

NRL Memorandum Report 3725

Possible New Irdome Materials for Transmission to 4.5-5 Micrometers

3

32

33

A 05

AD

DOC FILE C

• 15

R. W. RICE

Ceramics Branch Engineering Materials Division



February 1978



3.41



NAVAL RESEARCH LABORATORY Washington, D.C.

Approved for public release; distribution unlimited.

REPORT DOCIMENTATION PAGE	READ INSTRUCTIONS
REPORT DOCUMENTATION PAGE	BEFORE COMPLETING FORM
1. REPORT NUMBER 2. GOVT ACCESSION	N NO. 3. RECIPIENT'S CATALOG NUMBER
NRL-Memorandum Report 3725	
4. TITLE (and Subtitle)	S TYPE OF REPORT & PERIOD COVERE
DOGUDE D NEW IDDOME MATERIAL C FOR	(9) Interim report on a continuing
POSSIBLE NEW IRDOME MATERIALS FOR	NRL problem.
TRANSMISSION TO 4.5-5 MICROMETERS.	6. PERFORMING ORG. REPORT NUMBER
AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(.)
Row Rice	
Koy)	
PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Naval Research Laboratory 🗸	
Washington, D.C. 20375	NRL Problem C03-26B
11 CONTROLLING OFFICE HAVE AND ADDRESS	12 REPORT DATE
CONTROLLING OFFICE NAME AND ADDRESS	11 February 178
9	12 NUMBER OF PAGES
6	12 19 0.
14 MONITORING AGENCY NAME & ADDRESS(It different from Controlling Of	15. SECURITY CLASS. (of this report)
Naval Air Systems Command	UNCLASSIFIED
Washington, D.C. 20361	15. DECLASSIFICATION DOWNGRADING
	SCHEDULE
18. SUPPLEMENTARY NOTES	
19. KEY WORDS (Continue on reverse side if necessary and identify by block nu Infrared	uan ber)
Optical properties Thermal expansion Irdomes	
Optical properties Thermal expansion Irdomes 20 ANTRACT Continue on reverse elde II necessary and identify by block num Results of a preliminary survey of possible new IR mat is reported. While some tentative candidate materials are ic report is to demonstrate that ternary and higher compound providing improved IR materials over the typical list of know pacing need for many new IR systems is thermal shock resis the possibility of finding materials with low thermal expanse DD . FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE .	terials for use out to 4.5-5 micrometers dentified, the primary purpose of this is provide a significant opportunity for own diatomic candidates. Since the istance, emphasis has been given to sion coefficients.
Optical properties Thermal expansion Irdomes 20 ANTRACT Continue on reverse side if necessary and identify by block num Results of a preliminary survey of possible new IR mat is reported. While some tentative candidate materials are ic report is to demonstrate that ternary and higher compound providing improved IR materials over the typical list of known pacing need for many new IR systems is thermal shock resis the possibility of finding materials with low thermal expanse DD : FORM 1473 EDITION OF ! NOV 65 IS OBSOLETE i	terials for use out to 4.5-5 micrometers dentified, the primary purpose of this is provide a significant opportunity for own diatomic candidates. Since the istance, emphasis has been given to sion coefficients.
Optical properties Thermal expansion Irdomes 20 ANTRACT (Continue on reverse elde II necessary and identify by block num Results of a preliminary survey of possible new IR mat is reported. While some tentative candidate materials are ic report is to demonstrate that ternary and higher compound providing improved IR materials over the typical list of known pacing need for many new IR systems is thermal shock resis the possibility of finding materials with low thermal expanse DD : FORM 1473 EDITION OF ! NOV 65 IS OBSOLETE i S.N. 0102-014-6601 SECURITY	terials for use out to 4.5-5 micrometers dentified, the primary purpose of this ds provide a significant opportunity for own diatomic candidates. Since the istance, emphasis has been given to sion coefficients.
Optical properties Thermal expansion Irdomes 20 ANSTRACT (Continue on reverse elde II necessary and identify by block nuc Results of a preliminary survey of possible new IR mat is reported. While some tentative candidate materials are ic report is to demonstrate that ternary and higher compound providing improved IR materials over the typical list of kno pacing need for many new IR systems is thermal shock resi the possibility of finding materials with low thermal expanse DD + JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE i S N 0102-014-6601 SECURITY	terials for use out to 4.5-5 micrometers dentified, the primary purpose of this ds provide a significant opportunity for own diatomic candidates. Since the istance, emphasis has been given to sion coefficients.



