls and eventually the viscosity attains values which are so high that for all practical purposes the substance behaves as a rigid solid. Thus the glassy state is like the liquid state, but is distinguished from the normal liquid state by the high

magnitude of viscosity. It is thus clear that the glass may be regarded as a supercooled liquid, since the melt is cooled through the temperature zone in which crystallization might occur, but the liquid-like structure is retained. Like other supercooled liquids glass is a substance in a metastable state which would achieve a lower free energy by crystallizing. Glasses appear to be completely stable, however, except within a fairly restricted range of temperatures.

The transparency of glass may be thought of as a property more usually characteristic of the liquid state than of the solid crystalline state. It is true that non-metallic single crystals are often transparent but polycrystalline materials are not and the transparency of glass is the result of complete absence of grain boundaries which could cause scattering of light. The X-ray diffraction pattern of glass shows only diffuse halos as compared with the sharp pattern of lines given by a crystalline substance. The pattern given by glass is thus virtually indistinguishable from that given by a liquid and this provides confirmation of the liquid-like nature of glass.

Conditions of glass formation:- Some oxides can be readily obtained in the form of glass when they are cooled from the molten state whereas others invariably crystallize. Whether or not an oxide can be obtained

in the form of a glass is of considerable scientific interest.

Goldschmidt (4) made one of the earliest attempts to discover characteristics common to glassforming oxides and suggested that the ability of an oxide to form glass might be related to the way in which the oxygen ions were arranged around the cation to form the unit cell of the crystal structure. In stable crystal structures the number of ions immediately surrounding a cation (co-ordination number) is determined by the relative sizes of the anions and cations. Goldschmidt pointed out that for a number of glass-forming oxides including SiO_2 , GeO_2 and P_2O_5 a tetrahedral arrangement occurred in the crystalline state. He suggested that this might be the criterion of glass-forming ability. Because of the exceptional behaviour of BeO , Zachariasen (5) rejected Goldschmidt's theory and developed a better accepted random net-work theory of glass structure. He deduced that the atoms must be linked in the form of a 3-dimensional net-work in the glass as in crystals. The net-work in glass could not be a periodic one, since glasses unlike crystals do not give sharp X-ray spectra. Zachariasen also proposed that the energy content of a substance in the glassy state must not be greatly different from that of the corresponding crystal net-work. It follows from this that

for a glass-forming oxide the co-ordination number of the cation must be closely similar in the glass to that observed in the crystal. This means that the units of structure in the glass and in the crystal will be practically identical. In the crystals these structural units are built up to give a regular lattice but in the glass there is sufficient distortion of bond angles to permit the structural units to be arranged in a non-periodic fashion giving a random net-work. Figs. 1a & 1b show the differences between the regular crystalline lattice and the random net-work for an oxide having the formula M_2O_3 . In both cases the structural units are MO_3 triangles. This view of glass structure is entirely consistent with the liquid-like nature of glass. Fig. 2 shows the settlement of foreign oxides in the structural net-work of glass. According to Zachariasen the following are the conditions for glass formation:

- (a) An oxygen atom must not be linked to more than two M atoms.
- (b) The number of oxygen atoms surrounding M must be small.
- (c) The oxygen polyhedra must share corners only and not edges or faces.

The oxides M_2O and MO cannot meet the conditions proposed by Zachariasen. The oxides M_2O_3 can do so if the

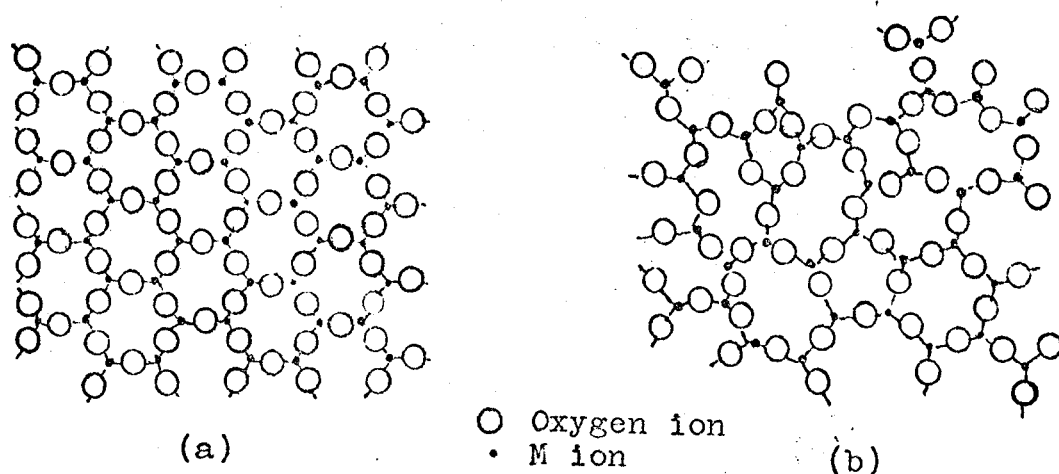


Fig.1. Two-dimensional representation of an oxide M_2O_3 in (a) the crystalline form (b) the glassy form.

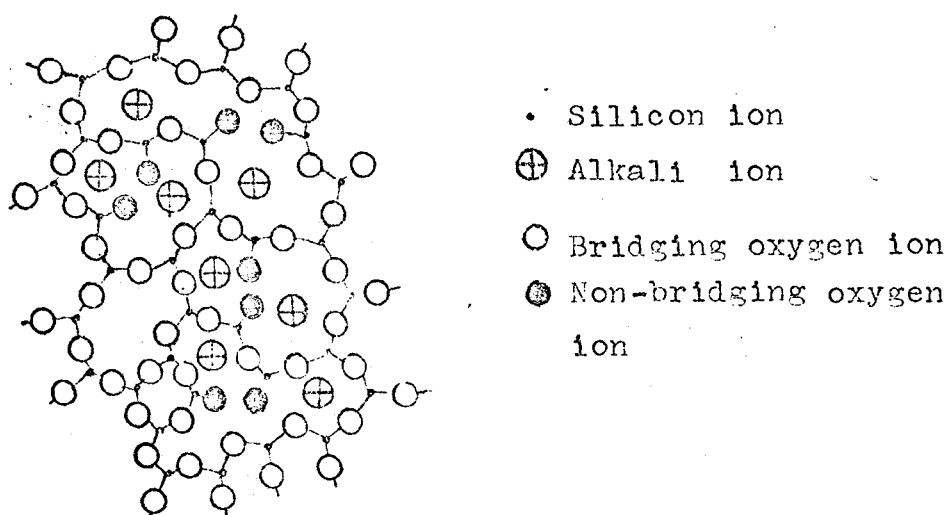


Fig. 2. Two dimensional representation of the structure of a silicate glass.

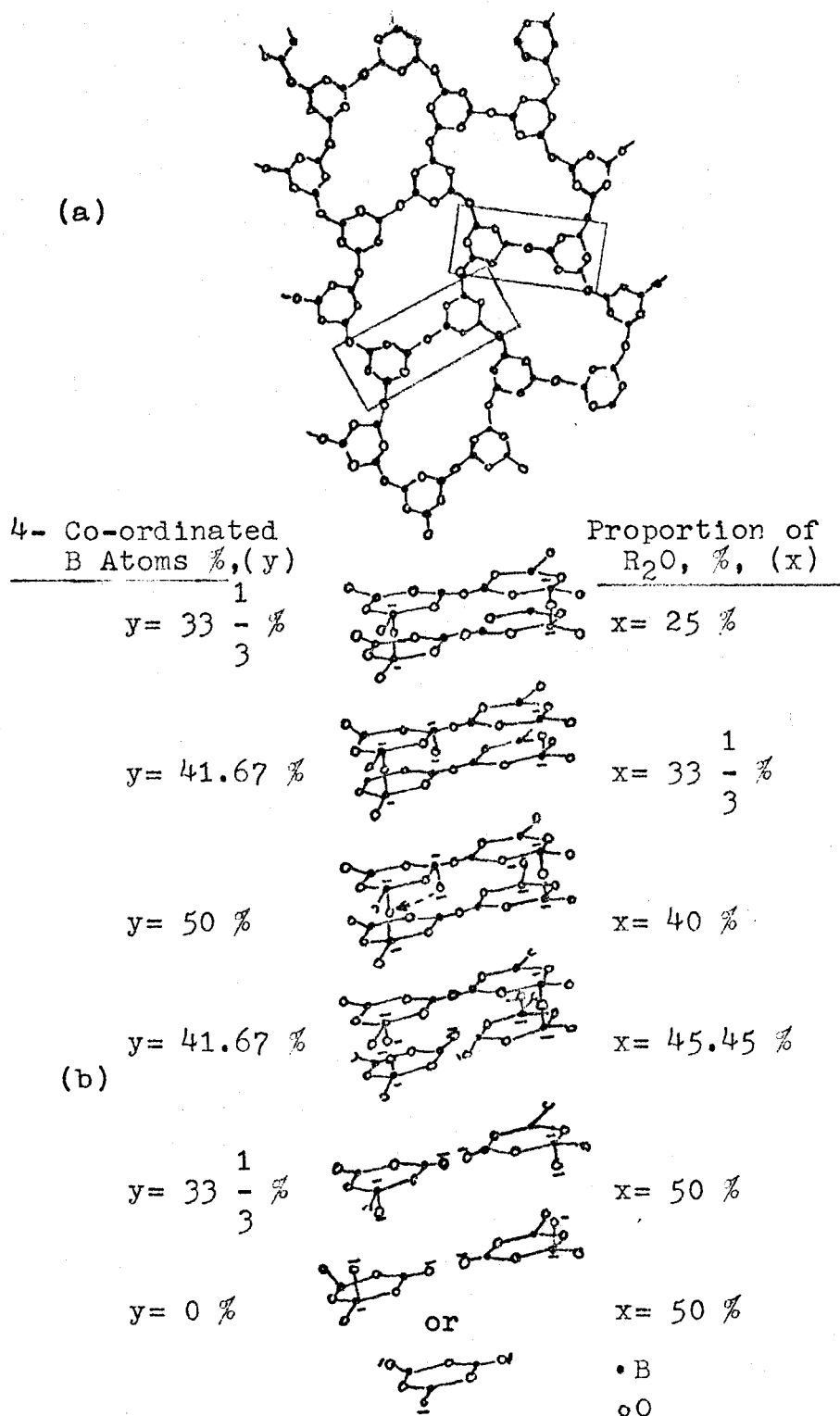


Fig.3(a) Structure of glassy boric anhydride.

Fig.3(b) Consecutive schemes of three dimensional structure formation (polymerization) and depolymerization of $B_2O_3 + R_2O$ glasses, based on the model of Fig.3(a).

oxygens form triangles around each M atom and the oxides MO_2 and M_2O_5 can do so if the oxygens form tetrahedra around each M atom.

Vitreous boric oxide (B_2O_3) is a good example of a glass whose structure is built up of triangular units. These units are found in many crystalline borates. V.V. Tarasove (6) has recently suggested a structure of glassy B_2O_3 . The whole structure could be subdivided into repeated units of the composition $3B_2O_3$, as presented in Fig. 3a.

The modifiers:- Oxides which form glasses when melted and cooled are glass-forming or net-work forming oxides because of their ability of building up a continuous 3-dimensional random net-work. A modifying oxide is one that is incapable of building up a continuous net-work. The effect of such oxides is to weaken the glass net-work. Consecutive schemes as reported, of 3-dimensional structure formation (polymerisation) and depolymerisation of $B_2O_3 + R_2O$ glasses (6) based on the model of B_2O_3 of Fig. 3a have been shown in Fig. 3b. R_2O is a modifying alkali oxide in this figure. A number of modifying oxides, which are usually not capable of forming a glass, can take part in the glass net-work. Aluminium oxide is a good example of such an oxide. This type of oxide is classified as an intermediate oxide. The functions of different types of ions, in glass, can be explained on the concept

of ionic field strength of different ions (7). The ionic field strength is defined as Z/r^2 , where Z is the valency of the ion and r is the ionic radius. The ionic field is a measure of the electrostatic force which the ion can exert upon neighboring oxygen ions. Examination of field strength* values for various ions shows that net-work forming cations have the highest values of field strengths.

Glass forming ability of Group-II metal oxides:- The concept of field strength represents a simplified view point since it considers ions to behave as rigid spheres. This is not strictly true since large ions of low charge and non-noble gas cations are deformable. Considering members of Group-II in the periodic chart the electronic configurations of the Group-IIA and Group-IIB metals differ in that the divalent ions of Group-IIA assume the rare gas configuration as contrasted with those of Group-IIB. The non-rare gas electronic configuration effects greater anion deformation than the rare-gas configuration, even when charge and ionic sizes are comparable as in the case of Group-IA and Group-IB ions (8). The higher polarization ability of the non-rare gas configuration results from the lower electronic screening effect of these cations as compared with those with rare gas configuration.

*Ions which exert an intermediate effect on glass structure generally have field strengths between those of net-work formers and modifiers.

