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CASTING OF HALIDE AND FLUORIDE ALLOYS FOR LASER WINDOWS

R. T. Newberg, et al

Raytheon Company

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Waltham, Massachusetts 02154

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20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

During the second six months of this program high quality castings of both CaF_2 and SrF_2 were fabricated regardless of the starting material. That is, either high purity single crystal chips or "reagent" grade powder pre-treated at elevated temperatures in teflon vapor may be used to yield equivalently cast ingots. The calorimetrically measured 5.25μm bulk absorption coefficient of cast CaF_2 has been consistently attained near $4.2 \times 10^{-4} cm^{-1}$ regardless of starting material. In preliminary results for cast SrF_2, the 5.25μm bulk absorption coefficient lies near $6.7 \times 10^{-5} cm^{-1}$ and $1.7 \times 10^{-4} cm^{-1}$ for

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Abstract (Cont'd.)

ingots cast from single crystal chips and pre-treated powder, respectively. Strained ingots of CaF_2 were successfully strain annealed at 900°C either in a vacuum or in an inert atmosphere. Strained ingots of SrF_2 were successfully strain annealed at 1000°C in a high vacuum.

Preliminary mechanical measurements on cast and single crystal CaF_2 and cast and single crystal SrF_2 show average fracture strengths ranging from 8000 psi to 28,200 psi, from 7200 psi to 26,500 psi, from 10,800 psi to 16,000 psi, and from 11,300 psi to 16,400 psi, respectively, depending both on the quality of polished surfaces and edges and on whether or not the polished samples are annealed prior to testing. This dependence is evidence that the fracture strength is limited by surface and/or edge flaws. The preliminary results show the equivalence in strength of CaF_2 and SrF_2 and of polycrystalline cast and single crystal material.

TECHNICAL PROGRAM SUMMARY

The main objective of this program is to demonstrate the feasibility of fusion casting of alkali halides and alkaline earth fluorides for high power laser window applications. The main effort deals with the fabrication and property evaluation of the alkaline earth fluorides.

During the second six months of this program high quality castings of both CaF_2 and SrF_2 were fabricated, regardless of the starting material. That is, either high purity single crystal chips or pre-treated "reagent" grade powder can be used as starting material to yield equivalently cast ingots.

Castings of CaF_2 were attempted in an inert atmosphere of purified argon (1-50 torr). The advantage over vacuum casting is that unidirectional solidification is better accomplished because of the better heat transfer provided by the gas.

Preliminary hot forgings of polycrystalline cast CaF_2 were done at 1000°C. At the high temperature a large grain size results so that not much advantage in grain size reduction is gained.

Calorimetrically measured 5.25μm bulk absorption coefficients for cast CaF_2 are being consistently attained near 4.2×10^{-4} cm^{-1} regardless of the starting material. Those castings of CaF_2 fabricated in an inert atmosphere (purified argon) have 5.25μm apparent absorption coefficients typically greater than 1×10^{-3} cm^{-1}, although one excellent casting was obtained (4.1×10^{-4} cm^{-1}).

In preliminary results the 5.25μm bulk absorption coefficient of cast SrF_2 lies near 6.7×10^{-5} cm^{-1} for an ingot using single crystal chips as starting material and lies near 1.7×10^{-4} cm^{-1} for an ingot cast from purified "reagent" grade powder.

Strain annealing of highly strained cast CaF_2 has been successful at

900°C either in a vacuum or in an inert atmosphere. Similarly strained ingots of cast SrF_2 have been successfully strain annealed at 1000°C, but only in a high vacuum furnace.

Mechanical measurements on cast CaF_2 show average fracture strengths ranging from a minimum near 8000 psi to near 28,200 psi, depending on both the quality of polished surfaces and whether or not the polished samples are annealed at 900°C (a strain relief procedure) prior to testing. The values are equivalent to the values obtained for single crystal CaF_2 for which similar polishing and annealing procedures show average fracture strengths ranging from 7200 psi to 26,500 psi. In preliminary results, the average fracture strengths for cast and single crystal SrF_2 range from 10,800 psi to 16,000 psi and from 11,300 psi to 16,400 psi, respectively. The best (for CaF_2) surface polish has not yet been evaluated for SrF_2, but these results show that for both CaF_2 and SrF_2 the dependence of fracture strength on both surface polish and annealing history is evidence that fracture may be determined by surface and/or edge flaws. The preliminary results also show that SrF_2 is equivalent in strength to CaF_2 and that polycrystalline cast material is equivalent in strength to single crystal material.

PREFACE

This report was prepared by Raytheon Company, Research Division, Waltham, Massachusetts under Contract No. F19628-74-C-0148 entitled "Casting of Halide and Fluoride Alloys for Laser Windows." This work is supported by the Advanced Research Projects Agency and is monitored by the Air Force Cambridge Research Laboratories, Bedford, Massachusetts.

At Raytheon the investigation is being carried out in the Advanced Materials Department under the direction of Dr. J. Pappis, principal investigator, and Dr. R. Newberg. Assisting with material fabrication and processing are T. Wong and A. De. Optical polishing is provided by R. Cosgro; Dr. T. Kohane and T. Varitimos are performing the laser calorimetry measurements. Dr. O. Guentert, W. Tye, and D. Howe are providing the SEM micrographs, microprobe analyses, and X-ray diffraction analyses. P. Roman is assisting with the mechanical property measurements. This report has been given an internal number of S-1864.

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1.0 INTRODUCTION

The primary objective of this program is to demonstrate the feasibility of fusion casting of alkali halides and alkaline earth fluorides for use as windows for high power lasers. In a previous program, initial work on alkali halide alloys, particularly $SrCl_2$-doped KCl, indicated that casting was a promising fabrication process.

The work on the alkaline earth fluorides is being stressed because they are more amenable to fabrication by fusion casting due to their smaller volume change on solidification and their better thermal and mechanical properties compared to the alkali halides, as was discussed in a previous report.[1] Therefore, this program investigates the effects of casting parameters and annealing procedures on the microstructure, mechanical properties, and optical properties of the alkaline earth fluorides. In addition, the effects of impurities and alloy additions on microstructure and properties are being evaluated. Equally significant is the study of the importance of starting materials and purification schemes on the optical absorption and scatter of the cast ingots.

2.0 RESULTS

2.1 Vacuum Casting

During the second six months of this program, the main effort was directed toward the fusion casting of pure alkaline earth fluorides, with most emphasis having been placed on SrF_2. Both large vacuum furnaces were used, with most of the casting (92 runs) having been done in the vacuum hot press (VHP) furnace capable of ingots of about five and one-half inches in diameter. The two-zone (CF) furnace was used for casting (11 runs), annealing (35 runs) and purification of "reagent" grade powder (17 runs). Two hot forging runs and two purification runs were also done in the VHP furnace.

Tables I and II list all the runs done in the two furnaces. Figures 1 and 2 show several polished windows of pure CaF_2 and SrF_2, respectively, cast in the laboratory. The grain size of such castings is large – typically on the order of 1 - 2 cm.

As mentioned above, nearly all of the castings were produced in the VHP furnace (an all graphite system). During the third quarter, six runs (CF91 - 96) were attempted in the two-zone furnace as listed in Table II. Earlier in this furnace, as was discussed in a previous report,[1] there had been a problem with the reaction of fluoride vapors with the insulating supports for the molybdenum elements and with the thermocouple insulating tubes. However, these six runs demonstrated that the problem is associated only with CaF_2 and not with SrF_2; i.e., with the present castings of SrF_2 no such reactions occurred up to 1500°C. The castings were generally discolored, probably a result of the poor vacuum (1 - 10μm) capability provided by the mechanical pump vacuum system. A diffusion pump was installed late in this reporting period providing vacuum capability of at least 10^{-5} torr. Five initial casting runs (CF 126-130) were attempted using SrF_2. Transparent material with no discolorations was obtained but cooling procedures to promote unidirectional solidification still need to be improved.

TABLE I

VACUUM HOT PRESS (VHP) RUNS

PURE FLUORIDES

VHP No.	Material	Comments
284, 285	SrF_2	Small castings; cracked
286-297	CaF_2	Large castings; good runs
300	SrF_2	Large casting; cracked
301	CaF_2	In argon 50 mm; colorless casting
302, 303	CaF_2	Hot forged samples (VHP-269) at 1000°C
304	CaF_2	In < 1mm argon; bluish casting
306	CaF_2	In 5 mm argon; yellowish casting
307, 308, 309	CaF_2	From purified powder; castings cracked
311, 312	SrF_2	Fast cooled; castings cracked
313	CaF_2	In 15 mm argon; bluish casting
314	CaF_2	In 50 mm argon; yellowish casting
316	CaF_2	Small casting; intergranular cracks
317	CaF_2	Remelt VHP-309; In 50 mm argon intergranular cracks; colorless casting
318	CaF_2	In 50 mm argon; no cracks; yellow-blue casting
319-321	SrF_2	Trouble with power supply; no melting
324	CaF_2	Purification of powder plus two percent teflon
325	SrF_2	Purification of powder plus two percent teflon
326, 327	SrF_2	Cooled nominal 75°C/hr.; cracked
329	SrF_2	Melt VHP-325; cooled 45°C/hr.; cracked cloudy ingot (white precipitates)
332	SrF_2	Remelt VHP-326; cooled 25°C/hr.; good
333	CaF_2	Two crucibles in furnace; cooled 75°C/hr.
334	SrF_2	Cooled 15°C/hr.; no good
335	SrF_2	Purified powder (vacuum baked); cooled 25°C/hr.; good
338	SrF_2	Cooled 25°C/hr.; white precipitates
339	CaF_2	Not melted
340	SrF_2	Cooled 60°C/hr.; good casting

TABLE I (Cont'd.)

341, 350	CaF_2	Cooled 75°C/hr.; good
342	SrF_2	Cooled 75°C/hr.: power failure; cracked
343	SrF_2	Remelt VHP-342; cooled 75°C/hr.; good
344, 345	SrF_2	Cooled 75°C/hr.; cracked
346	SrF_2	Cooled 45°C/hr.; cracked
348, 349, 353	SrF_2	Cooled 35°C/hr.; good
352	SrF_2	Cooled 20°C/hr.; cracked
354	CaF_2	Cooled 35°C/hr.; cracked
356	SrF_2	Cooled 35°C/hr.; cracked
357	SrF_2	Purified powder (vacuum baked); cooled 75°C/hr.; opaque
358	SrF_2	Remelt VHP-357; cooled 35°C/hr.; cracked
360, 361	SrF_2	VHP-361 remelt of VHP-360, cooled 25°C/hr.; good
363	SrF_2	Remelt VHP-358; not melted completely
364	SrF_2	Molybdenum crucible; cracked due to sticking
365	SrF_2	Cooled 25°C/hr.; cracked
368	SrF_2	Too high temperature; melt evaporated
369, 370	SrF_2	VHP-370 remelt of VHP-369; cooled 35°C/hr.; good
373, 374	SrF_2	Remelts; cooled 25°C/hr.; no good
375	SrF_2	In 25 mm argon; thermocouple broke, power off; cracked
378-380 382, 383	SrF_2	Remelts; no good
384	SrF_2	Remelt VHP-383; cooled 25°C/hr.; good
387	CaF_2	Remelt crystals; manually cooled; cracked
388, 389, 393	SrF_2	Purified powder (teflon + roast); opaque, discolored; cracked
390	SrF_2	Purified powder (teflon + roast); cracked but transparent
394	SrF_2	Purified powder (teflon - no roast); cracked but clear
395	SrF_2	Remelt VHP-390 and VHP-394; cooled 35°C/hr.; good
398	SrF_2	Remelt VHP-384; cooled 25°C/hr.; good

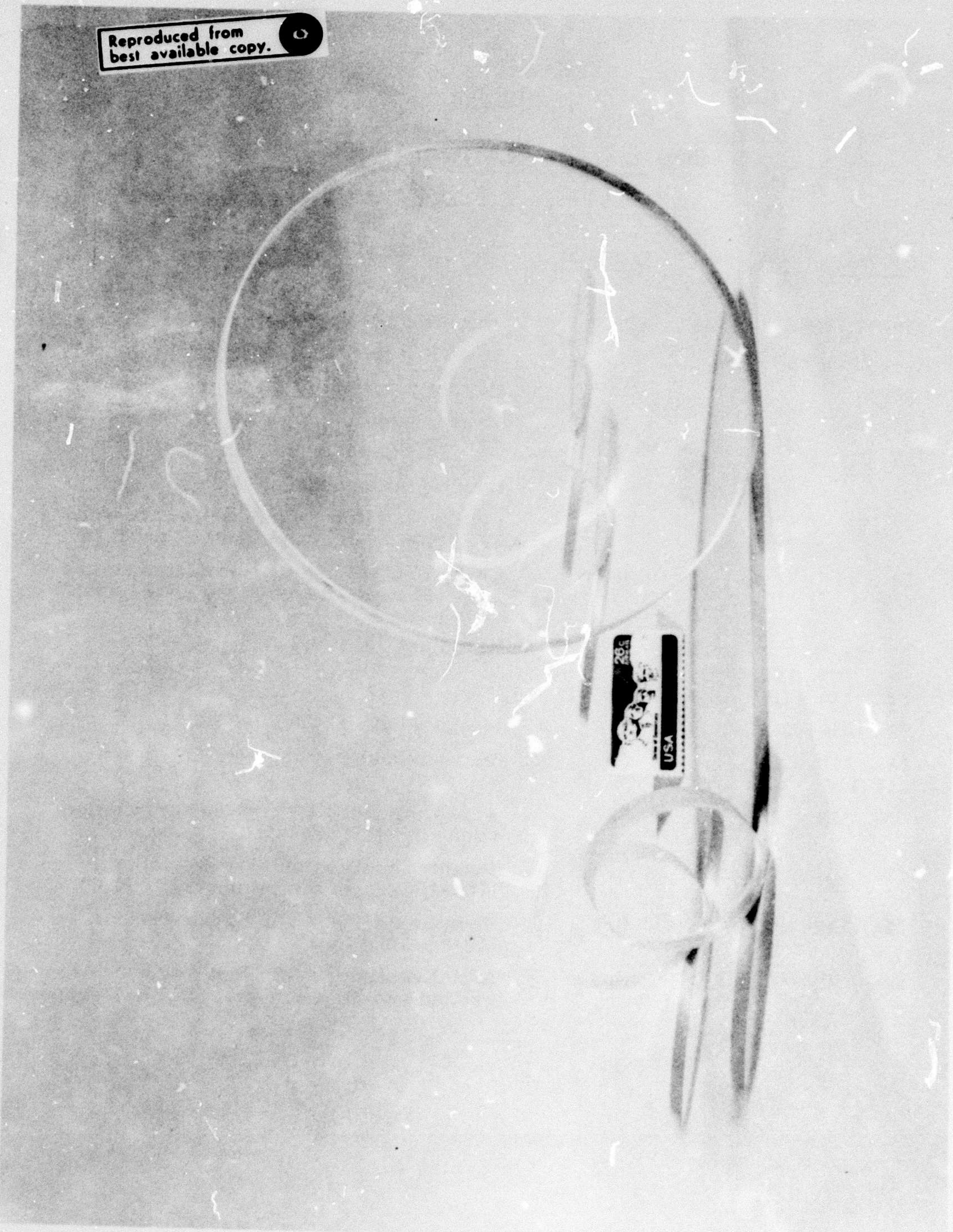
TABLE I (Cont'd.)

399	SrF_2	Purified powder + remelt deposits, cooled 25°C/hr.; good
400, 402	SrF_2	Remelts of VHP-393 and VHP-399, cooled 25°C/hr.; good
403	CaF_2	Manually cooled; good
404	SrF_2	Remelt; cooled 25°C/hr., discolored (green); cracked
405, 409, 411	CaF_2	Purification with PbF_2
408	SrF_2	Remelt VHP-404; cooled 20-25°C/hr.; good
412	CaF_2	Remelt; manually cooled; no good

