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QUARTERLY PROGRESS REPORT

HYDROTHERMAL CRYSTAL STUDIES

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Report Prepared by

Rustum Roy
R. C. DeVries
D. E. Rase
M. W. Shafer
E. F. Osborn

The Pennsylvania State College
State College, Pa.

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ABSTRACT

Investigations of the systems $\text{CaO-TiO}_2\text{-SiO}_2$, and BaO-TiO_2 are nearing completion. The presence of immiscible liquids in the former system appears to cover a large area of the diagram and extend to the binary system $\text{TiO}_2\text{-SiO}_2$. A fifth barium titanate - BaO.2TiO_2 - has been confirmed and its properties recorded, it appears to have a stability minimum at 1260°C .

Investigations of the system $\text{BaO-TiO}_2\text{-H}_2\text{O}$ provide information on the possibilities of hydrothermal growth of BaTiO_3 crystals. Essentially complete p-t curves describing the equilibrium in the system $\text{In}_2\text{O}_3\text{-H}_2\text{O}$ have been obtained, and preliminary data in the system $\text{Sc}_2\text{O}_3\text{-H}_2\text{O}$ fail to show agreement with earlier work. The application of infra-red spectra and single crystal electron diffraction techniques to certain relevant problems is being explored.

I. FACTUAL DATA

A. Equipment

No significant additions have been made to the equipment during this period. The high frequency "Ordway" type furnace was not used as extensively during this quarter as we hope to use it in the future. No satisfactory evaluation of the possibilities can therefore be given at present. However, one of the chief difficulties with our present design (which may not have been present in Ordway's original) is the fact there is no control on the cold junction temperature. In our furnace the thermocouple is attached directly to brass leads. Calibration with known materials does not solve this problem since each small thermocouple-resistor combination differs slightly and, moreover, the heating of the brass terminals is very largely a function of time. The solution of this problem is to introduce heavy leads, one of platinum and one of platinum -10% rhodium of sufficient length to prevent the heating of the remote end, or to permit its introduction into an ice-bath.

Some investigations have been started of the infrared spectra of certain of the phases encountered, using a Perkin-Elmer Model 12C instrument. The details regarding experimental techniques are given in the relevant section. Our differential thermal analyses have been partly repeated with much greater success using different equipment. It was mentioned in earlier reports that at temperatures above about 1250°-1300°C recording of the differential temperature by means of an electronic recorder was extremely difficult in cases where high sensitivity was desirable. This has been noted by all the workers in this field (Jaeger in 1929⁽¹⁾) ascribed it to the electron emission from the heated metal and subsequent conduction through the hot refractory). However, a well-damped ordinary d'Arsonval galvanometer does not respond to these extraneous currents, and moreover increasing the sensitivity does not require any sensitive

electronic circuits but rather a simple extension of the optical lever. The tedious part of taking numerous galvanometer readings (or of having to use a photographic method) may be eliminated by using a divided photocell* attached to an ordinary Brown recorder as shown by Keith and Tuttle⁽²⁾. The rest of the equipment was the same as previously described, all the thermocouple leads being shielded.

B. Results

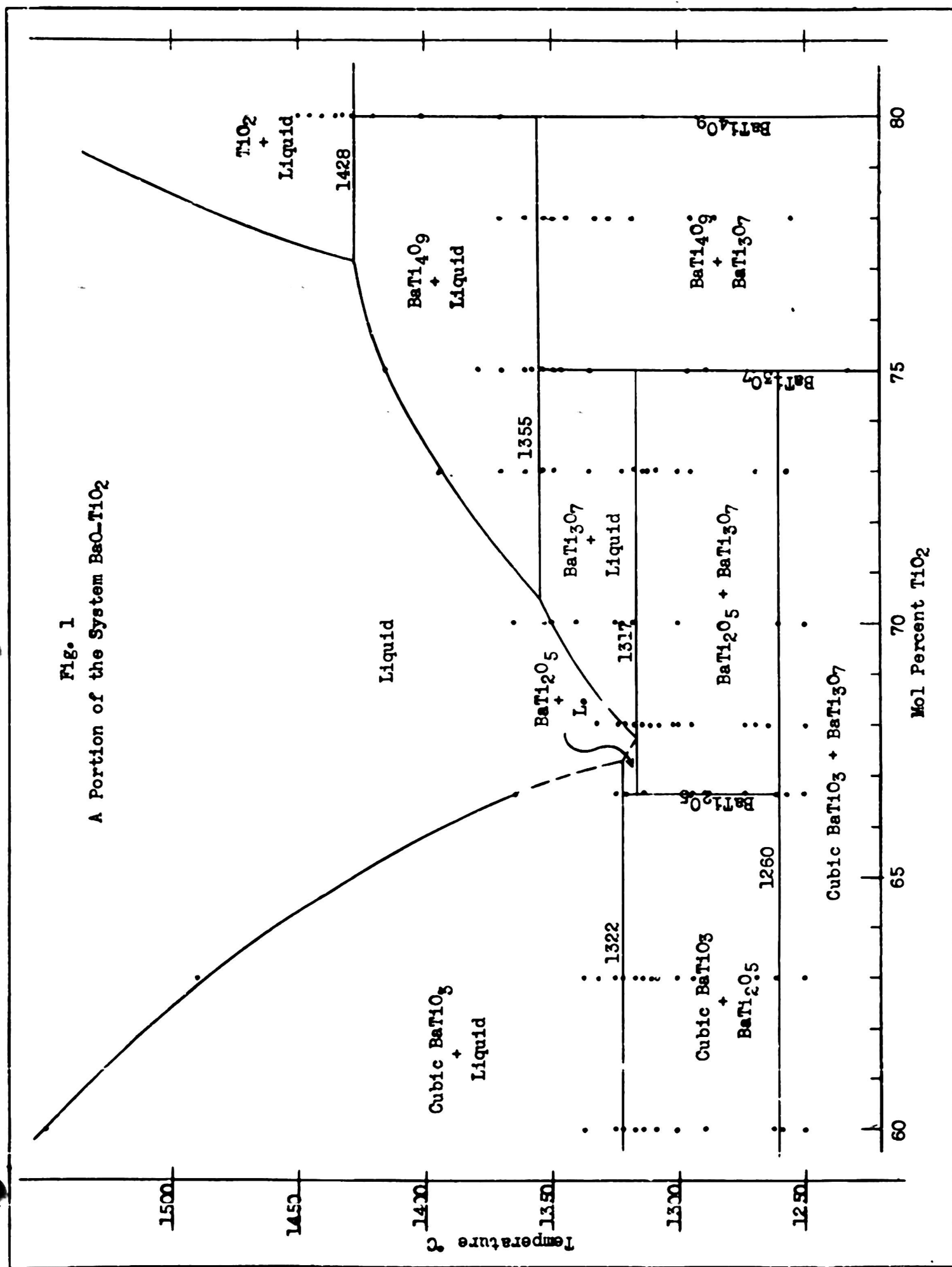
(1) The System BaO-TiO₂

In an attempt to complete the work on the system BaO-TiO₂ all the invariant points were checked as far as possible with the quenching furnace technique. Especial attention was paid to three general questions: (1) The nature of the effect of additions of BaO and TiO₂ to the hexagonal-cubic transition, (2) The congruent or incongruent melting of BaO.4TiO₂, (3) The question of the existence of the compound BaO.2TiO₂. Fig. 1 shows the general area of the diagram studied and some of the runs made; all the samples have been subsequently examined microscopically and by X-ray diffraction patterns.

(a). The Cubic-Hexagonal BaTiO₃ Transition. The equilibrium temperature we have assigned to this inversion is 1460°C. Very long runs show that this temperature is not appreciably affected by the addition of BaO, i.e., the inversion temperature remains constant in the two-phase region BaTiO₃ + Ba₂TiO₄. The phase changes on the high titania side of BaTiO₃ appear to be consistent with our earlier presentation of the diagram, and here the question of the composition of the solid phase formed arises again. It has been claimed that hexagonal barium titanate could be made from mixtures in

* We are indebted to Prof. M. L. Keith for the use of the recording mechanism described above.

Fig. 1
A Portion of the System BaO-TiO₂



the system $\text{BaTiO}_3-(\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3)$, although precise temperatures and compositions were not given⁽³⁾. With mixtures of 10-20 mol % BaTiO_3 we have indeed been able to obtain a few euhedral crystals of the hexagonal phase on cooling from 1350°C to 900°C. This would indicate one of two things: either these crystals are growing metastably - a very common occurrence with similar substances - or the inversion temperature is lowered by solid solution in a manner similar to that causing the inversion temperature to be raised in the system BaO-TiO_2 . The latter possibility is of considerable importance if these crystals have been used for further study. The important conclusion which may perhaps be drawn by analogy from the BaO-TiO_2 system is that it would require only a very few percent of the foreign ion to alter the inversion temperature by 100°-200°C. Furthermore, with reference to the equilibrium diagram it should be remembered that not all observations are made at equilibrium and many data will be in apparent conflict with the diagram as presented here. Thus we have among our own data a large number of runs which can only be explained by assuming non-equilibrium conditions. The diagram presented is that which is in best accord with the facts, and which with reasonable assumptions can explain the behavior of all melts in this system.