Fig. 4 shows crudely how the term polarization is conceived. A portion of the negative cloud of the anion is pulled over toward the region of the positive cation. As the distortion is increased the bond between anion and cation takes on a more covalent character. An easily deformable ion is said to be highly polarizable. The polarization ability of a cation (i.e., its ability to distort or deform a nearby electron cloud) depends on its concentration of positive charge; a cation with a large ratio of charge to size should be a good deformer. However cations having a non-rare gas configuration are more prone to form covalent bonds than are cations with the same charge -size ratio but with a rare gas configuration. Such a difference is based on differences in screening effects. The nuclei of rare gas structure ions are adequately screened by the spherical shell of p electrons on the outside of the atom. For other ions the screening is less complete and more of the excess positive charge is presumably available for distortion of the partner anion. As a result of the increased covalency between an anion and a cation the distance between them i.e., the interatomic distance may be considerably shorter than that predicted strictly from ionic radii . The strong polarizing effect of the Group II-B promotes immiscibility

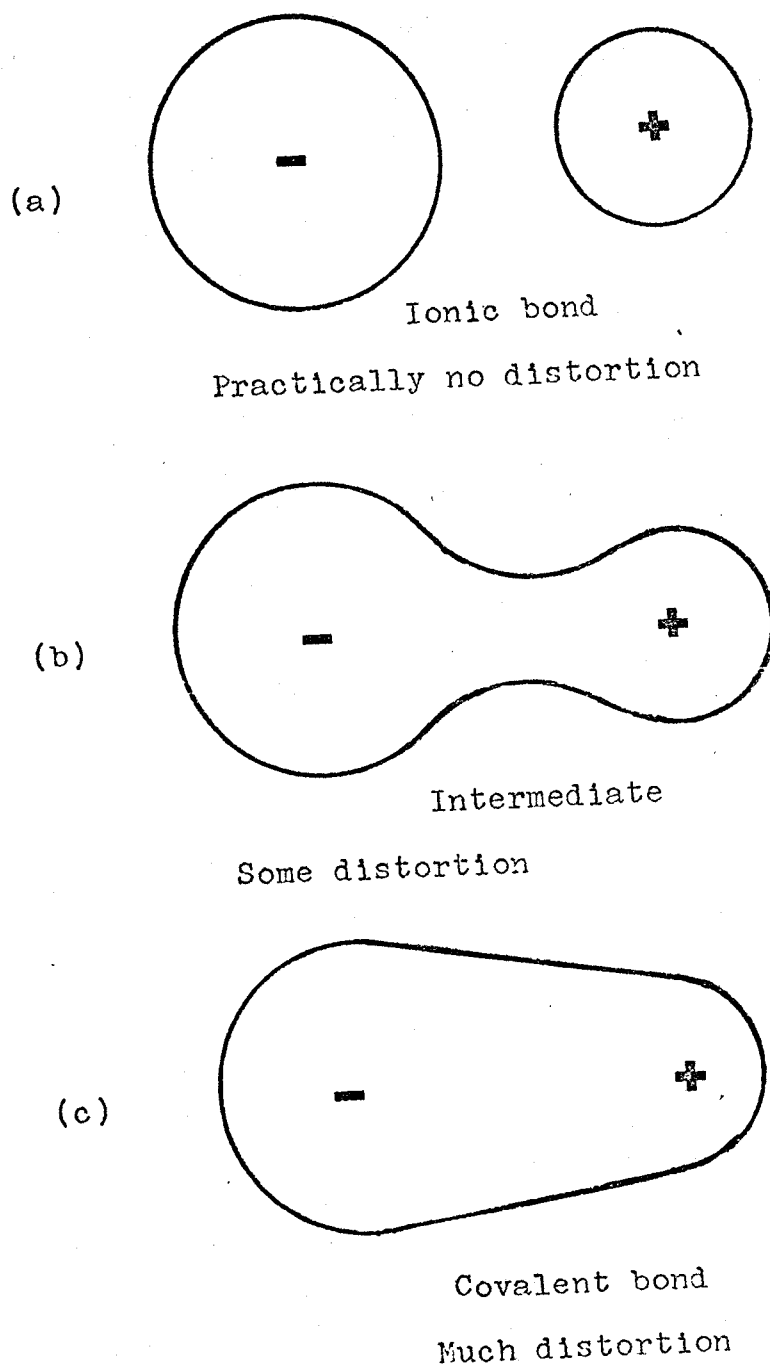


Fig. 4. Covalent character and distortion.

in the binary borates of these metals. In these systems, the magnitude of the glass-forming region is of particular interest in that it depends to an appreciable degree on the strength of the bond between the metal ion and the oxygen in the glass net-work. Qualitatively the degree of immiscibility in these binary systems is a function of the ionic potential Z/r of the cation and of the bond strength, $Z/C.N.$, in which r is the Pauling ionic radius, Z the ionic charge and $C.N.$, the co-ordination number of the cation in glass (9). Levin and Block (10) found that divalent ions with ionic radii greater than that of Ca^{++} belong to the group which in the binary borates corresponds with bond strength $Z/C.N.$ of $1/3$ or greater. The immiscibility of this group of ions is greater than that with $Z/C.N.$ of $1/4$ or smaller.

Lanthanum possesses a large ionic radius and a stronger bond with oxygen ions in comparison with other elements of the third group: aluminium and gallium (11). There exists a limited solubility in the system $La_2O_3-B_2O_3$. Miscibility, in terms of glass formation, of La_2O_3 in this system has been reported as 19-23.2 mole% (12). The presence of SrO and BaO is expected to increase the solubility range and make it possible to produce glasses of various compositions.

The influence of temperature and fusion time

on glass formation:- Generally speaking for a glass forming system there are upper and lower temperature limits of glass formation. Compositions which are rich in the high melting point constituents require high temperature for fusion and longer periods where necessary. It is, however, not advisable to prolong fusion time especially at the higher temperature limit of glass formation because this would increase the loss of glass through volatilization and consequently change the composition of the glass. Prolonged fusion beyond a certain stage causes devitrification of glass in many cases (13).

Unfortunately, the use of high temperatures for promoting solubility is of little use to the glass technologist. If the temperature is high the kinetic energy available for promoting solubility is also available for nucleation and hence these high melting systems are not suitable for stable glass formation (14). Glass formation at temperatures above 1500°C is rare (15).

Compositions of glass-formation:- Regions of glass formation in the system, $\text{MgO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{SrO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{BaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{ZnO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ and $\text{CdO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ as shown in Fig. 5 have already been worked out (16). These are of interest because aluminum along with lanthanum and gallium belongs to Group-III of the periodic chart. A glass forming region has also been determined for $\text{CdO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ system very recently (2). The boundaries of glass formation in the latter system include 50 to 80 mole% B_2O_3 , 0 to 25 mole% La_2O_3 and 0 to 25 mole% CdO . These compositions have been plotted in Fig. 6.

The boron in the borate glasses may exist in both three and fourfold co-ordination, the extent of fourfold co-ordination depending on the concentration of metal in the borate glass. Huggins and Abe (17) concluded that there is a maximum of four fold co-ordination of boron at a metal oxide concentration of 20 mole%. Beyond this concentration there is no further increase in the co-ordination of the boron. Krogh-Moe (18), however, has reported that the co-ordination of the boron continues to increase to fourfold until at least 50% of the boron is in the fourfold co-ordination. Huggins & Abe found support in the observed changes in the physical properties of borates with metal oxide concentration, such as a minimum expansion coefficient

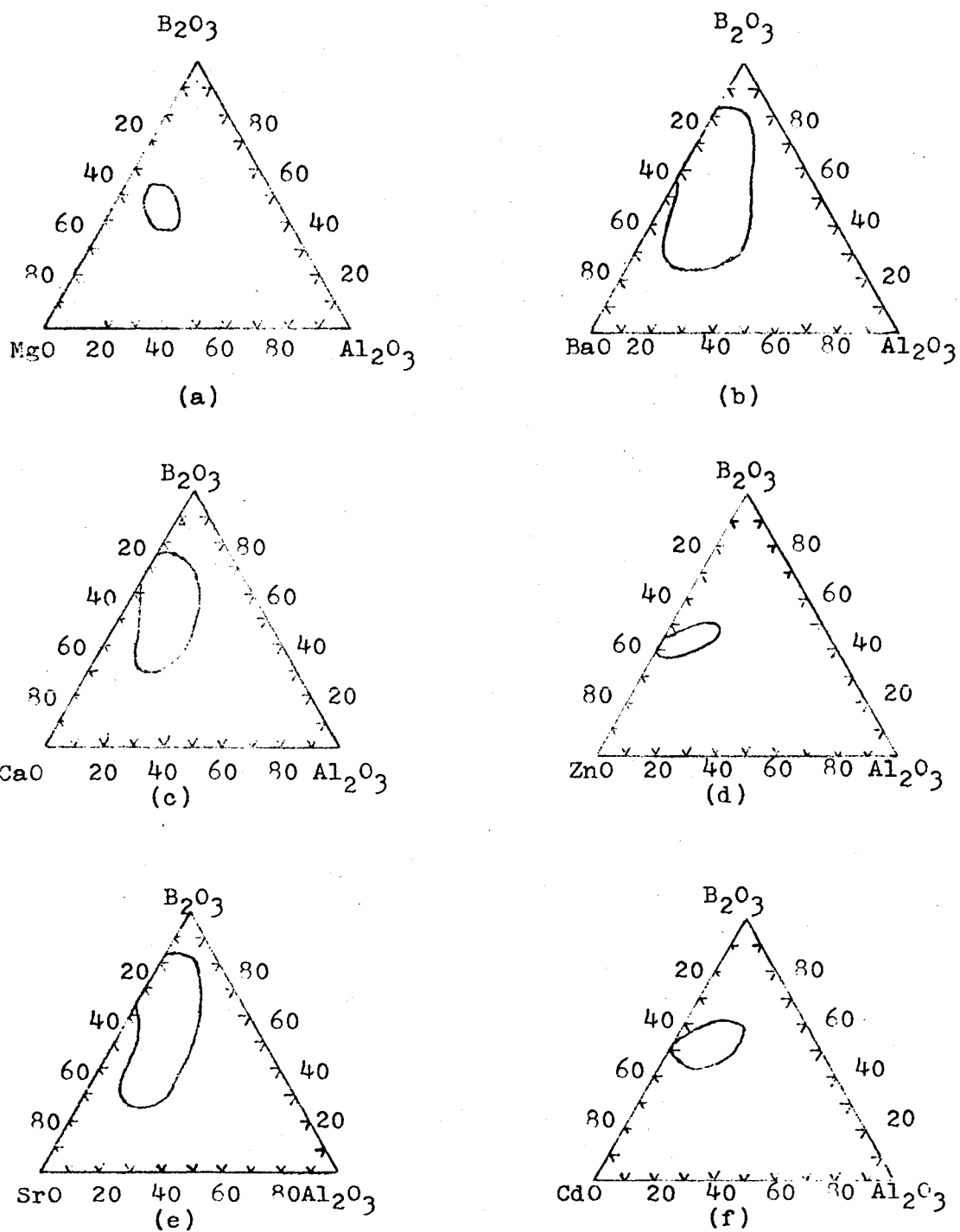


Fig. 5. Glass formation regions in (a) MgO-Al₂O₃-B₂O₃ (b) BaO-Al₂O₃-B₂O₃ (c) CaO-Al₂O₃-B₂O₃ (d) ZnO-Al₂O₃-B₂O₃ (e) SrO-Al₂O₃-B₂O₃ (f) CdO-Al₂O₃-B₂O₃ systems.

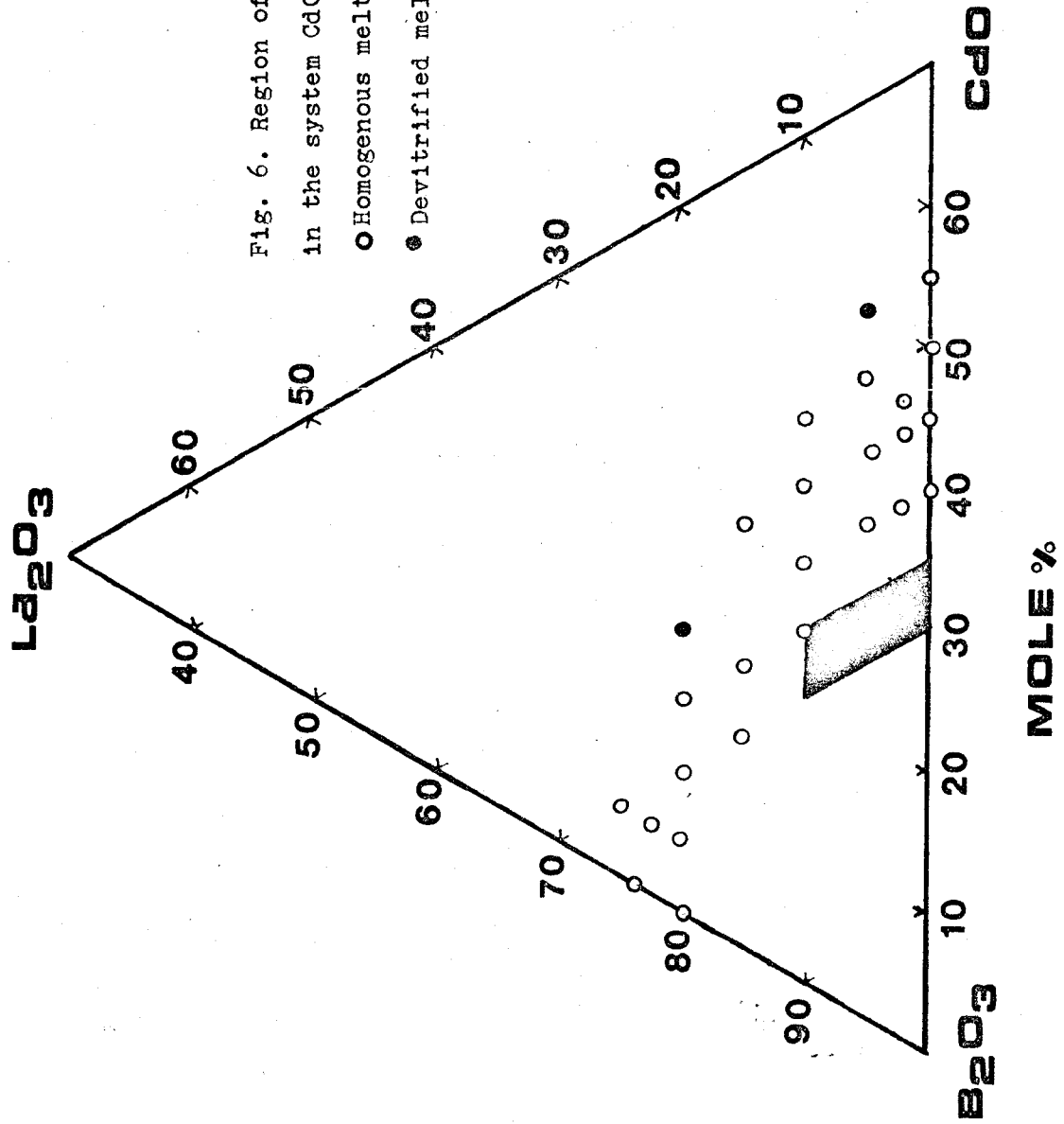


Fig. 6. Region of glass formation
in the system CdO-La₂O₃-B₂O₃.

- Homogenous melt which gave glass.
- Devitrified melt

at 20 mole% metal oxide, whereas Krogh-Moe found his principal support in the nuclear magnetic resonance data reported by Silver and Bray (19).

A consistent increase in the size of the aluminoborate glass forming region with an increase in atomic weight of the alkaline earth metal was observed. The region for the zinc and cadmium oxide also increased with increase in atomic weight. The characteristics of the glass forming regions for these Group-IIB systems differed markedly, however, from those of the alkaline earths. The covalent nature of the Group-IIB ions, as compared with the Group-IIA ions has been shown in the higher degree of immiscibility of the Group-IIB aluminoborates, with resultant smaller homogeneous glass forming regions.