TABLE II

TWO-ZONE FURNACE (CF) RUNS
PURE FLUORIDES

CF No.	Material	Comments
70-77, 79-81, 83-85	CaF_2	Annealing (900°C) cast ingots
82, 88, 89, 97, 98	SrF_2	Annealing (900°C) cast ingots
78	CaF_2	Powder purification in teflon vapors (900°C)
86, 90	SrF_2	Powder purification in teflon vapors (900°C)
87	SrF_2	Vacuum bake powder (900°C)
91	SrF_2	Casting failed because it did not melt
92, 93	SrF_2	Casting in teflon vapor(partial pressure 50 - 100μm). Ingots clear but cracked
94 - 96	SrF_2	Casting in teflon vapor(partial pressure 300 - 400μm). Ingots discolored (pink) and cracked
97, 98, 100, 104 106, 107, 109, 110 113, 117-119	SrF_2	Annealing (900°C) cast ingots
99, 101-103	SrF_2	Vacuum bake powder (900°C)
105, 111, 112 114-116	CaF_2	Vacuum bake powder (900°C)
108, 122	SrF_2	Annealing (1000°C) cast ingots in teflon vapor (partial pressure 100μm)
121, 121a, 123	SrF_2	Powder purification in teflon vapor (100-200μm partial pressure) (600°C).
124, 125	SrF_2	Annealing (1000°C) in higher vacuum (10^{-4} - 10^{-5} torr)
126-130	SrF_2	Initial casting runs to test new vacuum system and Mo elements. Ingots transparent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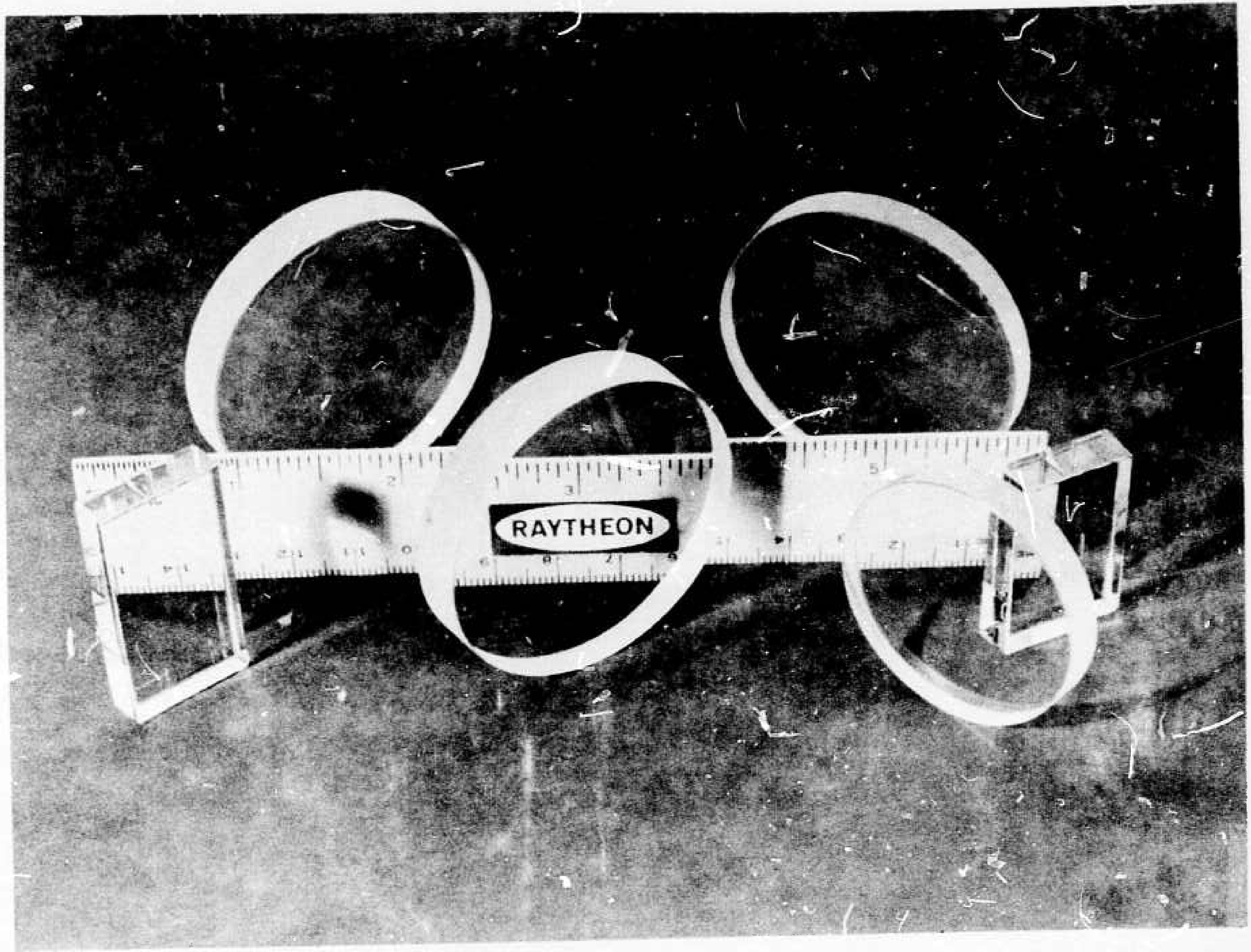


Fig. 2 Polished Windows of Cast SrF_2

At the beginning of the casting program for SrF_2, it was noted that the cast ingots were more susceptible to cracking (probably from thermal shock) than were similar CaF_2 ingots. The problem was in general remedied by modifying the VHP furnace to include temperature control over the entire range necessary (room temperature to over 1500°C) as well as controlled cooling at rates as low as 10°C/hr. For casting CaF_2 bare wire Pt; Pt-13percent Rh thermocouples can be used for temperature control, with an optical pyrometer being used as an auxiliary check of the temperature. For SrF_2, as mentioned above, alumina-sheathed Pt; Pt-13 percent Rh thermocouples can be used.

With such modifications, the present procedure for obtaining castings of SrF_2 and CaF_2 is as follows (for the vacuum hot press furnace): The charge to be melted (fluoride plus lead fluoride added as an oxide scavenger – usually 2 - 5 percent by weight) is loaded in a covered ATJ graphite crucible and placed in the furnace. The crucible rests on a PG (pyrolytic graphite) pedestal ("a" axis parallel to the desired direction of solidification) which in turn rests on the bottom water-cooled ram. A vacuum is drawn and, when it reaches 10^{-4} torr, the furnace is brought slowly up to temperature in about three hours. The charge is held at 1500°C for one hour to insure complete melting. During this time the water-coolant to the bottom pedestal is turned off to maximize the temperature. In the final 15 minutes of melting, the water coolant is turned on to establish a thermal gradient in the crucible from top to bottom, in order to promote unidirectional solidification. The furnace is then switched to controlled cooling at the desired rate by adjusting the clock-drive controls. After complete solidification is assured, the water-coolant to the pedestal is again turned off to minimize the thermal gradient in the ingot, and the cooling rate may be reset to the desired cooling to room temperature. The total process requires about three days in the case of SrF_2. CaF_2 can be cooled more quickly and the process requires only one day. All of the castings produced in the above manner are still quite strained (probably due to residual thermal gradients in the furnace). Consequently, each sample must be subsequently strain annealed in the two-zone vacuum furnace prior to further handling, as will be discussed below.

Starting material for most castings was high purity, single crystal chips of CaF_2 (Optovac) or SrF_2 (Harshaw). However, a number of castings of CaF_2 and SrF_2 were made from in-house purified "reagent" grade powder with equal success. As listed in Tables 1 and 2, several purification schemes were used. One has been discussed before,[1] using teflon vapors at elevated temperature according to the following thermodynamically favorable reactions:

$$2\ CaO + C_2F_{4(g)} \rightarrow 2\ CaF_2 + 2\ CO_{(g)} \qquad \text{or}$$

$$2\ SrO + C_2F_{4(g)} \rightarrow 2\ SrF_2 + 2\ CO_{(g)} \qquad .$$

The other procedure is to vacuum bake the "reagent" grade powder at 900°C to remove as much absorbed water as possible. The partially sintered powder can then be melted in the normal way with only lead fluoride being added as an oxide scavenger according to the reactions:

$$CaO + PbF_2 \rightarrow CaF_2 + PbO \qquad \text{or}$$

$$SrO + PbF_2 \rightarrow SrF_2 + PbO \qquad ,$$

with the PbO and any excess PbF_2 being removed by volatilization under vacuum at the elevated temperatures.

In purifying the "reagent" grade SrF_2 powder (obtained from Barium and Chemicals, Inc., Steubenville, Ohio), both procedures were used. In using the teflon vapor technique at 900°C (CF-86 and 90), the teflon also pyrolyzes (as is the case with CaF_2[1]), and the resulting graphite contamination is difficult to remove by subsequent roasting in air at 500°C. The one casting (VHP-329) made from such powder was opaque (white precipitates), but upon subsequent remelting with additional lead fluoride added, transparent castings were obtained (VHP-346 and 349). Subsequent teflon vapor purifications were run at 600°C (CF-121, 121a, and 123) resulting in little or no pyrolysis with no obvious graphite contamination. Nonetheless several such purification runs were roasted in air (500°C) prior to casting with mixed results. One ingot

(VHP-388) was opaque and one (VHP-390) was clear. The former was remelted several times (VHP-389, 393, and 400) and was purified to transparency. However, the best results were obtained from the 600°C teflon-treated powder with no subsequent roasting. Two runs (VHP-394 and 399) produced clear castings.

In the purification scheme of the SrF_2 powder, it was noticed that the as-received powder is contaminated with small black particles. The particles, being magnetic, are somewhat effectively removed by passing a magnet repeatedly through the powder. (X-ray diffraction and ion probe analysis show the contaminants to contain Fe – probably iron oxide due to the reddish brown colored powder obtained upon grinding – plus trace amounts of Al, Si, and Ti.) After such a mechanical separation some contamination remains because the vacuum-baked (or 600°C teflon-treated) powder is discolored pink. Mixed results were obtained in casting vacuum-baked powder (VHP-335 and 357), the ingots being clear and opaque, respectively. However, on remelting the opaque ingot, transparent ingots were subsequently cast (VHP-358 and 363).

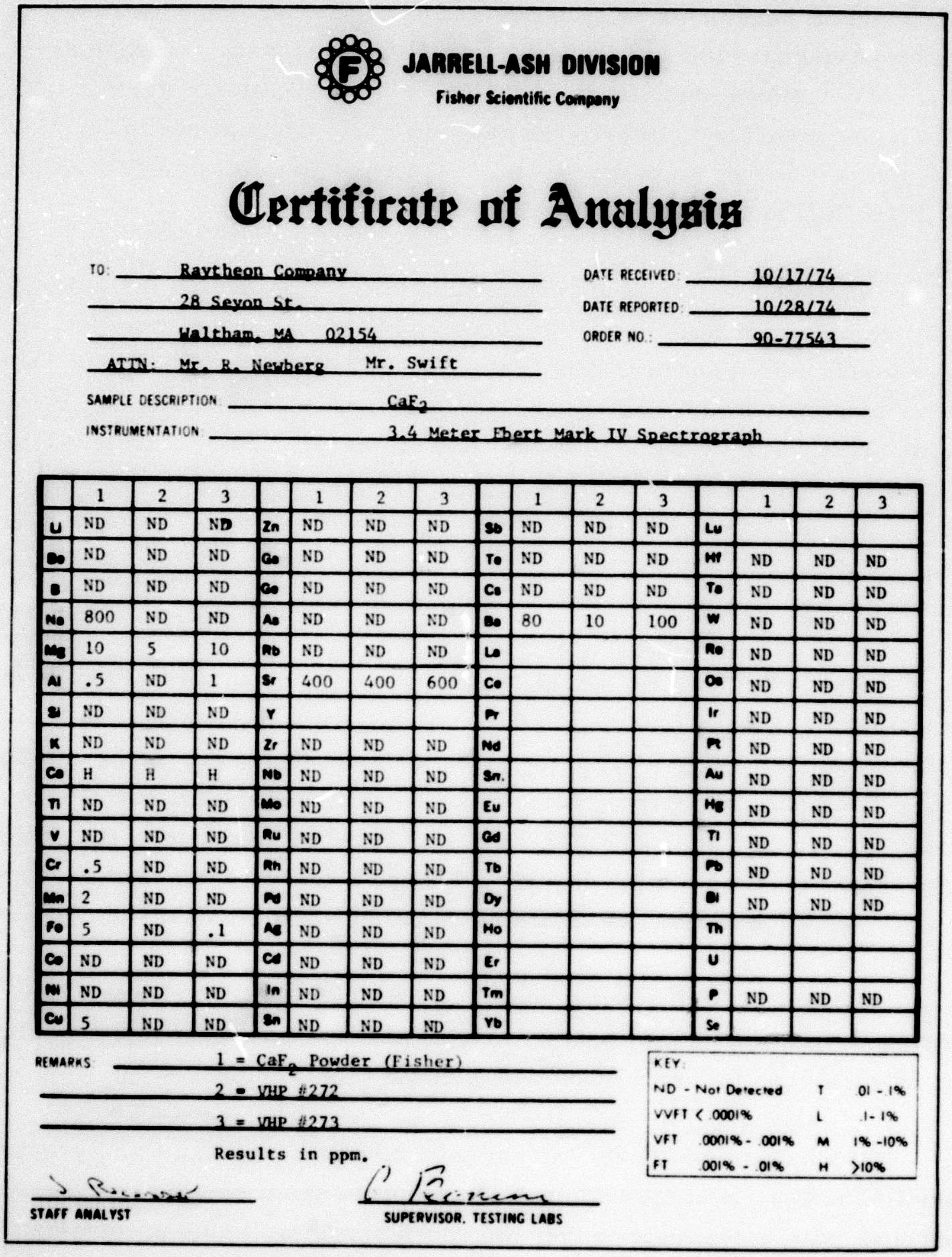
Teflon-treated CaF_2 (900°C) gives consistently good results (VHP-307, 308, 309, and 317).

It was at first noticed that castings produced from purified powder (both SrF_2 and CaF_2) seemed to be especially sensitive to intergranular cracking by thermal shock. It may have been due to trace residual impurities (e.g., residual Pb) at the grain boundaries with increased sensitivity to thermal shock, as will be discussed below. The problem was alleviated by using a crucible cover with a hole – the hole presumably allowing more volatile impurities to escape more readily. Subsequently some castings cracked but failure was predominantly transgranular in nature, i.e., cleavage across large grains.

Selected samples of "reagent" grade CaF_2 and SrF_2 were analyzed by emission spectroscopy (Jarrell-Ash, Waltham, Massachusetts). Table III shows the results of the analyses on the following CaF_2 samples: 1) As-received "reagent" grade powder, 2) A casting (VHP-272) using teflon-treated powder, and 3) A casting (VHP-273) using untreated powder. As

TABLE III

ANALYSES OF "REAGENT" GRADE CaF_2 SAMPLES



JARRELL-ASH DIVISION
Fisher Scientific Company

Certificate of Analysis

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28 Seyon St.
Waltham, MA 02154
ATTN: Mr. R. Newberg Mr. Swift

DATE RECEIVED: 10/17/74
DATE REPORTED: 10/28/74
ORDER NO.: 90-77543

SAMPLE DESCRIPTION: CaF_2

INSTRUMENTATION: 3.4 Meter Ebert Mark IV Spectrograph

	1	2	3		1	2	3		1	2	3		1	2	3
Li	ND	ND	ND	**Zn**	ND	ND	ND	**Sb**	ND	ND	ND	**Lu**			
Be	ND	ND	ND	**Ga**	ND	ND	ND	**Te**	ND	ND	ND	**Hf**	ND	ND	ND
B	ND	ND	ND	**Ge**	ND	ND	ND	**Cs**	ND	ND	ND	**Ta**	ND	ND	ND
Na	800	ND	ND	**As**	ND	ND	ND	**Ba**	80	10	100	**W**	ND	ND	ND
Mg	10	5	10	**Rb**	ND	ND	ND	**La**				**Re**	ND	ND	ND
Al	.5	ND	1	**Sr**	400	400	600	**Ce**				**Os**	ND	ND	ND
Si	ND	ND	ND	**Y**				**Pr**				**Ir**	ND	ND	ND
K	ND	ND	ND	**Zr**	ND	ND	ND	**Nd**				**Pt**	ND	ND	ND
Ca	H	H	H	**Nb**	ND	ND	ND	**Sm**				**Au**	ND	ND	ND
Ti	ND	ND	ND	**Mo**	ND	ND	ND	**Eu**				**Hg**	ND	ND	ND
V	ND	ND	ND	**Ru**	ND	ND	ND	**Gd**				**Tl**	ND	ND	ND
Cr	.5	ND	ND	**Rh**	ND	ND	ND	**Tb**				**Pb**	ND	ND	ND
Mn	2	ND	ND	**Pd**	ND	ND	ND	**Dy**				**Bi**	ND	ND	ND
Fe	5	ND	.1	**Ag**	ND	ND	ND	**Ho**				**Th**			
Co	ND	ND	ND	**Cd**	ND	ND	ND	**Er**				**U**			
Ni	ND	ND	ND	**In**	ND	ND	ND	**Tm**				**P**	ND	ND	ND
Cu	5	ND	ND	**Sn**	ND	ND	ND	**Yb**				**Se**			

REMARKS: 1 = CaF_2 Powder (Fisher)
2 = VHP #272
3 = VHP #273

Results in ppm.

KEY:			
ND - Not Detected		T	.01 - .1%
VVFT	< .0001%	L	.1 - 1%
VFT	.0001% - .001%	M	1% - 10%
FT	.001% - .01%	H	>10%

STAFF ANALYST

SUPERVISOR, TESTING LABS

can be seen, the teflon-treated material has the lowest cation impurity content, containing only alkaline earth impurities (Mg, Sr, and Ba) with no Na, Al, Cr, Mn, Fe, or Cu as is present in the as-received powder. The untreated casting is somewhat improved over the as-received powder but is not as impurity-free as teflon-treated material. The casting analyses compare (except for Mg, Sr, and Ba) with those of single crystal chips and castings made from such chips which have small amounts of Mg, Si, Cu and possibly Al and Fe for total analyzed cation impurity levels of 1.7 ppm and 1.1 ppm, respectively.[1] Table IV gives the limits of detection of impurities in CaF_2 in these analyses.

In Tables V and VI are the results of the analyses on the following SrF_2 samples: Table V — 1) As-received "reagent" grade powder, 2) Vacuum-baked powder, and 3) A casting (VHP-358, a remelt of VHP-357) initially using vacuum-baked powder and Table VI – 1) A casting (VHP-390) using 600°C teflon-treated and air-roasted powder, 2) A casting (VHP-393, a remelt) using 600°C teflon-treated and air-roasted powder, 3) A casting (VHP-394) using 600°C teflon-treated — no subsequent roast-powder, and 4) A casting (VHP-399) using teflon-treated material. Table VII gives the limits of detection of impurities in SrF_2 in these analyses.