TABLE OF CONTENTS

FOREWARD	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	iv
INTRODUCTION		•		•			•	•		•	•	•	•	•	•	1
SURVEY OF MATERIALS	•		•					•	•	•		•		•		2
SUMMARY AND CONCLUSION	•							•	•		•				•	5
ACKNOWLEDGMENT					•	•		•								6
REFERENCES																6

NTIS DDC		White Section Buff Section	
UNANNOU JUSTIFIC	NCED Ation		
DISTRIBL	ITION/AV	AILABILITY COD	ES

Constant and the second

FOREWARD

This report represents a limited updating of a paper by the same title given by the author at the Workshop on Radomes and Irdomes for Tactical Missiles held at the Naval Weapons Center, China Lake, California, 1-4 March 1976. This paper was also presented by Dr. A. M. Diness for the author at the TTCP Meeting, Subgroup P2 (Ceramics) held in Adelaide, Australia, 14-16 July 1976. Abstracts published in Report TTCP/AUS/P 2/2/76, "Performance and Evaluation of Electro-Ceramic Materials in Military Systems," edited by L. M. Gillin.

iv

POSSIBLE NEW IRDOME MATERIALS FOR TRANSMISSION TO 4.5-5 MICROMETERS

INTRODUCTION

Increasing demands are being placed on irdome materials that can transmit in the 1 to ~ 4.5 to 5 μ m region. These increased demands are primarily for substantially greater thermal shock resistance and secondarily for increased rain erosion resistance. Commonly used or proposed alternate IR materials are typically drawn from a limited list of familiar materials that have been studied and/or developed a fair amount which is important for near term development. Table 1 lists some of the common candidates. However, these commonly proposed materials do not offer great improvement over widely used MgF₂ and hence are not expected to meet many future requirements.

The thesis of this paper is thus two-fold. First, that there are many, at least hundreds and possibly thousands of materials that can meet the basic transmission needs. The list of suitable candidates is, of course, greatly reduced as demands for other necessary properties, mainly low, thermal expansion and reasonable hardness and Young's modulus, are considered. Also, as discussed later, the number of candidates can be measurably effected by how close to 5 microns transmission is required. The second thesis is that even with drastic reductions in the number of candidate materials to meet the other requirements, especially low thermal expansion to have good thermal shock resistance, a number of materials that could be much better than the common candidates should be feasible. Therefore, the main purpose of this paper is to present the results of an initial survey to show the potential opportunity of finding better materials, not to be a comprehensive survey to identify final candidates. Thus, the secondary purpose to indentify some areas or materials of opportunity, is meant to be a demonstration of the possible improved materials rather than proposing these specifically, as definite candidates.

Note: Manuscript submitted February 8, 1978.

1

SURVEY OF MATERIALS

First, for reference, consider the properties of commonly available or used materials for transmission to ~ 5 microns (Table 1). Of the traditional materials, only fused silica has a sufficiently low thermal expansion to have good thermal shock resistance; however, it transmits only to ~ 4 microns and hence is not usable for many applications of interest that typically require transmission to at least 4.5 microns. Further, fused SiO₂ is probably marginal in rain erosion resistance. Note that one of the next lowest transmission materials in this list is alumina; however, it's expansion of ~ 9-10 x 10^{60} C is high and is, thus, a major factor in its poor thermal shock resistance. Note also the relative high expansion, low hardness, and low Young's modulus of MgF₂, currently the most commonly used material.