Properties of glass:- Knowledge of the properties of glass such as density, thermal expansion, refractive index and hardness helps in the selection of proper material for a specific purpose. Density measurements are well established in the technological laboratories and are widely used for quality control. Precision methods have been worked out for the purpose of discovering the minute deviations which are introduced by faulty changes in the batch composition, inhomogeneities and even by different degree of annealing. Density measurements reflect the change of constitution during annealing as well as during crystallization (20).

W. Biltz, F. Weibke and S. Traeger (21) claim that molecular refractivity values (calculated on the basis of density and refractive index) of certain simple glasses are strictly additive, like density, and that their calculation from the oxide contents leads to fairly accurate results. V. N. Pollukhin (22) studied the effect of the addition of La_2O_3 on the molecular refractivity of silicate and borosilicate glasses. He found a linear relationship between the quantity of La_2O_3 and the corresponding molecular refractivity.

The refractive index of a glass and its change with the composition and heat-treatment are of primary importance for optical glasses but it cannot be related directly to structural changes because the refractive index, n_D depends upon two properties namely the molar refractivity and the density. The molecular refractivity resembles the density in as much as it cannot give us any structural details because it integrates over the whole system. There is no simple relationship between the refractive index of a glass and its composition and structure (21).

The degree of crystallinity in polymers can however be estimated on the basis of X-ray diffraction , density or refractive index.

The thermal expansivity is one of the first properties found to be characteristic for the glassy state. Volume change of solids on heating is the result of the following phenomena(23).

(i) Increase in temperature causes the mutual polarization of the ions (over a time range) to decrease so that they behave more like excess point charges. For this reason many crystals that have a smaller molecular volume and a low symmetry at ordinary temperature due to strong mutual polarization of their ions change in to the more symmetrical and less dense modifications if the temperature is raised.

(ii) Atoms that are bonded together by strong forces have vibrations with small amplitude. They resemble simple harmonic oscillators. Atoms with weaker binding forces have larger amplitudes of vibration at the same temperature than strongly bonded atoms. Their anharmonicity is greater and their relationship leads to the statement which can be found in the literature that strong bonds result in low expansivities. The anharmonicity however is not only a function of the bond strength or amplitude of vibrations but also is dependent upon the symmetry of the environment of the oscillator. In spite of the average binding forces in quartz, being stronger than in the glass, quartz has a much higher thermal expansivity than glass. Low thermal expansivity of

vitreous silica is attributed to a combination of three features : (i) low polarizability of all the ions , (ii) strong binding forces, (iii) highly symmetrical structural units. The thermal expansivity of B_2O_3 is very high in spite of this compound having a low polarizability and strong binding forces. This indicate the importance of the symmetry of the structural units in determining thermal expansivity. At ordinary temperatures a chilled glass can have a higher thermal expansivity than the same glass in an annealed condition in spite of having a more spacious structure. The higher expansivity of chilled glasses at ordinary temperatures must be the result of the lower symmetry of their structural units.

Significance of hardness of glass and its determination:-

According to Powell and Preston (24) hardness is a property that must be closely related to the mechanical strength of a glass and its low temperature viscosity.

Considering the conditions of testing under a diamond point, R.W. Douglas (24) asserted that when the loaded diamond point first touches the surface, the viscosity of glass under the intense load is sufficiently reduced to allow flow to take place.

He added that the flow would continue until the area of contact between diamond and glass is increased sufficiently to reduce the shear stress to such a magnitude that the viscosity assumes its normal value and no further flow can take place.

Weyl and Marboe (24) described the effect of shear stresses as a disproportion of the binding forces and the ability of the system to flow because of the weaker forces.

Ainsworth (24) used a diamond pyramid indenter under conditions that did not lead to fracture and that involved a small volume of glass so that the chances of avoiding Griffith flaws were very good. This method of determining the DPH gave precise and reproducible results which were independent of the applied load.

Devitrification of glass:- Devitrification implies the growth of crystalline material in the glass.

In normal glass making practice, steps are taken to prevent its occurrence. Devitrification occurring during the shaping of glass has a very harmful effect since it can lead to sudden and unpredictable changes of viscosity which interfere with the working of glass shaping machinery. Devitrification can occur due to the selection of an unsuitable glass composition.

In the devitrification of ordinary glasses, during reheating, the surface appears to play an important role since crystallization occurs much more rapidly on the surface than in the body of the glass. It is quite likely that crystallization is almost always initiated at the surface. The following reasons for this occurrence have been reported (25).

(i) Loss of volatile constituents from the glass surface during melting could account for composition difference, (ii) those constituents which lower the surface energy tend to be concentrated at the surface. (iii) the existence of surface heterogeneities which can act as nucleation catalysts for the crystallization process.

Practical examples of oxide nucleation catalysts:-Perhaps the best known example of an oxide nucleation catalyst is TiO_2 and its use has been described by S. D. Stookey (26) who showed that it was effective in amounts of 2 to 20 wt.% in a wide variety of glass composition. The TiO_2 is soluble in molten glasses but during cooling or subsequent reheating large numbers of microscopic particles are precipitated and these can be utilized to assist the development of major crystalline phases. The processes involving TiO_2 -catalyzed crystallization of glasses are complex and so far they have not been fully understood.

The use of ZrO_2 as a catalyst has been described by Swai (27) but it is not very soluble in most of the glass formers.

A net-work forming oxide used as a catalyst is P_2O_5 . Its use has recently been reported by McMillan and co-workers (28). The P^{5+} assumes tetrahedral co-ordination and therefore provides an example of phase separation due to a charge difference between the principal net-work forming ions, Si^{4+} and the foreign net-work forming ion P^{5+} , when the glass for crystallization is of the silicate type. Electroneutrality cannot be ensured if the phosphorus-oxygen bonds are of the type P-O. Therefore it is assumed that one phosphorus-oxygen bond has to be a double bond. The presence of this type of double bonded oxygen ion within the silicate net-work creates conditions favouring separation of phosphate grouping from the silicate net-work. It is unlikely that these groups would separate as P_2O_5 but rather that this oxide would separate out in combination with an alkali or alkaline earth oxide. The phase which separates out may be crystalline but it is quite likely to be glassy (29).

Heterogeneous nucleation:- Gernez in the nineteenth century, showed that while crystallization could be induced in supersaturated solutions by seeding with "foreign" crystals these were less effective than

crystals of the actual phase to be precipitated.

Vonnegut (30) has confirmed and extended these general observations in experiments directed towards a practical application of heterogeneous nucleation. The object was to bring about the crystallization of supercooled clouds for the purpose of inducing rainfall. He searched for a crystal, with lattice parameters closely matching those of the ice crystal, to work as a potential nucleation catalyst. He selected silver iodide and its effectiveness supported his selection. A number of his other experiments proved that the potency of nucleation catalyst is related to the degree of similarity between its structure and that of the phase being nucleated.

Kinetics of nucleation:- The phenomenon of nucleation of a metastable phase makes it possible to prepare compounds that have no stability region but form only because of their higher rates of nucleation. From the phase diagram for the system CaO-SiO_2 , it is found that a mixture of 1 mole CaO with 2 moles of SiO_2 is in equilibrium only when CaO is combined with SiO_2 in the form of wollastonite, CaO.SiO_2 . One-half of the SiO_2 remains unreacted. On heating the mixture to approximately 1000°C , it is found that in spite of the excess of silica the orthosilicate of calcium, Ca_2SiO_4 is formed first and not the metasilicate which is the stable phase. As the reaction proceeds further the compound $3\text{CaO}.2\text{SiO}_2$

is formed next and that it requires considerable time to change the system to the stable wollastonite-silica mixture (31). These facts are explained on the basis of polarizability. Ca_2SiO_4 has a higher polarizability than CaSiO_3 . Once a nucleus of Ca_2SiO_4 has formed, it will guide the reaction and cause the nucleus to grow. The most polarizable is grown first until, by chance, a new nucleus forms. The compound, next in line, $3\text{CaO} \cdot 2\text{SiO}_2$ has a better chance of forming nuclei than the least polarizable $\text{CaO} \cdot \text{SiO}_2$ (32).

The fascinating aspect of this phenomenon is that in order to guide a reaction towards a certain metastable product one does not even need a nucleus or a seed of that phase: a crystal which resembles it geometrically may be sufficient. In this case we speak about a nucleation catalyst. Here we meet one of the fundamental differences between experimentation in the field of equilibria (phase diagram) and rate processes.

Selection of glass types for conversion to glass-

ceramics:- The glass composition must be capable of being melted and shaped by economic means so that in the formulation of glasses for glass-ceramic production the influence of composition upon these factors must be borne in mind. Many glass shaping processes depend on the fact that glass is a plastic over a wide temperature

range. Another important aspect of the working characteristics concerns the possibility of devitrification during the cooling of the glass in the shaping operation. Perhaps the most important criterion in selecting a glass composition for glass-ceramic production is that it shall be capable of being crystallized without the use of prohibitively long heat-treatments. It is also important that the constituents be chosen in proper ratios so that crystal types can be developed which will possess the desired physical properties. Glass which will crystallize easily during the reheating process will be that containing fairly high proportions of modifying oxides. This is because the oxides weaken the glass net-work structure by introducing non-bridging oxygen ions in place of bridging oxygen ions. As the proportion of non-bridging oxygen ions increases the net-work structure becomes progressively weakened and the atomic rearrangements necessary for crystallization become increasingly probable (33).

The role of differential thermal analysis in the selection of temperature range for heat-treatment:-

The heat-treatment required to convert glass into glass-ceramics is normally carried out between the annealing temperature of the primary glass and the

lowest eutectic or melting point of the crystalline phase(s) in the devitrified material. Differential thermal analysis (DTA) can be used to determine the annealing temperature and the various eutectics, liquidii or melting points in the glass/ glass-ceramic systems. These appear as endotherms on the DTA trace (34). Devitrification is exothermic and the DTA exotherm peak temperatures can be used to characterise the glass-ceramic conversion process (35). The main object in heat-treatment is to produce as many nuclei as possible which will only grow into small crystals. A good compromise is obtained by treatments at or near the main DTA exotherms (34).

The significance of electron microscopy:- Crystals in glass-ceramics are usually so small that they are below the limit of resolution of an optical microscope. Even for the fully heat-treated glass-ceramics the majority of the crystals are 1 micron or less in diameter and some may be only a few hundred Angstrom units in size. For this reason the greater resolution of the electron microscope is used (36).

it as indicated in a number of DTA thermograms and corresponded closely to that defined by Lillie (37) i.e., it corresponded to a viscosity of about $10^{14.5}$ poises. None of the annealed specimens showed any evidence of devitrification.

Materials and equipment used:- Reagent grades of strontium and barium carbonates, fused boric acid (boric oxide) and lanthanum oxide were used for the batch making.

Two electric tube furnaces equipped with automatic temperature control systems of $\pm 5^{\circ}\text{C}$ accuracy, one capable of being used up to 1250 C and the other up to 1500°C , were employed for firing the batches for glass formation. The temperature was also periodically checked by means of a calibrated Pt-Rh thermocouple and a Leeds & Northrup potentiometer. An electric muffle furnace, in addition to the tube furnaces, was used for the heat-treatment of the specimens.

Measurement of properties of glass:- The densities of glass pieces were measured at room temperature by hydrostatic weighing in toluene with an accuracy of $\pm 0.01\%$.

The refractive index of glass was measured according to "Beke line" method (38). Small size grains were immersed in immersion liquids of known refractive indices and examined under a microscope using Na-D light.

By immersing a grain in the liquids of successively higher indices the point was reached where the refractive index of the grain corresponded to that of the immersion liquid.

The molecular refractivity of glass was calculated using the Lorentz-Lorenz equation, given in Appendix I.

The coefficient of thermal expansion was measured in the range 100-350°C, using rods 4-in. (± 0.1) long and 1/6 in. in diameter on a vertical quartz dilatometer with accuracy of $\pm 3\%$. The temperature was raised by about 2°C/minute. Similar equipment has been used by a number of researchers (11,16&39). Some of the rods were prepared by mould casting whereas the others were successfully drawn from the melts. Calculations were made using the equation given in Appendix I.

Heat treatment of glass for conversion to glass-ceramics:-

DTA curves of a few selected compositions were prepared through the courtesy of the Pakistan Council of Scientific and Industrial Research Laboratories (Lahore, Pakistan). Three of these curves have been shown in Fig. 12. The heat-treatment conditions were chosen on the basis of the results of a differential thermal analysis, for the composition (mole%) 15 BaO, 20 SrO, 20 La₂O₃ and 45 B₂O₃. In compounding the batch, 0.3 % by weight of a catalyst, phosphorus pentoxide, was added. A glass with this composition

was selected for heat-treatment because of its superior workability. Various heat-treatments in the range of 500-830°C, were given for different time periods.

Crystallization occurred so fast that 1/2 hr. was generally adopted as sufficient time for each temperature studied. The heating period was, however, extended up to 12 hrs. for temperatures in the precrystallization range. During heat-treatments at temperatures above 830°C significant surface fusion of the samples occurred. This would appear to indicate that the industrial feasibility of the process above this temperature is in doubt. Therefore the heat-treatment was terminated at 830°C.

Determination of properties after crystallization:- In addition to the determination of the physico-chemical properties of glass-ceramics, microhardness, a mechanical property, was also determined using the recognized methods. Microhardness was tested on a Leitz-Wetzlar microhardness tester, using a diamond pyramid indenter under a load of 50 gms.

X-ray phase analysis of heat-treated samples:- The samples, which had been cooled rapidly in order to freeze in the conditions obtained at the critical temperatures, were subjected to X-ray diffraction analysis using a Philips

diffractometer. Diffraction maxima were compared with the literature data (40) for ortho and meta-borates.

Determination of chemical durability of glass:-

Specimens of known dimensions and weights were exposed to steam for 200 hrs. After the termination of each experiment the specimens were towel dried, further dried in an oven at 60° C for ten minutes and then weighed.

IV RESULTS AND DISCUSSION

Regions of glass formation:- The glass forming regions for the systems studied are shown in Figs. 7 & 8. The compositions which formed clear glass on quenching are shown by open circles. Those compositions which crystallized on cooling are shown by semi-closed circles whereas areas of immiscibility are indicated by closed circles. The limits of glass formation for the binary $\text{SrO-B}_2\text{O}_3$, $\text{BaO-B}_2\text{O}_3$ and $\text{La}_2\text{O}_3\text{-B}_2\text{O}_3$ systems closely agree with those reported by others (12 & 16).