One example will suffice to illustrate this. If a platinum crucible full of barium metatitanate is melted in the gas furnace and extracted rapidly at a temperature of say 1700°C and "quenched" in water, one would expect to find hexagonal barium titanate as the phase which forms in contact with the liquid. As a matter of fact in several such runs only the cubic (tetragonal at room temperature) form is obtained. This is explained by assuming that the melt cooled below 1460° so rapidly that no structure was formed at all and that when the material finally crystallized it did so in the stability range of the cubic phase yielding cubic crystals.

The other consideration which we regard as being of considerable importance in connection with both the melting and inversion of barium titanate is that of partial reduction. It is undoubtedly true that much of our equilibrium data, and the

data obtained by most workers on various properties, really apply to phases in the system $\text{BaO-TiO}_2\text{-Ti}_2\text{O}_3$. It has been assumed, with some justification, that the amount of reduction is small and that it will not noticeably affect equilibria in the system. This assumption is examined critically in a subsequent section.

(b) The Melting of BaO.4TiO_2 . This problem is not of great importance as it does not make much difference to the diagram whether BaTi_4O_9 is congruently melting or not. Actually the diagram presented earlier showed it as incongruently melting, although it was stated that this could not be unequivocally established. The evidence now, although considerably increased in volume, is not much less equivocal. Careful runs made at intervals of a few degrees from 1400° to 1450°C indicated that possibly the BaO.4TiO_2 composition did not develop liquid till $1428^\circ \pm 4^\circ$ and liquid was developed in mixtures containing 82, 85 and 90% TiO_2 at temperatures within the experimental error range. The only criteria which can be used to determine the appearance of liquid are observation in the binocular microscope, and the x-ray diffraction patterns. Microscopic observations can be misleading, since sintering at temperatures a few degrees below the liquidus is so pronounced that crystals grow together considerably. Hence larger single crystals of BaO.4TiO_2 were grown from a 73% TiO_2 melt and also used as starting material. Moreover, all automatic regulators "overshoot" a little if the sample is introduced after the furnace is at the desired temperature, hence these runs were repeated and the sample was introduced at a temperature some 25°C below the desired temperature. The furnace was heated up slowly -- the maximum temperature being carefully observed. It was hoped that if the compound was incongruently melting, by quenching from a temperature just above the melting point it would be possible to obtain indications of the presence of rutile from the X-ray diffraction patterns. Neither in this, nor in microscopic observations was any indication of rutile found. The compound is, therefore,

still shown as melting just incongruently. This is in accord with the rough liquidus data which can be obtained on the strip furnace, but which cannot be relied upon in "non-glass forming" systems.

(c) The Existence of a Compound of Composition $\text{BaO} \cdot 2\text{TiO}_2$.

In our earlier reports we have indicated the possible existence of such a compound and stated that there were unresolved questions regarding the area of the diagram near this composition, between 60 and 70% TiO_2 . It is now established that a fifth compound does exist in the system -- most probably with the composition $\text{BaO} \cdot 2\text{TiO}_2$ (although the composition is not certain and may conceivably be 70% TiO_2). The compound's stable existence, in accord with our earlier data, appears to be only at temperatures just below the solidus. Thus, the data obtained earlier which showed $\text{BaTiO}_3 + \text{BaTi}_3\text{O}_7$ in equilibrium for compositions between 50 and 75% TiO_2 are correct at the temperatures for which they were reported. However, at 1260°C about 40° below the first appearance of liquid, the BaTiO_3 and BaTi_3O_7 react to give a new phase. The same phase is detectable in all the mixtures between 55% and 70% TiO_2 which have been held for a few hours above this temperature. However, even after 200 hours the conversion is not complete in any of the mixtures, considerable evidence for BaTiO_3 being found in the powder patterns even in the 66% and 70% mixtures. This is one reason why it is not possible to assign the composition of the compound definitely; for if complete reaction were to take place in a few days, the 66.6% TiO_2 mixture should convert completely to the new phase. The X-ray powder diffraction pattern for this phase is very "weak" - undoubtedly due partly to a low multiplicity factor-making its detection in small quantities altogether impossible. That this phase is stable at the higher temperatures and in the presence of liquid is easily established, since melted mixtures such as those with 63%, 66% and 68% TiO_2 , yield on crystallization, among other phases well-formed crystals with an X-ray pattern corresponding to that obtained from the phase formed below the solidus. These crystals grow very

easily and in a 30 ml platinum crucible have attained lengths up to 1 cm. They were carefully separated from the ground-mass under the binocular microscope, and a spectroscopic analysis revealed the absence of any Pt or other impurity in excess of a few tenths of one percent. It was expected that the composition could be determined by other considerations, but chemical analysis is being undertaken to determine their composition directly. Microscopically they are length fast needles, with parallel extinction, biaxial negative with $2v = \text{ca. } 80^\circ$. The X-ray diffraction pattern is quite characteristic and distinct from the other phases. Furthermore, it should be noted that prima facie evidence has not been obtained to prove that this phase is not the stable phase at lower temperatures, although the evidence is strongly against it. Runs of 200 hours duration failed to convert the crushed needles into a mixture of BaTiO_3 and BaTi_3O_7 , although at the same time mixtures of barium carbonate and titania reacted completely to give the latter assemblage. In many instances the failure of such a phase once formed to convert to the stable assemblage is known. Moreover, hydrothermal runs undertaken for this purpose showed that at 830°C in 7 days the raw batches would react to yield only $\text{BaTiO}_3 + \text{BaTi}_3\text{O}_7$. However, even hydrothermally it was not found possible to convert the new phase to this assemblage in 5 days at 800°C and 5000 psi water pressure. The phase relations above the solidus are even more difficult to determine, since their composition has such a great effect and since several different invariant points appear to lie within a very narrow range. Furthermore, in this region the liquids when quenched do not yield phases with X-ray patterns of crystals, although they do not yield what may be called glasses. Each run in this region has to be made separately since the highly fluid melts tend to run out of the envelopes. This leads to the additional serious difficulty that after the first development of liquid it runs out from around the crystals into the folds of the platinum envelope, thereby changing the composition of the body of the sample. Equilibrium could, therefore, never be attained under these conditions. The question to be decided

is whether $\text{BaO} \cdot 2\text{TiO}_2$ melts congruently or whether it melts in the primary field of BaTiO_3 or the field of BaTi_3O_7 . We hope to decide this issue on the basis of careful differential thermal analysis accompanied by the "filtering" of the mixtures at various temperatures.

(2) The System $\text{CaO-TiO}_2\text{-SiO}_2$

Investigation of this system is nearing completion and an up-to-date diagram is presented. In our earlier work we had wished to avoid the controversy regarding the $\text{TiO}_2\text{-SiO}_2$ system, assume that the diagram by Bunting⁽⁴⁾ was essentially correct, and extrapolate our data towards the binary system. However, this became impossible because relations found for the ternary system required a new interpretation of the binary system. Work was therefore started on this binary system and is reported on in a later section. However, a reconsideration of one aspect, viz., that of reduction of TiO_2 is common to much of the work that has been done here and is therefore dealt with first.

(a) The Reduction of TiO_2 . All workers in this field have recognized that TiO_2 can be reduced very easily although the extent of reduction in air is quite small at temperatures below the melting point of TiO_2 . Most people regard this reduced TiO_2 as "a non-stoichiometric" compound, wherein there are vacant oxygen sites, a property also used to account for the semiconducting nature of reduced rutile. While this is a useful concept, especially when discussing properties which are essentially non-colligative and dependent on the outermost electrons, it is not helpful and often quite misleading when used in connection with phase equilibrium work. We propose, therefore, that in such cases the quite general applicability of the phase rule to such compositions be recognized and its standard terminology used. The system Ti-O was investigated nearly 20 years ago by P. Ehrlich⁽⁵⁾ who recognized at least 4 oxide phases which would correspond in all probability the following compounds: TiO , Ti_2O_3 , Ti_3O_5 and TiO_2 . The

