

AFOSR-TN-57-391
ASTIA Document No. AD 132 466

ENGINEERING RESEARCH INSTITUTE
THE UNIVERSITY OF MICHIGAN
ANN ARBOR

ADDITIONS OF Fe_2O_3 TO BaTiO_3 - SrTiO_3
FERROELECTRICS

Technical Report No. 3
Solid State Devices Laboratory
Department of Electrical Engineering

H. Diamond
V. Chang

Project 2495

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
AIR RESEARCH AND DEVELOPMENT COMMAND
SOLID STATE SCIENCE DIVISION
CONTRACT NO. AF 18(603)-8, DIVISION FILE NO. 40-24

December 1957

ENSM

UNIR1224

LIST OF ILLUSTRATIONS

Fig. No.		Page
1	Dielectric constant at 1000 cps versus temperature for small additions of Fe_2O_3 to BaTiO_3 ceramics.	5
2	Shift and splitting of the Curie temperature with increasing additions of Fe_2O_3 to a BaTiO_3 - SrTiO_3 ceramic.	6
3	Ternary diagram with respect to the solubility of Fe_2O_3 in BaTiO_3 - SrTiO_3 .	7
4	Sintering Fe_2O_3 with BaO and TiO_2 in varying stoichiometric proportions.	8

ABSTRACT

If small percentages of Fe_2O_3 are added to polycrystalline BaTiO_3 and fired at 1400° as a ceramic, the Curie Temperature of the ceramic remains constant while the peak permittivity is lowered. However, if the Fe_2O_3 is added to BaO and TiO_2 , the iron goes into the lattice predominately in the titania sites and decreases the Curie Temperature as well as the peak permittivity.

Additions of Fe_2O_3 to mixed BaTiO_3 - SrTiO_3 compositions result both in a lowering of the Curie Temperature and a depression of the peak permittivity of the single phase system. No changes in lattice dimensions with the additions were observed when the Ba to Sr ratio was held fixed.

ADDITIONS OF Fe_2O_3 TO BaTiO_3 - SrTiO_3 FERROELECTRICS

Several investigators,^{1,2} working with ferroelectric single crystals, have observed that BaTiO_3 single crystals containing small percentages of Fe_2O_3 have lowered Curie temperatures. However, experiments in our laboratory on polycrystalline ceramic ferroelectric compositions, both of the pure BaTiO_3 type and the $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ compositions, have yielded some rather interesting results with respect to the addition of Fe_2O_3 . Sintering the pure BaTiO_3 with the Fe_2O_3 additives did not, as is the case for the single crystals, have any affect in shifting the cubic to tetragonal ferroelectric transition to lower temperatures. What is observed is a gradual suppression of the peak permittivity of the material as more and more of the Fe_2O_3 was added to the BaTiO_3 . This was found to hold when as little as .2 mol percent or as much as 6 mol percent of the Fe_2O_3 was added, and under the rather severe firing schedule of 1400°C for two hours. Figure 1 shows this behavior where the incremental permittivity for BaTiO_3 compositions containing varying quantities of the Fe_2O_3 additive are plotted against temperature. It is clear that the Curie peak remains at about the same temperature regardless of the amount of Fe_2O_3 present.

On the other hand, when a "sufficient" amount of strontium ion is present in a composition of the form $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ and the composition is sintered with small quantities of the Fe_2O_3 additive, the effect of the iron ion in shifting the Curie temperature is much more marked than the same effect due to the strontium. It was found, however, that for a given amount of strontium present, only a certain maximum amount of iron could enter the lattice before a separate phase makes its appearance. This is seen in the dielectric data of

Figure 2 for a typical composition of $\text{Ba}_{.91}\text{Sr}_{.09}\text{TiO}_3$ fired with increasing amounts of the Fe_2O_3 . The barium to strontium ratio is held constant so that the effect of the lowering of the Curie temperature is due to the iron entering the perovskite lattice. It is observed that the Curie temperature is gradually lowered and the peak permittivity is suppressed as more and more of the iron enters into the lattice. A point is then reached where the downward shift in Curie temperature stops and apparently a new phase appears as is evidenced by the occurrence of a new peak in permittivity at around 125°C --- the Curie temperature of the pure BaTiO_3 . This effect is first noticed for .5 mol percent of Fe_2O_3 additive in the composition described above.