A comparison of the sizes of the glass forming regions in the present study with that reported for the $\text{CdO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ system in the literature (2) shows that these regions are wider. This may be explained on the basis that Sr^{++} and Ba^{++} are members of Group-IIA in the periodic chart and assume the rare gas configuration whereas Cd^{++} which is a member of Group-IIB assumes the non-rare gas electronic configuration. The non-rare gas configuration produces a greater anion deformation than the rare gas configuration even when the charge and ionic sizes are comparable. The higher polarization ability of the non-rare gas

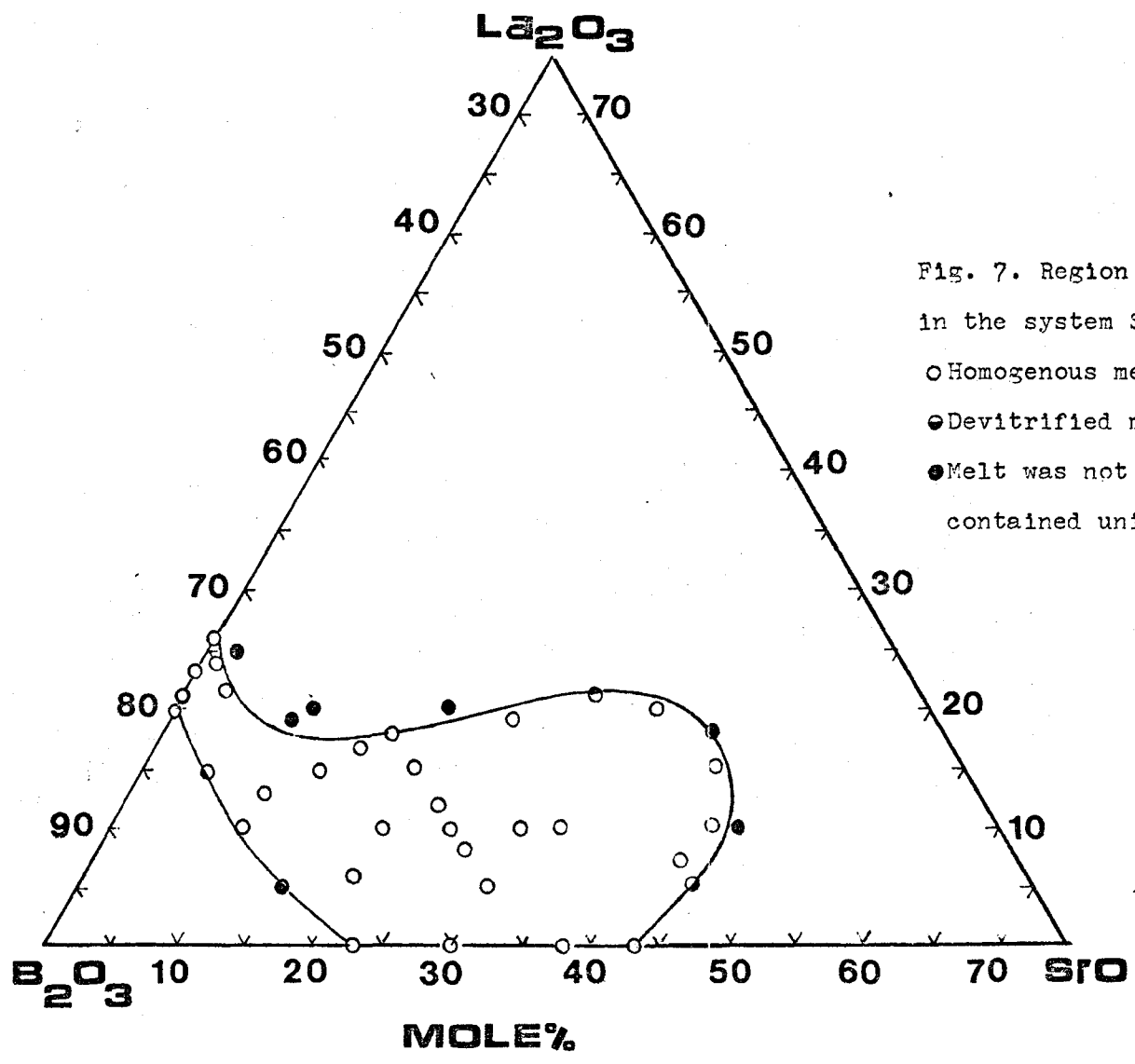


Fig. 7. Region of glass formation in the system SrO-La₂O₃-B₂O₃.
○ Homogenous melt which gave glass
● Devitrified melt
● Melt was not homogenous and contained unincorporated material

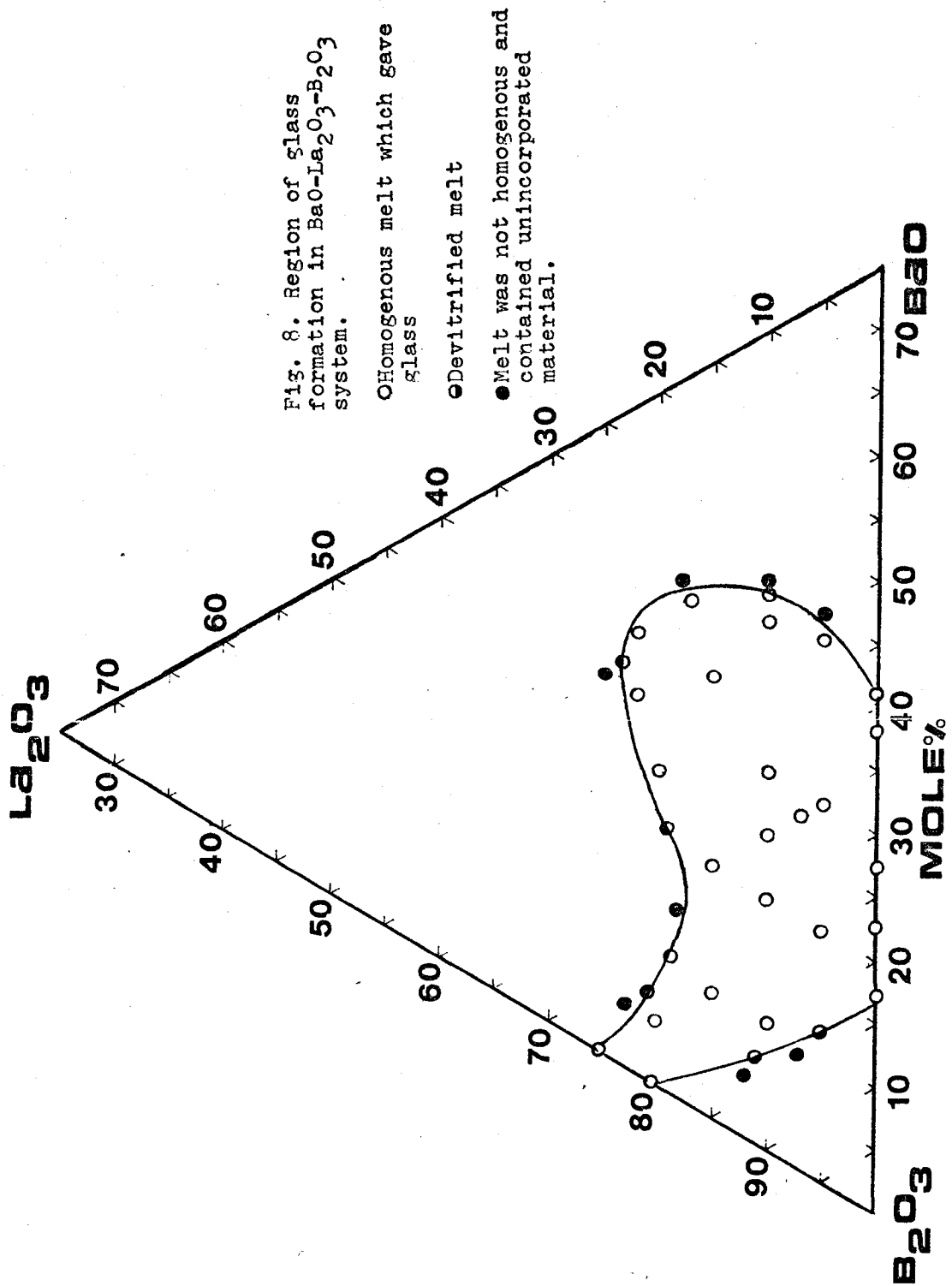


Table I. Compositions of Glasses Studied from the Systems SrO-La₂O₃-B₂O₃ and BaO-La₂O₃-B₂O₃.

Glass No.	Mole%			Glass No.	Mole%		
	SrO	La ₂ O ₃	B ₂ O ₃		BaO	La ₂ O ₃	B ₂ O ₃
1S	1	24	75	1B	10	10	80
2S	3	22	75	2B	10	15	75
3S	10	10	80	3B	20	5	75
4S	10	13	77	4B	20	10	70
5S	13	15	72	5B	20	15	65
6S	20	6	74	6B	25	10	65
7S	20	10	70	7B	28	7	65
8S	20	15	65	8B	30	5	65
9S	23	12	65	9B	30	10	60
10S	25	10	65	10B	35	15	50
11S	27	8	65	11B	35	22	43
12S	30	5	65				
13S	30	10	60				
14S	33	10	57				
15S	35	20	45				

Table II. Properties of Glasses of the System SrO-La₂O₃-B₂O₃

Glass No.	Density, gm/cm ³	Refractive index		Thermal Expansion	
			nd	Coefficient, (α ₁₀₀₋₃₅₀) · 10 ⁶ , deg ⁻¹	
1S	4.397		1.712	-	-
2S	-		1.710	-	-
3S	3.933		1.684	14.3	
4S	3.980		1.688	17.5	
5S	3.904		1.696	-	
6S	4.118		1.680	15.0	
7S	4.130		1.688	16.3	
8S	4.159		1.700	17.2	
9S	-		1.696	17.8	
10S	4.094		1.692	18.1	
11S	4.051		1.684	18.4	
12S	3.910		1.688	19.0	
13S	-		1.692	19.4	
14S	4.157		1.696	-	
15S	-		1.705	-	

Table III. Properties of Glasses of the System BaO-La₂O₃-B₂O₃

Glass No.	Density, gm/cm ³	Refractive index n _D	Thermal Expansion Coefficient, (α ₁₀₀₋₃₅₀) · 10 ⁶ , deg. ⁻¹
1B	3.942	1.688	14.2
2B	4.020	1.700	20.3
3B	4.199	1.684	15.2
4B	4.247	1.692	16.7
5B	4.294	1.700	17.5
6B	4.372	1.696	18.4
7B	-	1.688	19.2
8B	4.231	1.692	19.5
9B	4.251	1.700	19.9
10B	4.552	1.710	-
11B	-	1.716	-

configuration arises from the lower electronic screening effect of these cations when compared with those with the rare gas configuration. As a result there is an increased covalency when an anion is bonded to a cation with non-rare gas configuration. Because of the increased covalency, the interatomic distance between anion and cation may be considerably shorter than those predicted for strictly ionic radii. The magnitude of the glass forming region is of particular interest in that it depends to an appreciable degree on the strength of the bond between the metal ion and the oxygen ion. The strong polarizing effect of cadmium ions promote immiscibility in borate systems.

The present glass forming regions are comparatively smaller in size than the reported aluminoborate glass forming regions as shown in Fig. 5, when SrO and BaO are present in the two glass forming systems. Taking in to account the effect of cations of elements belonging to the same group in the periodic chart, Al³⁺, because of its small radius and high charge, may be present in the glass as a net-work former as well as a modifier. La³⁺, on the other hand, has a large radius and acts only as a modifier in the structure of glass. This

explains why the tendency for glass formation is higher in the aluminoborate glass forming systems.

Variation of density and refractive index of annealed glass with the introduction of lanthanum oxide:-

It may be seen from Tables II & III that the density and refractive index of glass increased with the substitution of La_2O_3 , for MO (SrO or BaO) and B_2O_3 .

The study of molecular refractivity when related to the addition of La_2O_3 to 30 mole% SrO-70 mole% B_2O_3 glass revealed a linear relationship as shown in Fig. 9. This behaviour agrees with the work of Pollukhin (22) who plotted mole% La_2O_3 vs. molecular refractivity in silicate and borosilicate glasses.

Variation of thermal expansion with the introduction of lanthanum oxide:- Results of this study have been presented in Tables II & III. The substitution of La_2O_3 for MO decreased the coefficient of thermal expansion of glass at 65 mole % B_2O_3 . These results have been plotted in Figs. 10 & 11.

The addition of La_2O_3 at 10 mole% MO resulted in a sharp increase in the thermal expansion. At 20 mole% MO, the increase in thermal expansion

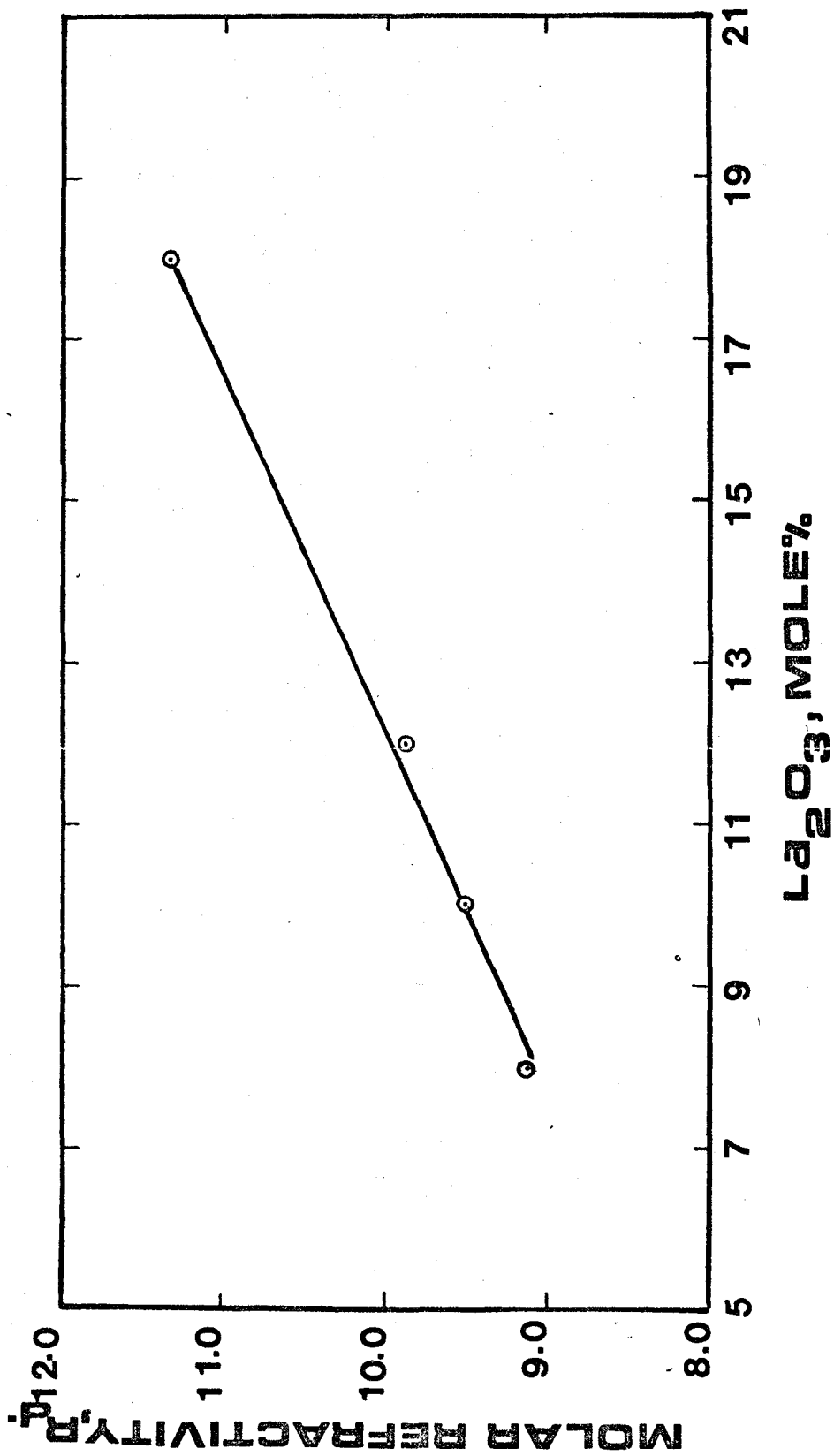


Fig. 9. Variation of molecular refractivity with the molecular contents of lanthanum oxide.