same phase in all these cases was found to exist with compositions both richer and poorer in oxygen. Agamawi and White⁽⁶⁾ thought that the Ti_3O_5 compound was not as well established as the others. However, the extensive work by Rusakov and Zhdanov⁽⁷⁾ on reduction of TiO_2 and the formation of anosovite, $TiO_2 \cdot Ti_2O_3$ establishes it beyond any doubt. From the phase equilibria point of view, the system Ti-O would be described as one having four compounds each with considerable solid solution on both sides of the compound. There is no need whatsoever to regard the "reduced" TiO_2 case as exceptional in any way. It is simply a solid solution of TiO_2 towards Ti_2O_3 (or containing more Ti than TiO_2). Thermodynamic calculations by Kubaschewski and Evans⁽⁸⁾ have shown that very low partial pressures of oxygen of the order of 10^{-5} mm. of mercury would be required for the complete reduction of TiO_2 to Ti_2O_3 . This, of course, does not provide us with any quantitative basis for predicting the extent of reduction or, in other words, the composition of the solid solution in equilibrium with partial pressures of oxygen of the order of 150 mm. of Hg or perhaps considerably less in a crucible or well-sealed platinum envelope. Some indication of the actual extent of reduction under approximately similar conditions as those used in these experiments may be obtained by studying the loss in weight of the original mixtures when fired to a certain temperature for a certain length of time. A similar approach was used by Agamawi and White (op. cit.) who heated TiO_2 to $1550^\circ C$ and found a loss of approximately 0.785% of which 0.284% was lost below $500^\circ C$ and was attributed by them to loss of volatiles. The amount of the loss which could be regained on cooling was, however, only .025%. They make the unwarranted assumption that this is the only part that may be attributed to oxygen loss. No attempt was made to bring the TiO_2 in the platinum crucible into equilibrium with the surrounding atmosphere and it is hardly likely that powdered TiO_2 in the bottom of a crucible could be expected to come to equilibrium with the atmosphere above the top of the powder under static conditions. We have studied the weight

loss of ten mixtures on the TiO_2 - SiO_2 join and the percentage weight loss for the high titania mixtures is of the same order of magnitude as that reported by Agamawi and White (op. cit.). If TiO_2 were completely reduced to Ti_2O_3 it would lose 10% of its weight; the above authors found a weight loss at 1000°C of approximately 0.785% and after deducting volatiles lost below 500°C give a value of ca. 0.5%. Our weight loss for the 90% TiO_2 mixtures was 0.7% at constant weight; this does not include the loss of volatiles which we find to be of the order of 0.2%. If we estimate the percentage of Ti_2O_3 required to give these amounts of loss we obtain a magnitude of approximately 5% Ti_2O_3 present in the TiO_2 . This is by no means inconsiderable in any consideration of phase equilibria. This estimate is based on the assumption that most of the loss is actually due to the loss of oxygen. There is a little justification for this insofar as we have found that, under similar conditions of heat treatment, other mixtures in various oxide systems including the ternary system $\text{CaO-TiO}_2\text{-SiO}_2$ and the quaternary system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ lose approximately 0.25% or less of a 10.00 gm batch. Losses significantly and consistently greater than this are only found in the high TiO_2 part of the system. The possibility remains, of course, that TiO_2 itself volatilizes, i.e., that both Ti and O are lost but, excepting this, one must consider the conclusion that the reduction is of such an order as to yield a few percent of Ti_2O_3 . Thus investigations of the systems $\text{TiO}_2\text{-SiO}_2$ under atmospheric conditions and the usual quenching technique may very well be really an investigation of a join in the ternary system $\text{TiO}_2\text{-Ti}_2\text{O}_3\text{-SiO}_2$. However, because of the complete solid solution relationships apparently obtaining up to these compositions, none of the relations will be very markedly changed as far as phase equilibria go. Our views of structural and color changes of phases may be affected by these considerations. Thus, the well-known "yellow" and "black" types of BaTiO_3 may find an explanation along these lines, and it may also have some bearing on the metastable appearance of the hexagonal polymorph.

A plot of refractive indices of glasses in the system $\text{CaO-TiO}_2\text{-SiO}_2$ is shown in Fig. 2, and an up-to-date equilibrium diagram is shown in Fig. 3. The data were obtained from 128 mixtures, most of which are plotted on the diagram.

(b) The System $\text{TiO}_2\text{-SiO}_2$. At least five versions of this system are now available (4, 9, 10, 11, 12). These are shown in Fig. 4. The Umezu-Kakiuchi⁽¹⁰⁾ version, which antedates all but Rieke's diagram was found in an obscure Japanese journal. Since the diagrams of Bogatskii and Rieke are similar, only Rieke's is shown. The discrepancies, particularly in the location of the eutectic, are extraordinary. The introduction of a two liquid region in the Japanese worker's diagram is significant in view of the large two liquid region found in the ternary system $\text{CaO-TiO}_2\text{-SiO}_2$. A series of mixtures made in our laboratory on the binary system show a similar phenomenon over the range of at least 30% - 85% TiO_2 at a temperature of $1800^\circ \pm 30$. C. (a slightly greater range than Umezu and Kakiuchi's 42.5% - 80%). The rather flat liquidus defining the rutile field in Bunting's diagram is not incompatible with such a representation.

The present data from the ternary system $\text{CaO-TiO}_2\text{-SiO}_2$ (Fig. 3) are not compatible with either a eutectic at about 40% TiO_2 , according to Rieke and Bogatskii⁽¹¹⁾, or with one at 85% TiO_2 , as in the Japanese diagram. The temperatures of the latter diagram seem much too low also. The high temperatures involved, the fact that most liquids near the $\text{TiO}_2\text{-SiO}_2$ side of the diagram do not quench to glasses and the possible consequences of reduction (previously discussed) all have to be contended with here.

It is possible for purposes of discussion to construct a theoretical, "not-impossible" diagram of the system $\text{TiO}_2\text{-SiO}_2\text{-Ti}_2\text{O}_3$ (largely by analogy with $\text{Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ ⁽⁶⁾) which might be the basis of an explanation of the disagreement existing for the binary system $\text{TiO}_2\text{-SiO}_2$. If it is assumed that the high TiO_2 mixtures all contain some Ti_2O_3 , these systems may be shown as joins in the ternary system

Fig. 2
 Refractive Indices of glasses
 in the system
 $\text{CaO} - \text{TiO}_2 - \text{SiO}_2$
 (weight per cent)
 (Na light)

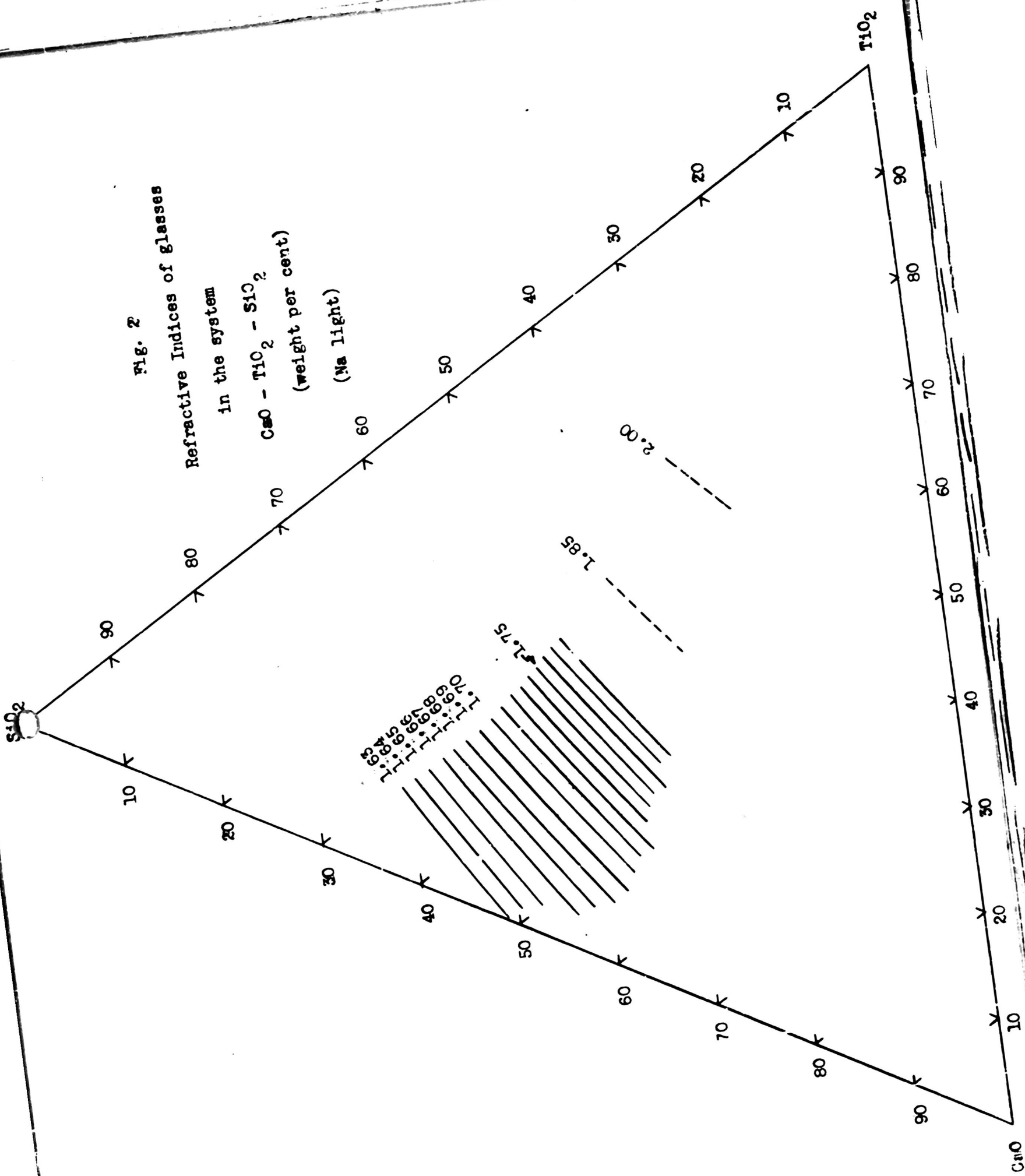


Fig. 3

The System $\text{CaO} - \text{TiO}_2 - \text{SiO}_2$

(weight per cent)

Data of Iwase, Fukusima, Nisioka
is incorporated.