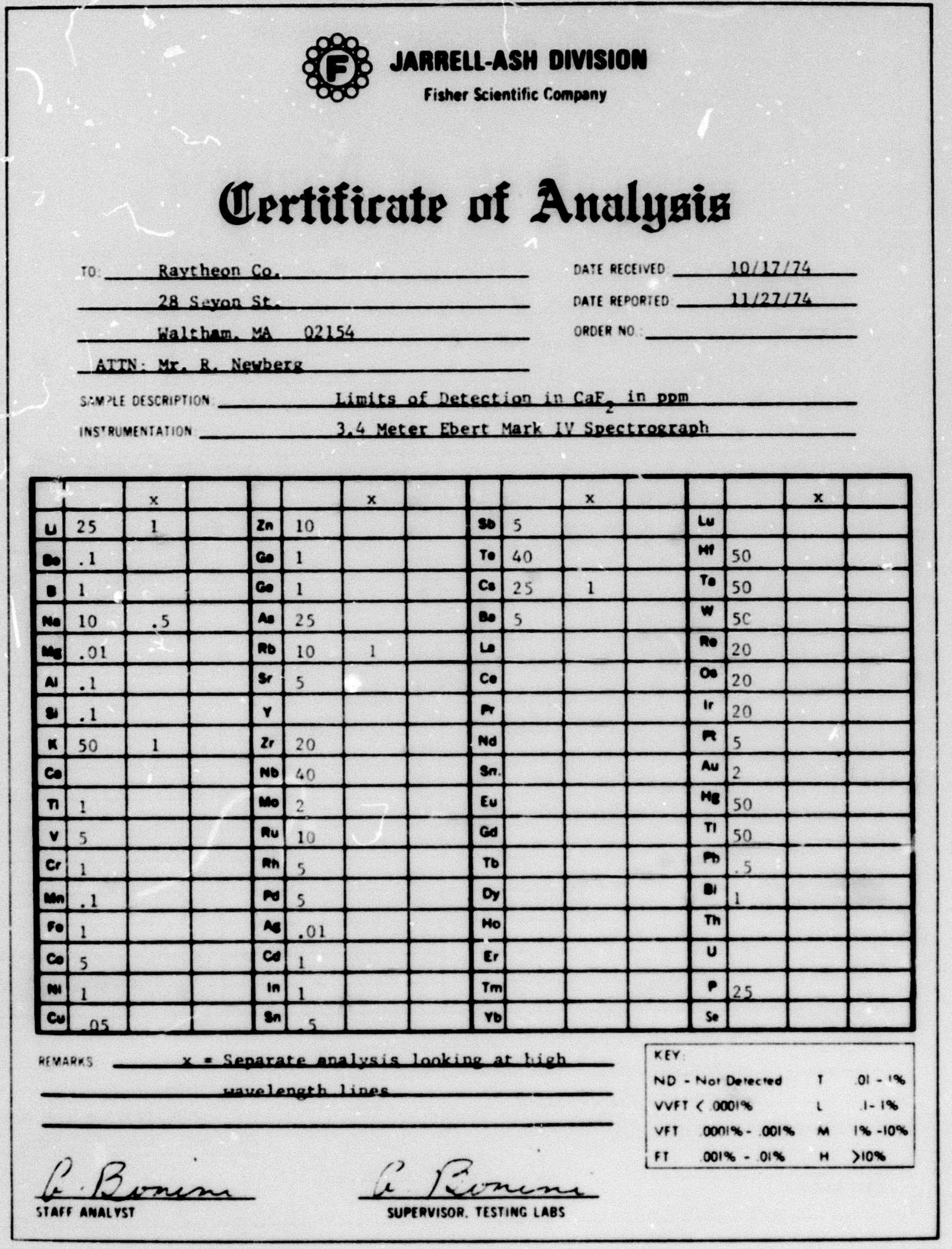
As can be seen in Tables V and VI, the as-received powder, vacuum-baked powder, and the casting from such are all rich in impurities as is the casting (VHP-390) from teflon-treated, air roasted powder. The casting (VHP-394) using teflon-treated-no roast-powder and the two remelts of powder (VHP-393 and 399) have mainly alkaline earth impurity (Ba, Ca, and Mg) contamination. Single crystal chips and a casting from such chips had similar alkaline earths as contaminants but at different levels of contamination.[1]

Clearly, these results show that castings of both CaF_2 and SrF_2 can be obtained with low cation impurity levels (with the exception of the alkaline earths) as was the case for ingots cast using single crystal chips.

As mentioned above, the early castings of SrF_2 and CaF_2 prepared from purified powder (and several castings prepared from single crystal chips) seemed quite susceptible to thermal shock cracking, being predominantly intergranular in nature. This behavior suggested weakened grain boundaries due to

TABLE IV

LIMITS OF DETECTION FOR ANALYSIS OF CaF_2 SAMPLES



JARRELL-ASH DIVISION
Fisher Scientific Company

Certificate of Analysis

TO: Raytheon Co.
28 Seyon St.
Waltham, MA 02154
ATTN: Mr. R. Newberg

DATE RECEIVED: 10/17/74
DATE REPORTED: 11/27/74
ORDER NO.:

SAMPLE DESCRIPTION: Limits of Detection in CaF_2 in ppm
INSTRUMENTATION: 3.4 Meter Ebert Mark IV Spectrograph

		x				x				x				x	
Li	25	1		Zn	10			Sb	5			Lu			
Be	.1			Ga	1			Te	40			Hf	50		
B	1			Ge	1			Cs	25	1		Ta	50		
Na	10	.5		As	25			Ba	5			W	5C		
Mg	.01			Rb	10	1		La				Re	20		
Al	.1			Sr	5			Ce				Os	20		
Si	.1			Y				Pr				Ir	20		
K	50	1		Zr	20			Nd				Pt	5		
Ca				Nb	40			Sm				Au	2		
Ti	1			Mo	2			Eu				Hg	50		
V	5			Ru	10			Gd				Tl	50		
Cr	1			Rh	5			Tb				Pb	.5		
Mn	.1			Pd	5			Dy				Bi	1		
Fe	1			Ag	.01			Ho				Th			
Co	5			Cd	1			Er				U			
Ni	1			In	1			Tm				P	25		
Cu	.05			Sn	.5			Yb				Se			

REMARKS: x = Separate analysis looking at high wavelength lines

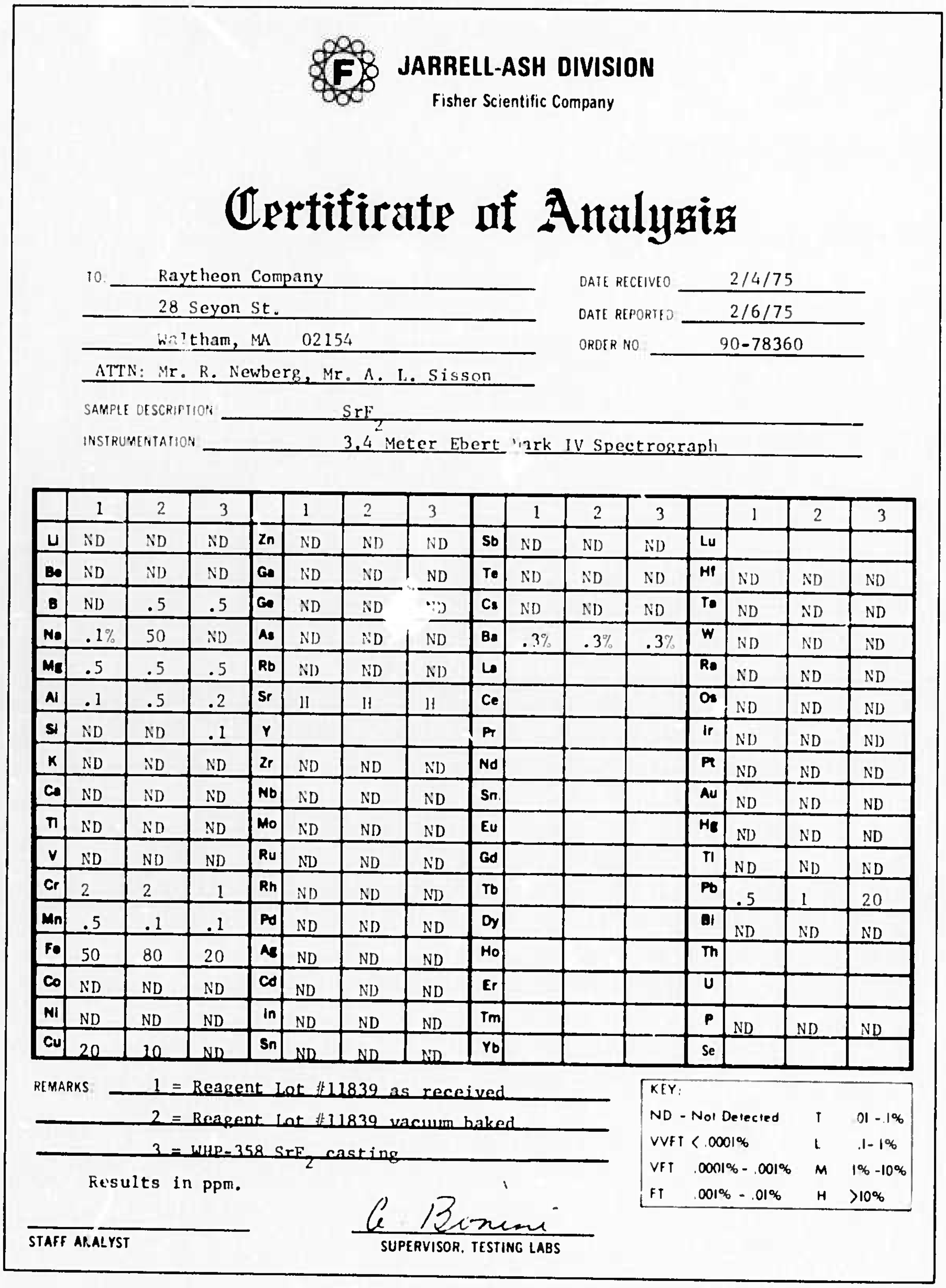
KEY:
ND - Not Detected
VVFT < .0001%
VFT .0001% - .001%
FT .001% - .01%
T .01 - 1%
L .1 - 1%
M 1% - 10%
H >10%

C. Bonini
STAFF ANALYST

C. Bonini
SUPERVISOR, TESTING LABS

TABLE V

ANALYSES OF "REAGENT" GRADE SrF_2 SAMPLES



JARRELL-ASH DIVISION
Fisher Scientific Company

Certificate of Analysis

TO: Raytheon Company
28 Seyon St.
Waltham, MA 02154
ATTN: Mr. R. Newberg, Mr. A. L. Sisson

DATE RECEIVED: 2/4/75
DATE REPORTED: 2/6/75
ORDER NO: 90-78360

SAMPLE DESCRIPTION: SrF_2
INSTRUMENTATION: 3,4 Meter Ebert Mark IV Spectrograph

	1	2	3		1	2	3		1	2	3		1	2	3
Li	ND	ND	ND	Zn	ND	ND	ND	Sb	ND	ND	ND	Lu			
Be	ND	ND	ND	Ga	ND	ND	ND	Te	ND	ND	ND	Hf	ND	ND	ND
B	ND	.5	.5	Ge	ND	ND	ND	Cs	ND	ND	ND	Ta	ND	ND	ND
Na	.1%	50	ND	As	ND	ND	ND	Ba	.3%	.3%	.3%	W	ND	ND	ND
Mg	.5	.5	.5	Rb	ND	ND	ND	La				Re	ND	ND	ND
Al	.1	.5	.2	Sr	H	H	H	Ce				Os	ND	ND	ND
Si	ND	ND	.1	Y				Pr				Ir	ND	ND	ND
K	ND	ND	ND	Zr	ND	ND	ND	Nd				Pt	ND	ND	ND
Ca	ND	ND	ND	Nb	ND	ND	ND	Sm				Au	ND	ND	ND
Ti	ND	ND	ND	Mo	ND	ND	ND	Eu				Hg	ND	ND	ND
V	ND	ND	ND	Ru	ND	ND	ND	Gd				Tl	ND	ND	ND
Cr	2	2	1	Rh	ND	ND	ND	Tb				Pb	.5	1	20
Mn	.5	.1	.1	Pd	ND	ND	ND	Dy				Bi	ND	ND	ND
Fe	50	80	20	Ag	ND	ND	ND	Ho				Th			
Co	ND	ND	ND	Cd	ND	ND	ND	Er				U			
Ni	ND	ND	ND	In	ND	ND	ND	Tm				P	ND	ND	ND
Cu	20	10	ND	Sn	ND	ND	ND	Yb				Se			

REMARKS: 1 = Reagent Lot #11839 as received
2 = Reagent Lot #11839 vacuum baked
3 = WHP-358 SrF_2 casting

Results in ppm.

KEY:

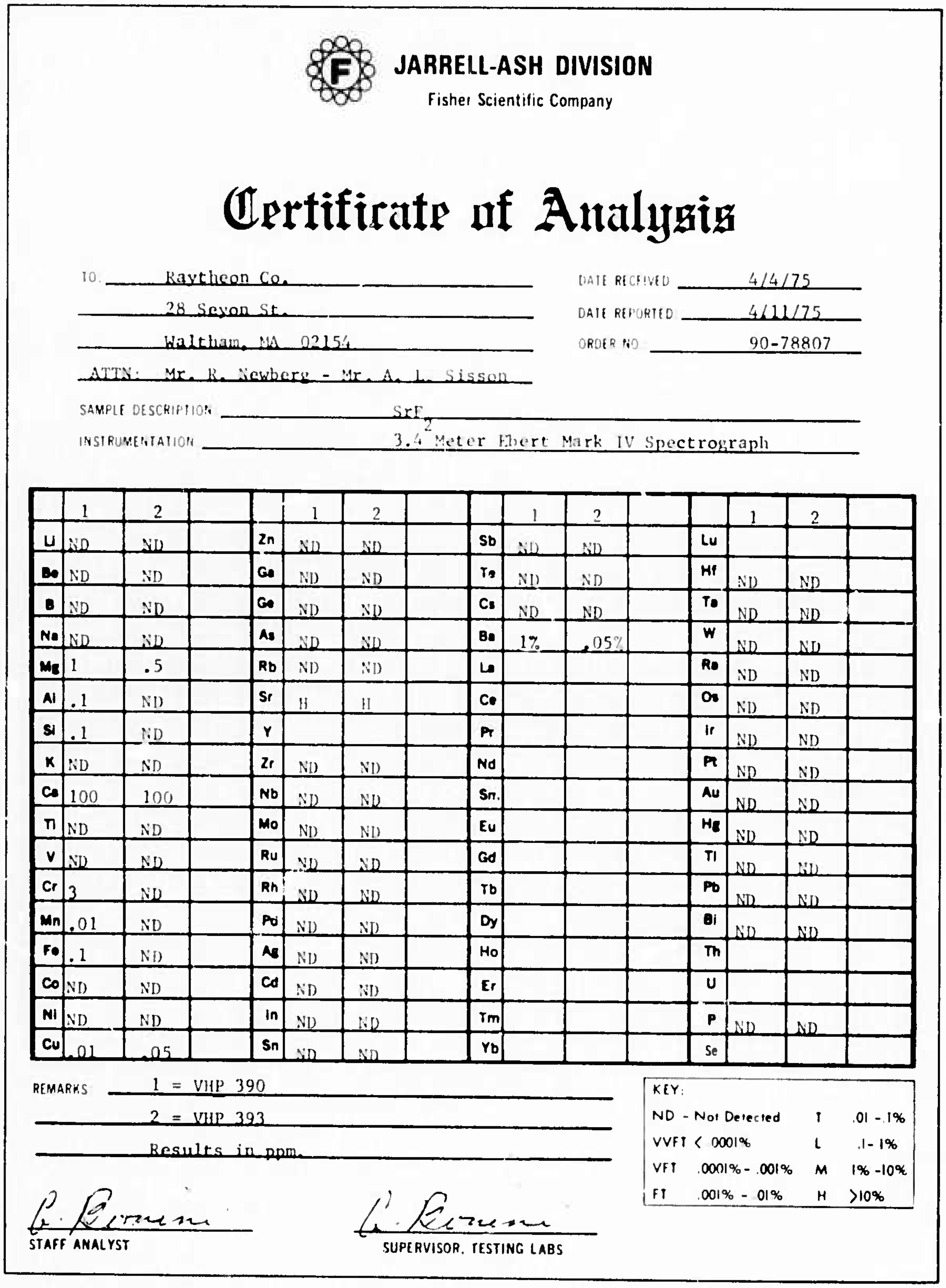
ND - Not Detected		T	.01 - .1%
VVFT	< .0001%	L	.1 - 1%
VFT	.0001% - .001%	M	1% - 10%
FT	.001% - .01%	H	>10%

STAFF ANALYST

Bonini
SUPERVISOR, TESTING LABS

TABLE VI

ANALYSES OF "REAGENT" GRADE SrF_2 SAMPLES



JARRELL-ASH DIVISION
Fisher Scientific Company

Certificate of Analysis

TO: Raytheon Co.
28 Seyon St.
Waltham, MA 02154
ATTN: Mr. R. Newberg - Mr. A. L. Sisson

DATE RECEIVED 4/4/75
DATE REPORTED 4/11/75
ORDER NO. 90-78807

SAMPLE DESCRIPTION SrF_2
INSTRUMENTATION 3.4 Meter Ebert Mark IV Spectrograph

	1	2			1	2			1	2			1	2	
Li	ND	ND		Zn	ND	ND		Sb	ND	ND		Lu			
Be	ND	ND		Ga	ND	ND		Te	ND	ND		Hf	ND	ND	
B	ND	ND		Ge	ND	ND		Cs	ND	ND		Ta	ND	ND	
Na	ND	ND		As	ND	ND		Ba	1%	.05%		W	ND	ND	
Mg	1	.5		Rb	ND	ND		La				Re	ND	ND	
Al	.1	ND		Sr	H	H		Ce				Os	ND	ND	
Si	.1	ND		Y				Pr				Ir	ND	ND	
K	ND	ND		Zr	ND	ND		Nd				Pt	ND	ND	
Ca	100	100		Nb	ND	ND		Sm				Au	ND	ND	
Ti	ND	ND		Mo	ND	ND		Eu				Hg	ND	ND	
V	ND	ND		Ru	ND	ND		Gd				Tl	ND	ND	
Cr	3	ND		Rh	ND	ND		Tb				Pb	ND	ND	
Mn	.01	ND		Pd	ND	ND		Dy				Bi	ND	ND	
Fe	.1	ND		Ag	ND	ND		Ho				Th			
Co	ND	ND		Cd	ND	ND		Er				U			
Ni	ND	ND		In	ND	ND		Tm				P	ND	ND	
Cu	.01	.05		Sn	ND	ND		Yb				Se			

REMARKS 1 = VHP 390
2 = VHP 393
Results in ppm.