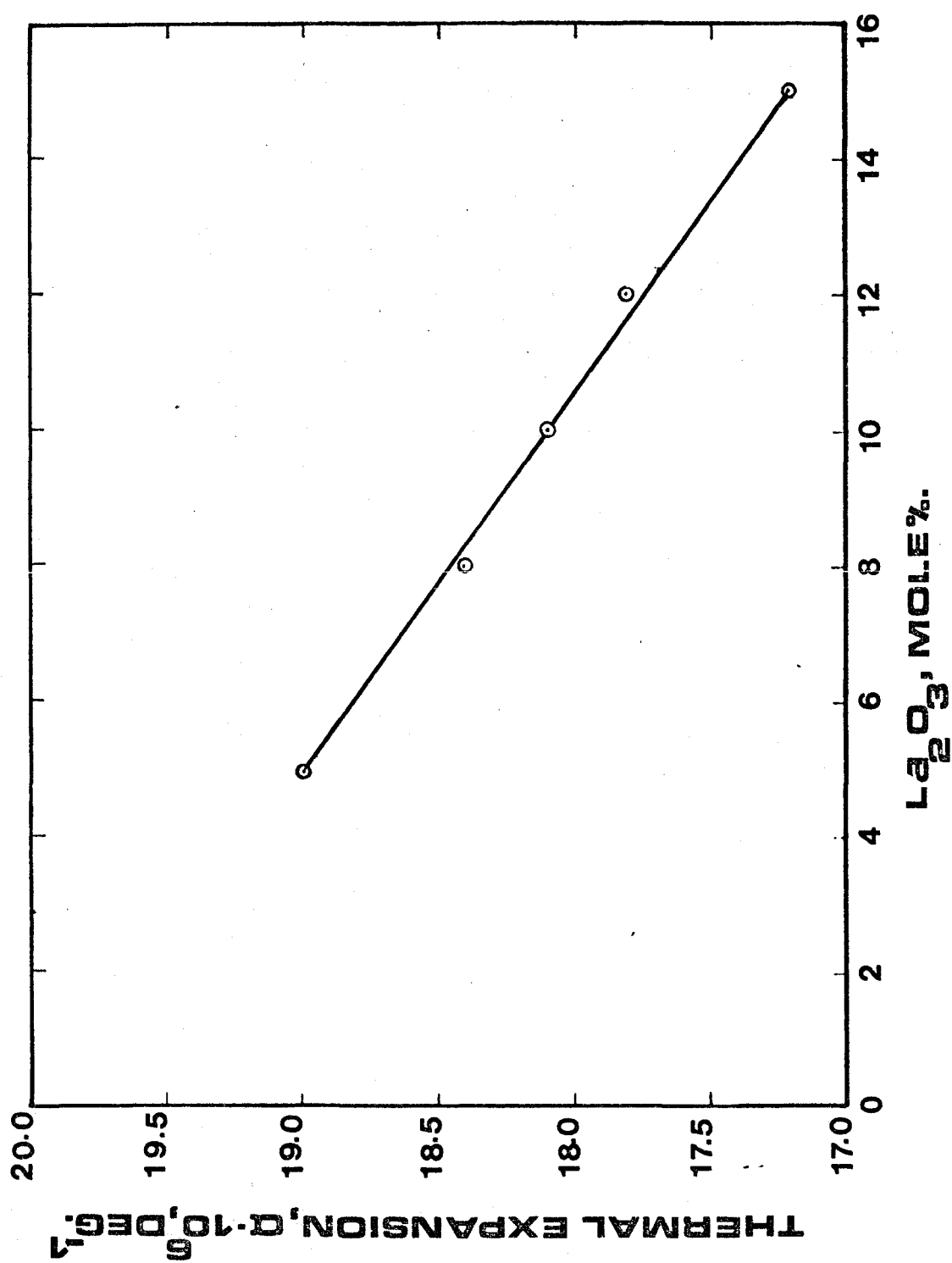


Fig. 10. Effect of replacement of SrO by La_2O_3 on thermal expansion of glass at 65 mole% B_2O_3 .

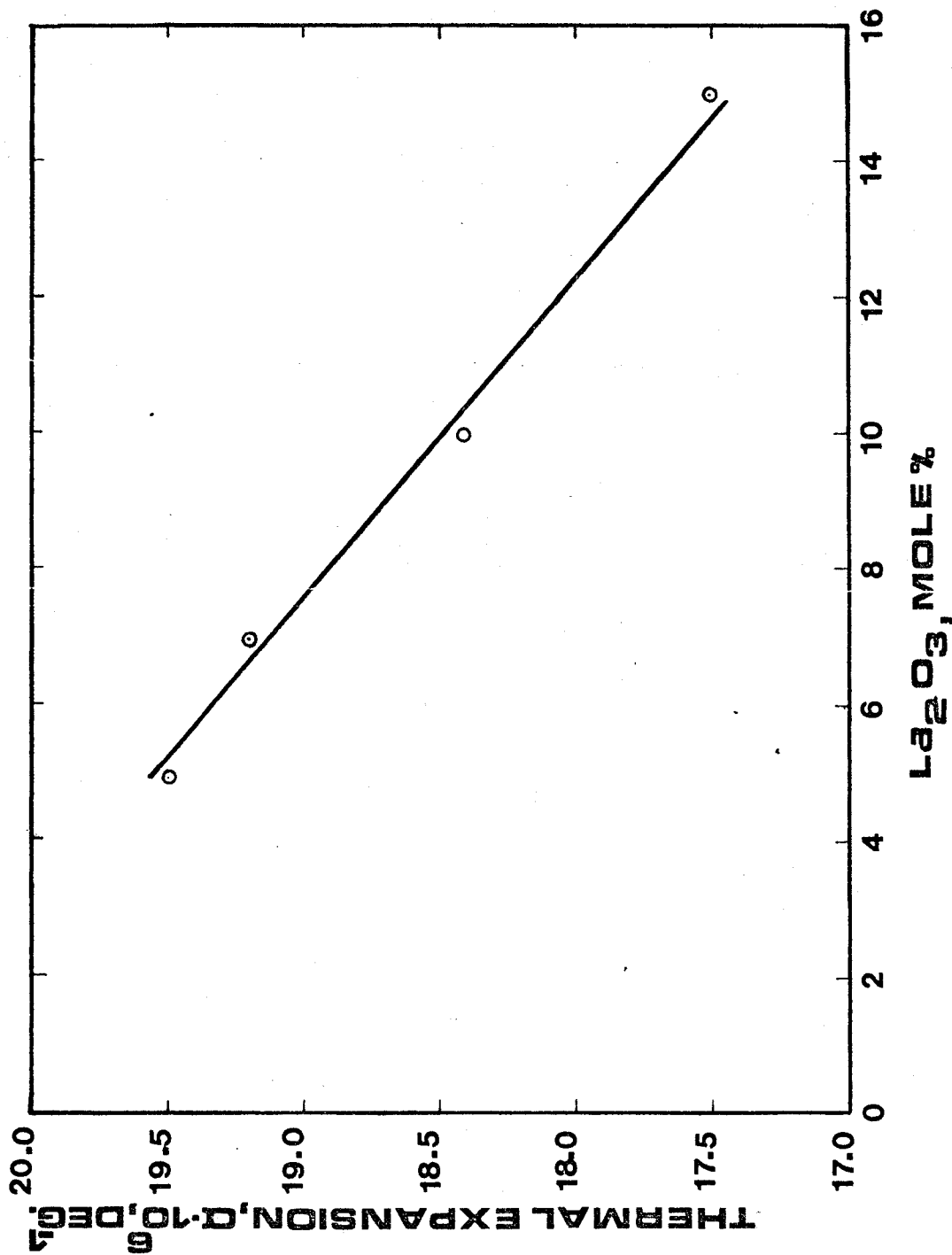


Fig. 11. Effect of replacement of BaO by La_2O_3 on thermal expansion of glass at 65 mole % B_2O_3 .

was comparatively small and was negligibly small at 30 mole % MO.

Thermal expansion is a constitutive property and is related to the nature of the bonds in the structure of glass. In low alkaline earth glasses, when the boron-oxygen net-work is sufficiently polymerised, cleavage of the strong B-O-B bonds, by the introduction of lanthanum with a lower force field, leads to an increase in the coefficient of expansion. In glasses with high contents of alkaline earths the net-work is depolymerised to a certain degree and the introduction of a second triply charged modifier strengthens the lattice. This in turn leads to the weakening of the vibrations and thus a lessened increase in the thermal expansion takes place.

Examination of DTA diagrams:- Fig. 12 shows the traces of DTA curves for the compositions numbered 11S, 9S and the composition (mole%) 15 BaO, 20 SrO, 20 La₂O₃ and 45 B₂O₃. The latter composition was selected for DTA and subsequent heat-treatment due to its superior workability as determined experimentally. 0.3 % by weight, P₂O₅ was added to the batch of this composition as a catalyst.

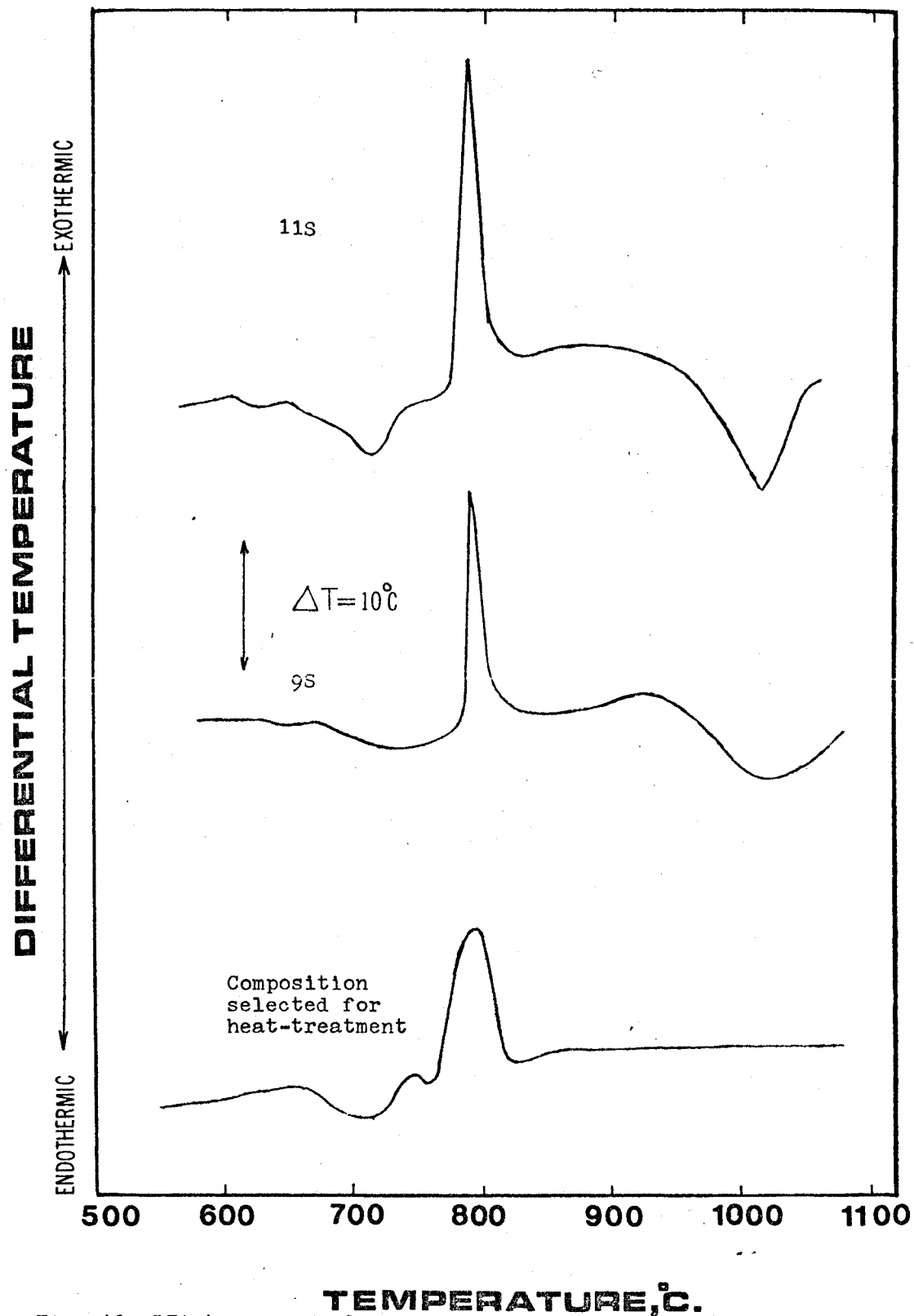


Fig. 12. DTA traces of glasses of compositions 11S, 9S and the one selected for heat-treatment.

