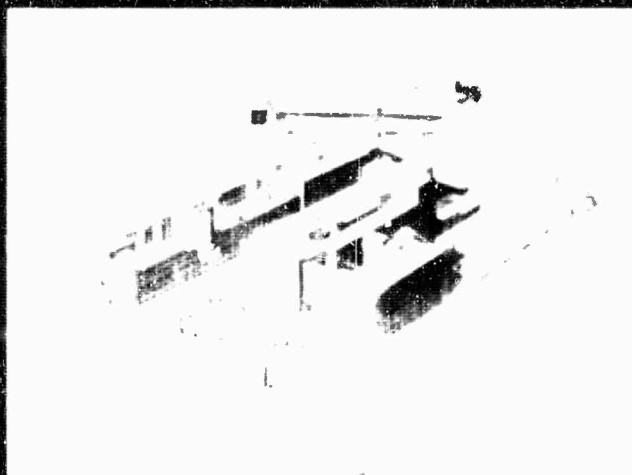


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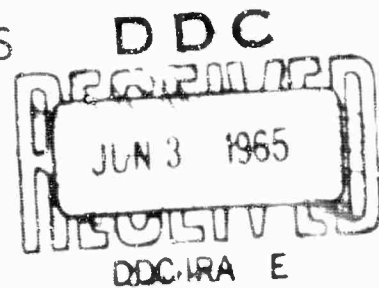
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STUDY OF NON-OXIDE MATERIALS

with

DEFECT STRUCTURES

ANNUAL REPORT 31 DECEMBER 1964



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STUDY OF NON-OXIDE MATERIALS WITH DEFECT STRUCTURES

Contract No. NONr 3632(00)
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ANNUAL REPORT FOR THE PERIOD ENDING 31 DECEMBER 1964

Prepared by:

D. A. Buckner and P. C. Velasquez

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FORWARD AND ACKNOWLEDGMENT

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The suggestions of our consultant, Dr. Rustum Roy, Director of Materials Research at The Pennsylvania State University, have been incorporated into this work. We acknowledge the many generous contributions made by the Pennsylvania State group in the Department of Geophysics-Geochemistry headed by Dr. Rustum Roy and Dr. Della Roy.

I. INTRODUCTION

Statement of Work:

To evaluate known and prepare new fluorides expected to possess controllable gross defects and determine their properties, especially as a function of the amount and nature of the defect; and to perform an intensive study of the mechanical, optical and electrical properties of polycrystalline aggregates formed under high pressure and temperature conditions.

The fundamental character of the study was designed to explore non-oxide materials which were expected to have controllable gross defects. The exploration was to delineate several types of defects in uncommonly considered materials and to demonstrate the feasibility of controlling some physical properties by a chemical control over defects.

Gross lattice defects were conveniently defined as those existing in concentrations of several percent, in contrast to the more familiar consideration of lattice defects in the parts per million range. The following list summarizes the types of defects expected:

<u>Type</u>	<u>Example</u>
A. Substitutional	$\text{MgF}_2-(\text{NiF}_2)$
1. Equivalent valence; cations proxy on a 1:1 ratio	
2. Half-Breed structures; two cations of host structure (e.g. CaF_2) replaced by one cation of higher electrical charge and one of lower electrical charge.	$\text{CaF}_2-(\text{NaYF}_4)$
B. Interstitial; Electrical neutrality maintained by filling lattice interstices with ionic species to compensate for valence variations at neighboring lattice sites.	$\text{CaF}_2-(\text{YF}_3)$
C. Vacancy	
1. Anion vacancies; anions omitted in host structure to compensate for lower cation charges.	$\text{LaF}_3-(\text{SrF}_2)$
2. Cation vacancies; higher charged cation (e.g. Sc^{3+}) proxies for lower valence cation with electrical neutrality maintained by omission of cation in a different site.	$\text{KMgF}_3-(\text{ScF}_3)$

Since similar gross defects are known to occur in large molar concentrations, it was expected that a systematic study could demonstrate the proposed method of property control in the design of materials.

Several factors influenced the selection of fluoride systems for this study. With fluorides, the well-known oxide structures can be easily imitated at lower temperatures. Furthermore, they comprise a class of compounds possessing valuable infrared transmitting properties. Finally, since considerably less work has been done on fluorides than oxides, worthwhile contributions to the field were anticipated.

Property measurements were to be made using specimens of hot-pressed compositions. These would be polycrystalline aggregates of the materials having intrinsic physical properties very similar to those of single crystals.

The study program was generally divided into three categories:

1. A survey of systems likely to demonstrate the various defect types.
2. The selection of representative systems and the detailed characterization of the defect structures.
3. Preparation of specimens suitable for physical property measurements to compare the effects of defect type and amount.

The first two annual reports have illustrated from the broad survey aspect that the principles are sound and that all expected defects do exist to a substantial degree. In addition to illustrating the applicability of the broad principles, previous reports have presented data which substantiate the nature of the defect structures and help to characterize them, as intended under category (2). The present report amplifies the characterization of the defects found in several of the interesting systems. In addition the principal work of the past year emphasizing the third phase, i.e., acquiring physical property data, is reported.

II. SUMMARY

During the report period three systems were examined which provided data to illustrate three principal types of defects under consideration.

Compositions of $3 \text{ NaF} \cdot 5 \text{ YF}_3 - \text{CaF}_2$, with up to 40 mole % CaF_2 , displayed a "Half-Breed" type of structure containing, as well, interstitial anion defects. In the case of the "pure" half-breed derivative of CaF_2 , $\text{NaF} \cdot \text{YF}_3$, 2 Ca^{2+} ions have been replaced by one monovalent Na^+ ion plus one trivalent Y^{3+} ion. In the present study, replacement of 8 Ca^{2+} ions by 3 Na^+ ions plus 5 Y^{3+} ions resulted in the interstitial anion-containing half-breed, $3 \text{ NaF} \cdot 5 \text{ YF}_3$. In the crystalline solutions prepared, as Ca^{2+}

ions were incorporated "back" into the cubic lattice; i.e., as the $\text{Ca}^{2+}/\text{Na}^+\cdot\text{Y}^{3+}$ ratio increased, the crystal unit cell, the density, and the refractive index, were observed to decrease.

Compositions of up to 30% of YF_3 in solid solution with CaF_2 demonstrated the interstitial anion defect type. For each divalent Ca^{2+} ion replaced by a trivalent Y^{3+} ion electroneutrality was maintained by the incorporation of one F^- ion into an interstitial crystal lattice site. In the experiments performed, increases in the unit cell size and refractive index were observed as YF_3 increased.

Anion vacancies were produced in the solid solution of SrF_2 in the tysonite structure of LaF_3 . As the divalent Sr^{2+} ion replaced La^{3+} , in concentrations of 10% - 15%, electroneutrality was shown to be maintained by the omission of F^- ions. The increase of Sr^{2+} in LaF_3 caused a marked decrease in both density and refractive index of the material.

Large batches of some of the above compositions were prepared and hot-pressed specimens were made in order to obtain some physical property measurements. Most of this work is in progress and will be reported in the final summary report.

III. EXPERIMENTAL

A. Preparation of materials

The general method adopted for preparation of the materials involved the following four steps: (1) co-precipitation of the mixtures for maximum homogeneity; (2) calcination under a partial $\text{NH}_3\cdot\text{HF}$ atmosphere to remove moisture with minimum hydrolysis; (3) sintering or melting at elevated temperatures under a N_2 atmosphere to effect complete solid solution formation; (4) milling to the desired fineness.