Dielectric measurement techniques were used to determine the ferroelectric cubic to tetragonal crystallographic transition that is indicated by the Curie peaks in the perovskite type ferroelectrics. The smooth shifting of the Curie temperature upon variation of the percentages of one iron or another in the ternary indicates a homogeneous ferroelectric composition. On the other hand, as is corroborated by x-ray data, if a second Curie peak suddenly makes its appearance it can be said that the composition is no longer homogeneous but that it contains a separate ferroelectric phase. It has been therefore possible to construct a phase boundary line in a ternary diagram of BaTiO_3 - SrTiO_3 - Fe_2O_3 , as seen in Figure 3, for small percentage-wise additions of the Fe_2O_3 . Compositions in the narrow region to the left of the phase boundary form a solid solution and the compositions indicated to the right of this line all show the additional characteristic small peak at about 125°C . Along the boundary, the ratio of mol percent of SrTiO_3 to Fe_2O_3 is about eight to one.

X-ray powder photographs were made with a series of compositions of constant barium - to - strontium ratios in order to study the influence of the

iron on the perovskite lattice. It was found that the mean lattice constant did not change within the limits of $\pm .01 \text{ \AA}$ over a range of Fe_2O_3 content of from zero to ten mol percent, even though over this same range the Curie temperature shifted from approximately room temperature down to -70°C . This, plus the fact that the atomic radius of iron is very close to that of titanium, leads one to believe that the iron enters the titanium sites in the lattice. That is, the lattice dimensions are more or less set by the comparatively large barium and strontium ions, whereas the Curie temperature is changed by the modification of the binding forces upon the addition of the iron. The favoring of the titanium site for the iron additive was also shown by the following. Instead of sintering the Fe_2O_3 with a pre-reacted BaTiO_3 , BaO and TiO_2 in varying stoichiometric proportions were reacted with Fe_2O_3 . Of these compositions, one was stoichiometrically balanced, the second was deficient in the TiO_2 , and the third deficient in the BaO . The amount of added Fe_2O_3 for all the samples was the same and amounted to 2 mol percent. Figure 4 shows that for these compositions, the iron goes into solution and that the Curie point is shifted to lower temperatures. There is no evidence of a separate BaTiO_3 phase as would be observed by the occurrence of a peak at 125°C . The lowest Curie temperature is found for the sample deficient in TiO_2 and the highest (except for the case of the pure BaTiO_3 , used as a control sample) for the sample with the excess of TiO_2 . From this it is evident that the iron favors the titanium sites, although results of paramagnetic resonance experiments³ have indicated a divalent form for iron in BaTiO_3 .

We wish to express our appreciation to Professor Lars Thomassen for his helpful discussions and valuable suggestions.

REFERENCES

1. J. P. Remeika, J.A.C.S. 76, 940-941 (1954).
2. A. Nishioka, K. Sekikawa, N. Owaki, J. Phys. Soc. Japan 11, 180-191 (1956).
3. A. W. Hornig, E. T. Jaynes, H. E. Weaver, Phys. Rev. 96, 1703 (1954).