As the proportion of La_2O_3 increased, changes in the thermograms occurred. The size of annealing range varied with the composition. The trace of composition 9S showed a wide annealing range. The first crystallization peak which appeared in the trace of composition 11S disappeared in the trace of composition 9S and then reappeared in the trace of the composition given above. The endotherm corresponding to the melting points of the crystalline phases in the last case exceeded 1100°C and was therefore beyond the recording range of the instrument used.

Effect of crystallization on properties of glass:-

The results of the determination of the properties are given in Tables V-VII, and Figs. 13-17 & 20. An examination of Fig. 13 shows that the density of the glass is unchanged by heat-treatment for 1/2 hr. in the temperature range $500-700^\circ\text{C}$. The heating of the glass at 745°C , the first temperature of crystallization, raises the density from 4.564 to 4.596. The density is unchanged by heat-treatment in the temperature range $745-760^\circ\text{C}$ for 1/2 hr. At higher temperatures it decreases rapidly reaching

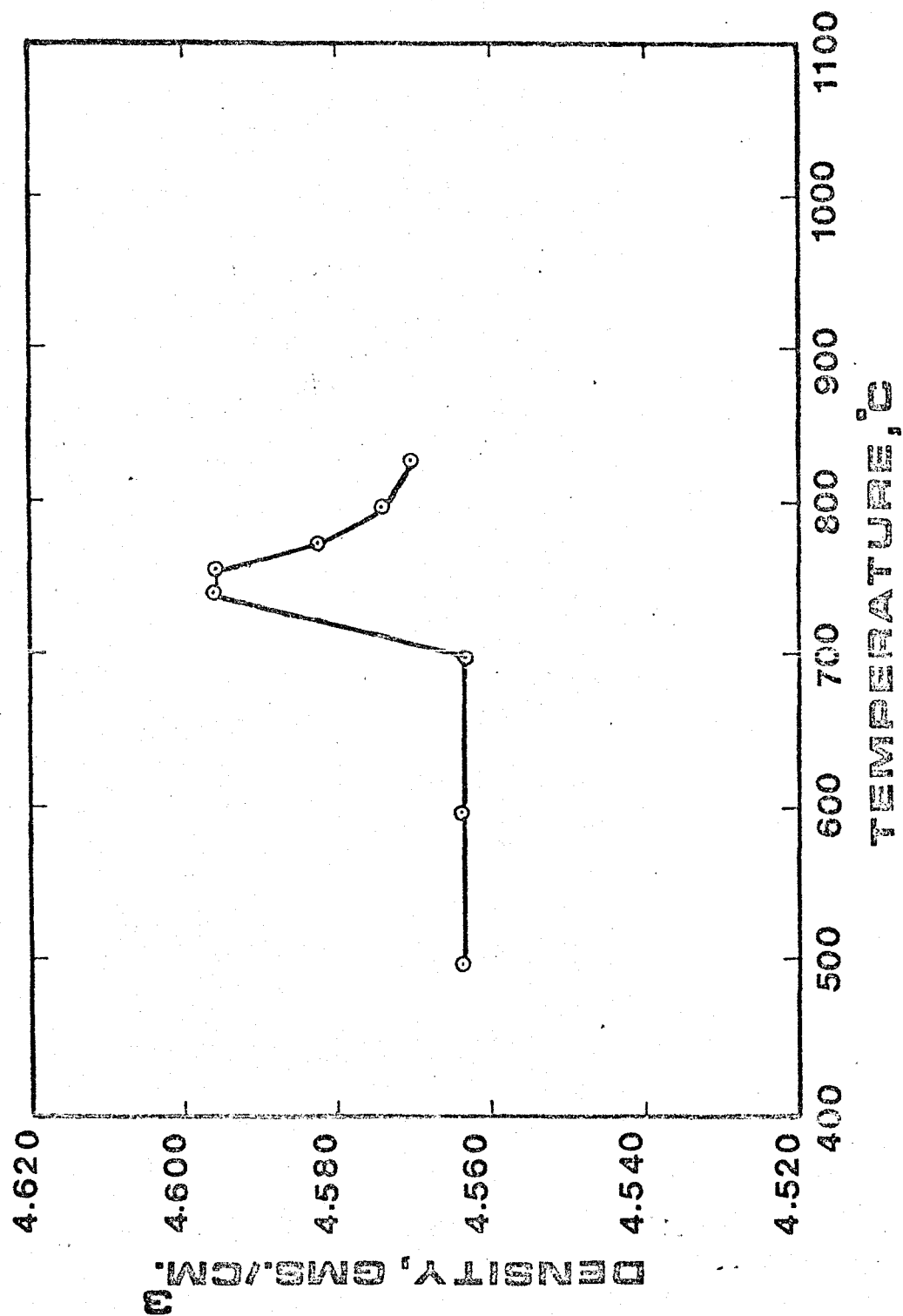


Fig. 13. Variation of density of glass of the composition (mole %)
15 BaO, 20 SrO, 20 La₂O₃ and 45 B₂O₃ with heat-treatment

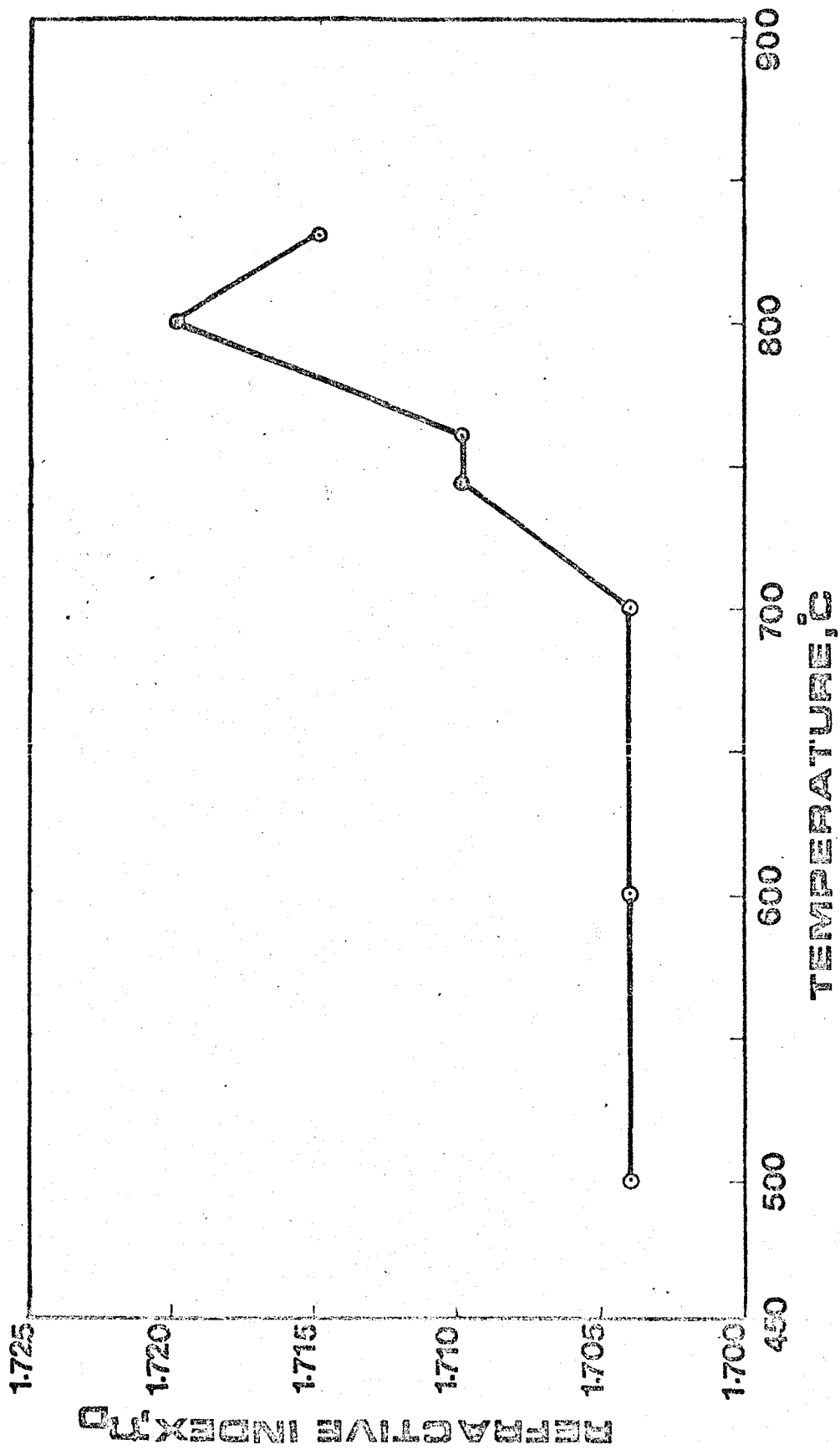


Fig. 14. Variation of refractive index of glass of the composition, 15 BaO, 20 SrO, 20 La₂O₃ and 45 B₂O₃ (mole%) with heat-treatment

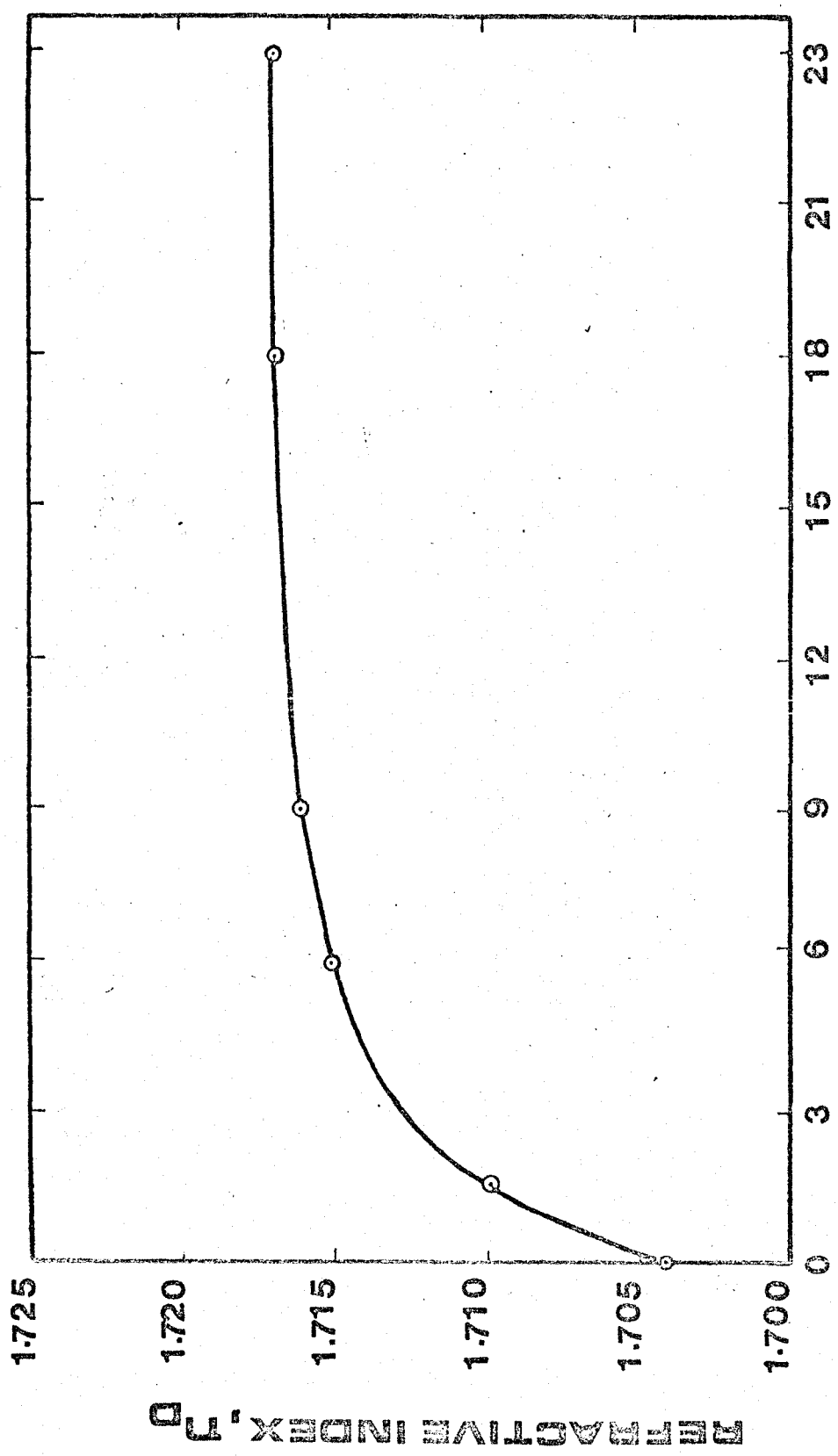
the minimum value of 4.570 at 830°C. The density increase observed in the 700-745°C range may be associated with the crystallization of lanthanum metaborate in the glass. The density decrease observed in glass crystallized at temperatures above 760°C may be attributed to crystallization of lanthanum orthoborate. The presence of the two lanthanum compounds has been confirmed by X-ray results. It is assumed that the decomposition of lanthanum metaborate into lanthanum orthoborate produces glassy boron trioxide with some swelling action which could be observed visually. The changes in refractive index, with heat-treatment, follow the same route as density up to 760°C. The refractive index continues to increase until 800°C after which a gradual decrease occurs. The increase in refractive index has been attributed to the high refractive indices of the crystalline meta and orthoborates of lanthanum. The refractive index of the orthoborate is higher than that of the metaborate.

Two characteristic regions can be distinguished in the investigation of glass in the range 500-830°C. The upper boundary of the precrystallization range (the rising branch of the endotherm in DTA diagram) shifts somewhat towards lower temperatures with increasing time of heat-treatment. It may be assumed that at these

temperatures the glass has a crystallization tendency with time. In the precrystallization region, certain properties of the glass are altered during heat-treatment. The curve in Fig. 15 represents variations of the refractive index at 715°C.

The variation of microhardness of glass, crystallized at various temperatures of heat-treatment follows the same course as the density variations up to about 760°C whereas above this temperature the microhardness decreases sharply. The greatest increase of microhardness is 9.2 %. The decrease in the microhardness of glass crystallized above 760°C may be attributed to the considerable increase in brittleness as was shown by the numerous cracks and individual signs of breakdown around the indentation.

The linear thermal expansion increases in the range 700-745°C and then after a small steady range as in the case of other measurements, decreases sharply. At 830°C the lowest value of thermal expansion is obtained. At this temperature a sufficient amount of B_2O_3 is released to become part of the remaining glass which in turn decreases the thermal expansion considerably.



TIME, HRS.