The co-precipitation was effected in polyethylene containers. Stoichiometric quantities of the desired metal nitrates, in aqueous solution, were reacted with a 48% hydrofluoric acid solution. The resulting mixture was evaporated to dryness in polypropylene or Teflon containers on a steamplate. After drying, the batch was covered once with 48% HF solution and once with a solution of 5% NH_4F , and evaporated to dryness both times. The batch was then crushed with a heavy Teflon rod, sieved through a 40-mesh stainless steel screen, and calcined at 500°C for 1-1/2 hrs. in platinum containers. Residual H_2O and NH_4F fume off during this operation; the $\text{NH}_3\cdot\text{HF}$ atmosphere permeates the furnace chamber and suppresses possible hydrolysis.

After calcining, the batch was allowed to cool to room temperature in a desiccator; then sieved through an 100-mesh screen in preparation for firing. The firing was effected in an iridium (or platinum) pot in a glass melting furnace. The firing schedule involved placing the material in the furnace at room temperature, adjusting the atmosphere, heating to a given temperature and holding for one hour. Air or water quenching of the fired batch suppressed exsolution of components.

Final processing involved washing and drying the batch, crushing the mass, and milling in a high purity alumina ball mill to -60 mesh. The hardness of the prepared fluorides made it imperative that the milling be kept to a minimum to reduce alumina contamination.

B. Hot-Pressing

In order to obtain fully dense polycrystalline compacts for evaluation, the sample powders were hot-pressed. A charge of powder was compacted into a mold which could be evacuated while hot. When thermal equilibrium was established and gases evacuated, pressure was applied through a hydraulic ram. Optimum pressure-temperature conditions varied according to the material under study. First experiments were made using 650°C at 30,000 psi with a dwell time under pressure of 20 minutes. Examination of the results led to adjustments in P-T parameters.

Attainment of the best results was, in practice, dependent on the amount of material available for experimentation. Often the hot-pressed pieces cracked even when slow cooled in the mold. No attempts at annealing were made.

The span of temperatures and pressures generally used was 650°C, using 30,000 to 68,000 psi. In addition, a few hot-pressings were attempted between 900 and 1100°C at 6,000 psi in a system which had no provision for evacuation during pressing.

C. Evaluation of Materials

The optical polarizing microscope was used extensively to examine materials for homogeneity plus any observable optical characteristics. Usually it was possible to determine whether the individual grains, as well as the compacts, were isotropic. Refractive indices were measured using oil immersion techniques. Significant change of refractive index of materials reacted to homogeneity was one of the criteria used to demonstrate crystalline solubility and hence defect concentrations where components were not of similar formal formula.

Powder x-ray diffraction techniques were relied upon to confirm homogeneity and obtain phase data and crystal structure. Changes in lattice parameters plus the lack of x-ray detection of expected second phases confirmed the occurrence of prepared defect materials.

The x-ray equipment used was a Tem-Press XD Model No. 1. Copper target radiation was used exclusively. Geiger tube detection was read out on a strip chart recorder. Variable goniometer drive speed and ability to record high angle back reflections enabled quite sensitive measurement of lattice parameter changes.

Comparison of pycnometric densities and densities calculated using parameters obtained from x-ray data formed the *prima facie* line of evidence used in categorizing the defect materials into the major groupings of net vacancies or net interstitials.

IV. RESULTS

Extensive study of crucible size (15-25 gm) batches of proposed defect systems established both feasibility and the conditions for preparing pound-lot quantities of the solid solutions. Pound-lots were necessary to achieve successfully hot-pressed specimens upon which to perform the proposed measurements. Scale-up proved to be no routine matter. With available equipment, NaF-YF₃-CaF₂ and CaF₂-YF₃ compositions could be prepared relatively simply, those of the system LaF₃-SrF₂ with a little more difficulty, and those of the systems NiF₂-MgF₂ and KMgF₃-NiF₂, not at all. The systems receiving most of the attention were NaF-YF₃-CaF₂, CaF₂-YF₃, and LaF₃-SrF₂.

A. The System NaF-YF₃-CaF₂

As stated in previous reports, efforts with this system were concentrated on a solid solution of the composition 3NaF·5YF₃; altering its structure through the purposeful substitution of CaF₂ into the lattice. Assuming the undistorted fully disordered cubic fluorite structure to obtain, the 3NaF·5YF₃ solid solution contains interstitial F⁻ ion defects at an average of one per unit cell. This postulation was verified by comparing the measured with the calculated density. Incorporation of the Ca²⁺ ion in increasing amount should result in a proportional dilution of the interstitial F⁻ ion stuffing.

At 20 mole % CaF₂, the average interstitial F⁻ ion defect content of the crystal should be 0.8 F⁻ ions per unit cell, as Ca²⁺ ion assumes the Na⁺ and Y³⁺ ion positions. Related observed changes included contraction of the unit cell, decrease in density, and lowering of the refractive index.

Batches containing approximately 3 lbs. of the compositions 90 mole % (3NaF·5YF₃) -10 mole % CaF₂, and 80 mole % (3NaF·5YF₃) -20 mole % CaF₂, were prepared as described. All were melted at 1250°C, quenched in air, and the mass crushed and milled to -60 mesh. Subsequent spectroscopic analysis revealed slight alumina contamination.

X-ray diffraction and microscopic analysis of the powders, prior to reaction at 1250°C, indicated considerable, though incomplete, solid solution formation at the calcining temperature.

X-ray diffraction analysis of the reacted powders at slow scanning speeds verified the fluorite cubic structure with no superstructure. Repeated measurements of the d-spacing between {111} planes indicated the expected lattice contraction. The changes were small, varying from $d_{\{111\}} = 3.176$ for the solid solution containing 20 mole % CaF_2 to $d_{\{111\}} = 3.183$ for the non- CaF_2 containing solid solution. Measurement of the same d-spacing of a 60 mole % $(3\text{NaF} \cdot 5\text{YF}_3)$ -40 mole % CaF_2 sample verified the continuity of the trend, $d_{\{111\}}$ being 3.163 (see Appendix, Table I).

Microscopic analysis revealed the solid solutions to be composed of very homogeneous, well-formed grains. Some contamination was apparent, but the majority of this could be attributed to Al_2O_3 contamination from the ball mill. The observed changes in refractive index were from 1.475 to 1.444 (see Appendix, Table I).

When hot-pressed, excellent 1"-diameter compacts, well-accreted and translucent, were obtained at 650°C and 68,000 psi. A noticeable cloudy effect within the polycrystalline aggregates was believed to be due to the Al_2O_3 contamination. Cracking of the compacts was somewhat alleviated by allowing the samples to cool to room temperature within the die before removal.

Displacement methods were used to determine the density of the polycrystalline compacts. The results corresponded closely to the theoretical values for the interstitial F^- defect structure and are included in the Appendix, Table I.

All of the compositions within this system exhibited coloration upon exposure to ionizing radiation, viz. x-rays. This observation was completely qualitative, but supports the other evidence for the existence of defects.

B. The System CaF_2 - YF_3

In the system CaF_2 - YF_3 the case for interstitial F^- defects is opposite to that of the system $3\text{NaF} \cdot 5\text{YF}_3$ - CaF_2 . In the latter system, the starting $3\text{NaF} \cdot 5\text{YF}_3$ solid solution is inherently defective. Systematic reduction of the interstitial defect concentration was brought about through substitution of Ca^{2+} ions into the Na^+ and Y^{3+} ion positions. In CaF_2 - YF_3 solid solutions, interstitial defects were created when F^- ion was "stuffed" into the lattice to maintain electrical neutrality as the higher valency Y^{3+} ions replaced the Ca^{2+} ions in the lattice. Proportional increases in the unit cell size, density, and refractive index, were expected with increasing YF_3 content.

Batches containing approximately 3 lbs. of the compositions 90 mole % CaF_2 -10 mole % YF_3 and 80 mole % CaF_2 -20 mole % YF_3 were prepared as described. Reaction under N_2 was effected at 1300°C , followed by a water quench. As with the $\text{NaF-YF}_3\text{-CaF}_2$ materials, milling to -60 mesh in an alumina mill introduced slight alumina contamination.