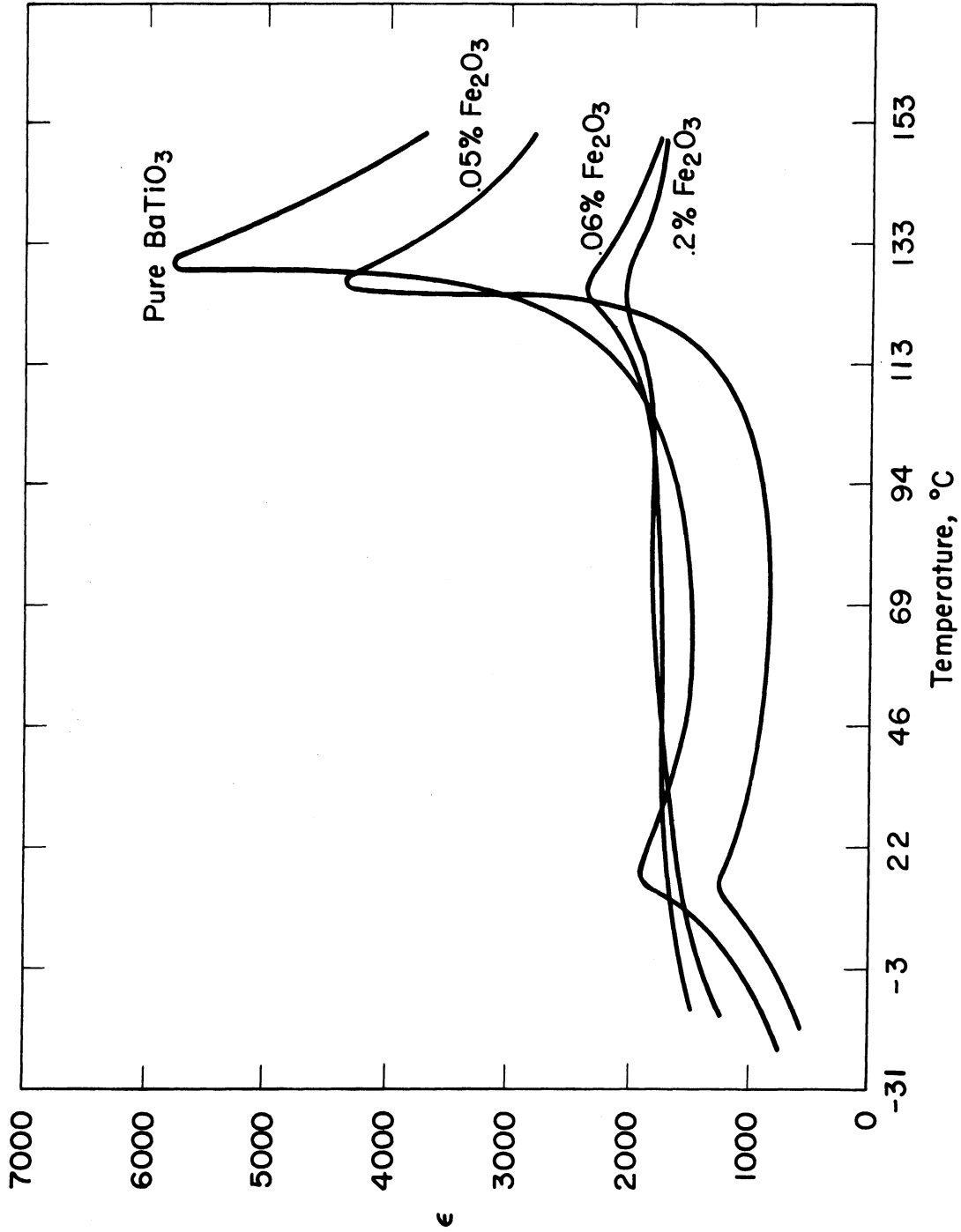


Fig. 1. Dielectric constant at 1000 cps versus temperature for small additions of Fe₂O₃ to BaTiO₃ ceramics.