Fig. 15. Variation of refractive index of glass of the composition (mole%)
15 BaO, 20 SrO, 20 La₂O₃ & 45 B₂O₃ with heat-treat-treatment

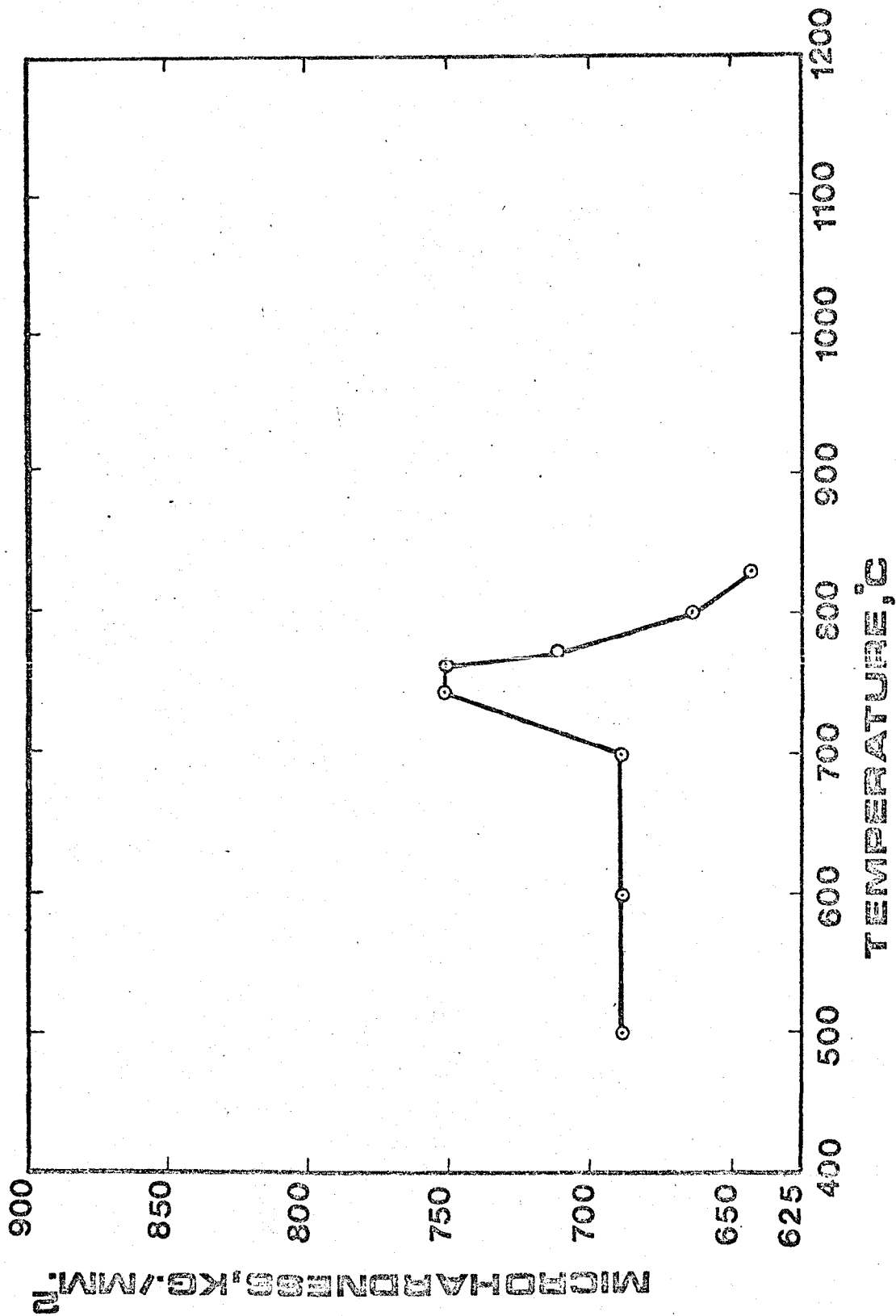


Fig. 16. Variation of microhardness of glass of the composition (mole%)
15 BaO, 20 SrO, 20 La₂O₃ & 45 B₂O₃ with heat-treatment

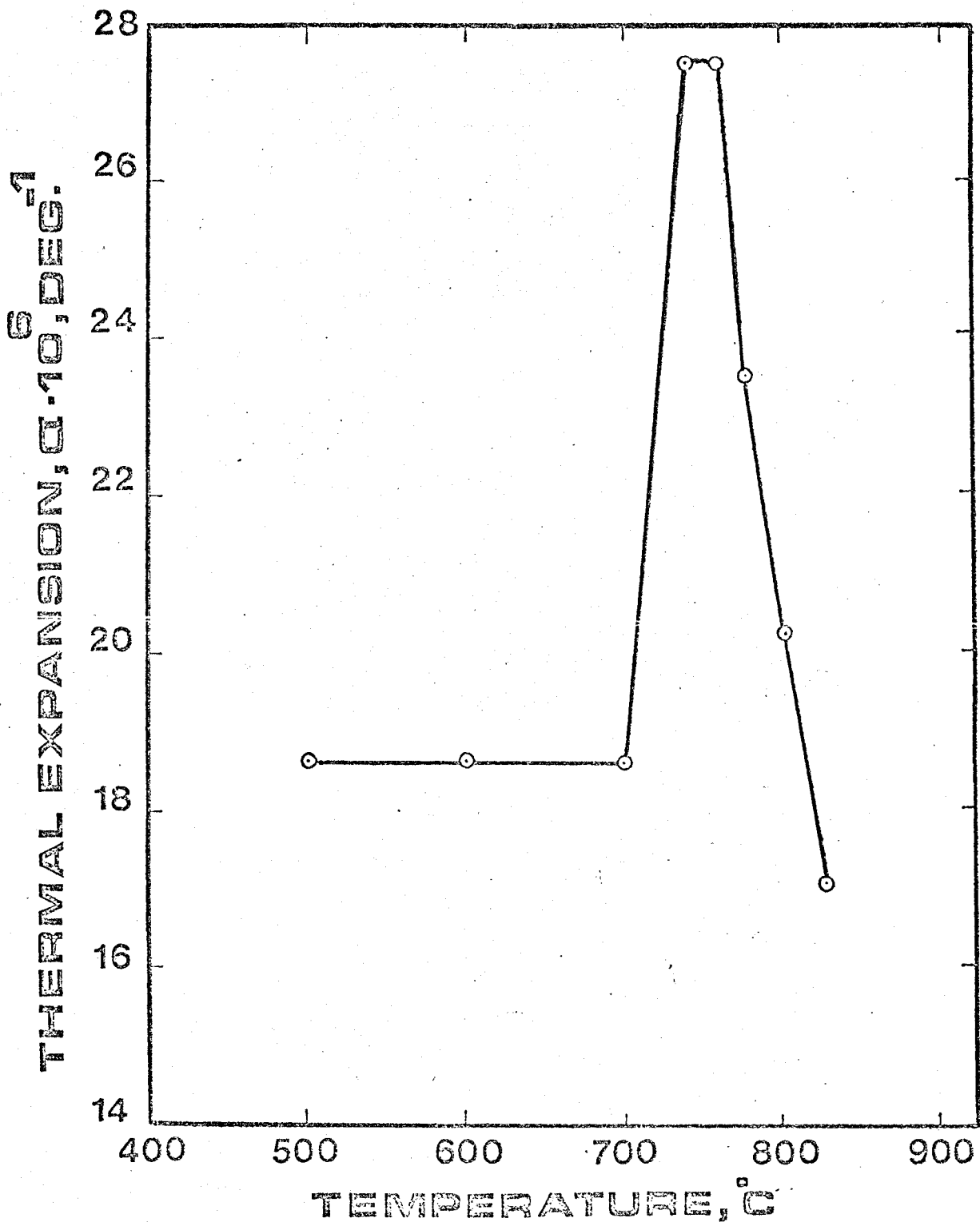
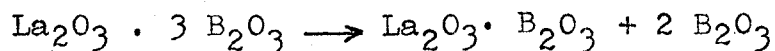


Fig. 17. Variation of thermal expansion of glass of the composition (mole%), 15 BaO, 20 SrO, 20 La₂O₃ & B₂O₃ with heat-treatment

X-ray diffraction analysis:- X-ray diffraction intensity curves of products of different critical heat-treatments are presented in Fig. 18 & 19. Identification of diffraction maxima ($d = 3.23, 3.12, 3.05, 2.87, 2.84, 2.57, 2.08, 2.03$ and 1.89) with the help of literature data (41) shows that the primary crystalline phase (at temperature 745°C) consists of a metastable solid solution of lanthanum metaborate ($\text{La}_2\text{O}_3 \cdot 3\text{B}_2\text{O}_3$). A small number of unidentified peaks are also present in the X-ray diffraction curve. The intensity of diffraction maxima is lower in the curve corresponding to the heat-treatment at 760°C . At a temperature around 775°C decomposition of lanthanum metaborate occurs and lanthanum orthoborate is formed. The curve corresponding to heat-treatment at 775°C shows characteristic peaks ($d = 3.49, 3.38, 2.92, 2.43, 2.42, 2.39, 2.17, 2.03, 1.92$ and 1.86) of lanthanum orthoborate ($\text{La}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$). The reaction may be written as:



A few peaks characteristic of lanthanum metaborate are also present in the curve. At 800°C , diffraction maxima are almost solely due to the orthoborate. A very small number of unidentified peaks are, however, still present. The crystallization of borates of lanthanum in the presence of other modifying cations is explained on the basis that the ionic field strength (Z/r^2)

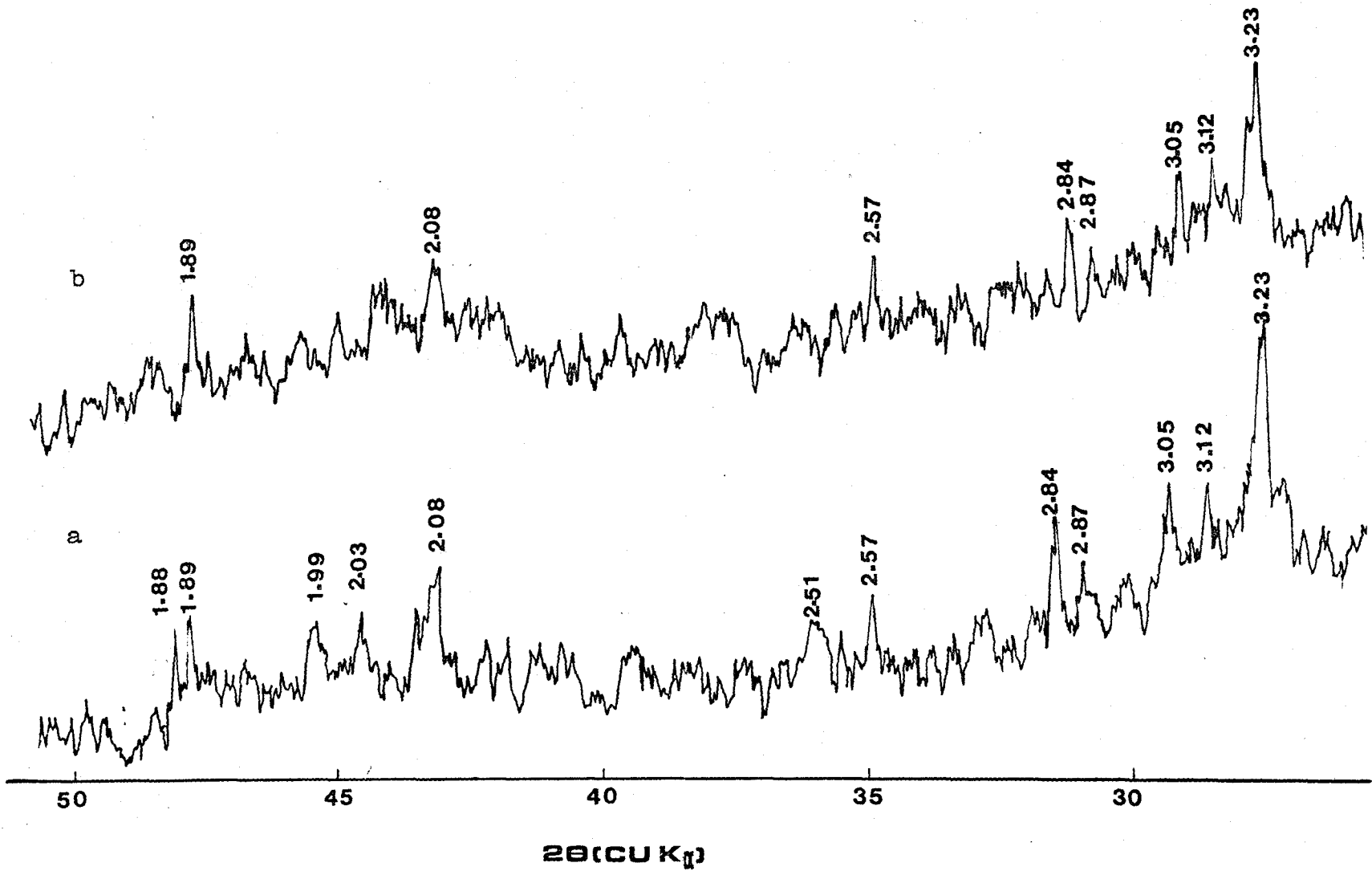


Fig. 18. X-ray intensity curves of glass after heat-treatment: a) 745°C , $1/2$ hr.
 b) 760°C , $1/2$ hr.