Next, consider the more common non-oxide materials (Table 2). The author knows of no borides or silicides that are dielectric, i.e. that are not electrical conductors, and hence that would be possible dielectric IR transmitting materials. At least two carbides, berylium carbide and silicon carbide are not intrinsic conductors; however, berylium carbide is felt to be impractical because of its toxicity and its deliquescence. Silicon carbide is a material currently being given some consideration for IR purposes although it does not give usable transmission completely to 5 microns and it has quite a high index or fraction.1 Several nitrides may be possible candidates with silicon nitride currently receiving some consideration.1 However, it only transmits to ~ 4.5 microns and also has a fairly high index or fraction. Many mixed nitride compounds are believed to exist and a substantial number of these may have useful IR transmission, but no data whatsoever, is known about these. Some phosphides should meet the IR transmission requirements but these generally have high indices of fraction. Many sulfides, other chalcogenides, and semi-conductors can also meet the IR requirements but also have high indices or refraction and also sufficiently low hardnesses that most of them have serious rain erosion problems.

Table 3 shows a partial listing of single oxide materials. Transition metal oxides have not been included since data is generally lacking and many are expected to not meet the transmission requirements because of the intrinsic absorption band they have that extends into the IR, e.g. Fig. 1. No really attractive single oxide candidates are seen; the only one of these expected to meet transmission requirements to at least 4.5 microns with a relatively low expansion is tin oxide. However, its potential as a candidate material is probably limited by its expected fairly high refractive index, its fairly easy reduction, its possible semi-conducting character, and its low Young's modulus and hardness.

A major opportunity for new IR materials is seen to lie in the mixed oxides, primarily the binary oxide systems, i.e, oxide compounds of two metals (Table 4 and 5). There are many families of these materials. Table 4 is only a partial listing of one such family, the aluminates. Many of these materials are expected to meet IR wavelength transmission requirements. Note that amongst this partial listing even with incomplete property determination, there is at least one possible candidate; namely, calcium aluminate with a thermal expansion in the range of 2-3. While possible questions of its stability with H₂O and its general phase stability exist, it does indicate some of the potential of surveying, the wide variety of available materials.

Turning now to a broader survey, Table 5 lists some of the other possible mixed oxide systems that may provide candidate materials, and properties for some of the members of these families. While some borates may be possibilities, it is generally expected that the light weight of the boron atom would make these compounds questionable in their ability to meet the high IR transmission requirement. However, many other systems should meet these requirements. Some of these materials have fairly low thermal expansions, e.g., aluminum niobate and titanium niobate. Two phosphates are known to have rather interesting expansion behavior. First, aluminum phosphate stabilized in the β form has a quite low expansion; unfortunately IR transmission measurements of this material shows that it does not transmit beyond ~ 4 microns² and hence is not suitable. Uranium phosphate, though clearly not of practical interest again illustrates the possibilities of looking beyond typical compounds in that its expansion ranges from a significant contraction to a positive expansion, indicating possibilities of developing very low expansion materials.

Many silicates probably will not meet the transmission requirement since fused SiO₂ itself fails to while corresponding germanates are more likely to because of the heavier germanium atom. However, the silicates generally offer the opportunity for lower expansion. Mullite is a particularly interesting possibility. Tests at the Naval Research Laboratory on transparent hot press samples kindly provided by Dr. J. Mazdiyasni of AFML, indicates that this material may be usable to ~ 4.8 microns (Fig. 1). This is one example illustrating the important question of exactly how close to 5 microns transmission is required. Mullite has a relatively low thermal expansion coefficient of ~ 5 and compositions having thermal expansion approaching as low as ~ 3 have apparently been reported though they may possibly have higher silica content which may further compromise the transmission. Besides the above noted hot pressing, the material has been processed as a glass and then crystallized³ with this apparently resulting in strengths as high as 100,000 psi. Thus, this is a particularly good example of the possibilities of looking at new materials. Silicates having a heavy metal ion will generally give broader transmissions, e.g. bismuth titanate and probably zircon transmit closer to 5 microns, though the former and possibly the latter have a fairly high refractive index.

Aluminum titanate illustrates one of the pitfalls one must watch for, namely, this material can have a very low coefficient expansion. However, this is due to opening and closing of microcracks resulting from very anisotropic expansion of the individual crystallites giving apparent low net bulk thermal expansion. However, such microcracking is not tolerable for IR purposes because of the resultant high scattering. Dense, fine grain material, which would not have such microcracking, does not exhibit the desired low thermal expansion. Two other mixed oxide materials, which may have real relatively low thermal expansions, are aluminum and zirconium tungstates, but their phase stability is unknown.