KEY:

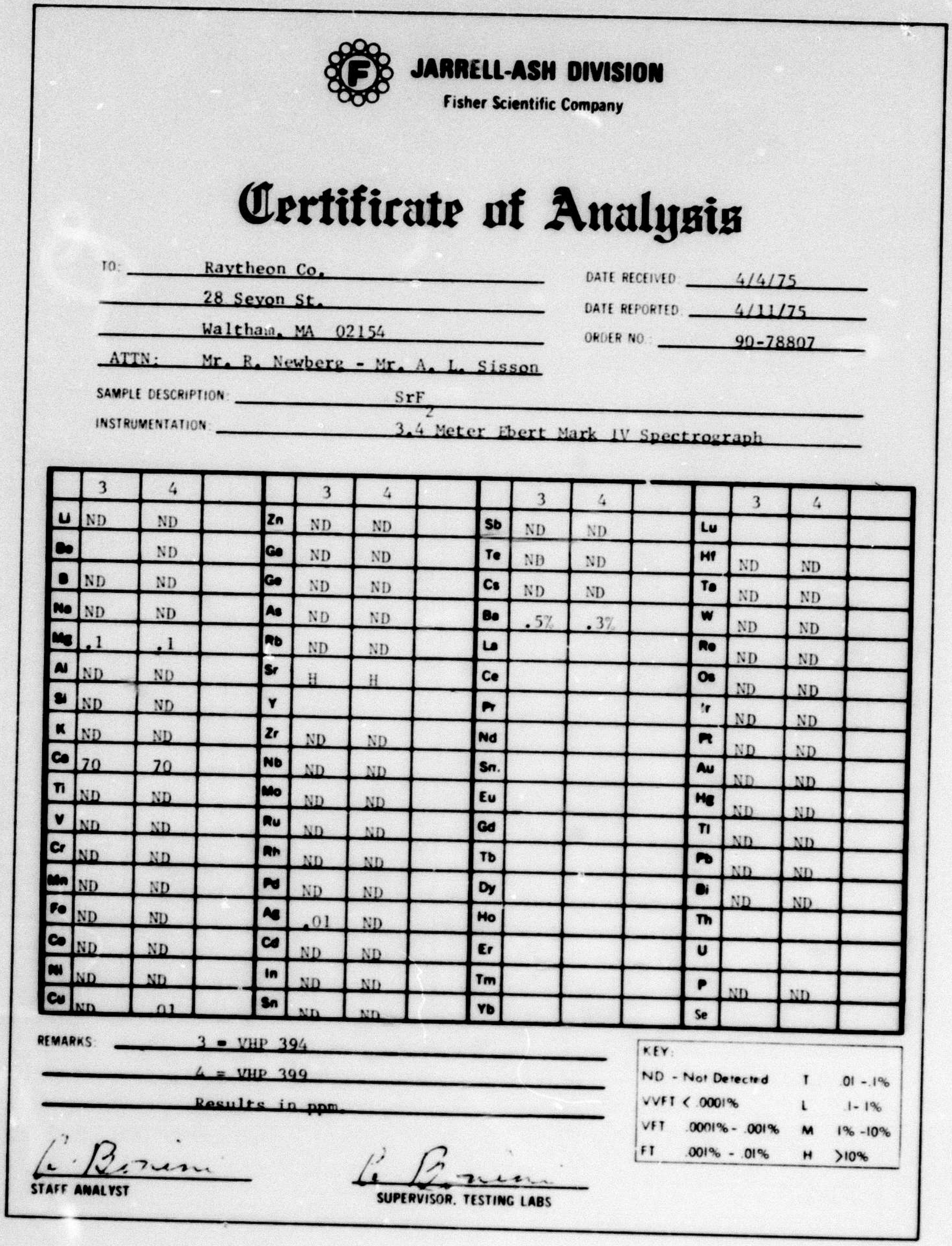
ND - Not Detected		T	.01 -.1%
VVFT	< .0001%	L	.1- 1%
VFT	.0001% - .001%	M	1% -10%
FT	.001% - .01%	H	>10%

STAFF ANALYST

SUPERVISOR, TESTING LABS

TABLE VI (Cont'd.)

ANALYSES OF "REAGENT" GRADE SrF_2 SAMPLES



JARRELL-ASH DIVISION
Fisher Scientific Company

Certificate of Analysis

TO: Raytheon Co.
28 Seyon St.
Waltham, MA 02154
ATTN: Mr. R. Newberg - Mr. A. L. Sisson

DATE RECEIVED: 4/4/75
DATE REPORTED: 4/11/75
ORDER NO.: 90-78807

SAMPLE DESCRIPTION: SrF_2
INSTRUMENTATION: 3.4 Meter Ebert Mark IV Spectrograph

	3	4			3	4			3	4			3	4	
Li	ND	ND		Zn	ND	ND		Sb	ND	ND		Lu			
Be		ND		Ga	ND	ND		Te	ND	ND		Hf	ND	ND	
B	ND	ND		Ge	ND	ND		Cs	ND	ND		Ta	ND	ND	
Na	ND	ND		As	ND	ND		Ba	.5%	.3%		W	ND	ND	
Mg	.1	.1		Rb	ND	ND		La				Re	ND	ND	
Al	ND	ND		Sr	H	H		Ce				Os	ND	ND	
Si	ND	ND		Y				Pr				Ir	ND	ND	
K	ND	ND		Zr	ND	ND		Nd				Pt	ND	ND	
Ca	70	70		Nb	ND	ND		Sm				Au	ND	ND	
Ti	ND	ND		Mo	ND	ND		Eu				Hg	ND	ND	
V	ND	ND		Ru	ND	ND		Gd				Tl	ND	ND	
Cr	ND	ND		Rh	ND	ND		Tb				Pb	ND	ND	
Mn	ND	ND		Pd	ND	ND		Dy				Bi	ND	ND	
Fe	ND	ND		Ag	.01	ND		Ho				Th			
Co	ND	ND		Cd	ND	ND		Er				U			
Ni	ND	ND		In	ND	ND		Tm				P	ND	ND	
Cu	ND	.01		Sn	ND	ND		Yb				Se			

REMARKS: 3 = VHP 394
4 = VHP 399
Results in ppm.

KEY:

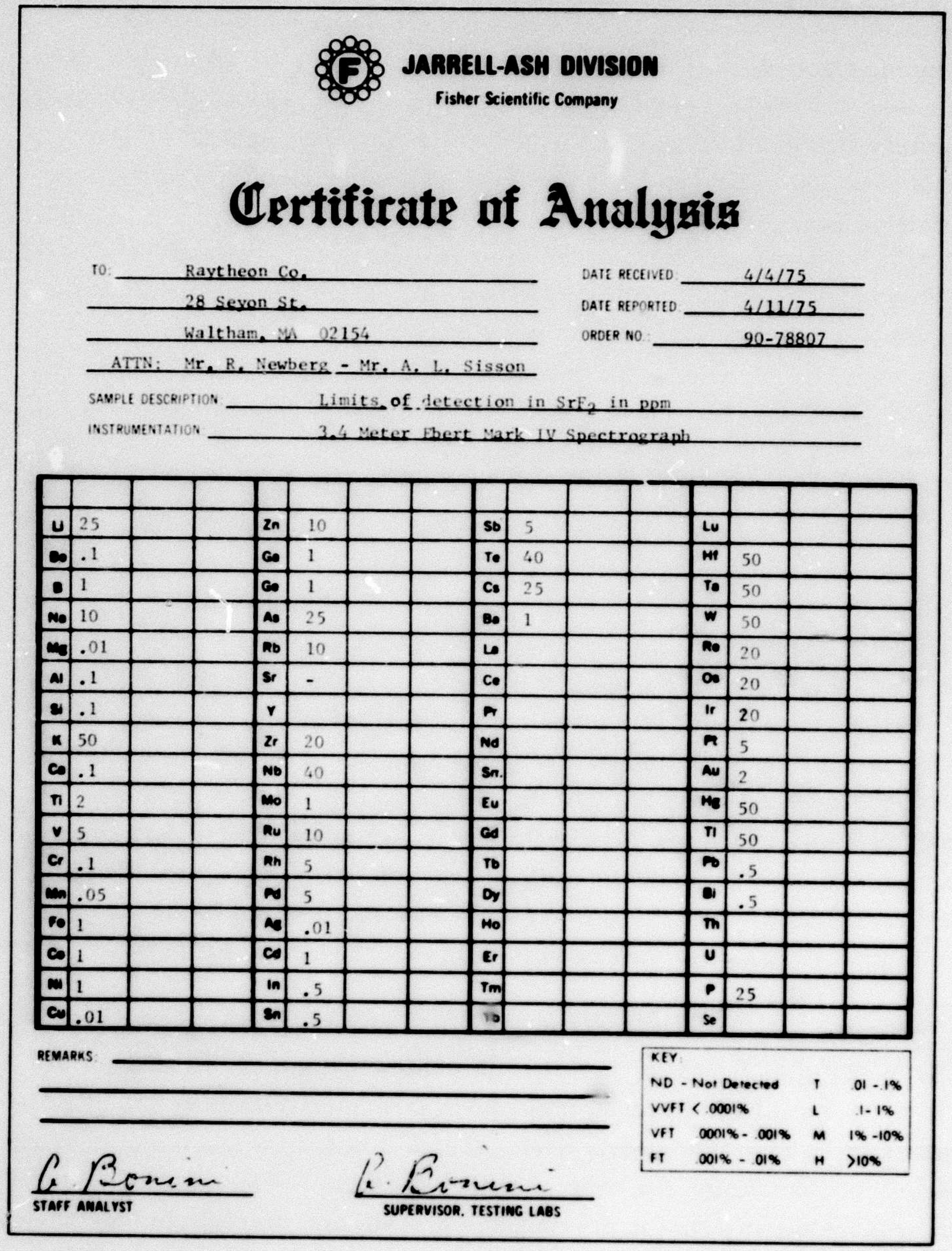
ND - Not Detected		T	.01 - .1%
VVFT	< .0001%	L	.1 - 1%
VFT	.0001% - .001%	M	1% - 10%
FT	.001% - .01%	H	>10%

STAFF ANALYST

SUPERVISOR, TESTING LABS

TABLE VII

LIMITS OF DETECTION FOR ANALYSIS OF SrF_2 SAMPLES



JARRELL-ASH DIVISION
Fisher Scientific Company

Certificate of Analysis

TO: Raytheon Co.
28 Seyon St.
Waltham, MA 02154
ATTN: Mr. R. Newberg - Mr. A. L. Sisson

DATE RECEIVED: 4/4/75
DATE REPORTED: 4/11/75
ORDER NO.: 90-78807

SAMPLE DESCRIPTION: Limits of detection in SrF_2 in ppm
INSTRUMENTATION: 3.4 Meter Ebert Mark IV Spectrograph

Li	25			Zn	10			Sb	5			Lu			
Be	.1			Ga	1			Te	40			Hf	50		
B	1			Ge	1			Cs	25			Ta	50		
Na	10			As	25			Ba	1			W	50		
Mg	.01			Rb	10			La				Re	20		
Al	.1			Sr	-			Ce				Os	20		
Si	.1			Y				Pr				Ir	20		
K	50			Zr	20			Nd				Pt	5		
Ca	.1			Nb	40			Sm				Au	2		
Ti	2			Mo	1			Eu				Hg	50		
V	5			Ru	10			Gd				Tl	50		
Cr	.1			Rh	5			Tb				Pb	.5		
Mn	.05			Pd	5			Dy				Bi	.5		
Fe	1			Ag	.01			Ho				Th			
Co	1			Cd	1			Er				U			
Ni	1			In	.5			Tm				P	25		
Cu	.01			Sn	.5			Yb				Se			

REMARKS:

KEY:
ND - Not Detected T .01 - .1%
VVFT < .0001% L .1 - 1%
VFT .0001% - .001% M 1% - 10%
FT .001% - .01% H >10%

C. Bonini
STAFF ANALYST

C. Bonini
SUPERVISOR, TESTING LABS

impurity precipitation and led to further investigation which solved the problem as mentioned above. Samples of three cast fluorides – BaF_2, SrF_2, and CaF_2 (VHP-147, 311, and 317, respectively) that failed intergranularly were investigated by X-ray microprobe analysis and SEM (scanning electron microscopy). Microprobe analysis of impurities and their distribution in these samples indicated a weak, uniformly distributed contamination of Al (in CaF_2 and BaF_2), Ca (in SrF_2), and Sr (in BaF_2). In addition, the grain boundary surfaces showed localized accumulations containing predominantly Na, S, Cl, K and occasionally also Mg, Si, Fe, and Zn. These accumulations seemed to be located in surface irregularities such as holes, cracks, and precipitates. To obtain a clearer correlation between surface appearance and impurity content, magnified maps of the grain boundary surfaces were produced from overlapping SEM pictures. Specific irregularities were identified and subjected to microprobe analysis, the results of which follow.

Figures 3 and 4 illustrate the example of BaF_2 (VHP-147). Figure 3a shows the general surface area with irregularity at the intersection of two grains. The precipitate is shown at higher magnification in Fig. 3b. Care was taken to avoid contamination of the surfaces during handling, but it is not entirely clear in this case if the precipitate is not a result of handling. Figure 4a is the overall X-ray spectra from microprobe analysis of both the general uniform distribution of the grain boundary surface (designated matrix) and the precipitate (designated location 1). Figure 4b is the stripped X-ray spectrum of the precipitate; i.e., the matrix spectrum is subtracted from the precipitate spectrum. Any differences in impurity concentrations between the two are shown as sharp peaks in the stripped spectrum. In this case the precipitate is enriched in K, S, and Cl.

Similarly, Figs. 5a and 5b show the grain boundary fracture surface of SrF_2 (VHP-311) with several irregularities and a magnification of a similar irregularity, respectively. Such irregularities appear to be precipitates torn from the matrix during fracture and are clearly not contaminants from handling. Figures 6a and 6b show the X-ray spectra for the two areas – the matrix (no precipitates probed) and precipitate (designated location 1, the latter showing the area to be enriched in Na, K, and Cl.

Fig. 3a Fracture Surface of Cast BaF_2 Sample. SEM 200×

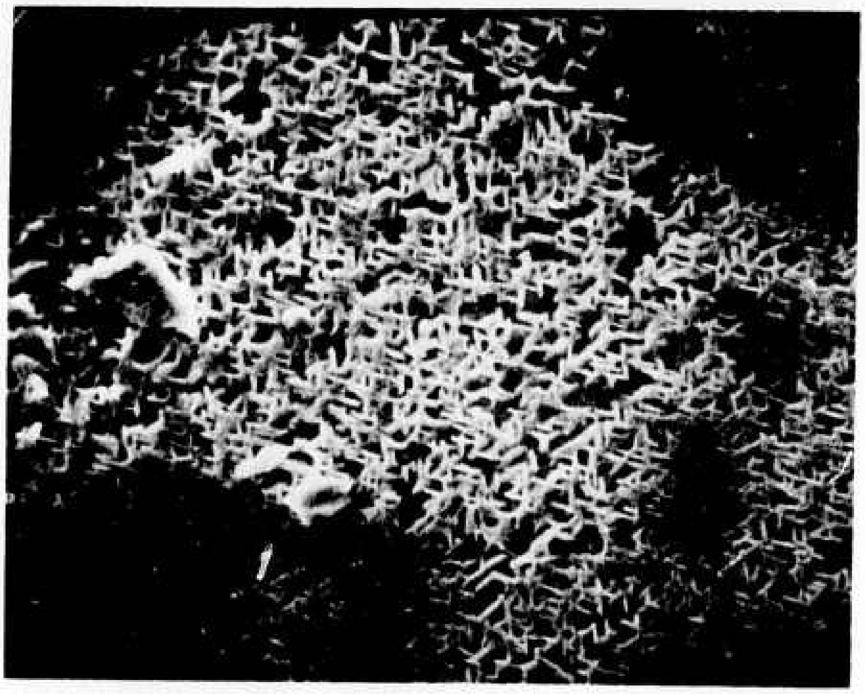


Fig. 3b Precipitate Area at Fracture Surface of Cast BaF_2 Sample. SEM 2000×

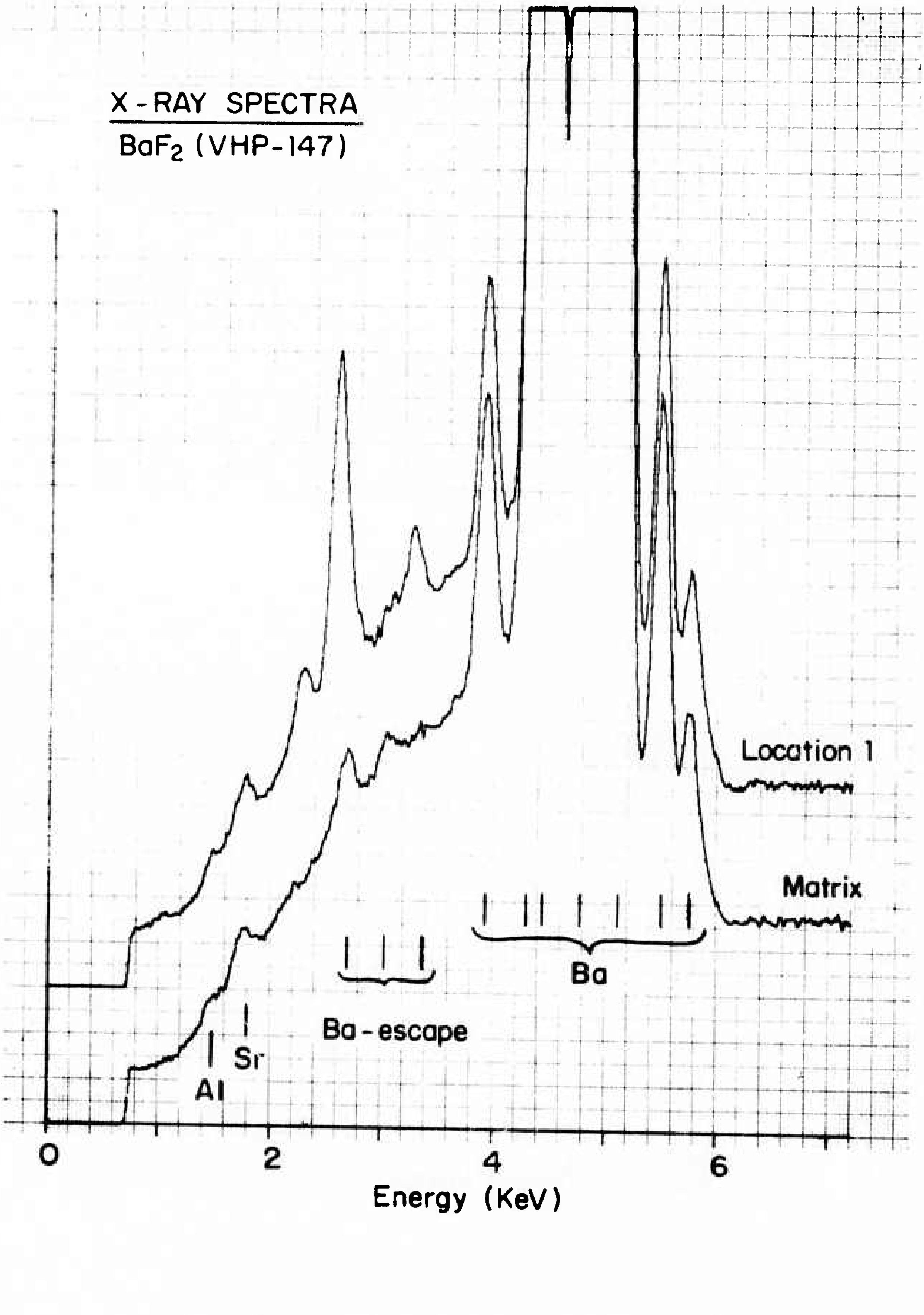
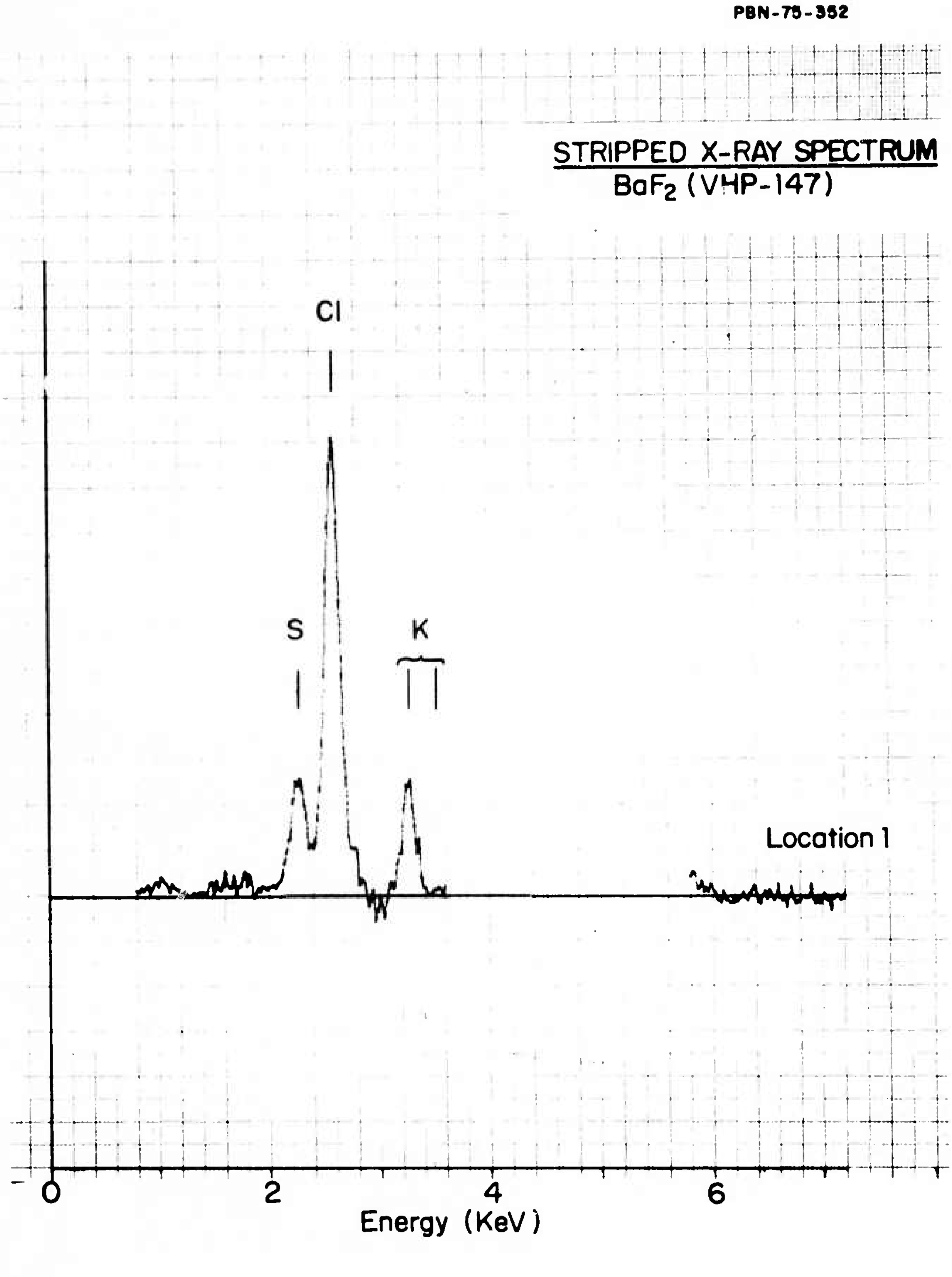