—x— limit of two liquid region

- a - 1400 °C
- b - 1395
- c - 1425
- d - 1345
- e - 1353
- f - 1310
- g - 1373
- h - 1365
- i - 1375
- j - 1365
- k - 1375

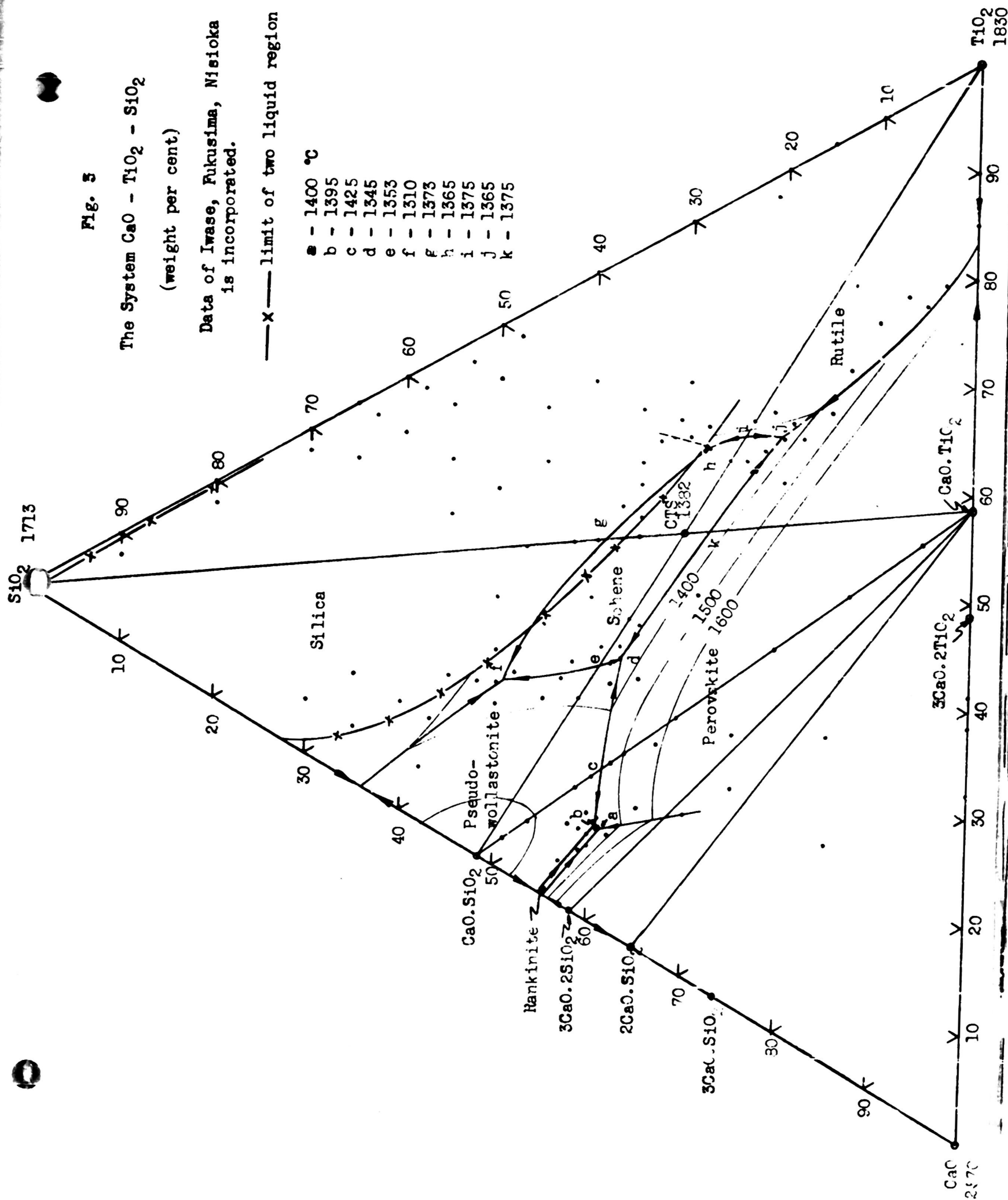
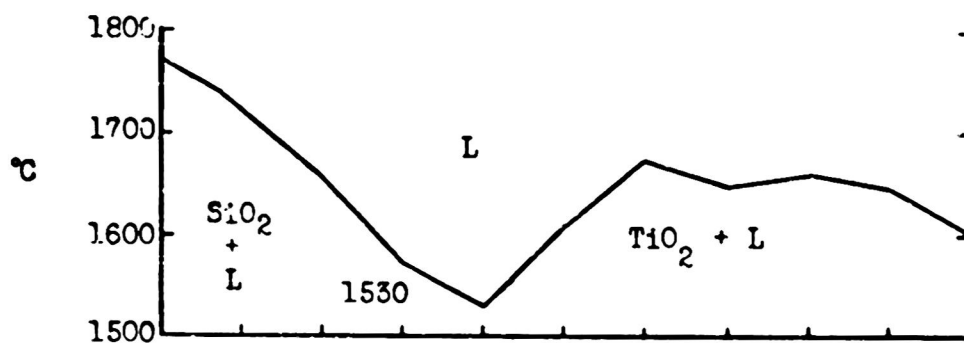