Another possible candidate again illustrating the potential of looking at new materials is calcium zirconate. The literature indicates thermal expansions ranging from approximately 5 to 11. The lower expansion value is reasonably interesting for thermal stress resistance, while the latter is not. Recent tests at NRL indicate a thermal expansion of \sim 7, which while not low is \sim 10 - 20% lower than that of magnesia alumina spinel, the only mixed oxide material that appears to have received any consideration for irdomes. Calcium zirconate clearly meets the transmission requirement and its refractory, reasonably hard character as well as some progress in its fabrication (e.g., it is currently skull melted and tests indicate reasonable promise in hot pressing) indicate it might be more promising than spinel.

Table 6 briefly summarizes some of the possibilities seen in this preliminary survey, again emphasizing the mixed oxides as the most substantial area of opportunity with several families of these showing some possibilities. Again it should be emphasized that the number of candidates can be substantially effected by exactly how far into the IR transmission is required; that is, if transmission is required to 5 microns, few if any of the silicates will meet this, while if transmission to somewhat less than 5 microns is required, then some promising silicates become candidates. Again, mixed nitrides or mixed compounds such as oxinitrides, oxisulfides, carbophosphides, etc., may have some possibilities, but so little is known about these materials that in general they cannot be considered particularly viable candidates, at this time or in the forseeable future, but should not be totally neglected in a more detailed survey. The recommendation as a result of this consideration is thus that a more detailed survey be made with some accompanying property measurement to fill out the survey and test possible candidate materials in order to select better IR candidates. This should be done in conjunction with designers to more closely determine the exact IR wavelength transmission requirements, since this in fact can be an important factor in considering some possibly attractive candidates, as noted above.

Table 7 summarizes some of the guidelines and pitfalls for a further more detailed survey. Thus, for example, the IR cut-off wavelength, λ , is proportional to the square root of quotient of the effective mass of the ions and the effective spring constant. The spring constant is basically a function of Young's modulus, E, and the effective mass for a diatomic system is simply as shown. It is also important to keep in mind whether the material is cubic or non-cubic; and if non-cubic, the degree of optical and thermal expansion anisotropy. High thermal expansion anisotropy requires fine grain sizes for mechanical integrity. High optical anisotropy may limit the range of usage at shorter wavelengths due to resultant scattering. Note also that while high thermal conductivity will limit thermal stresses under relatively low rates of temperature change, its effect in limiting thermal stress decreases with increasing heating rate, becoming negligible at high rates. Further, high thermal conductivity means higher internal dome or window temperatures which can be detrimental.

SUMMARY AND CONCLUSIONS

This preliminary survey shows that there can be substantial opportunity for improved IR materials amonst compounds consisting of three or more atoms, e.g. with mixed oxide compounds being a good example of the promise of such compounds. It is important that new materials for irdomes and windows have potential for meeting both near and far term needs. The commonly proposed candidates of more developed materials have, at best, limited potential for needs beyond those of the near term. Thus, a more comprehensive survey-testing program is warranted to investigate the potentially very promising area of new compounds. The focus of attention of this preliminary survey has been materials for use to ~ 5 μ m. However, it is clear that the possibility of ternary and higher compounds may offer important new materials opportunities for other wave length regions such as 8-14 μ m in where mixed halide or mixed chalcogenide materials may be possible candidate families.

ACKNOWLEDGMENT

The support of this work by the Naval Air Systems Command, monitored by Charles Bersch, is gratefully acknowledged.