X-ray diffraction and microscopic analysis of the above samples, of CaF_2 , and of a previous crucible-size batch of 70 mole % CaF_2 -30 mole % YF_3 , verified solid solution formation. As expected the refractive index changed progressively from 1.434 (CaF_2) to 1.48 over the series. The unit cell size increased from $a = 5.464 \text{ \AA}$ to $5.523 \text{ \AA}$ (see Appendix, Table I). These solid solutions also exhibited coloration upon x-ray irradiation.

Well-accreted, 1" diameter, polycrystalline compacts were hot-pressed at 650°C and 68,000 psi pressure. Density values of these samples compared favorably with the calculated "ideals" and are presented in the Appendix, Table I.

C. The System $\text{LaF}_3\text{-SrF}_2$

The phase LaF_3 gives its own mineral name, tysonite, to a family of compounds in which the laser industry has shown considerable interest recently. To our knowledge, no one has previously reported large defect concentration in the tysonite structure. In our study of the system $\text{LaF}_3\text{-SrF}_2$, where the hexagonal LaF_3 is the host matrix, it was believed that ion for ion replacement of La^{3+} by Sr^{2+} would result in the creation of an anion vacancy defect system. Although lattice contraction and decreases in density and refractive index with increasing SrF_2 content could be expected, the linearity of such a change could not be predicted due to the differing crystal structure of the end members. For this same reason, complete solid solution formation was not to be expected.

For studies in this system, batches containing approximately 3 lbs. of the compositions 80 mole % LaF_3 -20 mole % SrF_2 and 90 mole % LaF_3 -10 mole % SrF_2 were prepared. Calcination at 500°C yielded complete solid solution formation of the 90 mole % -10 mole % SrF_2 composition and partial solid solution formation of the 80 mole % LaF_3 -20 mole % SrF_2 composition. This is the first confirmation of a grossly defective tysonite phase. High temperature reaction to complete solid solution formation of the latter was not attempted because of its tendency to oxidize to LaOF . Furthermore, it was hoped that the combination of temperature-pressure applied during hot-pressing would dissolve the excess SrF_2 .

Refractive index measurements and x-ray diffraction analysis verified the single phase nature of the 90 mole % LaF_3 -10 mole % SrF_2 solid solution. Undissolved SrF_2 was detected both microscopically and by x-rays in the 20 mole % SrF_2 composition. The mean refractive

index changed from 1.590 to 1.566 for the 20% member and 1.574 for the 10% composition. It should be noted that the lattice parameters hardly change in these concentrated solutions. From the phase and refractive index data the limit of the solid solution can be set at about 15%. No coloration upon x-ray irradiation was observed for either composition.

Hot-pressing at 650°C and 68,000 psi pressure yielded excellent 1"-diameter compacts. In the case of the 10 mole % SrF_2 -containing solid solution these were well-accreted and transparent. General cloudiness of the 20 mole % SrF_2 sample was partially attributed to light scattering by the undissolved SrF_2 phase.

D. The System MgF_2 - NiF_2

Repeated efforts on a crucible size basis to prepare defect solid solutions of MgF_2 - NiF_2 without significant oxidation were not fruitful. A final attempt was made by buying custom elts of two compositions in 5-lb. quantities from a commercial supplier.

By so doing large competent facilities were made available and it was hoped that at least sizeable chunks of homogeneous material could be recovered. The first attempt was fired in vacuum and the whole charge was lost in the vapor phase. A second attempt will be made by firing under dry nitrogen.

V. CONCLUSIONS

Three types of defects have been described and were found to exist in high concentration. These defects were exemplified by:

- a. The system $3\text{NaF} \cdot 5\text{YF}_3$ - CaF_2 (The Half-Breed Defect Type)
- b. The system CaF_2 - YF_3 (The Interstitial Anion Defect Type)
- c. The system LaF_3 - SrF_2 (The Anion Vacancy Defect Type)

The existence and nature of the defects were characterized by documentation of several physical measurements such as density, refractive index, and x-ray determined lattice parameters.

In addition to the preparation of "test-tube" amounts of material, large batches were prepared and experiments in hot-pressing significant-size specimens of selected compositions were conducted. Resulting polycrystalline ingots were used in attempting some of the measurements of physical properties. A previously described system, MgF_2 - NiF_2 , displaying

the substitutional defect, was included in attempting large batch preparation, but no successful preparation was available within the report period.

Many of the preparations are currently being examined for meaningful physical property data. A request for contract extension to 1 April 1965 was made to cover this work in progress. Results of the current investigations will be reported in the final summary report.

A P P E N D I C E S

TABLE I

Summary of Observed Physical Properties

Composition	Lattice Spacing; d_{111}	$a(\text{\AA})$	Density		Refractive Index
			Calculated	Measured	
3NaF·5YF ₃ ss.	3.183	5.514	4.24	4.2	1.475
9(3NaF·5YF ₃) 1 CaF ₂ ss.	3.178	5.504	4.14	4.1	1.465
8(3NaF·5YF ₃) 2 CaF ₂ ss.	3.176	5.502	4.03	4.0	1.465
6(3NaF·5YF ₃) 4 CaF ₂ ss.	3.163	5.479	3.85		1.444

CaF ₂	3.154	5.464	3.18	3.17	1.434
9CaF ₂ 1YF ₃ ss.	3.167	5.485	3.42	3.3 3.40 *	1.45
8CaF ₂ 2YF ₃ ss.	3.183	5.514	3.62	3.6	1.47
7CaF ₂ 3YF ₃ ss.	3.189	5.523	3.88		1.48

LaF ₃			5.93	5.91	1.590
9LaF ₃ 1SrF ₂	(Anion Vacancy) (Interstitial Cation)		5.71 5.91	5.73	1.574
8LaF ₃ 2SrF ₂	(Anion Vacancy) (Interstitial Cation)		5.50 5.89	5.60	1.566

* Hot pressed at 1150°C and 4,000 psi

TABLE II

Reaction Data for the System NaF-YF₃-CaF₂

<u>Sample</u>	<u>Sample History</u>	<u>Reaction Time/Temp.</u>	<u>Remarks</u>
NaF•YF ₃	Crucible size sample. Mech. mixed; quenched in air after reaction under N ₂ in gold tubes and platinum crucibles.	1/2 hr. 700°C	Well sintered. Good grain quality and homogeneity. Strongly birefringent; n=1.47-1.48. Incompletely reacted; mainly hex. NaYF ₄
		1/2 hr. 800°C	Granular. Good grain quality; non-homogeneous. Strongly birefringent. Mixture of hex. and Fluorite cubic phases.
		1/2 hr. 900°C	Sintered-granular. Fair grain quality; non-homogeneous. Strongly birefringent. Mixture of hex. and cubic phases.
		1/2 hr. 1000°C	Fused. Fair grain quality and homogeneity. Strongly birefringent. Mixture.
		1/2 hr. 1100°C	Fused. Good grain quality; poor homogeneity. Weakly birefringent. Mixture of hex. and cubic phase.
9NaF•YF ₃ 1CaF ₂	Crucible size sample. Mech. mixed; quenched in air after reaction under N ₂ in gold tubes and platinum crucible.	1/2 hr. 700°C	Well sintered. Fairly good grain quality and homogeneity. Strongly birefringent. Incompletely reacted mixture; mostly hex. NaYF ₄
		1/2 hr. 800°C	Granular. Good grain quality; poor homogeneity. Strongly birefringent. Incompletely reacted mixture, mostly hex. NaYF ₄

TABLE II (Continued)