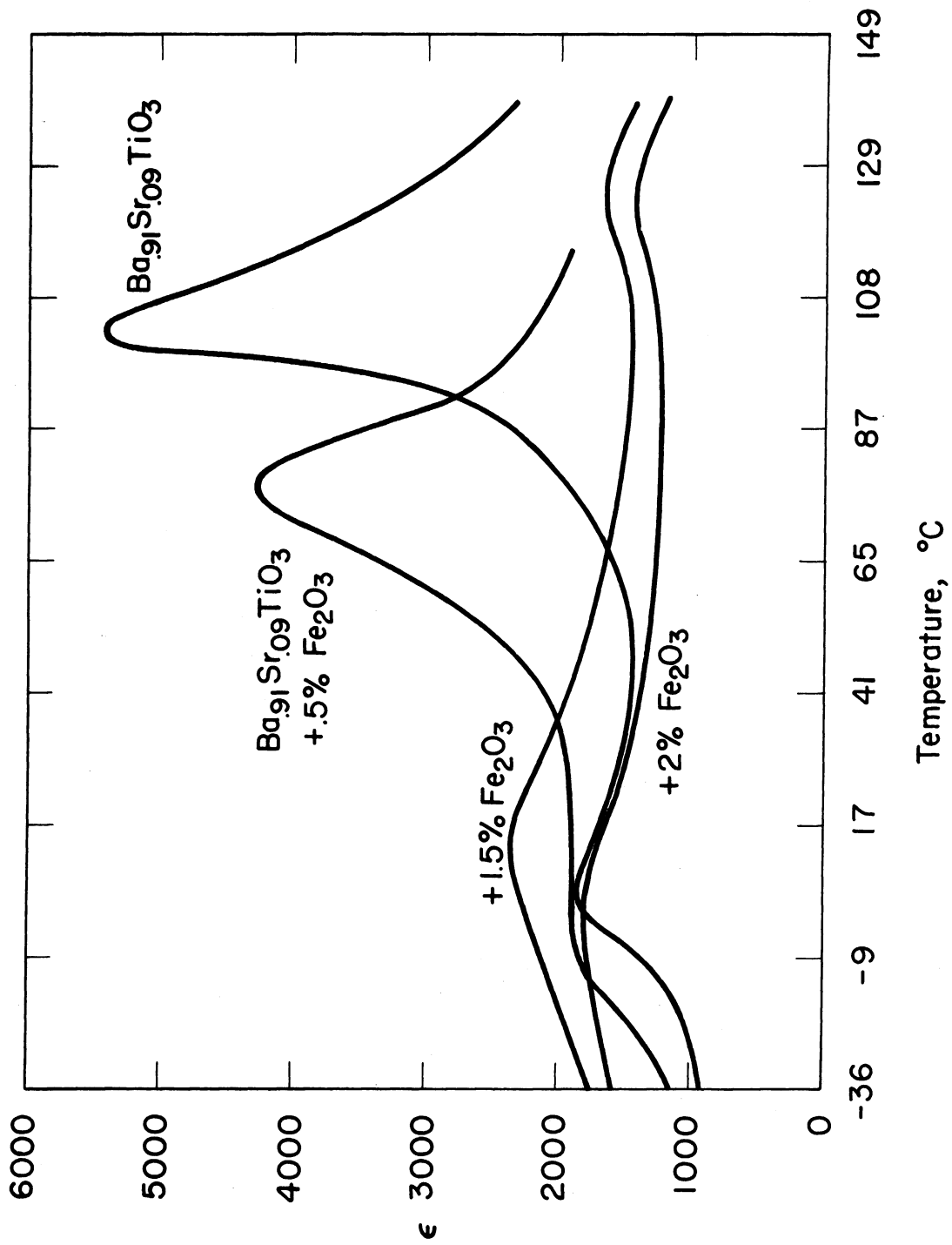


Fig. 2. Shift and splitting of the Curie temperature with increasing additions of Fe_2O_3 to a $BaTiO_3$ - $SrTiO_3$ ceramic.