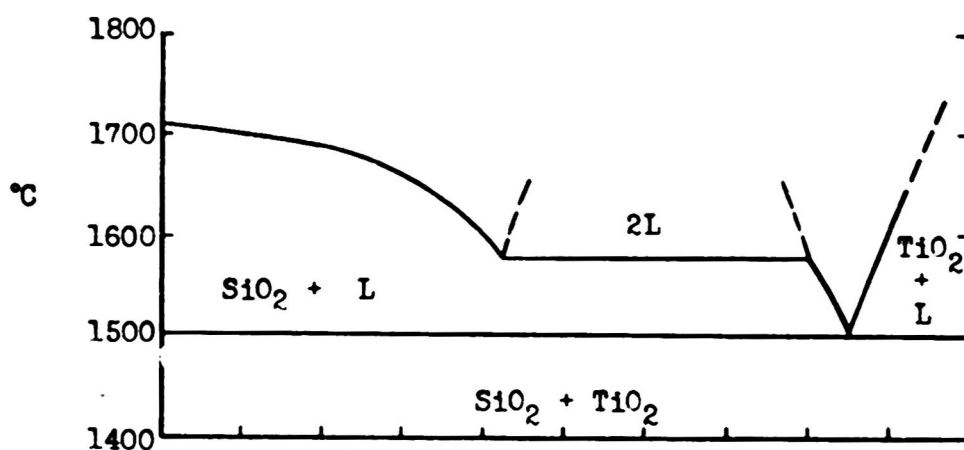
Fig. 4

Different Versions of the System TiO_2 - SiO_2

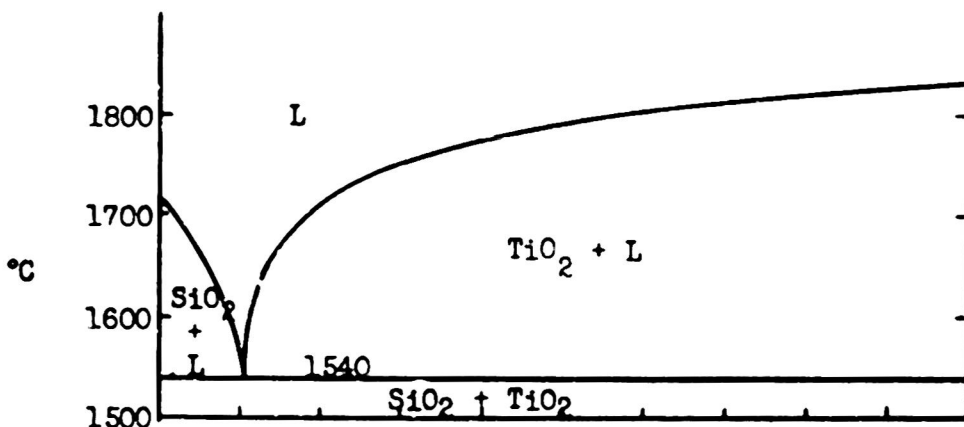


R. Rieke, 1908

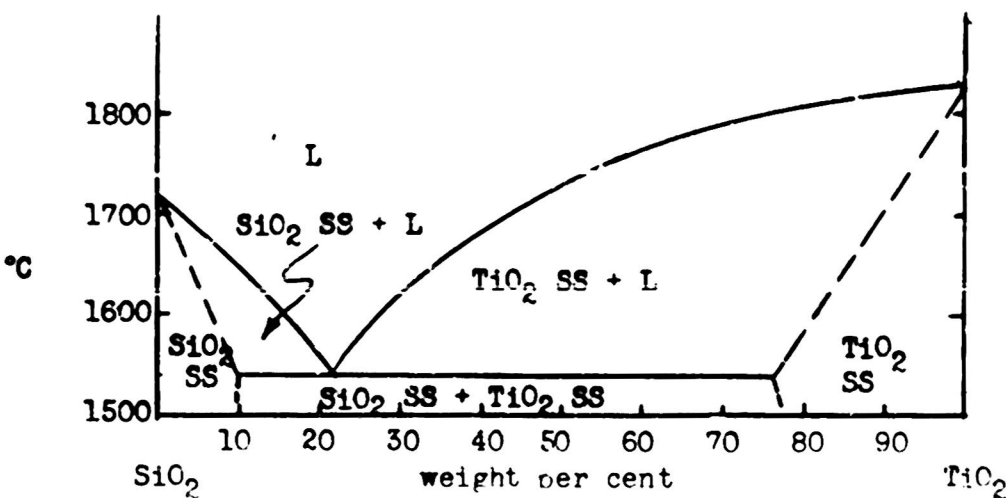
(D. Bogatskii, 1936
eutectic: 45% TiO_2 ; 1610)



S. Umezu and F. Kakiuchi,
1930



E. N. Bunting, 1933



R. W. Ricker and
F. A. Hummel
1951

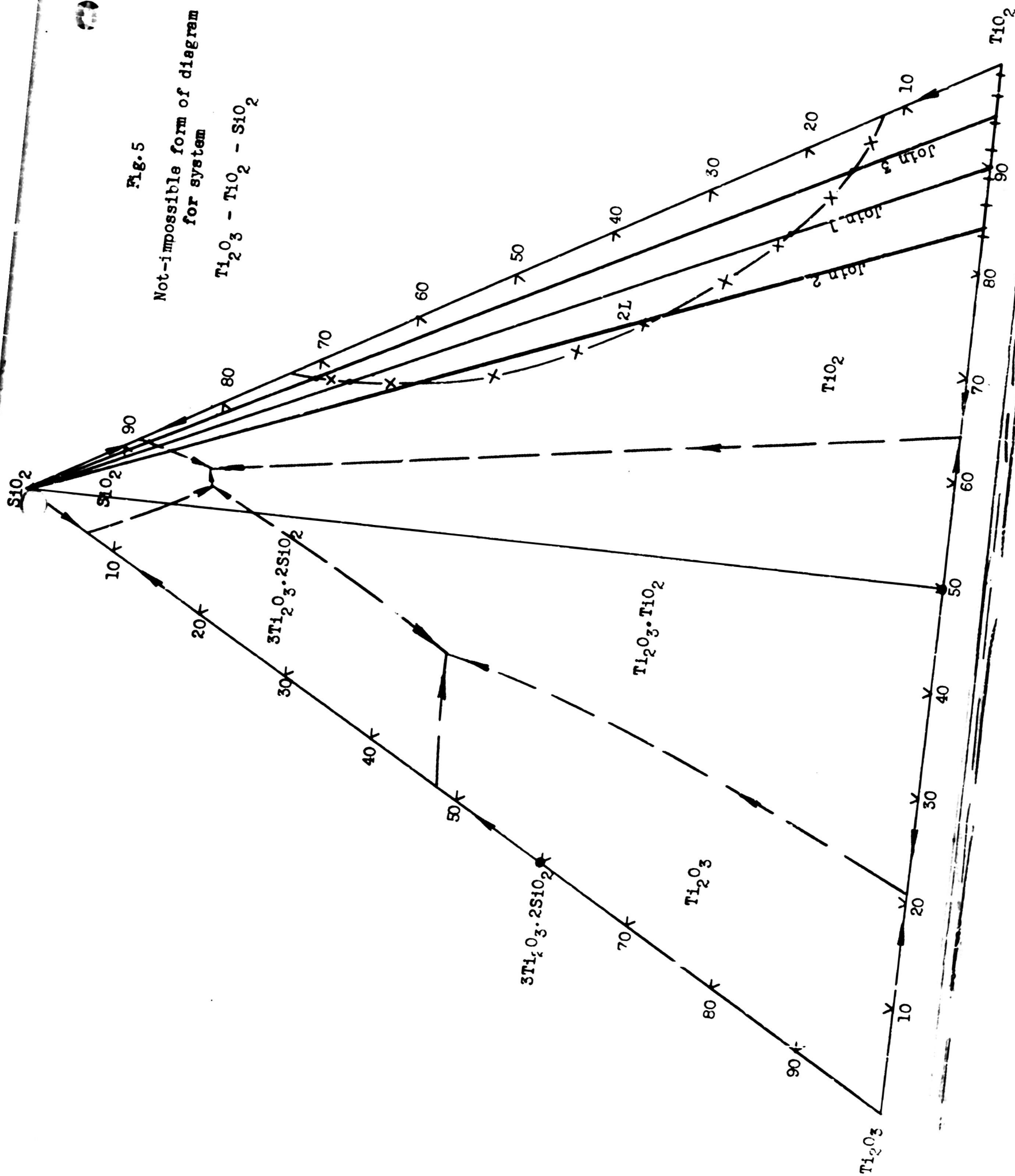
(Fig. 5). Thus the work of Umezu and Kakiuchi, which was done admittedly under strongly reducing conditions, might be well into the ternary system (join 1, Fig. 5) thus explaining the low temperatures and the smaller range of two liquids since the two liquid region might be expected to diminish. Their placing of the eutectic is not so easily explained. The eutectic of Rieke and of Bogatskii (join 2) may well be one limit of the two liquid region. Photomicrographs shown by Bogatskii⁽¹¹⁾ are suspiciously like the phenomenon which we call two liquids.

It may be advantageous to review the phenomenon we have been calling "two liquids". This effect occurs in all of the mixtures in the ternary system enclosed in the area marked by long dashes (see Fig. 3) and in the 30% - 85% TiO_2 mixtures on the binary system TiO_2 - SiO_2 . It is characterized almost invariably by the separation of a clear glass and devitrified glass. On the strip furnace the devitrified masses -- apparently as the result of high fluidity -- surround the clear glass. On melting a mixture in a crucible a separation takes place also. If the mixture is crushed and remelted, the separation takes place again. After quenching the crucible and melt, the center portion -- usually a blue glass in bulk -- can be easily separated from the gray crystalline mass around it. This can and will be used to advantage. Such a separation with subsequent chemical analysis should give the conclusive proof of a two liquid region -- if such exists -- because the tie lines representing the composition of the two liquids in equilibrium can then be plotted. If this phenomenon is not that of two liquids separating, it is one deserving of explanation.

(3) The System $\text{BaO-TiO}_2\text{-H}_2\text{O}$

In considerations of growth of single crystals of BaTiO_3 of sufficient size to be industrially valuable, two methods stand out. One of these, the growth from melts, (usually in the presence of other phases to lower the temperatures necessary) has been investigated extensively: the other method,

EX-8.5



that of growth under hydrothermal conditions has also gained some attention recently because of its success in the case of quartz. We have made reference to our work on this problem in earlier reports and, undoubtedly, this method has been attempted by people interested in growing large crystals of BaTiO_3 . For the successful hydrothermal growth of these crystals the following information will be necessary:

(i). Are BaTiO_3 and H_2O compatible phases under the conditions which may be used for the synthesis of this phase? If not (while it is possible to form phases metastably) these conditions would hardly be considered the best for the growth of large single crystals of BaTiO_3 .

(ii). Is BaTiO_3 appreciably soluble in water at the temperatures used?

(iii). Is there a sufficient difference of solubility with temperature in order that a temperature-gradient method may be used to grow the crystals.