REFERENCES

- 1. Private communications, Dr. R. Tanzilli, General Electric Co., Valley Forge, PA.
- 2. Private communication, Dr. M. Hills, Naval Weapons Center, China Lake, CA.
- 3. J. F. MacDowell, Corning Glass Works, U. S. Patent No. 1,005,338 (1965).

t

		Comments												
	IR	Cutoff		V 4	x 0	12	9	6	ŝ					
	n Refrac-	tive Index		1.3	1.3	1.4	1.8	1.7	1.6					
erials	α Thermal	Exp. Coeff.		0.5	п	22	9-10	13	9-10				×	
n IR Mate	Young's	Modulus 106 psi		10	16	14	60	45	20					
cal 1-5 µ	H	Hardness kg/mm ²		800	550	150	2400	~ 700	~ 700					
Typi	Р	Density gm/cc		2.2	3.2	3.2	3.98	3.58	3.1	exagona 1				
	TM	Melting Temp. ^{oC}		> 1500	1260	1360	2050	2800		1c; H: H				
	Crvstal*	Struc- ture		Glass	F	c	H	c	Glass	1; C: Cub				
		Material	Typical IR Materials	S102	MGF2	CaF ₂	A1203	·· MgO	CaO-BaO- MgO-A1203	*T: Tetragona				

TABLE 1

7

TABLE 2 NON-OXIDE CERAMICS

		TM	a	H	3	ø	a		
	Crystal' Struc- ture	Melting Temp. ^O C	Density gm/cc	Hardness kg/mm ²	Young's Modulus 106 ps1	Thermal Exp.Coeff. 10-6 oC-f.	Refrac- tive Index	IR Cutoff µm	Comments
								none	
									toxic deliquescent
	C (H)	d~2500	3.2	~3000	65	ŝ	~2.4	\$°	
		d~2300	3.26	~1300	50	4-6 1-25	~2.2	8	•
					,			;	toxic, reacts with $H_2^{-0.02}$
	H	d~1900	3.2	2000	45	ຊິຄ	~2.2	4.5	
	OECE	>2000 >2000 1620 ~1350	e	3200 3800 950 600		4 5 - 6 4 - 5 5 - 6	3-3.5 2.8 3.9		
-								none	
-				medium		medium	high	>5	
	pu			low		to high			
	lexagona l								
-									
_									

8

t

TABLE 3

011	
A G	
2	
T D D	
2	
-	
5	
0	
No.	
10.7	

			•	M	A	~	-		
	Crystal*				s, Suno,	Thermal	Refrac-	IR	
Material	Struc- ture	Melting Temp. ^{OC}	Bensity gm/cc	Hardness kg/mm ²	Modulus 106 psi	Exp. Coeff.	tive Index	Cutoff	Comments
Single Oxides									
A1,04	=	2050	3.98	2400	60	9-10	1.8	9	
Bao	c	1920	5.72	s500			~1.9	~20	Very extreme H ₂ O attack.
BeO	H	2530	3.02	1300	57	8-9	~1-6	5-6	Toxic
CaO	c	2600	3.32	s600		12-14		12	Some H20 attack.
Ce0,	c						~2.2	80	Fairly easy to reduce.
Cr.903	H	d~2000	5.21	~2400		6-8			
Ge02	1					~11~			
HEO	*	2800	9.68			5-6			
MgO	c	2800	3.58	~700	45	12-13	1.7	6~	Limited H ₂ O attack.
Nb ₉ 0 ₃	*				25				Variable expansion due to
\$10 ²	Glass	~1700		~700	10	0.5		7	anisotropy
Sn0,	T		7.00			3-5			Easily reduced.
Sro	c	2400		<600		13-14		~17	Extreme H2O attack.
Th0 ₂	c	3200	9.8		35	9-10		6	Limited Radioactivity (α).
T102	Ŧ	~1900	4.26	~1000	40	8-9	2.4	5.5	Susceptible to reduction.
Y203	c	2400	4.84	675	26	7-8		80	
ZnO	H		5.66	•	18	6-7			Easily reduced.
Zr02	T			1500	36	5-6			Requires stabilization.
		1							
H: Hexagon	11; C: Cu	ole; T: T	etragon	W: WO	oclinic				