<u>Sample</u>	<u>Sample History</u>	<u>Reaction Time/Temp.</u>	<u>Remarks</u>
		1/2 hr. 900°C	Sintered-granular. Good grain quality; fair homogeneity. Strongly birefringent. Mixture.
		1/2 hr. 1000°C	Fused. Good grain quality. Non-homogeneous; strongly birefringent. Mixture mostly hex. phase.
		1/2 hr. 1100°C	Fused. Good grain quality; poor homogeneity. Weakly birefringent. Mixture cubic and hex. phase.
3NaF·5YF ₃	Crucible size batch. Re-precipitated and calcined at 450°C. Reacted in gold tubes and platinum crucible under P ₂ . Quenched in air.	1/2 hr. 700°C	Sl. sintered. Poor grain quality; non-homogeneous. Incompletely reacted mixture.
		1/2 hr. 800°C	Well sintered. Poor grain quality; non-homogeneous. No birefringence. Incompletely reacted.
		1/2 hr. 900°C	Well sintered. Poor grain quality; non-homogeneous. No birefringence. Incompletely reacted.
		1/2 hr. 1000°C	Well sintered. Fair-good grain quality. Non-homogeneous. No birefringence. n=1.47. Incompletely reacted; mostly cubic phase.
		1/2 hr. 1100°C	Fused. Fair-good grain quality and homogeneity. n=1.47. A few birefringent particles discernable. Mostly cubic phase with sl. hex. phase present.

TABLE II (Continued)

<u>Sample</u>	<u>Sample History</u>	<u>Reaction Time/Temp.</u>	<u>Remarks</u>
9(3NaF·5YF ₃) 1CaF ₂	Crucible size batch. Co-precipitated and calcined at 450°C. Reacted in gold tubes and platinum crucible under N ₂ . Quenched in air.	1/2 hr. 700°C	Sl. sintered. Poor grain quality and homogeneity. Sl. birefringence. Incompletely reacted. Mostly cubic phase.
		1/2 hr. 800°C	Well sintered. Poor homogeneity; fair grain quality. No birefringence. n=1.45-1.47. Incompletely reacted mixture; mostly cubic phase.
		1/2 hr. 900°C	Well sintered. Fair grain quality; poor homogeneity. No birefringence. n=1.45-1.47. Incompletely reacted mixture; mostly cubic phase.
		1/2 hr. 1000°C	Strongly sintered. Fair grain quality; poor homogeneity. No birefringence. Incompletely reacted; mostly cubic phase.
		1/2 hr. 1100°C	Fused. Good grain quality and fair-good homogeneity. A few birefringent particles discernable. Mostly fluorite cubic phase with slight hex. phase present. n=1.47.
8(3NaF·5YF ₃) 2CaF ₂	Crucible size batch. Mech. mixed and reacted under N in gold tubes and platinum crucible. Quenched in air.	1/2 hr. 700°C	Very sl. sintering. Fair grain quality; poor homogeneity. Strongly birefringent. Incompletely reacted mixture.
		1/2 hr. 800°C	Sl. sintering. Poor homogeneity. Much birefringence but weak. Incompletely reacted mixture.

TABLE II (Continued)

<u>Sample</u>	<u>Sample History</u>	<u>Reaction Time/Temp.</u>	<u>Remarks</u>
		1/2 hr. 900°C	Granular. Fair grain quality; poor homogeneity. Sl. birefringence. Mixture cubic and hex. phases.
		1/2 hr. 1000°C	Sintered-granular. Fair-good grain quality; poor homogeneity. Very sl. birefringence. Mixture mostly cubic phase with sl. hex. phase present.
		1/2 hr. 1100°C	Fused. Good grain quality; fair homogeneity. Very sl. birefringence. Mostly cubic phase.
3NaF•5YF ₃	Crucible size batch. Coprecipitated and calcined at 400°C. Reacted under N ₂ in a platinum crucible and quenched in air.	1 hr. 1050- 1060°C	Fused. Glassy clear boule. Yellowish; excellent grain quality and homogeneity. No birefringence; n=1.47. Fluorite cubic ss.
9(3NaF•5YF ₃) 1CaF ₂	Crucible size batch. Coprecipitated and calcined at 400°C. Reacted under N ₂ and quenched in air.	1 hr. 1050- 1060°C	Sintered - fused. Milky white appearance. Good grain quality; n=1.46-1.47.
		1/3 hr. 1200°C	Fused. Glassy clear boule of excellent grain quality and homogeneity. A very few birefringent particles discernable. n=1.46-1.47.
NaF•YF ₃	Crucible size batch coprecipitated and calcined at 400°C. Reacted under N ₂ in a platinum crucible and quenched in air.	1/2 hr. 1200°C	Mat'l. opaque white. Good grain quality; some birefringence. Appears to be mixture of cubic and hex. phases.

TABLE II (Continued)

<u>Sample</u>	<u>Sample History</u>	<u>Reaction Time/Temp.</u>	<u>Remarks</u>
3NaF·5YF ₃	Crucible size sample co-precipitated and calcined at 400°C. Reacted under N ₂ and quenched in air.	1 hr. 1200°C	Clear yellowish boule. Excellent grain quality and homogeneity. No birefringence. n=1.47.
9(3NaF·5YF ₃) 1CaF ₂			n = 1.46-1.47
8(3NaF·5YF ₃) 2CaF ₂			n = 1.46-1.47
8(3NaF·5YF ₃) 2CaF ₂	Co-precipitated and calcined at 450°C. Reacted in a pt. crucible under N ₂ and cooled <u>slowly</u> to room temperature to check exsolution	1/2 hr. 1150°C	No exsolution discernable. Good grain quality and homogeneity.
6(3NaF·5YF ₃) 4CaF ₂	Mechanically mixed and reacted in air. Quenched in air. Pt. crucible used.	9 min. 1250°C	Fair-good general appearance under n liquids. n=1.44, approx.
3NaF·5YF ₃	3-lb. batch prepared by co-precipitation and calcination at 450°C. Reacted under N ₂ and quenched in air. Milled in Al ₂ O ₃ mill.	before high temp. reaction	Appears homogeneous. Sl. ss. formation. Hex. plus YF ₃ phase.
		1250°C	Fused. Good grain quality and homogeneity. Sl. contamination apparent. XRD indicates complete ss. Fluorite cubic phase of n=1.475.
9(3NaF·5YF ₃) 1CaF ₂	3-lb. batch prepared by co-precipitation and calcination at 450°C. Reacted under N ₂ and quenched in air. Milled in Al ₂ O ₃ mill.	before high temp. reaction	Appears homogeneous. Sl. ss. formation. Mixture of hex. and cubic phases.

TABLE II (Continued)

<u>Sample</u>	<u>Sample History</u>	<u>Reaction Time/Temp.</u>	<u>Remarks</u>
		1250°C	Fused. Good grain quality and homogeneity. Sl. contamination apparent. Fluorite cubic ss. $n=1.465$.
8(3NaF·5YF ₃) 2CaF ₂	3-lb. batch prepared by coprecipitation and calcination at 450°C. Reacted under N ₂ and quenched in air. Milled in Al ₂ O ₃ mill.	before high temp. reaction	Appears homogeneous. Sl. ss. formation. Mixture of cubic and hex. phase.
		1250°C	Fused. Good grain quality and homogeneity. Some contamination apparent. Fluorite cubic ss. of $n=1.465$.