A complete answer to the first point would be obtained from a knowledge of the system $\text{BaO-TiO}_2\text{-H}_2\text{O}$. In Fig. 6 we represent the compounds in the system as circles along the edges of a composition triangle, there being no hydrates of any of the barium titanates (to the best of our knowledge up to the present). We are interested in knowing whether the join BT-H is stable, say between 200° and 500°C ; if it is, it is quite likely that the phase assemblage will be quite similar to that shown in the (a) part of the figure. The other likely possibility is that at some temperature BaTiO_3 will react with water to yield either rutile + Ba(OH)_2 or Ba(OH)_2 with BT_2 , BT_3 or BT_4 . The consideration of the system is complicated by the fact that both the Ba(OH)_2 and $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ melt at these temperatures and may form liquids only partially miscible with water. Our earlier data showed that BaTiO_3 was stable in the presence of water at least as low as 500°C although it could not be formed from $\text{BaCO}_3 + \text{TiO}_2$ at temperatures below this value. The more recent data showed that BaTiO_3 does not decompose in the presence of water under any static conditions that have been used (in times less than two

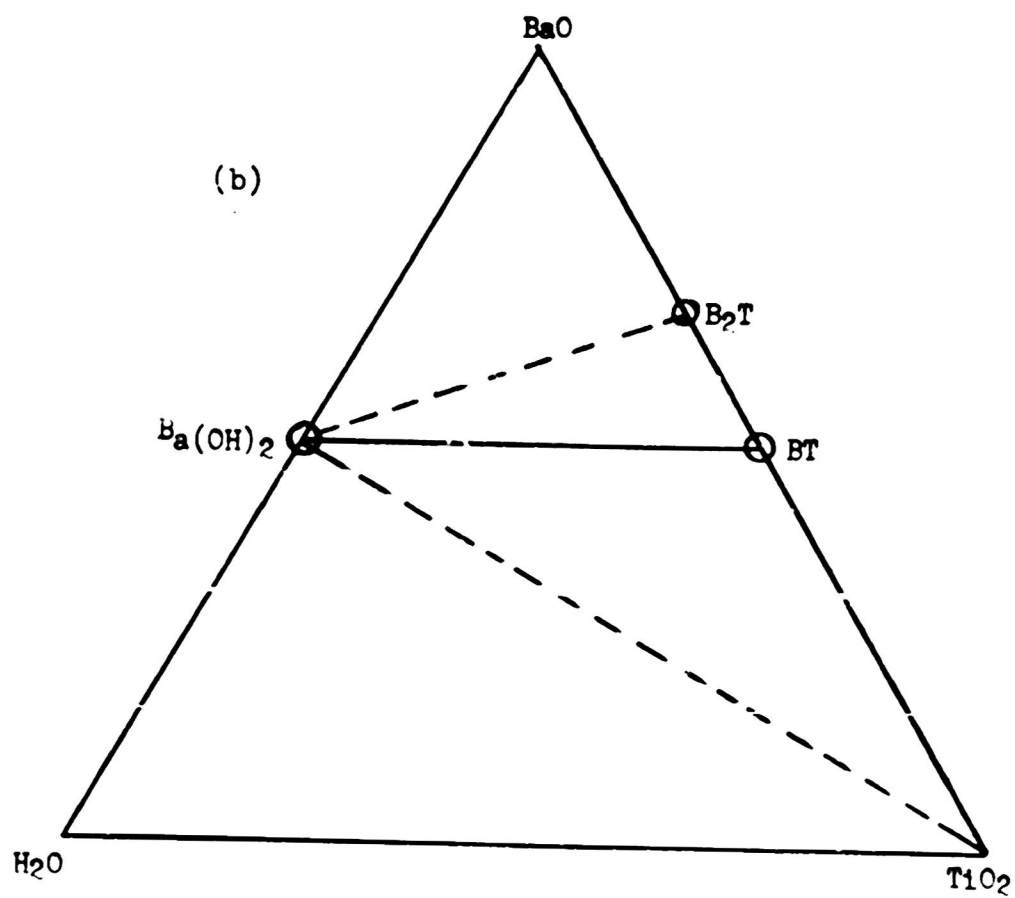
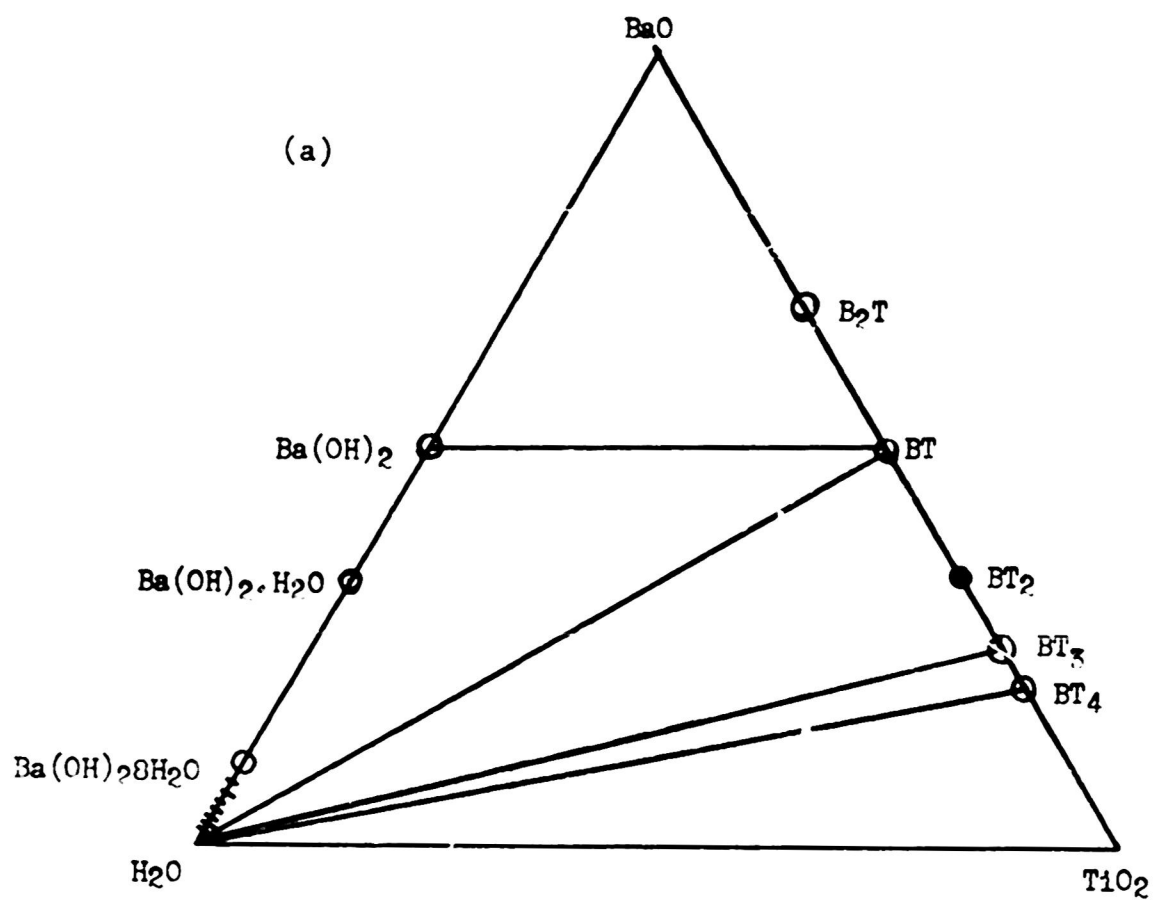
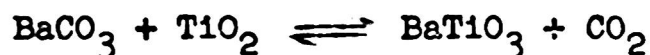


Fig. 6

weeks) at temperatures as low as 200°C. Moreover, $\text{Ba}(\text{OH})_2$ reacts vigorously with titania at 420° under low water pressures (less than one atmosphere) to yield $\text{BaTiO}_3 + \text{H}_2\text{O}$. The same reaction takes place at temperatures as low as 300°C and shows clearly the direction of equilibrium at these low water pressures. It would, therefore, appear that BaTiO_3 is stable in the presence of water down to room temperature. A few more runs will suffice to establish this positively. Furthermore, by studying the melting of mixtures, the join BaTiO_3 - $\text{Ba}(\text{OH})_2$ has been demonstrated to be a stable one at low water vapor pressures and is not likely to be affected by water pressure. In this connection, it is interesting to point out that the system $\text{Ba}(\text{OH})_2$ - BaTiO_3 thus provides a possible, not practical, system for the growth of BaTiO_3 in a very low temperature range from say 700°C to 400°C -- the approximate eutectic. We are not equipped to determine accurately the solubility at elevated temperatures and pressures (our vessels being too small) but very crude determinations yield values* indicating a solubility of the order of approximately 500 ppm in distilled water at 270° and the saturated vapor pressure - the value probably decreasing slightly at 370°C and 4000 psi. Thus, it would appear that the attempted hydrothermal growth of BaTiO_3 should be straightforward, using BaTiO_3 as starting material, and a temperature gradient method. The material obtained is, of course, the cubic (tetragonal at room temp.) phase; some interesting changes in intensities of the X-ray reflections have been noticed. The solubility of the compound may probably be increased by various additions, but the fundamental study of these is much more complex and tedious than in the case of a one component system such as SiO_2 .