9

Table 4

		Connents						Some Ho,O Attack?	•	Commercial IR material-	good rain erosion resis-	tance (Barr & Stroud	(B539B)	-				The second s																	
	2	Cutoff										2										0	1												
	notion	tive Index																															oclinic		
te Ceramics	Q Lange	Exp. Coeff.		7-8		8~		2-3				9-10		6-8	6-8	8-9				12-13	8-9			6-7				6-7	80			8-8	ic. M: Mor		
Alumina	E	Modulus 106 psi										20										56	35										rthorhom		
amples of	H	Hardness kg/mm ²													1700							1950	1500										al. 0: 0		
Ex	٩	Density gm/cc		3.99	3.64	3.76	2.90		2.98	3.00		3.10	6.17	4.37	7.70	6.05		4.35		2.55	3.60	3.60	3.59	4.12	. 45	CF. F		3.03	4.45		5.50	4.58	Hexagor		
	, T	Melting Temp. ^o C		2050	1860	1880	1760	1720	1620	1540			2100	2020	2120	1820	2040	1440	>1650	>1900		>1650	2130	1560	00114	1080	2010	1660	2040	1980		1950	bic. H:		
	*******	Struc- ture		C/H	H	0	-	•		c			0		•	0	c	c	c		c		c	c			,		c	c	c	c	C: C		
		Material	Alumina tes	Ba0.A1203	Ba0-6A1-0-	Be0. A1203	Ca0-241203	3Ca0-5A1203	Ca0-A1203	3Ca0-A1203	CaO-BaO-MgO-	A1203 glass	Ce0. A1203	Ca0-A1203	DyA103	Dy203-2A1203	Gd203-A1203	Fe0.A1203	K20-A1203	L120.A1203	Li20-5A1203	Li2A1508	Mg0-A1203	Wn0-A1203	COLL OTA	College and	Sr0. 1100	Sr0.241.02	2Y202. A1203	3Y202.5A1.00	Y.0. A1205	Zno. A1203			

10

,

Comments																					
IR Cutoff µm	None?	9										4	~	4.8	4-5+						
n Refrac- tive Index		~3													~2~						
α Thermal Exp.Coeff.			7-10	5-7	3-5 6-10	6-9	4-8	~3	~10	9	~2.5	3	-4-+5	~5		~4.5	7-8		9-10	6-8	
F Young's Modulus 106 psi														32		224					
H Hardness kg/mm2														~1800		~1500					
p Density gm/cc														3,16		4.6					
T _M Melting Temp. OC				-										1800		d>1750	- non	2070			
Crystal* Struc- ture		c	T	1	۲	T							c	0	c	t			c		
terial	tes	deg012	e04	e04	ie04	e04	na tes Ir Og	a tes 03 · Nb205	202 · Nb205	0.Nb205	22-Nb205	phates PO4	· P205	cates 203-25102	114S13012	rsi04	na tes 1 ₂ 0 ₃ • 28n0 ₂	aSn03	Poussio4	a 28n207	

Table 5 Some Major Mixed Oxide Ceramic Families

11

Carries

		TN	a	H	я	ø	=		
Material	Crystal Struc- ture	Melting Temp. ^o C	Density gm/cc	Hardness kg/mm ²	Young's Modulus 10 ⁶ psi	Thermal Exp. Coeff. 10-6 oc-f.	Refrac- tive Index	LR Cutoff µm	Comments
Titanates Al ₂ 0, Ti02	0	1860	3.68			041**	1.96		
Bariog	T (C>120°C)	1600	5.9	600±200	18.0	12-13	~2.3	9-11	
B1203.T103							~2.5	10-127	
CaT103	0	1975	4.10	~1000		12-13		~5.5	
SrT103	c		5.11	~800	45.0	12-13	2.2	0.1~	
PbT103	T (C>500)	1250	7.52		~11.0		~2.7		
Rare Earth Titanates									
Tungstates									
ALAW602		1250				e~			
Bawo	T					17-28			
CaNOA	T	2250				17-22			
3La203 . WO3		2050							
Zrw208						4~			
Zirconates									
BaZr03	c	2650	6.26			8-0			
CaZr03	c	2400	4.76	600		5-11		9 Z	
SrZr03	c	2700	5.48		12	10-11			
PbZr03	•	1550	7.42		~17~	~10			
**Due to micro	cracking	from ver	y aniso	ropic exp	ansion;	dense fine	grain ma	terial	for
IR windows	ould have	substar	tially h	igher exp	Ansion.				
*C: Cubic, 1	: Tetra	conal, 0:	Orthor	hombic					