Fig. 4a X-Ray Spectra of Cast BaF_2 Sample



4b Stripped X-Ray Spectrum of Cast BaF$_2$ Sample

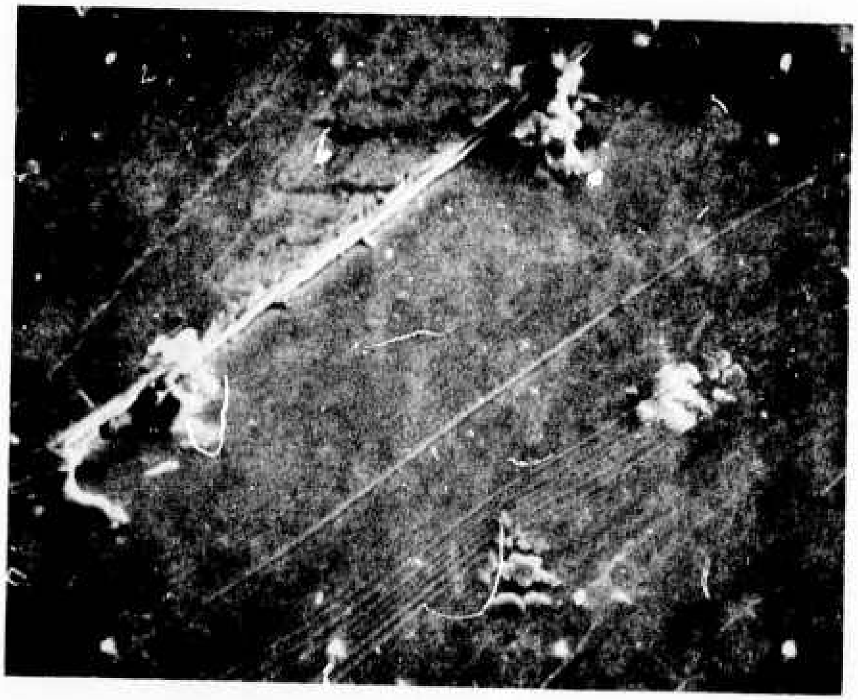


Fig. 5a Fracture Surface of Cast SrF_2 Sample. SEM 700×

Fig 5b Fracture Surface of Cast SrF_2 Sample. SEM 2000×

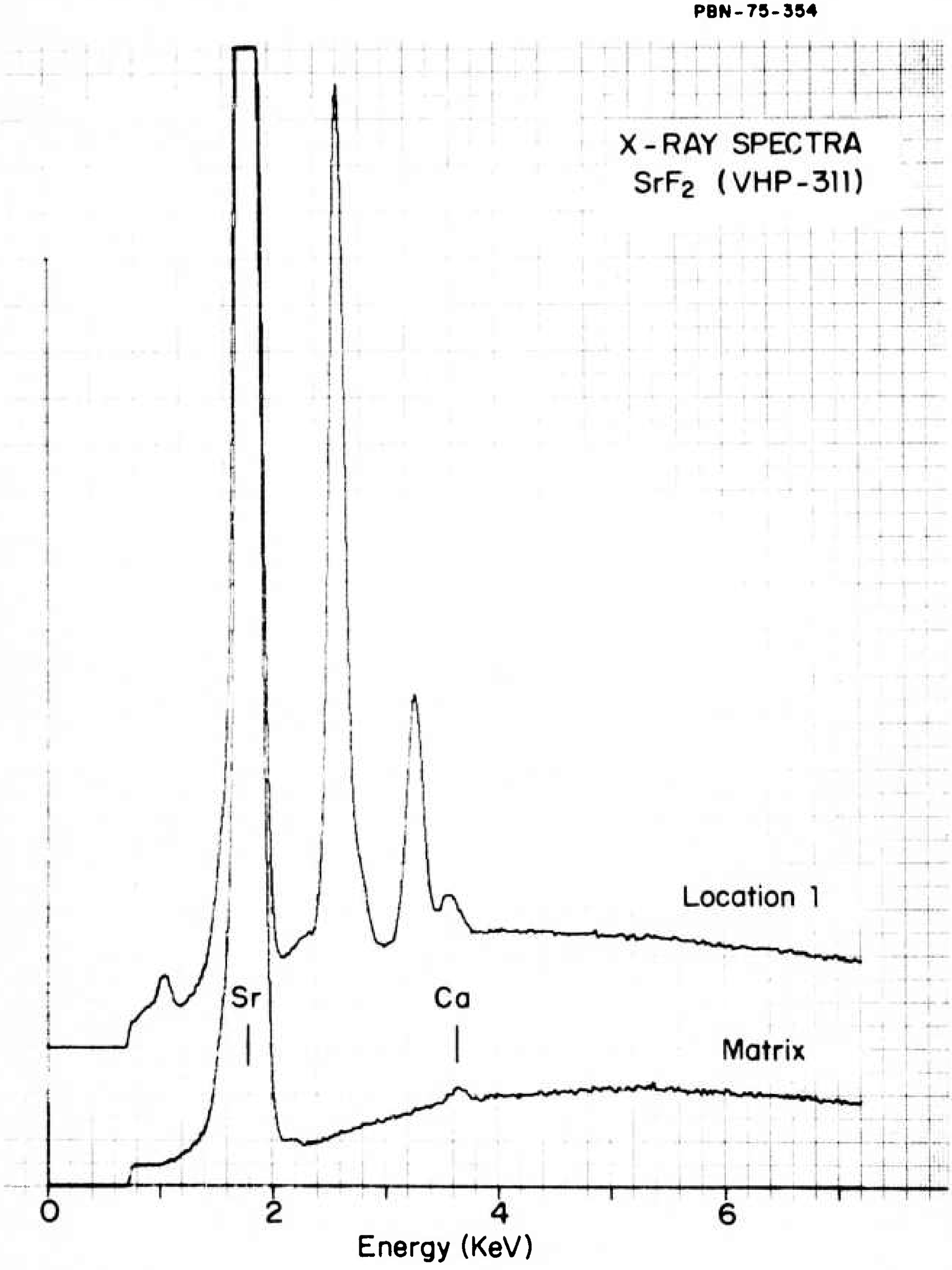


Fig. 6a X-Ray Spectra of Cast SrF_2 Sample

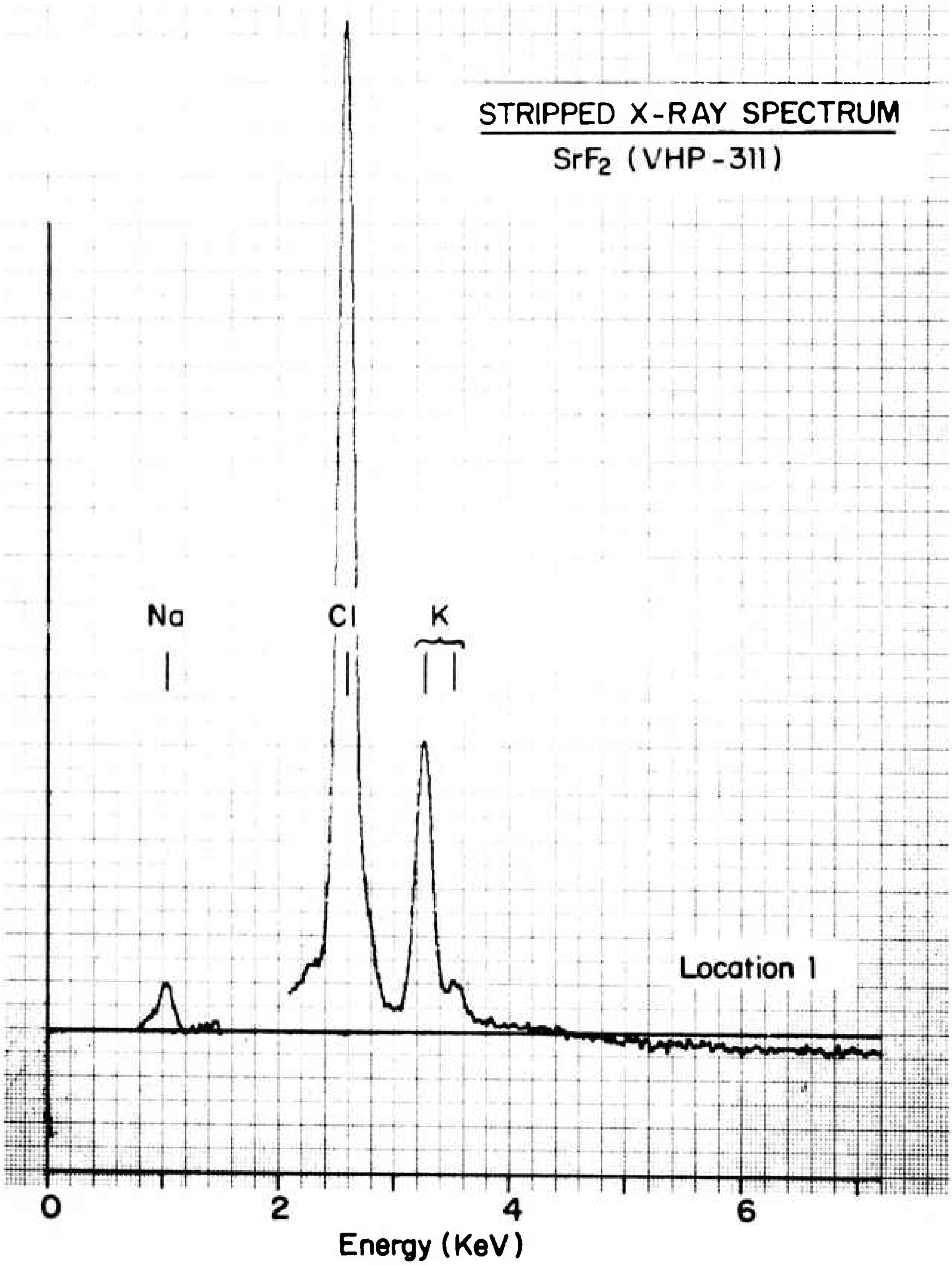


Fig. 6b Stripped X-Ray Spectrum of Cast SrF_2 Sample

Finally, Figs. 7a - e show similar grain boundary surfaces of cast CaF_2 (VHP-317) and three quite different surface irregularities (designated locations 1, 2, and 3 in the X-ray spectra of Figs. 8a and 8b). It can also be noted (Figs. 7a and 7b) by the ripply effect of the general surface that true intergranular failure occurred, whereas for the BaF_2 and SrF_2, cleavage steps are also present. From the X-ray spectra of Fig. 8a it can be seen that the CaF_2 matrix has few impurities. However, the irregularities are quite rich and substantially different from each other, as best seen in the stripped X-ray spectra of Fig. 8b. The protruding mass of location 1 is enriched mainly in Mg, Al, Si, and Fe; while what appears to be a hole at location 2 is enriched in Si, S, Cl, and K. Finally, the white precipitate at location 3 is enriched mainly in Na, Si, Cl, and K.

The above results indicate that the bulk of the contamination may be localized in accumulations at the grain boundaries. Whether or not these impurities seriously affect the mechanical properties (such as thermal shock resistance) is not quantitatively known. Further effort is being planned to fully evaluate their effect.

2.2 Inert Atmosphere Casting

During this period, work was initiated to develop a casting technique in an inert atmosphere instead of the high vacuum (10^{-4} torr or better) required normally. The advantage of inert atmosphere operation is that unidirectional solidification may be better accomplished due to the better heat transfer provided by the gas. It is also desirable because, in the event of scale-up to larger sizes, an inert atmosphere may be less expensive and more convenient to provide than a high vacuum system.

A series of castings of CaF_2 were attempted in the vacuum hot press furnace using dry, high purity argon (passed over titanium chips at 800 - 900°C to remove residual H_2O and O_2) to provide partial pressures of 1, 5, 15, 25, and 50 torr. The castings are listed in Table 1. As expected, better heat transfer resulted in complete unidirectional solidification in all but two of the castings (VHP-301 and 317). However, except for these same two castings, as well as VHP-375, the inert atmosphere castings were all