*These values are rendered inaccurate by the redeposition of material on cooling, and the rather high solubility of silver and should in no sense be considered quantitative.

(c) The Effect of CO_2 on BaTiO_3 . It was reported to us by several people and has been noted in the literature⁽¹³⁾ that commercially prepared BaTiO_3 contains BaCO_3 . It has been suggested that possibly the BaTiO_3 reacts with the CO_2 of the air to yield the carbonate and thus the reaction



which is used to prepare the compound proceeds from right to left. The only positive evidence for the existence of the carbonate is given by Sutherland et. al⁽¹³⁾ from the infrared spectra of some commercial samples. It has not been reported that any BaCO_3 may be detected in the X-ray diffraction pattern. We have not been able to find any BaCO_3 in our samples either by X-ray diffraction or by infrared absorption techniques (vide infra). To test this idea of the reversibility of the reaction further, BaTiO_3 was heated at 400°C under about 5000 psi of CO_2 . No detectable amounts (using X-rays) of the carbonate was formed. The experiment was repeated at 67°C (3000 psi CO_2) since it was argued that the higher temperature would favor the reaction from left to right. Again no appreciable amounts of carbonate could be found. It is, therefore, most probable that any BaCO_3 which is detected in commercial samples is present merely as unreacted material.

(4) The System BaTiO_3 - NaNbO_3

Work on this system has progressed slowly. Two objectives were in view: firstly, to obtain at least in broad outline the phase diagram, and secondly, to study the effect of solid solution on the various inversions. This latter would have special significance since the most interesting inversion is that at 636°C . Wood⁽¹⁴⁾ made the rather remarkable claim that NaNbO_3 behaved as a tetragonal crystal toward light and a cubic crystal towards X-rays in the range $470^\circ - 640^\circ$ (her values). Megaw⁽¹⁵⁾ following this idea calls NaNbO_3 cubic above 470° . This, of course, leaves

the inversion at 636° as some kind of anomalous second order effect. However, we have found it to be a large definite heat effect appearing consistently and through several cycles of heating and cooling at the same temperature. There is no reason to suppose that this is any other than the true tetragonal-cubic inversion in NaNbO_3 . The next lower inversion is apparently to some form which is strongly pseudo-cubic. The question then arises, which inversion, if any, corresponds to the BaTiO_3 inversion at 120°C at which ferroelectricity is lost. It was hoped that the phase diagram may provide some clue to this - especially if the inversion temperatures formed a simple solid-solution type of relationship. Unfortunately, it became obvious quite early that this was not so, since cubic or nearly cubic solid solutions of BaTiO_3 in NaNbO_3 could be obtained at room temperature in the composition range of approximately 30% - 60% BaTiO_3 . Moreover, high-temperature X-ray diffraction studies on the Geiger counter spectrometer type equipment had an inversion range below 120°C and was assigned the value of 100°C for the middle of the inversion range. However, the patterns are very much poorer and the changes much less sharp than in the endmember; part of this being accounted for by the breadth of the two-phase region in the binary system - a region in which the tetragonal and cubic forms exist together in equilibrium. In the high temperature region NaNbO_3 melts at about 1440°C and the system forms a series of solid solutions with a minimum at approximately 38% NaNbO_3 and 1320°C . The other observation of interest in this system is the fact that we were at first puzzled to find no evidence of superstructure in our NaNbO_3 as reported by earlier workers. It was later found that the non-superstructure form could be "quenched" quite easily if the sample was cooled rapidly from its melting point. This form persists metastably at room temperature for apparently indefinite periods, but on "annealing" at 300° - 700°C and cooling slowly it develops the characteristic superstructure.

(5) Multiple Substitutions in the Perovskite Structure

This study, reported on in our First Annual Report, is essentially complete and a manuscript is currently being prepared for publication. Some additional work has been done with the attempted syntheses of more oxide, hydroxide and fluoride-oxide combination structures. No data will be presented at this time since we hope to attach a copy of the manuscript to the next report.

(6) Hydrothermal Investigation of Equilibria in Trivalent Oxide-Water Systems

The system $\text{In}_2\text{O}_3\text{-H}_2\text{O}$ has been essentially completed. Three distinct phases occur in the system: the anhydrous oxide with the C-type rare earth oxide structure, a new, hitherto undescribed compound $\text{In}_2\text{O}_3\cdot\text{H}_2\text{O}$, and the cubic trihydrate $\text{In}(\text{OH})_3$. The pressure temperature diagram for this system has been determined and is shown in outline in Fig. 7. The monohydrate is formed from the trihydrate at 250°C at 1000 psi and 265°C at 16,000 psi, and the slope is quite probably steep at lower pressures. The monohydrate transforms to the oxide at approximately 450°C , the temperature being little affected by pressure. It should be noted that especially for the first of these univariant curves the actual runs showed the presence of both the monohydrate and trihydrate over a range of temperatures. This we ascribe to the non-attainment of equilibrium, the irreversible nature of the change, and the fluctuations in temperature. The unit-cell dimensions of the $\text{In}(\text{OH})_3$ was found to be 7.958 in fair agreement with earlier values which vary from 7.90 to 9.95. In such a case the purity of the oxide will play a very important part in actual value: our material was sold as 99.9% In_2O_3 but not analyzed by us. The pattern for $\text{In}_2\text{O}_3\cdot\text{H}_2\text{O}$ is not related to any of the other monohydrate structures known. The boehmite structure is ruled out since apparently aluminum is the largest ion which can be accommodated in it, as shown by Hill, Roy and Osborn⁽¹⁶⁾ in studies of the ternary