Table 5 (cont'd)

12

Stone Par

TABLE 6 SUMMARY OF 1-5 µ IR MATERIAL POSSIBILITIES

Materials	Opportunities and Limitations	
BORIDES	None - no transmission	
NITRIDES a) single b) mixed	Possibly AlN or GaN May be some possibilities	
OXIDES a) single b) mixed oxides	Possibly SnO2, probably no transition metal oxides	
aluminates	May be good possibilities, e.g. Ca aluminates	000
borates	Doubtful that any will transmit to 5 µm	SADI
germanates	May be good possibilities-better transmission than silica but higher expansion and refractive indices	ttes,
ha f na tes	May be some possibilities	
halides	Doubtful - high expansion, low hardness, and often moistu- attack	Ire
niobates	May be some possibilities	
phosphates	Uncertain	
silicates	Probably none	
stanates tantalates	Uncertain Unknown	
titanates	May be some possibilities) (typically have	
tungstates zirconates	May be good possibilities { { higher refractive May be some possibilities } { indices	
Phosphides, Chalcogen- ides and Semiconductors	Opportunity, but high refractive indices	
Silicides	None -•no transmission	
MIXED COMPOUNDS (e.g. Oxynitrides, oxy- sulfides, carbophos- phides, etc.)	May be possibilities, but least known area of material properties and preparation	

Senters

TABLE 7

GUIDELINES AND PITFALLS FOR NEW CANDIDATE IR MATERIALS

- 1. Transmission
- (a) longer wave transmission with heavier ions $\lambda \alpha \sqrt{M/k} k \alpha E$, $M = \frac{m_1 m_2}{m_1 + m_2}$; $E = Young's Modulus, m_1 = ion masses$
- (b) heavier ions increase refractories index
- (c) compounds with transition metal ions probably won't give necessary transmission because of intrinsic visible-IR absorption
- Hardness often not as critical, can be increased by alloying; e.g. fifty to several hundred percent, especially in ionic bonded systems.
- 3. Thermal Expansion
- (a) expansion tends to be lower for higher melting materials
- (b) expansion generally increases with increasing ionic bonding and generally decreases with increasing covalent bonding
- (c) expansion tends to increase with decreasing valence of a given ion
- (d) some low expansion coefficients are due to accommodation of highly anisotropic crystal expansion by cracks and pores. Also, some materials with low expansion at lower temperatures have high expansions at higher temperatures
- 4. Stability
- (a) some compounds are not stable, e.g. undergo reduction or decomposition
- (b) some undergo phase transformations between different crystal structures; some can be stabilized in a more desirable, e.g. lower thermal expansion structure by "alloying"



Fig. 1 - Transmission of polycrystalline (hot pressed) mullite and NiO single crystal as a function of wave length. While the mullite transmission is not corrected for surface reflections, the primary factor limiting its transmission is trace porosity left from the hot pressing operation which could be greatly reduced by further processing improvement. Since much of the porosity is quite fine, scattering from this increases as the wave length decreases and hence is the major factor in the drop-off in transmission with decreasing wave length. A critical question for the application of mullite for IR purposes is what the source of the absorption band at $\sim 4.4 \ \mu m$ is and the extent to which it may be reduced or eliminated. The Verneuil grown NiO crystals ($\rho \sim 7 \times 10^6$ ohm-cm) data is from R. W. Johnson and D. C. Cronemeyer, Physical Review 93, 3, p. 634-635, 1 Feb 1954. The wave lengths of the short wave length cut off ($\sim 2 \ \mu m$ for NiO) and the absorption band ($\sim 5 + \mu m$ for NiO) will vary some with the type of material. However, these effects are characteristic of transition metal oxides which thus makes most, or possibly, all such compounds unlikely candidates for IR usage in the 1 to 5 μ m region. Note the thickness for both samples is $\sim 1 \ \mu m$.