TABLE III

Reaction Data for the System $\text{CaF}_2\text{-YF}_3$

<u>Sample</u>	<u>Sample History</u>	<u>Reaction Time/Temp.</u>	<u>Remarks</u>
8 CaF_2 2 YF_3	Crucible size batch. Mech. mixed in alcohol. Reacted under N_2 in a platinum crucible and quenched in air.	1 hr. 1200°C	Sintered; white. Very good grain quality. Non-homogeneous; appears to contain sl. unreacted YF_3
8 CaF_2 2 YF_3	Crucible size batch. Co-precipitated and calcined at 500°C. Reacted under N_2 in a platinum crucible and quenched in air.	1 hr. 1090- 1100°C	Fair-good grain quality and homogeneity. $n=1.47$. Sl. YF_3 appears to be present.
		1/2 hr. 1300°C	Good grain quality and homogeneity. $n=1.47$.
		1 hr. 1300°C	
9 CaF_2 1 YF_3	Crucible size batches. Mech. mixed in alcohol. Reacted under N_2 in platinum crucible. Quenched in air.	1 hr. 1300°C	Excellent grain quality and homogeneity. No birefringence. $n=1.45$.
7 CaF_2 3 YF_3			Excellent grain quality and homogeneity. $n=1.48$.
6 CaF_2 4 YF_3			Fused. Translucent; very hard. Good grain quality and homogeneity. Very sl. birefringence discernable. $n=1.49-1.50$.

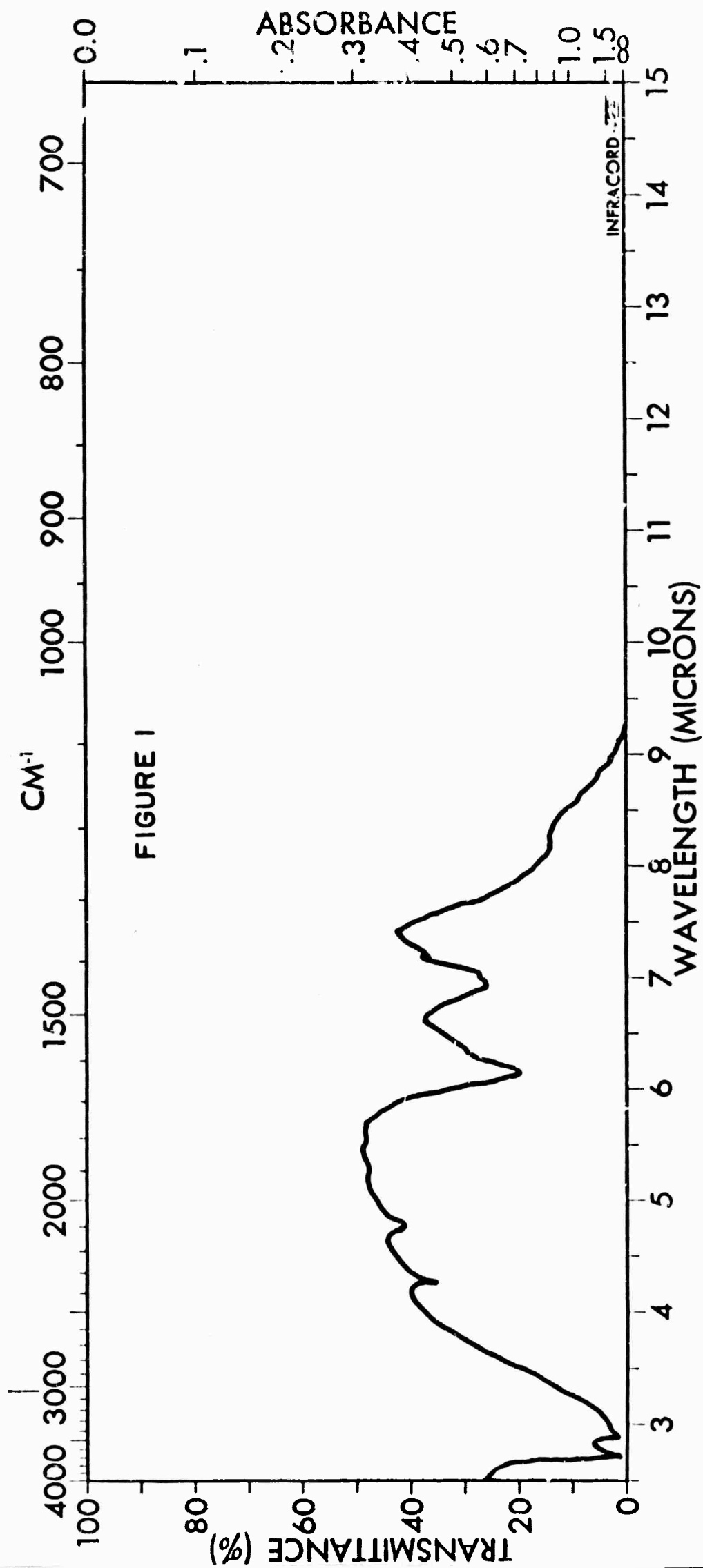
TABLE III (Continued)

<u>Sample</u>	<u>Sample History</u>	<u>Reaction Time/Temp.</u>	<u>Remarks</u>
9CaF ₂ 1YF ₃	3-lb. batches. Co-precipitated and calcined at 500°C. Reacted under N ₂ in a platinum pot and quenched in H ₂ O. Milled in an alumina mill.	before high temp. reaction	Some solid soln. formation.
		1300°C	Good grain quality and homogeneity. n=1.45.
8CaF ₂ 2YF ₃		before high temp. reaction	Some solid soln. formation.
		1300°C	Good grain quality and homogeneity. Fluorite cubic ss. of n = 1.47.

TABLE IV

Reaction Data for the System $\text{LaF}_3\text{-SrF}_2$

<u>Sample</u>	<u>Sample History</u>	<u>Reaction Time/Temp.</u>	<u>Remarks</u>
8 LaF_3 2 SrF_2	Crucible size batch. Co-precipitated and calcined at 450°C.	- - -	Mat'l. looks very good. Good grain quality and homogeneity. Very sl. birefringence discernable. $n = 1.565$.
	Reacted under N_2 and quenched in air.	3/4 hr. 800°C 1/2 hr. 830°C 1/2 hr. 1000°C 1/2 hr. 1100°C	Fair-good grain quality and homogeneity. Sl. oxidation discernable. Sl. sintered. Weakly birefringent. Sl. oxidation apparent. Sintered. Sl. birefringence discernable. Sl. oxidation. Sintered. Poor grain quality. Sl. birefringence. Sl. oxidation.
9 LaF_3 1 SrF_2	3-lb. batches co-precipitated and calcined at 500°C.		Very good homogeneity and grain quality. No free SrF_2 discernable. $n = 1.574$.
8 LaF_3 2 SrF_2			Good grain quality and homogeneity. Al. amt. of free SrF_2 discernable. $n = 1.566$.
8.5 LaF_3 1.5 SrF_2	Crucible size batch. Co-precipitated and calcined at 450°-500°C.	- - -	Good grain quality and homogeneity. Sl. amt. of free SrF_2 discernable. $n = 1.568$.



SPECTRUM NO. <u>2344</u>		LEGEND		REMARKS	
SAMPLE		HOT-PRESSED		1.	
80% Mg F ₂		PURITY		2.	
20% Ni F ₂		PHASE		DATE <u>1 July, 1963</u>	
		THICKNESS <u>2 mm</u>		OPERATOR <u>RR</u>	

FIGURE 2

THE RELATIONSHIP OF REFRACTIVE INDEX TO TOTAL COMPOSITION IN THE SOLID SOLUTION SYSTEM MgF_2 - NiF_2 .