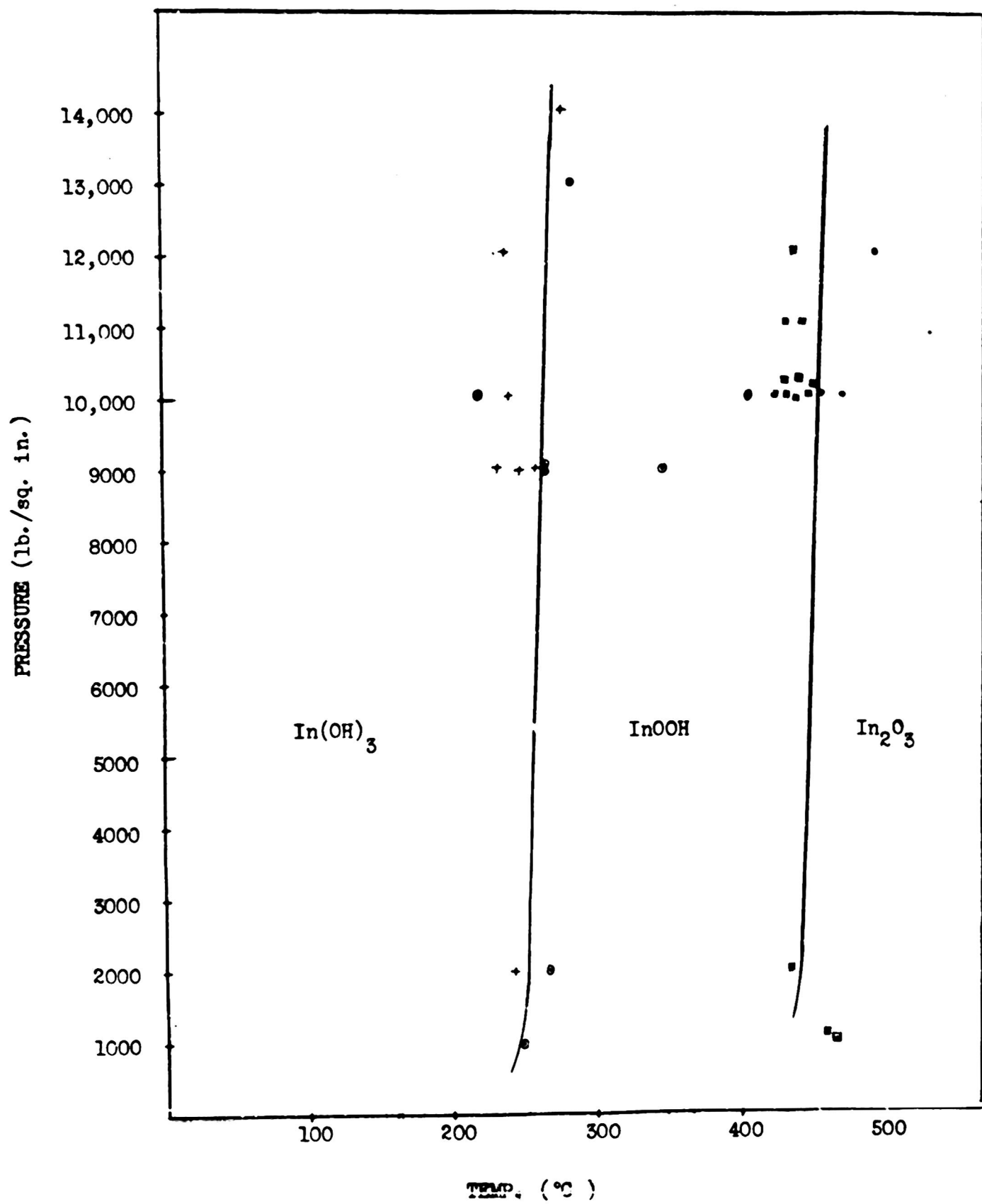


Fig. 7

system $\text{Al}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-H}_2\text{O}$. Diaspore appears able to accommodate ions from Al^{3+} through Ga^{3+} to Sc^{3+} (vide infra), but apparently will not accommodate one just larger than Sc^{3+} . It is more surprising, however, that neither the $\text{Y}_2\text{O}_3\cdot\text{H}_2\text{O}$ structure nor the $\text{La}_2\text{O}_3\cdot\text{H}_2\text{O}$ structure is assumed by $\text{In}_2\text{O}_3\cdot\text{H}_2\text{O}$. The difference of polarizability between the noble gas cations Y^{3+} and La^{3+} on the one hand and In^{3+} on the other probably accounts for this and should be reflected in the tendency to hydrogen bond formation.

In the system $\text{Sc}_2\text{O}_3\text{-H}_2\text{O}^*$ we have not been able to duplicate any of the earlier work. Thus, Fricke and Seitz⁽¹⁷⁾ claimed to have obtained a compound $\text{Sc}(\text{OH})_3$ at 160°C in a silver crucible from a 12 N NaOH solution in an autoclave. Working under essentially the same conditions we have obtained no evidence for the formation of this compound. In distilled water we are unable to obtain any crystalline phase whatsoever below approximately 250°C . Above this temperature we obtain a structure which corresponds apparently to a greatly enlarged diaspore structure. This appears to break down at about 375° (at 10,000 psi) to yield the oxide, Sc_2O_3 .

One of the difficulties in working with substances such as BaTiO_3 and its homologues is that the precise identification of phases is quite difficult. The petrographic microscope is virtually "neutralized" because of the very high refractive indices; and very often (as has already been noted in the case of NaNbO_3 ⁽⁵⁾) X-ray powder diffraction patterns may not yield sufficiently precise data. The infrared spectra of two other compounds, sillimanite ($\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) and mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$), have been reported in the literature⁽¹⁸⁾ and

*Spectroscopic analysis (kindly performed by H. L. Lovell) of the Sc_2O_3 (claimed by the manufacturer to be 99.9% Sc_2O_3) showed:

Ce, Y, Al	-	absent
La	-	doubtful, not exceeding 0.1%
Cr	-	.000x%
Si	-	.000x%
Mg	-	.000x%

appear quite different. However, these two phases have very similar X-ray diffraction characteristics. It was hoped, therefore, that perhaps infrared spectra may provide a rapid method for the identification of phases differing very slightly from each other. A more thorough investigation of the distinction between mullite and sillimanite was carried out, using three different samples of sillimanite from well known localities, and three samples of mullite (one consisting of electrically fused single crystals, another formed by heating kaolinite to 1400°C, and the last prepared hydrothermally). Both the method of mulling a fine dispersion in Nujol and of sedimenting and evaporating a fine fraction from an alcohol suspension (see Lamer⁽¹⁹⁾) were used. A note is being prepared for publication describing these results more fully. The patterns were distinct and reproducible, demonstrating the possible usefulness of the method in similar cases.

Spectra were therefore obtained for various preparations of BaTiO_3 (both hexagonal and tetragonal). They were similar to those shown by Sutherland (op. cit.) for "typical BaTiO_3 ", except for the fact that no carbonate impurity could be detected in these samples. No pronounced absorption bands are visible except for those near the 15 μ region. It was hoped that NaNbO_3 would prove to be sufficiently different to yield a characteristic spectrum in this region and permit identification of solid solution members of intermediate composition. This was not found to be the case. Further work on similar compounds is contemplated, our aim only being to search for a crude qualitative distinction.

We were privileged to have Dr. A. F. Moodie of the Council for Scientific and Industrial Research, Melbourne, Australia associated with the laboratories of the School for a few weeks. He introduced us to the techniques and possibilities of single crystal electron diffraction studies. Very marked success was obtained with natural and synthetic clay minerals, illustrating the abundance of, and relative ease with which, single crystal data may be obtained for such

structures. In attempting to apply the technique to compounds of interest to this project we were not so fortunate since the GaAlO_3 and the tetragonal BaTiO_3 did not yield any satisfactory patterns, and, indeed, behaved peculiarly in the beam. The GaAlO_3 appears to interact with the beam and "disintegrate". It has been suggested by de Bretteville (cited by Sutherland, 13) that the possibility exists of a strong absorption in the infrared spectrum of BaTiO_3 which would enable it to absorb enough energy to convert to the cubic modification. A somewhat similar case has been established⁽²⁰⁾ for the perovskite CsAuCl_3 under the electron beam. Large particles show single crystal patterns of tetragonal symmetry, whereas the finest particles apparently absorb enough energy from the beam to yield powder patterns which are cubic. The effect is apparently not attributable to heating. We had hoped to investigate the same phenomenon in BaTiO_3 .

II. CONCLUSIONS

A continuation of the determination of phase equilibria in the systems BaO-TiO_2 , $\text{CaO-TiO}_2\text{-SiO}_2$, $\text{BaTiO}_3\text{-NaNbO}_3$ is reported. Hydrothermal investigation of phases and relations in the systems $\text{In}_2\text{O}_3\text{-H}_2\text{O}$ and $\text{Sc}_2\text{O}_3\text{-H}_2\text{O}$ as well as $\text{ErO-TiO}_2\text{-H}_2\text{O}$ has been continued, the latter giving an indication of the conditions necessary for hydrothermal synthesis of BaTiO_3 . Recent investigations with infrared absorption spectra and single crystal electron diffraction are recorded.

III. PROGRAM FOR THE NEXT QUARTER

It is hoped to have several of the investigations reported on here in manuscript form during the next three months. The determination of equilibrium diagrams will concern those systems which involve BaTiO_3 as one endmember. Work on the hydrothermal stability of the micas which has

been done extensively on another project in the low temperature region will be attempted at higher temperatures where the equipment problem is much greater. The possible application of infrared and single crystal electron diffraction techniques will be explored further.

IV. IDENTIFICATION OF TECHNICIANS

No changes in personnel were made during this quarter.

V. REFERENCES CITED

1. F. M. Jaeger, Precise Measurements at High Temperatures, Cornell University Press, Ithaca, N.Y. (1937)
2. M. L. Keith and O. F. Tuttle, Am. J. Sci., Bowen Volume, 203-280 (1952)
3. H. Blattner, B. Matthias and W. Merz, Helv. Phys. Acta, 22, 225-228 (1947)
4. E. N. Bunting, N.B.S. Jour. Res., 11, 723 (1933)
5. P. Ehrlich, Z. Elektrochem., 45, 362 (1939)
6. Y. M. Agamawi and J. White, Trans. Brit. Cer. Soc., 51, 293-325 (1952)
7. A. A. Rusakov and G. S. Zhdanov, Dokl. Akad. Nauk. SSSR., 77, 411-414 (1951)
8. O. Kubaschewski and E. N. Evans, Metallurgical Thermo Chemistry, Butterworth-Springer Ltd., London (1951)
9. R. Fricke, Sprechsaal, 41, 406 (1908)
10. S. Umezaki and F. Kakiuchi, Japanese Mining Journal, 46, 867-876 (1930)
11. D. Bogatskii, Metallurg., 1, 59-67 (1936)
12. R. W. Ricker and F. A. Hummel, J. Am. Cer. Soc., 34, 271-279 (1951)
13. G. B. B. M. Sutherland, Infrared Studies of Crystals, Signal Corps. Contract DA-039 sc-5581, August 1952
14. E. A. Wood, Acta Cryst., 4, 353 (1951)
15. H. D. Megaw, Acta Cryst. 5, 739 (1952)
16. V. G. Hill, R. Roy, and E. F. Osborn, J. Am. Cer. Soc., 35, 135 (1952)
17. R. Fricke and A. Seitz, Zeit. anorg. Chem., 255, 13-15 (1947)

18. American Petroleum Institute, Project 49, Report
No. 8 (1950) Section I by H. H. Adler
19. P. J. Launer, Am. Min., 37, 764-784 (1952)
20. A. F. Moodie, personal communication