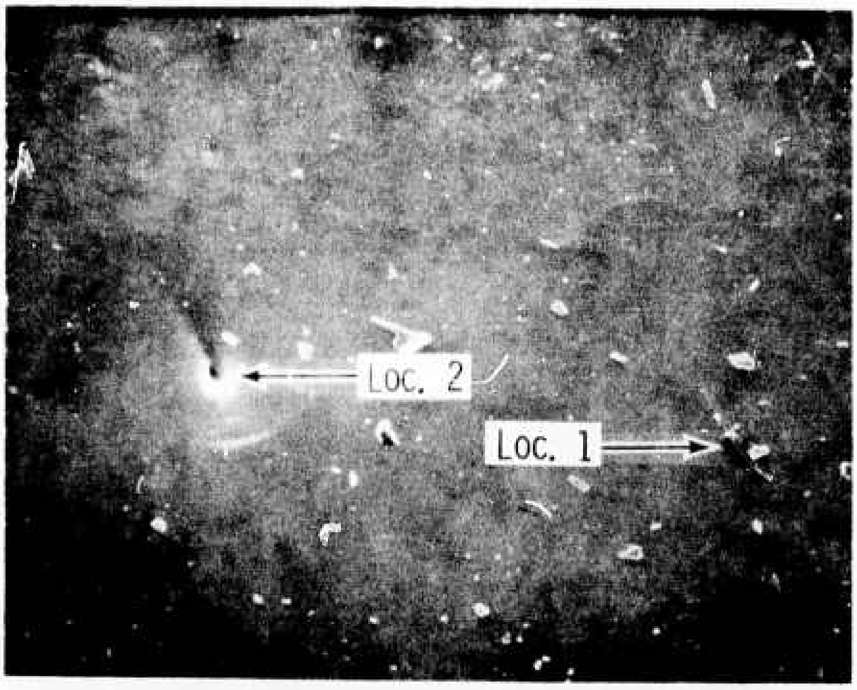


Fig. 7a Fracture Surface of Cast CaF_2 Sample. SEM 100×

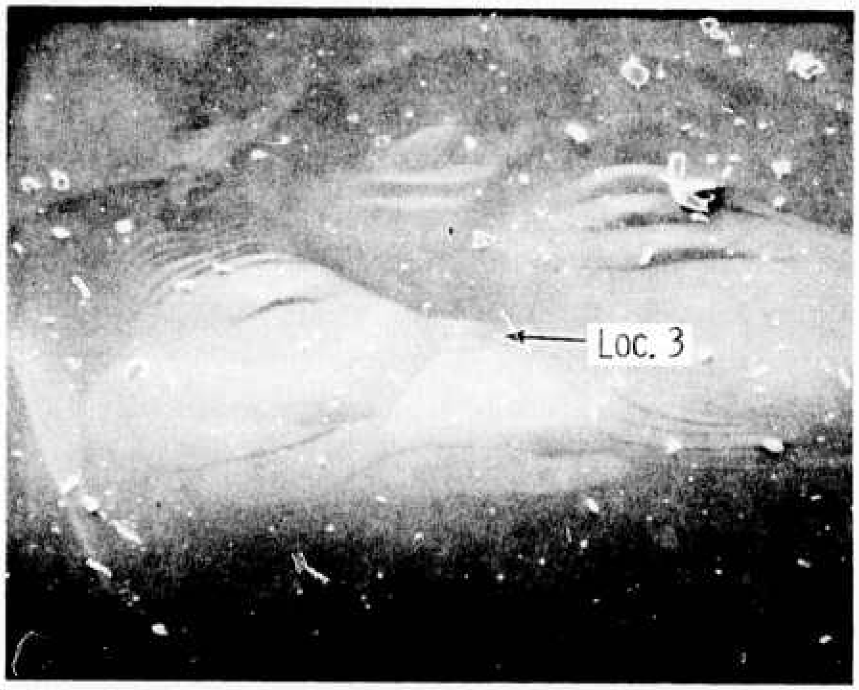


Fig. 7b Fracture Surface of Cast CaF_2 Sample. SEM 100×

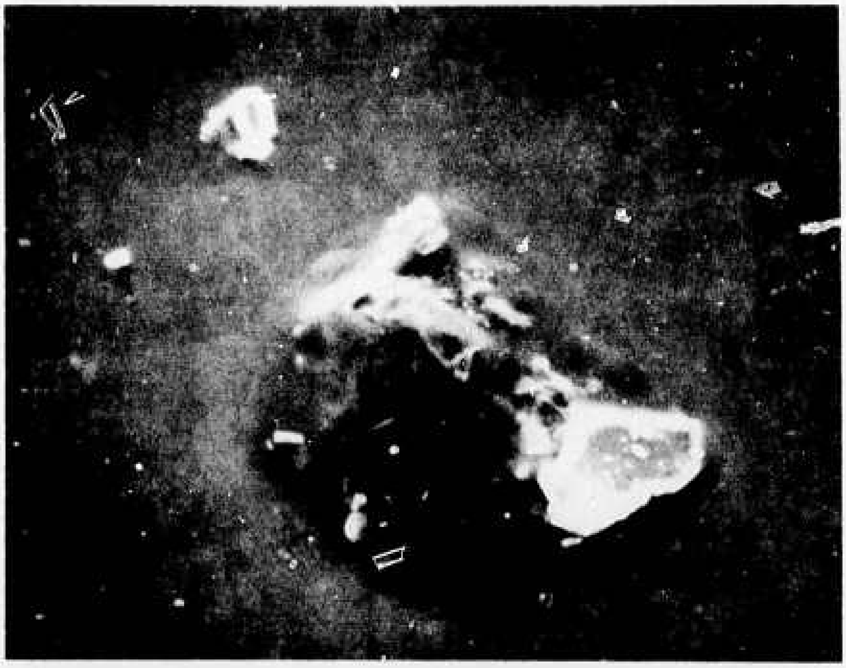


Fig. 7c Location 1. SEM 1000 ×

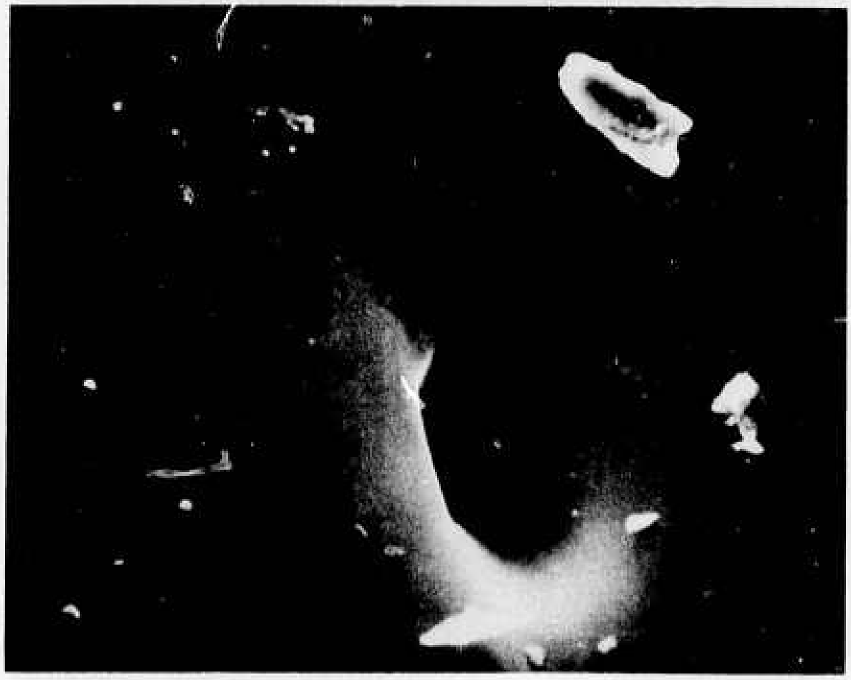


Fig. 7d Location 2. SEM 1000 ×

Fig. 7e Location 3. SEM 3000 ×

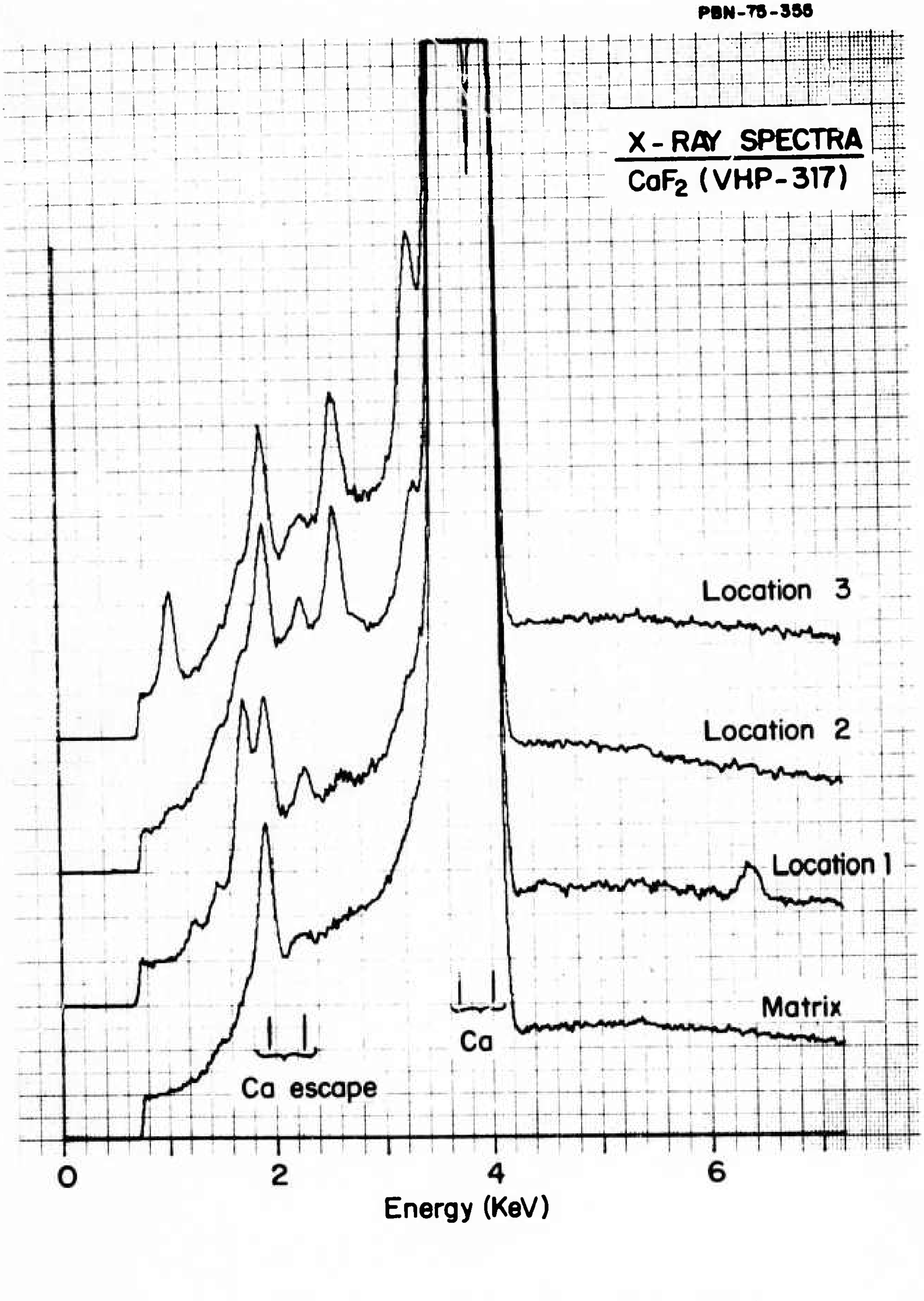


Fig. 8a X-Ray Spectra of Cast CaF_2 Sample

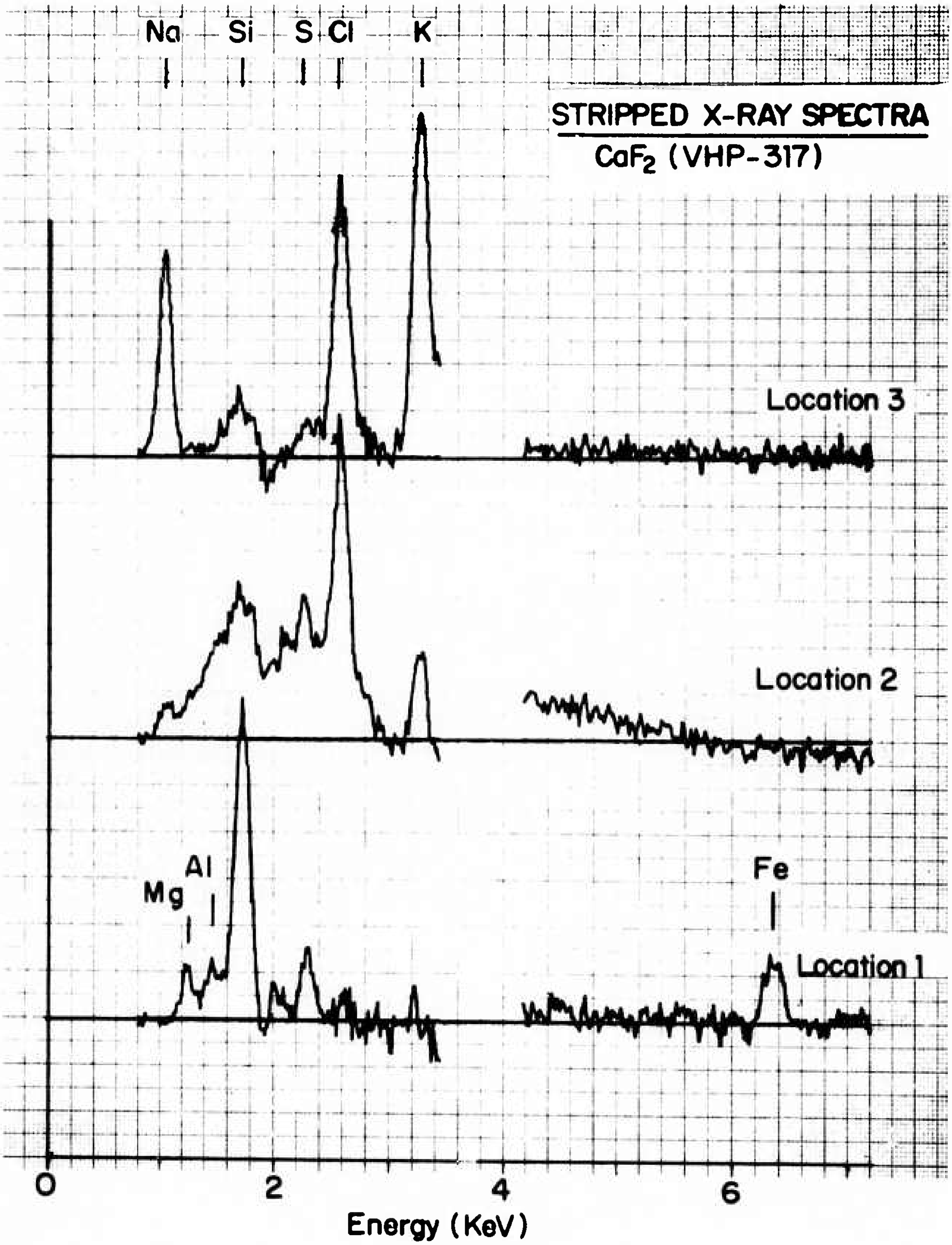


Fig. 8b Stripped X-Ray Spectra of Cast CaF_2 Sample

slightly discolored (a yellowish to bluish tinge) indicating that the atmosphere was not sufficiently inert and that there was impurity pickup in the castings. Further attempts are presently under way to improve the technique.

2.3 Hot Forging

During this reporting period only two hot forgings were attempted, as listed in Table I. One-inch diameter samples were core drilled from a polycrystalline casting of CaF_2 (VHP-302 and 303) in the vacuum hot press furnace. Both were successfully forged, but, as was the case with hot forged single crystal samples of CaF_2,[1] the resultant grain size was large (on the order of several millimeters) due to the high forging temperature. No further work on hot forging is presently being planned because of the very good mechanical properties of the castings as will be discussed later.

2.4 Strain Annealing

One of the major problems with the fusion casting of the fluorides is the residual strain present in the ingots cast in the vacuum hot press furnace, due to rapid or uneven cooling. The problem was alleviated somewhat, as mentioned earlier, by the furnace modification allowing controlled cooling to room temperature from the solidification temperatures. However, the cast ingots still come out strained (Fig. 9) and must be strain-annealed prior to subsequent handling. The strain annealing procedure that has been used extensively during this period is the same as that developed during the first six months, i.e., annealing at 900°C for 10 hours followed by controlled cooling at 25°C/hr. to room temperature. Samples of cast SrF_2 thus annealed show marked strain reduction, but as Fig. 10 illustrates, the procedure is not entirely successful in producing completely strain-free material. However, with the strain reduction achieved, further handling of the cast ingots could be done, e.g., core drilling, cutting, grinding, and polishing, without marked susceptibility to cracking. However, with the installation of the high vacuum system for the two-zone annealing furnace, several attempts were made late in this period to anneal SrF_2 at a higher temperature, i.e., at

PBN-75-357

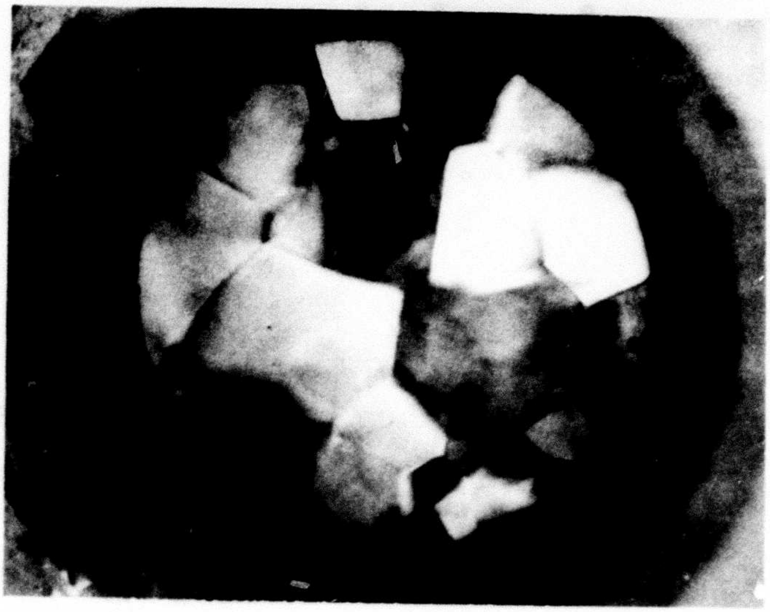


Fig. 9 Cast SrF_2, as Cast. Viewed through crossed polarizers.

PBN-75-88

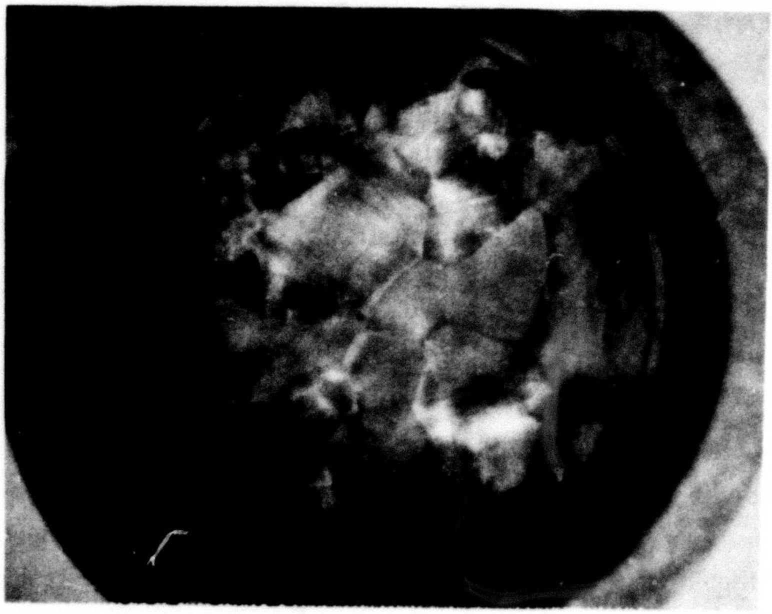


Fig. 10 Cast SrF_2 (VHP-343) After 900°C Anneal for 10 hrs. and Cooled at 25°C/hr. Viewed through crossed polarizers.

1000°C under high vacuum (10^{-4} - 10^{-5} torr). The initial results are successful as Fig. 11 illustrates. The ingot is fairly strain-free after annealing at 1000°C for 10 hours followed by controlled cooling at 25°C/hr. to room temperature.

During the third quarter, a large Lindberg box furnace was installed in the laboratory. It has heating and cooling capabilities at controlled rates of about 10 - 100°C/hr. (subject to the natural heating and cooling rates of the furnace) from room temperature to 1500°C.