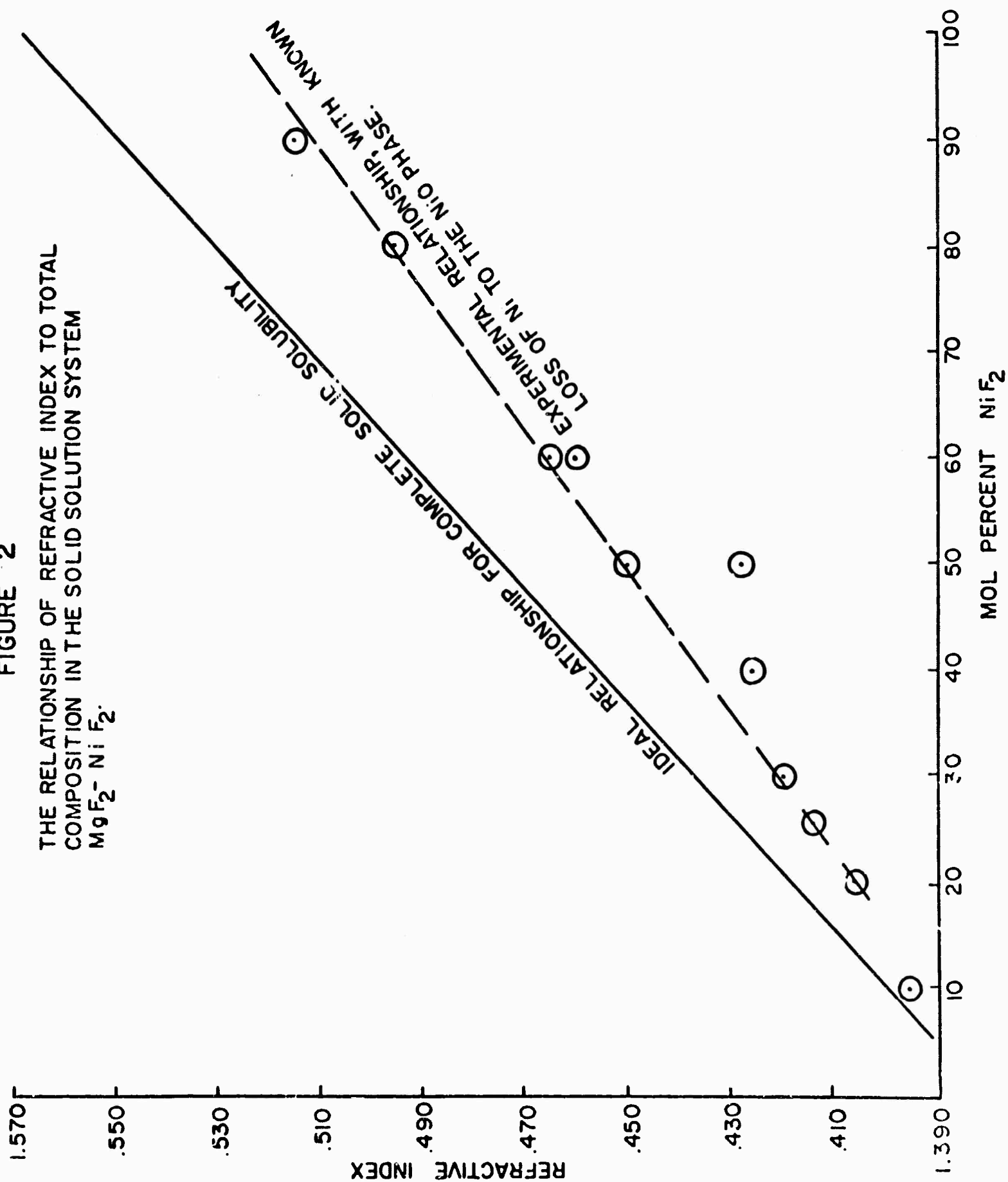


FIGURE 3

TERNARY COMPOSITIONAL DIAGRAM IN MOL
PERCENT FOR THE SYSTEM $\text{KF}-\text{MgF}_2-\text{ScF}_3$.

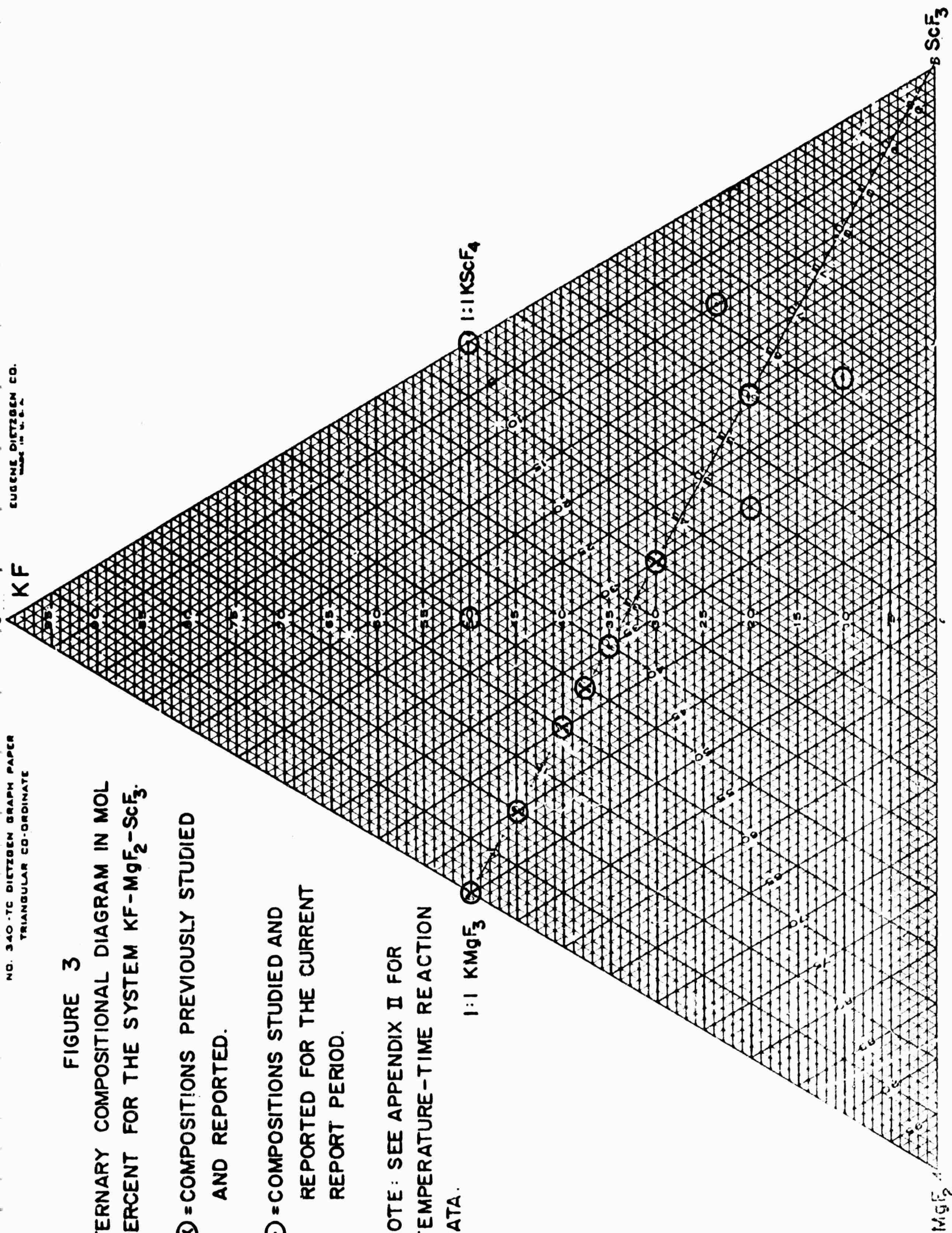
⊗ = COMPOSITIONS PREVIOUSLY STUDIED
AND REPORTED.