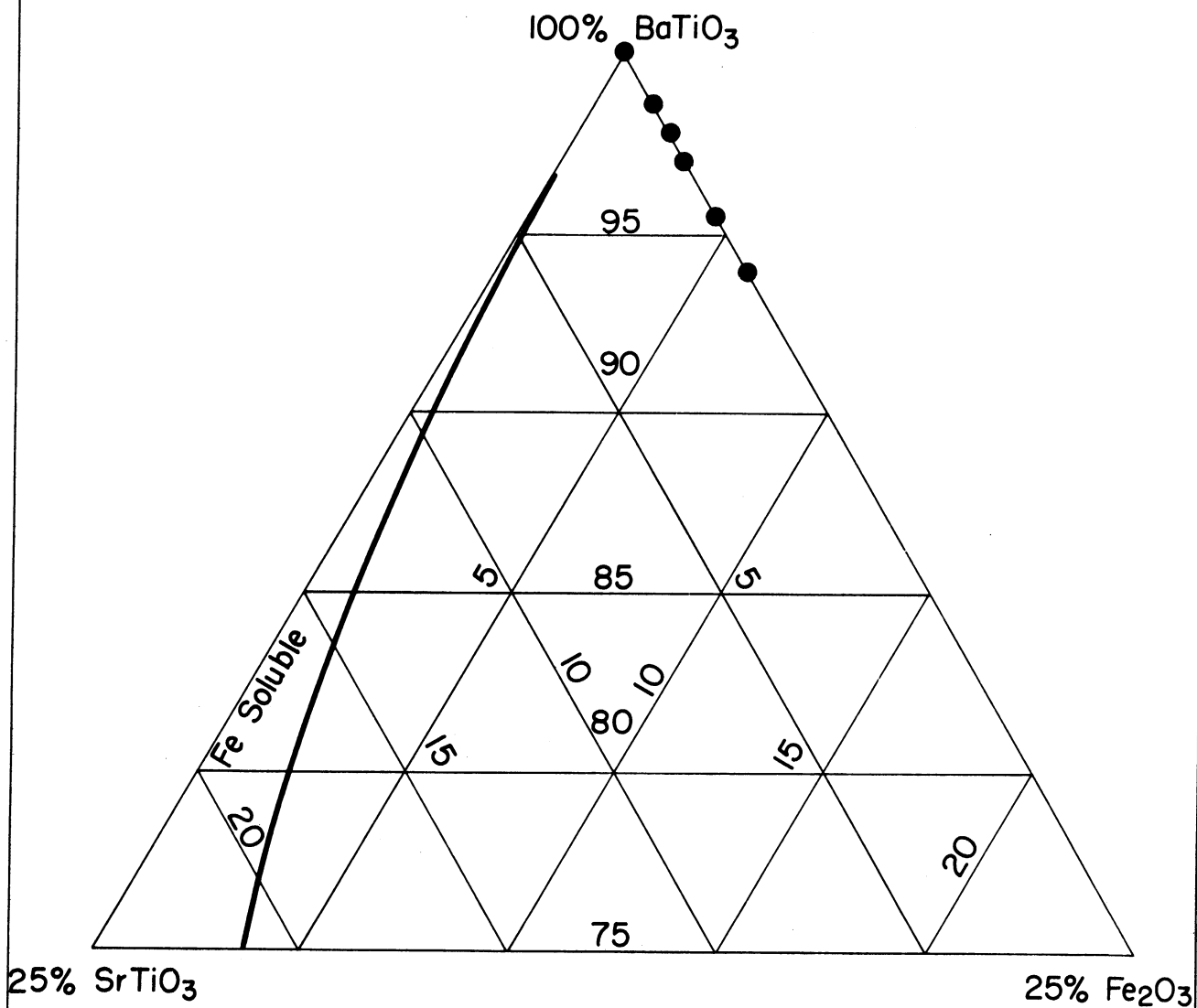


Fig. 3. Ternary diagram with respect to the solubility of Fe₂O₃ in BaTiO₃ - SrTiO₃.