By using an Inconel inert atmosphere retort (approximately 10 × 10 × 12 inches inner dimensions) preliminary strain anneal runs in an inert atmosphere were attempted in this furnace. Samples were one-inch diameter single crystals of CaF_2 (Optovac). The procedure for each heat treatment was to heat the furnace at 50°C/hr. to the soak temperature after purging the system as desired. The soak temperature (800, 900, or 1000°C) was held for ten hours, followed by cooling at 25°C/hr. to room temperature. Table VIII presents the results of these runs. The samples heated in air or argon at 1000°C showed fine white precipitates distributed either uniformly throughout (opacity) or as veils. Samples heated in argon or helium without sufficient purging at 900°C also showed some opacity. However, samples annealed at 800 or 900°C and properly purged with argon were as transparent as before and showed no scattering (as viewed with a He-Ne laser beam). So for CaF_2, annealing at 900°C in argon may be a viable alternative to vacuum annealing at 900°C.

However, since vacuum annealing of SrF_2 was more successful at 1000°C and since the above results for CaF_2 indicate a maximum useful annealing capability in argon of only 900°C without impurity pickup, an alternative was tried. That is, the SrF_2 sample to be annealed is placed in a closed crucible with pieces of teflon and subsequently annealed at 1000°C, the teflon vapors providing a "purifying" atmosphere. The results of several runs were mixed but encouraging. That is, there is strain reduction but the procedure must be developed further before a final analysis is given.

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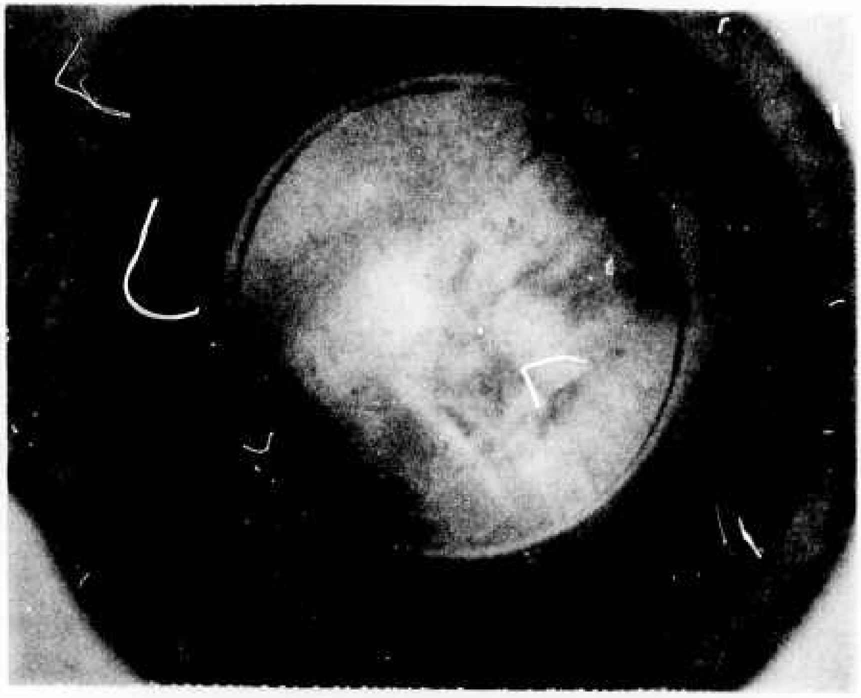

Fig. 11 Cast SrF_2 (VHP-395) After 1000°C Anneal for 10 hrs and Cooled at 25°C/hr. Viewed through crossed polarizers.

TABLE VIII

EFFECT OF HEAT TREATMENT ON CaF_2 SINGLE CRYSTALS

Heat Treatment Temperature (°C)	Atmosphere	Comments
1000	Air	Sample opaque
900	Argon (unpurged)	Sample uniformly hazy
900	Helium (unpurged)	Sample uniformly hazy
1000	Argon (purged 24 hrs.)	Veils throughout
900	Argon (purged 24 hrs.)	No haziness or scatter
800	Argon (purged 24 hrs.)	No haziness or scatter

2.5 Optical Properties

The feasibility of casting consistently high quality SrF_2 and CaF_2 has been demonstrated by using either high purity single crystal chips or purified "reagent" grade powder as starting materials. Loss measurements done by laser calorimetry were made at 5.25μm for CaF_2 (both purified powder and single crystal starting material), SrF_2 (single crystal starting material), and SrF_2 (purified powder starting material). Figures 12, 13, and 14, respectively, plot the total absorption versus length for these castings. Note that the measurements for cast CaF_2 fall on the same line regardless of the starting material (Fig. 12).

The results are summarized in Table IX for both CaF_2 and SrF_2. The average 5.25μm bulk* absorption coefficient of cast CaF_2 ingots is $(4.2 \pm 0.1) \times 10^{-4}$ cm^{-1} – 14 measurements on 10 ingots – results essentially equivalent to the measured value for single crystal CaF_2 and quite near the value of 1.8×10^{-4} cm^{-1} predicted[2] from the exponential law. The results for an ingot of SrF_2 cast from single crystal chips show an average 5.25μm bulk absorption coefficient – $(6.7 \pm 1.0) \times 10^{-5}$ cm^{-1} – near the value – $(4.1 \pm 0.7) \times 10^{-5}$ cm^{-1} – for single crystal SrF_2 as reported by Deutsch[2] and near the value of 2×10^{-5} cm^{-1} predicted[2] from the exponential law. The present results show a higher value – $(1.7 \pm 0.2) \times 10^{-4}$ cm^{-1} – for one ingot of SrF_2 cast from purified powder. However, further work is underway with purified-powder castings since the results for CaF_2 are so encouraging.

The above results show clearly that for both CaF_2 and SrF_2, the fusion casting process does not degrade the optical properties of high purity single crystal starting material. Furthermore, it has been shown that an all graphite system is capable of achieving high quality material, that polycrystalline material is equivalent in optical quality to single crystal material, and that at least for CaF_2, purified "reagent" grade powder is equivalent to single crystal chips when used as starting material.

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* The bulk absorption coefficient is defined as the total absorption per unit length less the correction for surface loss, as determined from the slope and intercept (zero length), respectively, of the absorption versus length plots. An apparent absorption coefficient is defined as the total absorption per unit length with no surface loss correction.

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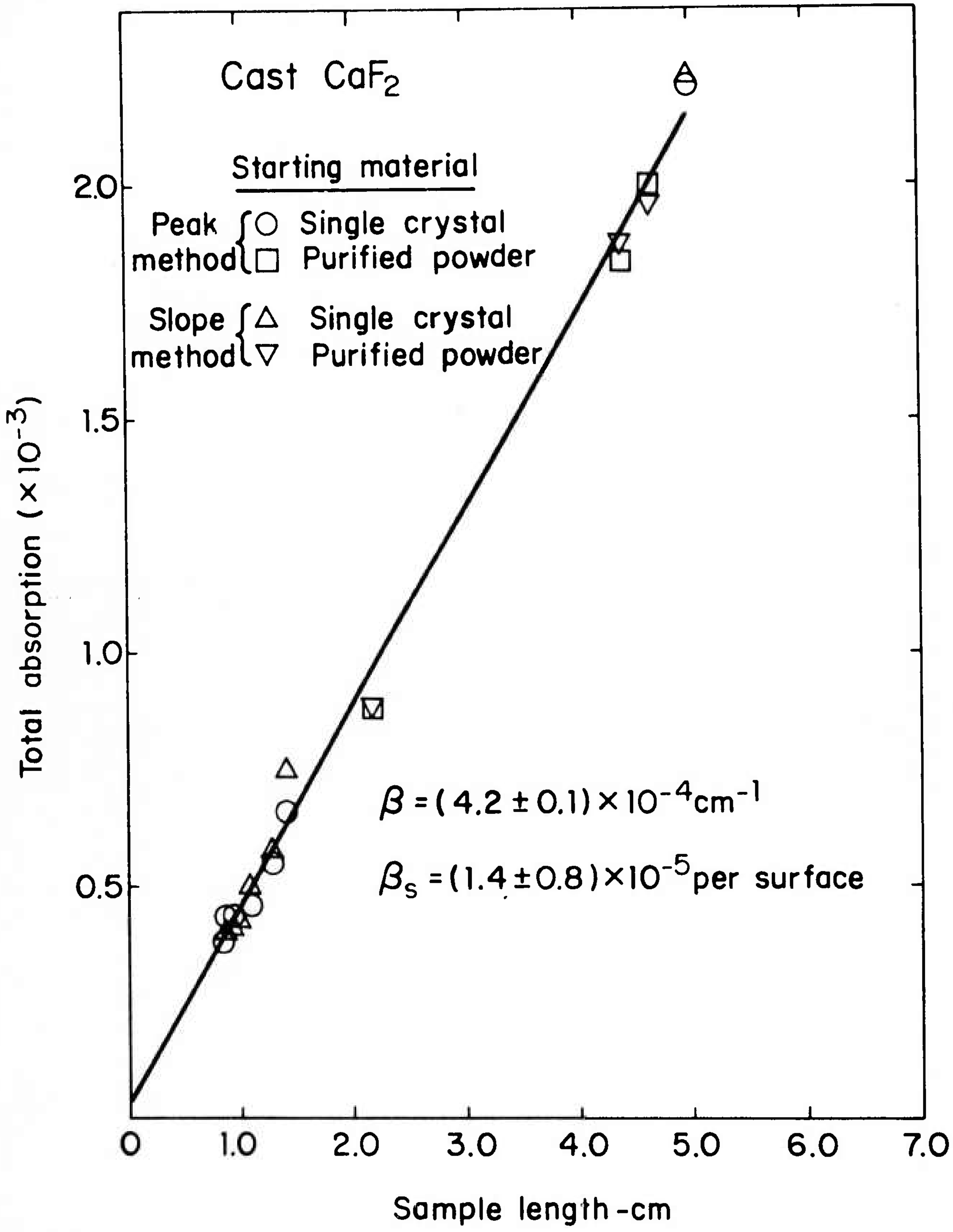

Fig. 12 5.25μm Optical Absorption vs Length for Cast CaF_2

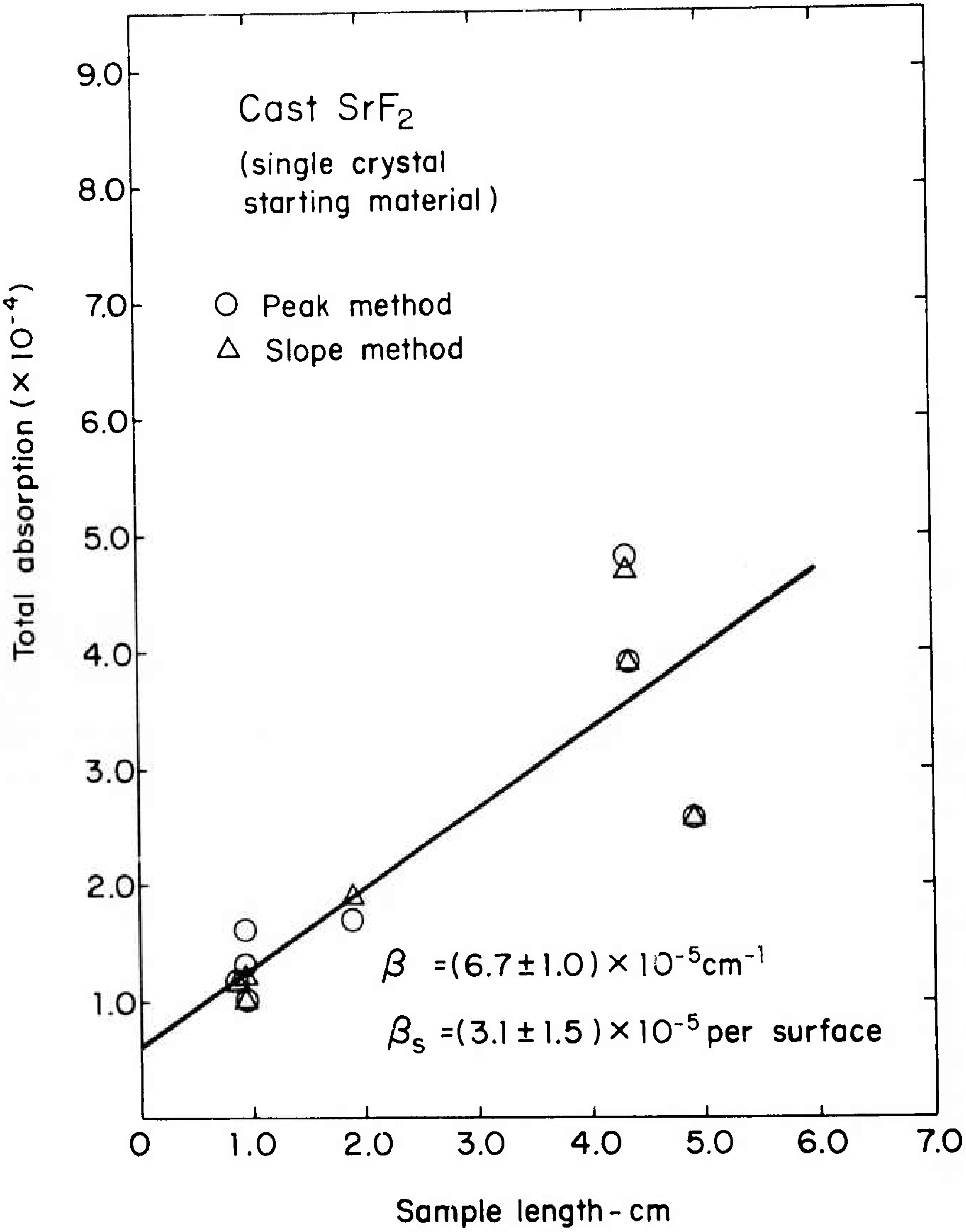

Fig. 13 5.25μm Optical Absorption vs Length for Cast SrF_2. Harshaw single crystal chip starting material

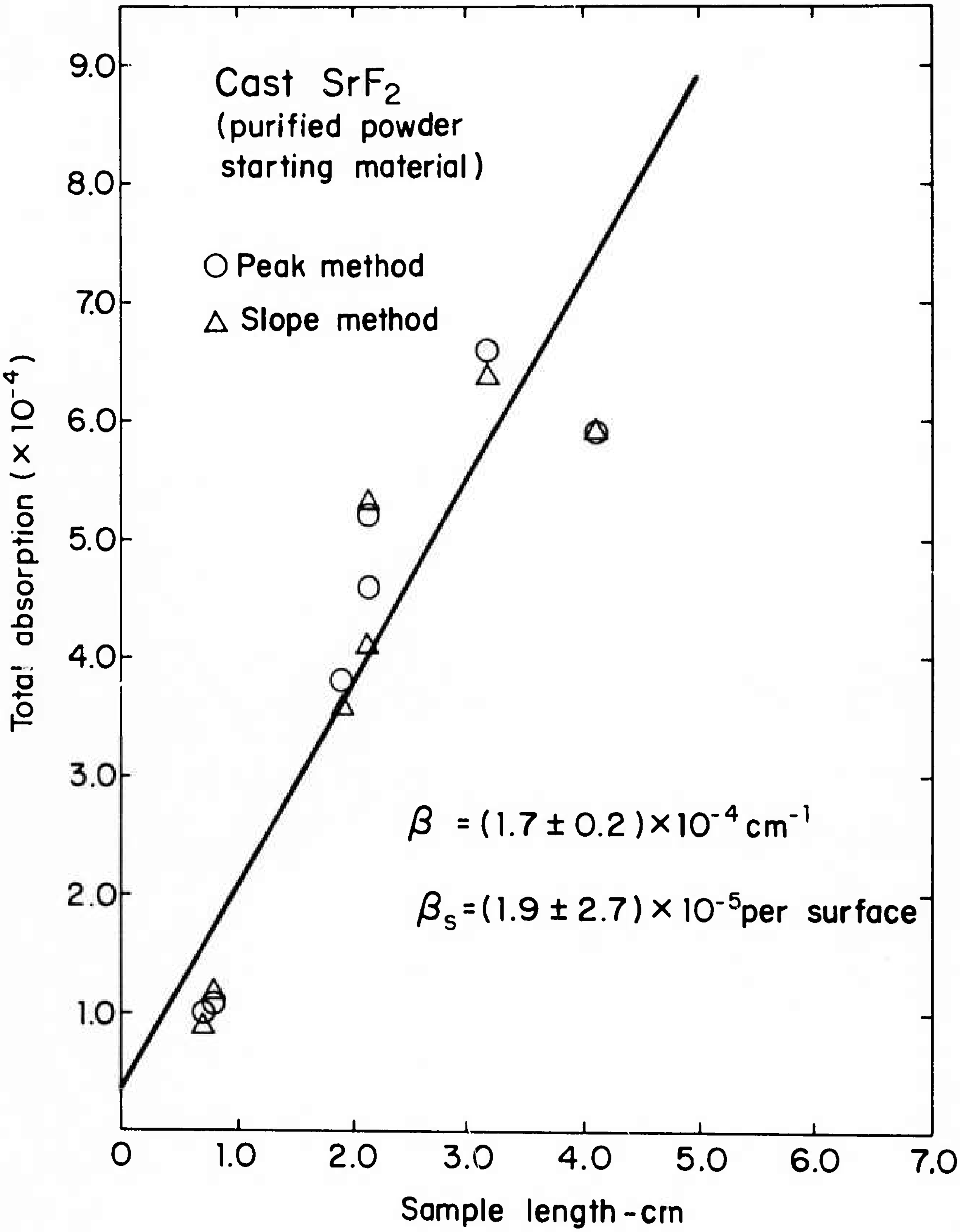

Fig. 14 5.25µm Optical Absorption vs Length for Cast SrF_2. Purified "reagent" grade powder starting material

TABLE IX

SUMMARY OF FLUORIDE MEASUREMENTS

Material	Starting Material	β Measured 5.25 μm	Surface Correction	β Predicted Exponential Law
Optovac CaF_2	--	$(4.7 \pm 0.3) \times 10^{-4} cm^{-1}$	No	$1.8 \times 10^{-4} cm^{-1}$
Cast CaF_2	Single crystal or purified powder	$(4.2 \pm 0.1) \times 10^{-4}$	$(1.4 \pm 0.8) \times 10^{-5}$ per surface	
Harshaw SrF_2	--	$(4.1 \pm 0.7) \times 10^{-5}$*	$(3.9 \pm 0.9) \times 10^{-5}$	2×10^{-5}
Cast SrF_2	Single crystal	$(6.7 \pm 1.0) \times 10^{-5}$	$(3.1 \pm 1.5) \times 10^{-5}$	
Cast SrF_2	Purified powder	$(1.7 \pm 0.2) \times 10^{-4}$	$(1.9 \pm 2.7) \times 10^{-5}$	

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* From reference 2.