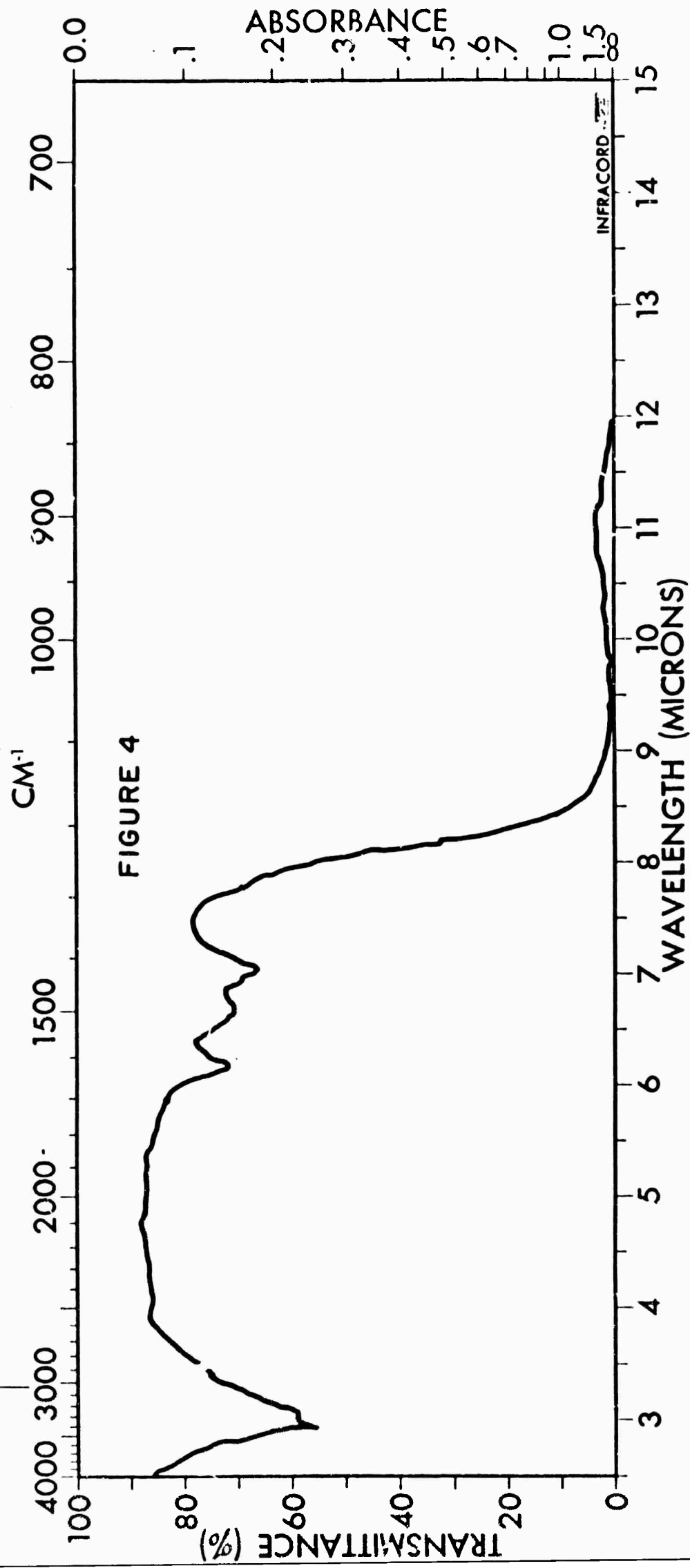
○ = COMPOSITIONS STUDIED AND
REPORTED FOR THE CURRENT
REPORT PERIOD.

NOTE: SEE APPENDIX II FOR
TEMPERATURE-TIME REACTION
DATA.