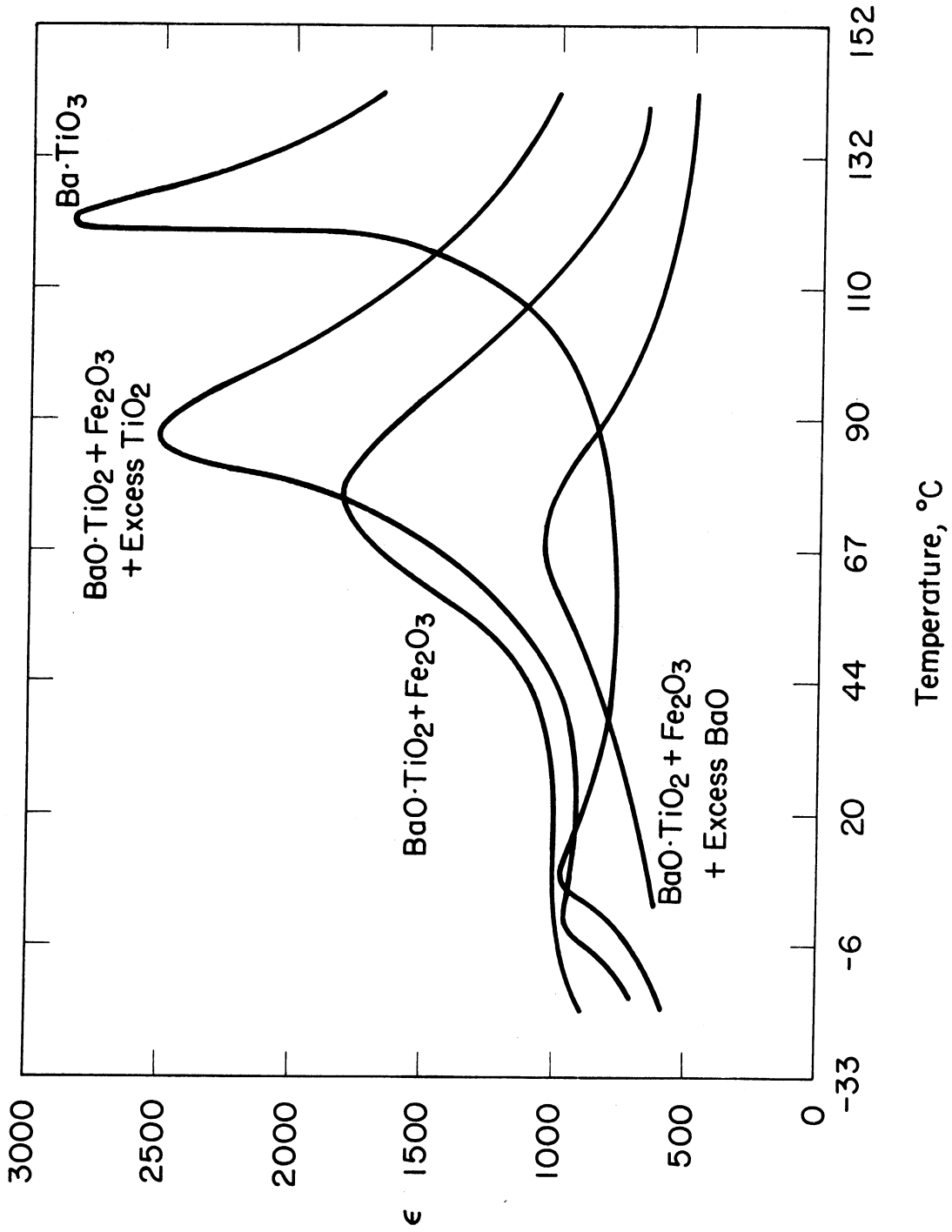


Fig. 4. Sintering Fe₂O₃ with BaO and TiO₂ in varying stoichiometric proportions.