Laser calorimetry measurements at 3.8μm (DF laser) have been made by other investigators on several samples of Raytheon-cast material and indicate excellent quality. An apparent absorption coefficient at 3.8μm for cast CaF_2 was measured to lie near 3.5×10^{-4} cm^{-1} at TRW.[3] At the University of Alabama, Huntsville, 3.8μm apparent absorption coefficients were measured near 6×10^{-4} cm^{-1}(4) and 2×10^{-4} cm^{-1}(5) for cast CaF_2 and cast SrF_2, respectively. No surface loss corrections were made on these above values.

For the samples of CaF_2 single crystals heat treated in the Lindberg box furnace, the results are as follows: For the samples annealed in purified argon at either 800 or 900°C (sufficiently purged), no increase in the 5.25μm apparent absorption coefficient ($4.7 \pm 0.3 \times 10^{-4}$ cm^{-1}) was measured as compared to unannealed single crystal CaF_2. At 1000°C (in argon) an increase is observed (1.2×10^{-3} cm^{-1}) with a corresponding increase in scattering (as viewed with a He-Ne laser). These results correlate with those reported earlier on vacuum (10^{-2} - 10^{-3} torr) annealing at 800, 900 and 1000°C.[1] In both cases it now seems clear that the systems are not sufficiently O_2-free, but that the damaging reactions occur only above 900°C, at least within the time period of these runs (10 hours) and with the low but unknown impurity concentration present.

For those samples of CaF_2 cast with a partial pressure of argon (inert atmosphere of 1 - 50 torr) present, the samples were typically discolored as mentioned previously. One sample (VHP-318) that was discolored a faint yellow-blue had a measured 5.25μm apparent absorption coefficient of 5.8×10^{-3} cm^{-1}; another similarly cast sample (VHP-317 - 50 torr argon) was colorless with a very good apparent absorption coefficient of 4.1×10^{-4} cm^{-1}. However, another colorless sample (VHP-301 - 25 torr argon) was higher, with a value of $1.16 \pm 1.2 \times 10^{-3}$ cm^{-1}. However, for the latter value the loss may be surface connected. After repolishing by an optician the value fell to $8.2 \pm 0.1 \times 10^{-4}$ cm^{-1}, and with an additional chemical etch the value was $6.7 \pm 0.6 \times 10^{-4}$ cm^{-1}. Clearly, the above results are mixed and further work is underway to improve the technique.

2.6 Mechanical Properties

Preliminary mechanical property measurements have been obtained on CaF_2 and SrF_2. Fracture strength as a function of surface preparation was determined for single crystal CaF_2 and SrF_2 and polycrystalline cast CaF_2 and SrF_2. The stress strain curves were determined in three-point bending on an Instron universal testing machine. The sample span was one inch and the cross-head speed was 0.05 cm/min. Nominal sample cross sections were 3/16 × 3/16 inches. Test bars were obtained from annealed ingots by cutting and polishing and were tested immediately or were either chemically polished in concentrated H_2SO_4 or annealed prior to testing. For a number of samples extra attention was given to polishing the edge bevels, as noted in the tabulated results. Sample dimensions were measured after testing to prevent surface damage. Grain size for the polycrystalline cast samples is generally on the order of one cm. In all cases fracture occurred with no apparent yielding.

The results as presented in Tables X and XI show the effects of polishing and annealing on the fracture strength of CaF_2, and indicate qualitatively the large effect surface preparation has. By going from a rough polish (wet 600 grit grinding paper – Fig. 15) to a normal in-house laboratory polish (Fig. 16) or to an optical polish (polished on a pitch lap by an optician) as shown in Fig. 17, the strength of cast CaF_2 is raised from 8000 psi to 14,600 psi and 13,900 psi, respectively. Moreover, the normal lab polished samples which were chemically polished prior to testing (calculated to remove about 1×10^5 Å from each surface) show a value of 12,500 ± 1800 psi. Note that for the samples on which extra attention was paid to polishing the edge bevels, the fracture strength is raised to an average of 18,000 psi but decreased to 11,700 psi for the lab and optical polishes, respectively.

For single crystal CaF_2 (Table XI) the polishing results are similar, i.e., going from a rough polish to lab and optical polishes, the fracture strength is increased from 7200 psi to 18,500 psi and 18,400 psi, respectively, values essentially equivalent to the cast material and not unexpected due to the large grain size of the castings.

TABLE X

FRACTURE STRENGTH OF CAST CaF_2

As-Polished					As-Annealed*				
Rough (psi)	Lab (psi)	Lab Edges** (psi)	Optical (psi)	Optical Edges** (psi)	Rough (psi)	Lab (psi)	Lab Edges** (psi)	Optical (psi)	Optical Edges** (psi)
6200	9500	12300	14900	7600	9600	10900	27000	21900	17900
7700	7900	18100	11900	13300	13800	20600	16100	26000	18800
5700	8300	24100	14500	17600	17000	17500	16800	22200	33500
8500	22800	19700	15400	8200	8900	19600	20500	20700	23900
5000	20700	19800	13300	11400	11700	22000	26400	53800	24500
6900	7800	13800	10800	11900	15300	5400	6700	24200	21600
2000	14700		19500			24100		28600	
24000	19100		18600			11500			
6400	20800		11100			18600			
8000	14600	18000	13900	11700	12700	16700	18900	28200	23400
±5900	±6000	±3900	±4300	±3300	±2900	±5800	±6900	±10700	±5100

* 10 hours at 900°C in 10^{-2} - 10^{-3} torr vacuum.

** Extra attention paid to polishing the edge bevels.

TABLE XI

FRACTURE STRENGTH OF SINGLE CRYSTAL CaF_2

As-Polished			As-Annealed*		
Rough (psi)	Lab (psi)	Optical (psi)	Rough (psi)	Lab (psi)	Optical (psi)
2900	30800	15400	13200**	36800	28400
5700	26600	12500	16700**	25200	16600
3000	21800	15700	17000**	20400	33000
2600	23200	17500	22500	22500	30100
8100	22000	28500	22800	10600	28800
14200	7800	20600	4800	10700	25000
9700			27500		23500
11400			3400		
			7600		
7200	18500	18400	15600	17800	26500
±4100	±6600	±5100	±1700	±7400	±5000

* Annealed 10 hrs. at 900°C in 10^{-2} - 10^{-3} torr vacuum.

** Annealed 7 hrs. at 1075°C in 10^{-5} torr vacuum.

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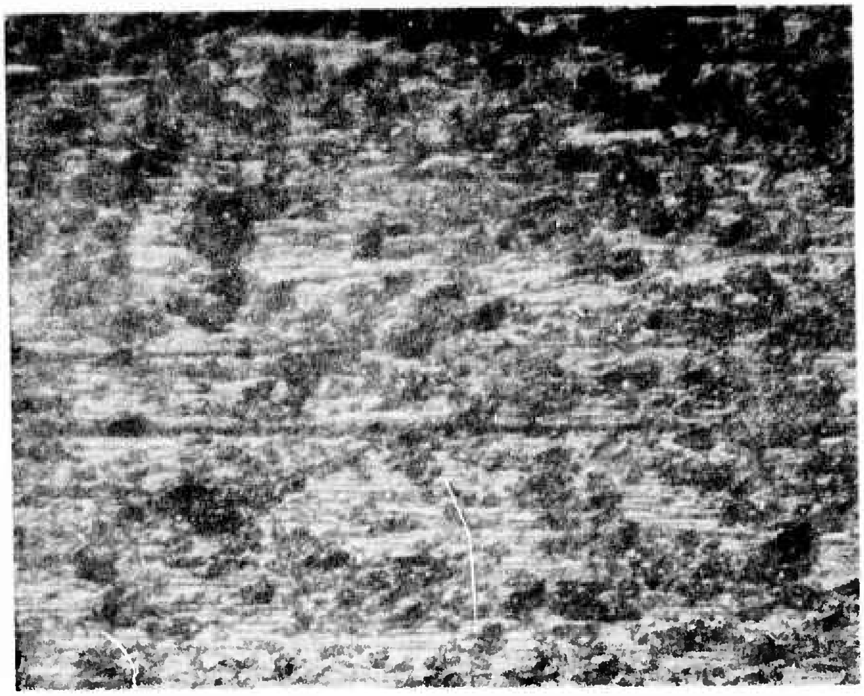

Fig. 15 Surface of CaF_2 Sample After Rough Polish (600 grit SiC Paper) 187 ×

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Fig. 16 Surface of CaF_2 Sample After Laboratory Polish. 187 ×

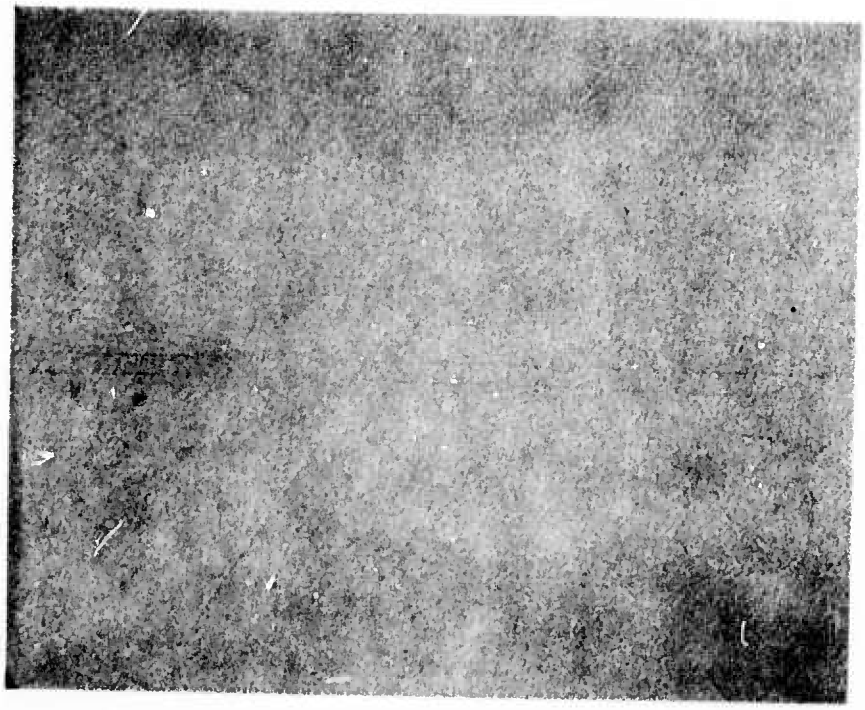

Fig. 17 Surface of CaF_2 Sample After Optical Polish (Pitch Lap). 187 ×

These polishing results (and the large scatter in the data) for both cast and single crystal material indicate that strength is limited by surface and edge flaws. Damaging flaws may be removed in part by more careful mechanical polishing.

Further evidence is seen in the effect of annealing individual test bars prior to testing as also indicated in Tables X and XI. Annealing significantly increases the fracture strength of both cast and single crystal specimens. Samples similarly polished as above - rough, lab, and optical polishes - and annealed prior to testing show increased fracture strengths of 12,700, 16,700, and 28,200 psi, respectively, for cast CaF_2 and 15,600, 17,800, and 26,500 psi, respectively, for single crystal CaF_2. As was the case for as-polished cast samples, those as-annealed test bars on which extra attention was paid to polishing the edge bevels, the fracture strength is raised (to 18,900 psi) and lowered (to 23,400 psi) for the lab and optical polishes, respectively.

Evidently by annealing the test bars, some surface damage is either reduced or removed, a further indication that the fracture strength of CaF_2 is limited by surface flaws. This assumes that bulk strain in all the bars are the same, supported qualitatively by viewing each specimen between crossed polarizers before testing and noting no differences. That is, all test bars appear macroscopically strain-free, whether they are to be tested as-polished or as-annealed (polished then subsequently annealed).

In all the above cases, fracture was predominantly transgranular in nature (i.e., cleavage). However, in the cases of samples of cast CaF_2 which were taken from castings annealed in the degrading anneal procedure[1] (1000°C in vacuum of 10^{-2} - 10^{-3} torr) fracture was totally intergranular in nature and strengths were markedly reduced to 4700 ± 600 psi (lab polished samples) from 14,600 psi. However, even in this instance, surface damage is limiting, since similar samples which were subsequently chemically polished show an increased strength to 6500 ± 1300 psi, but still far below the 12,500 psi level of similarly chemically polished specimens cut from castings annealed at 900°C. Thus it appears that annealing procedur not only degrades the optical properties[1] but also significantly affects the mechanical properties. Since fracture is intergranular, it suggests grain boundary weakening as a result of an impurity precipitation problem as previously discussed.

Preliminary results for single crystal and cast SrF_2 samples as listed in Table XII show a surface damage dependence similar to CaF_2, although rough polished SrF_2 is stronger than similarly polished CaF_2. For cast SrF_2 the as-polished samples (rough, lab, and lab edge polishes) show average fracture strengths of 10, 800, 11, 200, and 12, 800 psi, respectively. Similarly polished samples annealed prior to testing show an increased strength to 15, 000, 16, 000, and 16, 200, respectively. Single crystal SrF_2 shows an equivalent fracture strength compared to cast samples, i.e., the values for lab polished single crystal SrF_2 are 11, 300 psi and 16, 400 psi for as-polished and as-annealed samples, respectively.

Hardness measurements were also taken on samples of CaF_2 and SrF_2. Hardness is determined with a Vickers DPH indenter and a 50 gm load mounted on a Vickers M-55 metallograph. The results that appear in Table XIII show that there is no difference in hardness in single crystal or cast material for either SrF_2 or CaF_2 and that CaF_2 is slightly harder than SrF_2.

TABLE XII

FRACTURE STRENGTH OF SrF_2

As-Polished				As-Annealed			
Cast SrF_2			S.C. SrF_2	Cast SrF_2			S.C. SrF_2
Rough (psi)	Lab (psi)	Lab Edges (psi)	Lab (psi)	Rough (psi)	Lab (psi)	Lab Edges (psi)	Lab (psi)
10200	6500	11400	11800	17100	14500	14100	7700
10900	12200	6800	16100	14300	20900	18000	18900
11400	17700	8300	12500	13600	16700	14900	23400
	7900	15300	4800		11300	25600	15700
	7500	6200			21200	9400	
	19500	17700			9400	15100	
	6400	22900			25400		
	8300	5800			5000		
	14600	11300			19900		
		24400					
		9100					
		14800					
10300 ±500	11200 ±4700	12800 ±6000	11300 ±4100	15000 ±1500	16000 ±6500	16200 ±4900	16400 ±5700

* Annealed 10 hrs. at 900°C in 10^{-2} - 10^{-3} torr vacuum.

TABLE XIII

VICKERS HARDNESS* OF CaF_2 AND SrF_2

	SrF_2	CaF_2
Single Crystal	171 ± 2	191 ± 2
Polycrystalline Cast	173 ± 1	194 ± 2

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* Vickers Hardness Number, 50 gram load; average of four measurements.

3.0 SUMMARY AND CONCLUSIONS

3.1 Casting

Consistently high quality castings of both CaF_2 and SrF_2 have been fabricated regardless of the starting materials. That is, either high purity single crystal chips or pre-treated (vacuum baked or RAP-reactive atmosphere processing – treated in teflon vapors) "reagent" grade powder can be used as starting material to yield equivalent castings.

Castings of CaF_2 were attempted in an inert atmosphere – partial pressures of argon from 1 - 50 torr. The advantage is that unidirectional solidification is better accomplished because of the better heat transfer provided by the gas. The procedure needs more refinement because the castings are typically discolored.

3.2 Hot Forging

Preliminary hot forgings of polycrystalline cast CaF_2 have been done at 1000°C. At this high temperature a large grain size results so that not much advantage in grain size reduction is gained.

3.3 Optical Properties

5.25μm calorimetric bulk absorption coefficients of cast CaF_2 have been consistently obtained near 4.2×10^{-4} cm^{-1} regardless of the starting material. Those castings of CaF_2 fabricated in an inert atmosphere of argon have 5.25μm apparent absorption coefficients typically greater than 1.0×10^{-3} cm^{-1}, although one was as low as 4.1×10^{-4} cm^{-1}.

In preliminary results the 5.25μm bulk absorption coefficient of cast SrF_2 lies near 6.7×10^{-5} cm^{-1} for an ingot cast using single crystal chips as starting material and lies near 1.7×10^{-4} cm^{-1} for an ingot cast from purified "reagent" grade powder.

3.4 Strain Annealing

For highly strained ingots of cast CaF_2 strain annealing has been successful at 900°C either in vacuum or inert atmosphere furnaces. Highly strained ingots of cast SrF_2 have been successfully strained annealed at 1000°C in a high vacuum furnace.

3.5 Mechanical Properties

Mechanical measurements on cast CaF_2 show average fracture strengths ranging from a minimum near 8000 psi to near 28,200 psi, depending on both the quality of polished surfaces (and edges) and whether or not the polished test bars are subsequently annealed at 900°C (a strain relief procedure). The results are equivalent to the values for single crystal CaF_2 for which similar polishing and annealing procedures show average fracture strengths ranging from 7200 psi to 26, 500 psi. In preliminary results the average fracture strengths for cast and single crystal SrF_2 range from 10, 800 psi to 16, 000 psi and from 11, 300 psi to 16, 400 psi, respectively. The best (for CaF_2) surface polish has not yet been evaluated for SrF_2. The dependence of fracture strength on both surface polish and annealing history is evidence that fracture for the fluorides is determined by surface and/or edge flaws. The preliminary results also show that SrF_2 is equivalent in strength to CaF_2 and that polycrystalline cast material is equivalent to single crystal material.

4.0 PLANS FOR NEXT QUARTER

Work during the fifth quarter will include the following areas of effort:

1. Continue the investigation of purification treatments of "reagent" grade starting powder for fluoride castings, especially for SrF_2.

2. Continue the development of a casting procedure in an inert atmosphere.

3. Continue the mechanical property evaluation of cast fluorides (SrF_2 and CaF_2), including chemical-mechanical polishing procedures. Begin fractography analysis in order to determine points of fracture initiation in the fluorides.

4. Continue the evaluation of different annealing procedures, especially inert atmosphere operations at lower temperatures and teflon vapor operations at higher temperatures.

5. Investigate the effect of aliovalent additions to the fluorides under controlied casting conditions.

5.0 REFERENCES

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