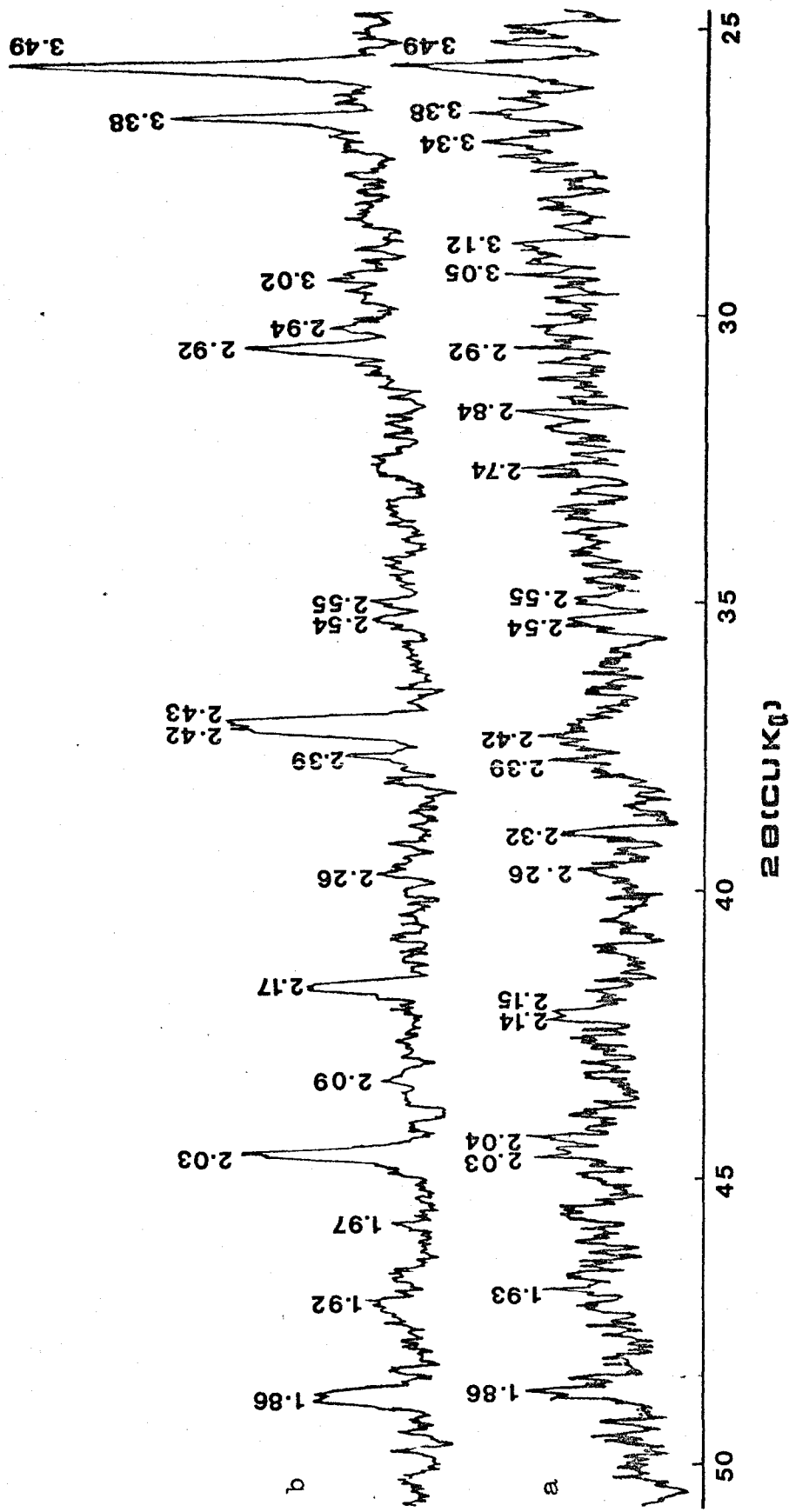


Fig. 19. X-ray intensity curves of glass after heat-treatment: a) 775°C, 1/2 hr.
b) 800°C, 1/2 hr.

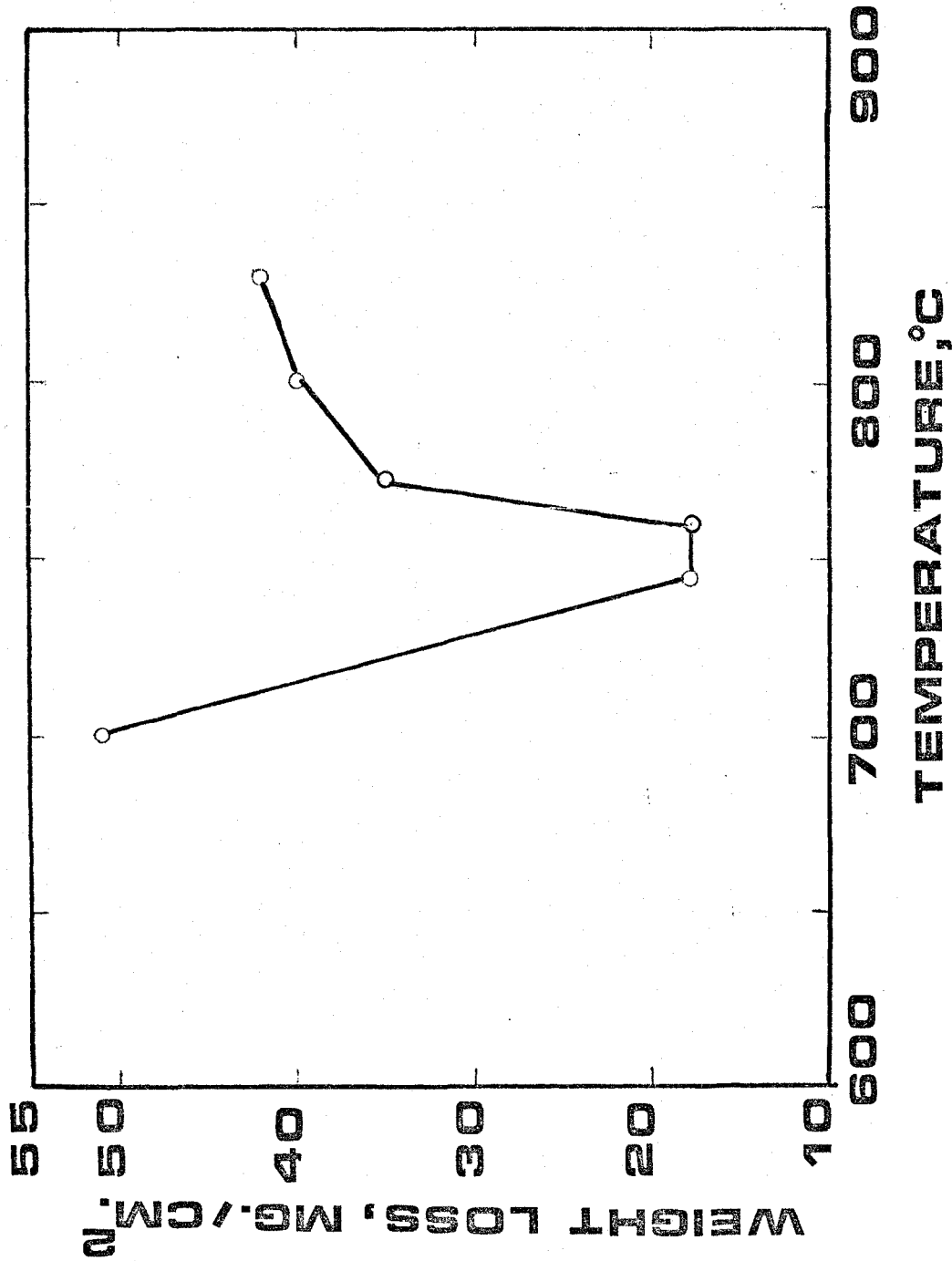


Fig. 20. Variation of chemical durability of glass* with heat-treatment

* Class of composition (mole%), 15 BaO, 20 SrO, 20 La₂O₃ & 45 B₂O₃

value for lanthanum (1.05) is higher than those for strontium (0.54) and barium (0.51). Cations of high field strength tend to be surrounded by more ordered arrangement (33).

Chemical durability of glass after crystallization:-

The results of the chemical durability determinations in terms of loss in weight when exposed to steam for 200 hrs., have been shown in Table VII and Fig. 20. It may be seen that glass, after heat-treatment in the metaborate crystallization temperature range, develops considerable resistance to steam attack and loses this improvement in the orthoborate crystallization range. The minimum loss in weight is 18 mg/cm^2 . This loss is not very high when compared with 9 mg/cm^2 for a commercial borosilicate glass, when tested under similar conditions as reported in the literature (39). Excessive loss of weight in the orthoborate crystallization range is probably due to attack of steam on B_2O_3 which is produced as a result of chemical decomposition of metaborate. B_2O_3 glass is soluble whereas lanthanum meta- and orthoborates are insoluble in hot water.

V CONCLUSIONS

- (1) Regions of vitrification or glass formation in $\text{SrO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ and $\text{BaO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ systems have been found to be wider than that reported in the literature for $\text{CdO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ system. This increase in width is attributed to the rare gas electronic configuration of divalent ions of strontium and barium which are members of Group IIA. This is in contrast to cadmium which has a non-rare gas configuration and belongs to Group IIB of the periodic chart. Cd^{++} , because of its strong polarizing effect, promotes immiscibility in the above mentioned borate systems so that smaller regions of glass formation occur.

- (2) Regions of glass formation in the systems $\text{SrO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ and $\text{BaO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ are comparatively smaller than those reported for corresponding aluminoborate glass formation i.e., $\text{SrO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ and $\text{BaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$. While aluminium and lanthanum both belong to Group III of the periodic chart, La^{+++} possesses a larger radius than Al^{+++} . The Al^{+++} , because of its high charge and small radius, may be present in glass predominantly as a net-work former rather than a modifier. La^{+++}

although of equal charge but because of its much larger radius, exists only as a modifier in the structure of glass.

- (3) The glass forming region of the $\text{BaO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ system is larger when compared to the $\text{SrO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ system. This has been attributed to the higher atomic weight of barium in the alkaline earth series and is in agreement with a number of published works for similar systems.
- (4) Considering the influence of composition on properties of glasses of the systems studied, density and refractive index increase with the substitution of La_2O_3 for MO (SrO or BaO) and B_2O_3 . The molecular refractivity of 30 mole % SrO- 70 mole % B_2O_3 glass increases linearly with the addition of La_2O_3 . The substitution of La_2O_3 for MO decreases the coefficient of thermal expansion of glass at 65 mole % B_2O_3 . The addition of La_2O_3 at 10 mole % MO results in a sharp increase in the thermal expansion. The magnitude of increase in the thermal expansion by the introduction of La_2O_3 decreases gradually between 20 and 30 mole % MO.
- (5) Assessing the improvement of glass properties as a result of catalyzed crystallization, the increase

in refractive index and microhardness and decrease in thermal expansion due to varied heat-treatments are 0.9, 9.2 and 8.0 % respectively.

(6) X-ray diffraction curves indicate the presence of lanthanum meta- and orthoborates in the glass after heat-treatment within specific ranges of temperature. The primary crystalline phase is identified as metaborate and its decomposition near to 775 C leads to the formation of orthoborate.

(7) The loss in weight of the crystallized glass is reduced to 18 mg/cm² by steam attack for 200 hrs. whereas under similar conditions of testing a commercial borosilicate glass is reported to lose 9 mg/cm². Borate glasses, due to their poor chemical durability, find limited use in actual practice. The present work suggests a possibility of producing a hard glass of high refractive index with a fairly good chemical durability.

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APPENDIX I

Calculations for the properties of glass:- Density was calculated using the equation:

$$\text{Density} = \frac{\text{Wt. of specimen in air}}{\text{Loss of wt. in toluene}} \times \text{Density of toluene}$$

Thermal expansion coefficient (α) was calculated according to the following relationship.

$$\alpha = \frac{\Delta L}{L \times T}$$
, where L is the increase in length between 100 and 350 C and L is the original length of the glass rod. T is the temperature difference over which thermal expansion has been studied (in the present case it is equal to 250).

Molecular refractivity was calculated using the Lorentz-Lorenz equation as given below:

$$R_d = \frac{n_D^2 - 1}{n_D^2 + 2} \left[\frac{N_1 M_1 + N_2 M_2 + N_3 M_3}{d} \right]$$
, where n_D and d are the refractive index and density of glass respectively. N_1 , N_2 , N_3 are the molar fractions and M_1 , M_2 , M_3 are the molecular weights of SrO, La₂O₃ and B₂O₃ respectively.

APPENDIX II

(Experimental Data on Molecular Refractivity
of Glass and Variations of Properties of
Glass With Heat-Treatment.)

Table IV. Effect of the Addition of Lanthanum Oxide on the Molecular Refractivity of SrO (30 mole%)-B₂O₃ (70 mole%) glass.

Quantity of La ₂ O ₃ (mole%) added to SrO-B ₂ O ₃ glass.	Density of final glass, gm/cm ³	Refractive index, n _D	Molecular Refractivity of final glass, cm ³
8	4.066	1.680	9.09
10	4.088	1.688	9.51
12	4.107	1.692	9.85
18	4.300	1.710	11.30

Table V.. Effect of Heat-Treatment on the Properties of Glass

Conditions of Heat-Treatment	Density, gm/cm ³	Microhardness, kg/mm ²	$\alpha_{100-350} \cdot 10^6$, deg. ⁻¹	Refractive index, n_D
Original glass	4.564	639	18.6	1.704
500, 1/2 hr.	4.564	639	18.6	1.704
500, 12 hrs.	4.566	701	19.0	1.705
600, 1/2 hr.	4.564	639	18.6	1.704
600, 12 hrs.	4.567	713	19.4	1.706
700, 1/2 hr.	4.564	639	18.6	1.704
700, 12 hrs.	4.569	726	20.0	1.710
745, 1/2 hr.	4.596	752	27.6	1.710
745, 15 mins.	4.590	739	24.7	1.708
760, 1/2 hr.	4.596	752	27.6	1.710
760, 15 mins.	4.591	739	24.9	1.708
775, 1/2 hr.	4.584	713	23.6	1.712
775, 15 mins.	4.582	701	22.5	1.710
800, 1/2 hr.	4.574	666	20.4	1.720
800, 15 mins.	4.573	666	20.2	1.718
830, 1/2 hr.	4.570	644	17.1	1.715
830, 15 mins.	4.570	644	17.1	1.715

Table VI.. Effect of Heat-Treatment on Refractive index of Glass at 715°C.

Heat-treatment time, hrs.	Refractive-index n_D
1.5	1.710
6	1.715
9	1.716
18	1.717
24	1.717

Table VII.. Effect of Exposure of Crystallized Glass to Steam for 200 Hrs.

Temperature of exposure for 1/2 hr.	Loss in weight, mg/cm^3
700°	51
745°	18
760°	19
775°	35
800°	40
830°	42

APPENDIX III

Table VIII. X-Ray Diffraction Data Consulted for
Lanthnum Borates (After Levin & Co-Workers, Ref.41)

La_2O_3 B_2O_3		La_2O_3 $3\text{B}_2\text{O}_3$	
d (a.u.)	I/I(%)	d(a.u.)	I/I(%)
3.49	100	3.235	100
3.38	44	3.200	47
2.936	24	3.123	34
2.552	31	3.050	28
2.431	33	2.870	26
2.422	30	2.842	68
2.036	47	2.572	21
1.947	17	2.535	22
1.926	27	2.433	17
1.868	37	2.144	17
1.784	21	2.088	63
1.769	17	2.065	21
1.517	15	2.035	25
1.298	15	1.896	31
1.255	19	1.880	29
		1.816	18

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