The University of Michigan • Engineering Research Institute

DISTRIBUTION LIST

<u>Agency</u>	<u>No. of Copies</u>	<u>Agency</u>	<u>No. of Copies</u>
Commander Hq., AF Office of Scientific Research, ARDC Attn: SRQB Washington 25, D. C.	5	Director of Research and Development Hq., U. S. Air Force Attn: AFDRD-RE-3 Washington 25, D. C.	1
Commander Wright Air Development Center Attn: WCRRH Attn: WCRRL Attn: WCRTL Attn: WCRTM-1 Wright-Patterson Air Force Base, Ohio	4	Department of the Navy Office of Naval Research Attn: Code 423 Attn: Code 421 Washington 25, D. C.	2
Commander Air Force Cambridge Research Center Attn: Technical Library Attn: CRRF L. G. Hanscom Field Bedford, Massachusetts	2	Office-in-Charge Office of Naval Research Navy No. 100 Fleet Post Office New York, New York	1
Commander Rome Air Development Center Attn: Technical Library Griffiss Air Force Base Rome, New York	1	Commanding Officer Naval Radiological Defense Laboratory San Francisco Naval Shipyard San Francisco 24, California	1
Director, Office for Advanced Studies Air Force Office of Scientific Research P. O. Box 2035 Pasadena 2, California	1	Director, Research and Develop- ment Division, General Staff Department of the Army Washington 25, D. C.	1
Document Service Center Armed Services Technical Information Agency Knott Building Dayton 2, Ohio	10	Division of Research U. S. Atomic Energy Commission 1901 Constitution Avenue, N. W. Washington 25, D. C.	1
		U. S. Atomic Energy Commission Library Branch Technical Information Division, ORE P. O. Box E Oak Ridge, Tennessee	1

The University of Michigan • Engineering Research Institute

DISTRIBUTION LIST (concluded)

<u>Agency</u>	<u>No. of Copies</u>	<u>Agency</u>	<u>No. of Copies</u>
Oak Ridge National Laboratory Attn: Central Files P. O. Box P Oak Ridge, Tennessee	1	Commander Western Development Division (ARDC) Attn: WDSIT, P. O. Box 262 Inglewood, California	1
Brookhaven National Laboratory Attn: Research Library Upton, Long Island, New York	1	Document Custodian Los Alamos Scientific Laboratory P. O. Box 1663 Los Alamos, New Mexico	1
Argonne National Laboratory Attn: Librarian P. O. Box 299 Lemont, Illinois	1	Arnold Engineering Development Center, Attn: Tech. Library P. O. Box 162 Tullahoma, Tennessee	1
Ames Laboratory Iowa State College P. O. Box 14A, Station A Ames, Iowa	1	Commanding Officer Ordnance Materials Research Office Watertown Arsenal Watertown 72, Massachusetts	1
Knolls Atomic Power Laboratory Attn: Document Librarian P. O. Box 1072 Schenectady, New York	1	Commanding Officer Watertown Arsenal Watertown 72, Massachusetts Attn: Watertown Arsenal Labs. Tech. Reports Section	1
National Bureau of Standards Library, Room 203 Northwest Building Washington 25, D. C.	1	Commander, Hq., AF Office of Scientific Research, ARDC Attn: SREC, Tech. Library Washington 25, D. C.	2
National Science Foundation 1520 H. Street, N.W. Washington 25, D. C.	1	Commander, WADC Air Technical Intelligence Center Attn: Deputy for Documentation WPAFB, Ohio	1
Director, Office of Ordnance Research, Box CM, Duke Station Durham, North Carolina	1	(Inner envelope--no postage) Commander, European Office c/o American Embassy, ARDC Brussels, Belgium	1
Office of Technical Services Department of Commerce Washington 25, D. C.	1	(Outer envelope--postage) Superintendent, Diplomatic Pouch Rooms, Department of State Washington 25, D. C.	1
NACA 1512 H. Street, N.W. Washington 25, D. C.	1		

UNIVERSITY OF MICHIGAN



3 9015 02828 4019