1:1 KMgF_3

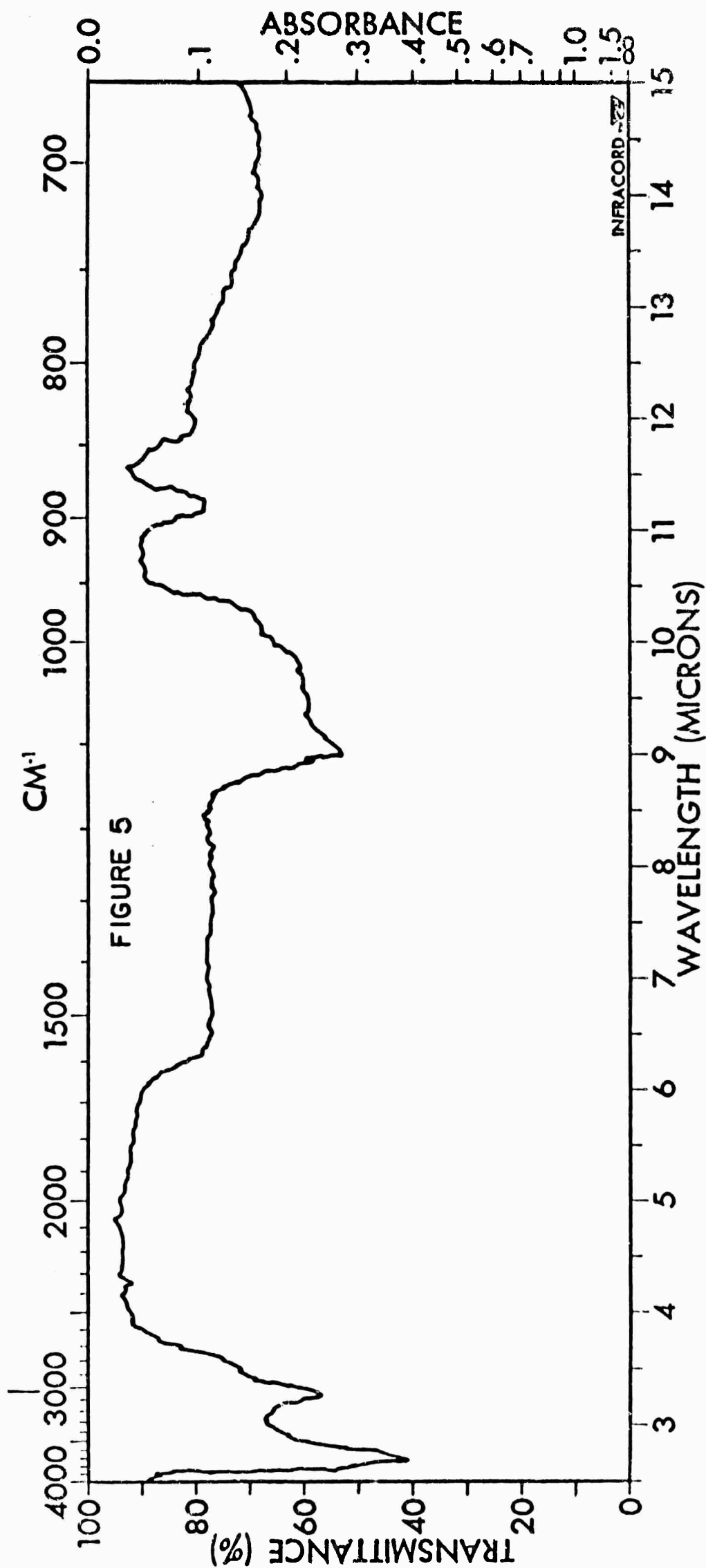
1:1 KScF_4



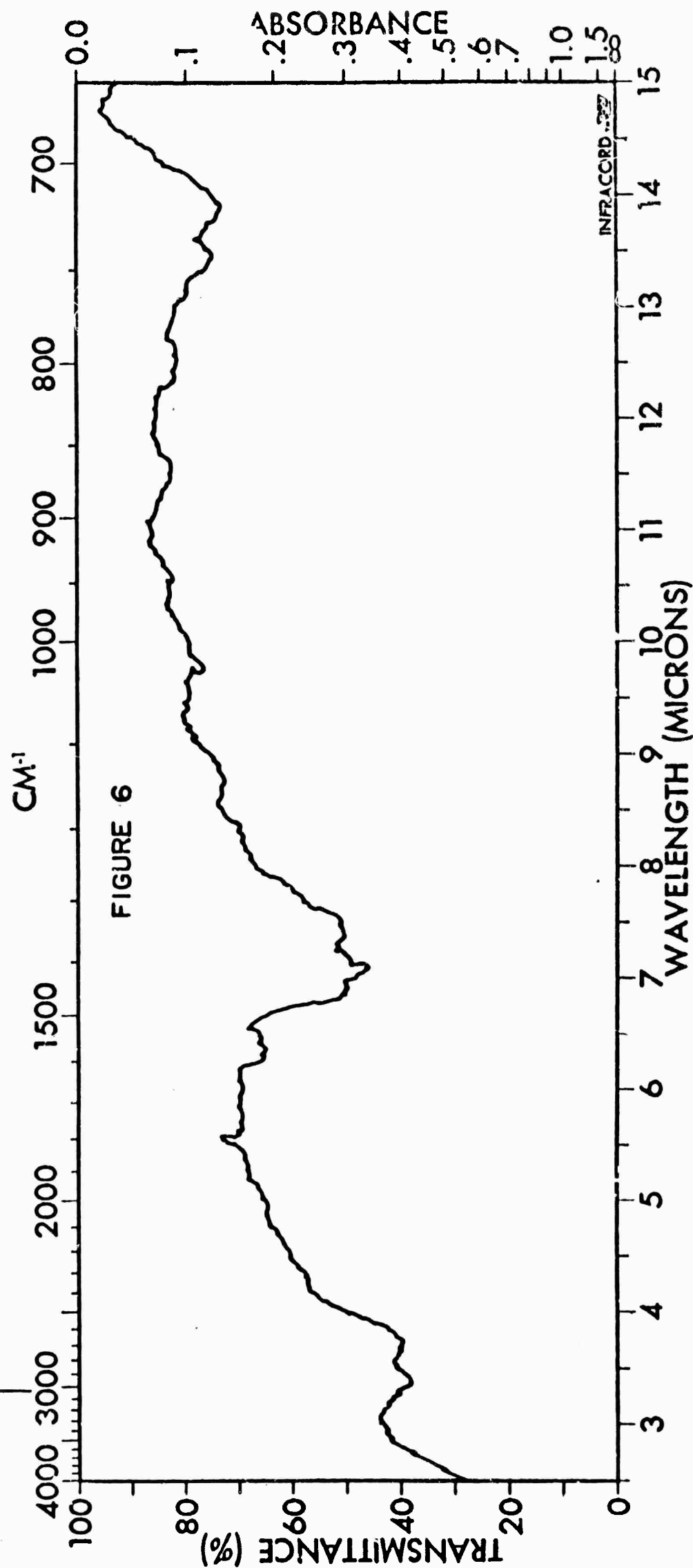


SPECTRUM NO. _____
SAMPLE

SPECTRUM NO. <u>2317</u>	ORIGIN _____	LEGEND _____	REMARKS _____
SAMPLE <u>CaF₂</u>	<u>HOT - PRESSED</u>	1. _____	_____
_____	PURITY _____	2. _____	_____
_____	PHASE _____	DATE <u>16 May, 1963</u>	_____
_____	THICKNESS <u>3.8 mm</u>	OPERATOR <u>RR</u>	_____



SPECTRUM NO. <u>5</u>		LEGEND		REMARKS	
SAMPLE <u>CdTe</u>		1.		POWDER PELLET	
PURITY		2.		PRESSED TO	
REACTED		DATE 26 FEBRUARY 1963		10 KILOBARS AT	
STOICHIOMETRIC WEIGHTS		OPERATOR <u>CSB</u>		ROOM TEMPERATURE	
THICKNESS					



SPECTRUM NO. <u>2</u>		ORIGIN _____		LEGEND _____		REMARKS _____	
SAMPLE <u>CdTe</u>		PURITY REACTED _____		1. _____		MINERAL OIL MULL	
STOICHIOMETRIC WEIGHTS _____		PHASE _____		2. _____		TECHNIQUE USED _____	
THICKNESS _____		DATE <u>27 MARCH 1963</u>		OPERATOR <u>DBP</u>		SPECTRUM NO. _____	

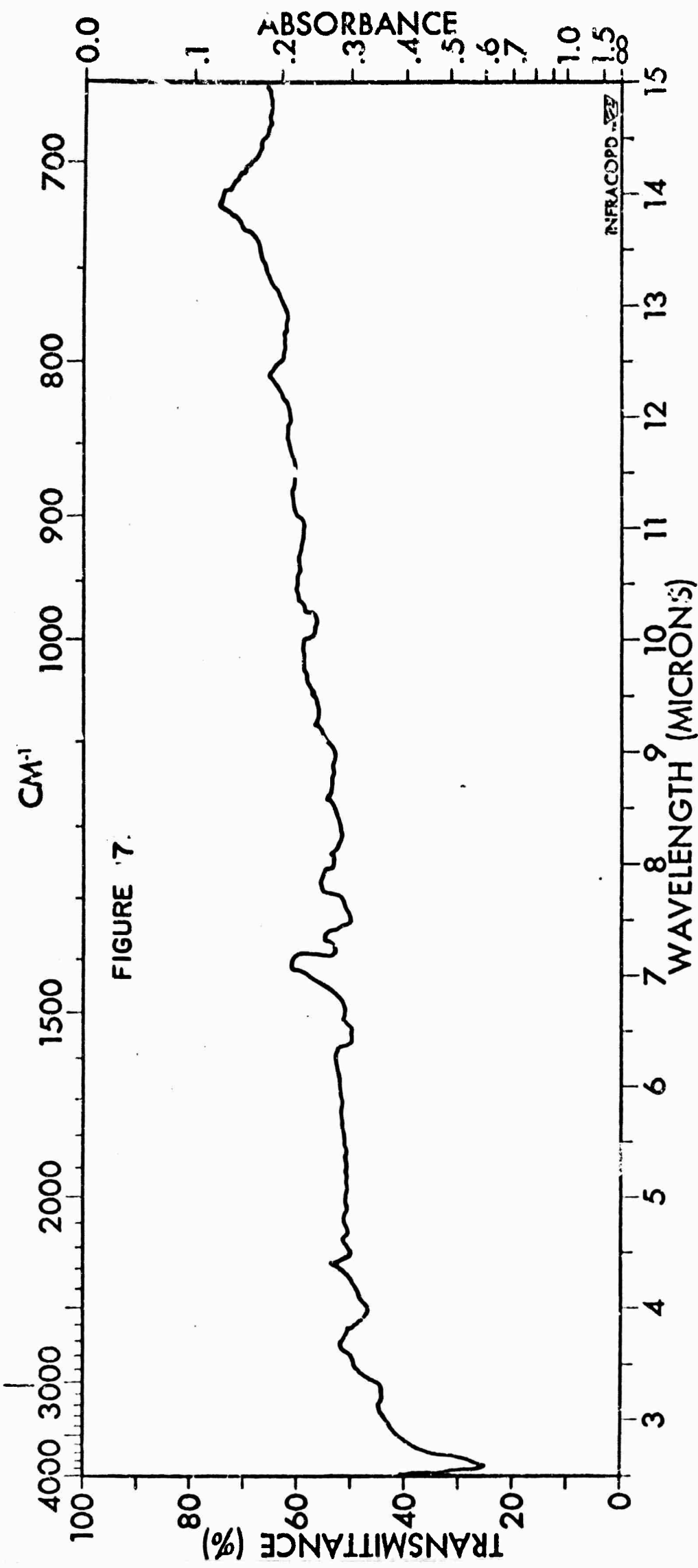


FIGURE 7.

SPECTRUM NO. <u>6</u>		ORIGIN _____		LEGEND _____		REMARKS _____	
SAMPLE <u>CdTe</u>		PURITY EVAPORATED _____		1. _____		MINERAL OIL MULL	
PHASE _____		THICKNESS _____		2. _____		TECHNIQUE USED _____	
DATE <u>27 MARCH 1963</u>		OPERATOR <u>DOB</u>		SPECTRUM NO. _____		SAMPLE _____	