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DIRECTED SYNTHESIS/FABRICATION AND SURFACE MODIFICATION
OF IR WINDOW MATE. (U) ROCKWELL INTERNATIONAL THOUSAND
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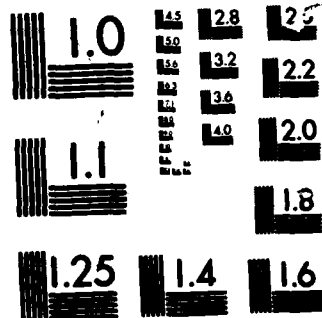
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**DIRECTED SYNTHESIS/FABRICATION AND
SURFACE MODIFICATION OF IR WINDOW
MATERIALS FOR THE 8-14 MICRON REGION**

AD-A166 661

**ANNUAL REPORT NO. 1 FOR THE PERIOD
March 1, 1985 through February 28, 1986**

CONTRACT NO. N00014-85-C-0140

Prepared for

**Engineering Sciences Program
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000**

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SELECTED
APR 17 1986
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**A. Harker
P. Morgan
Principal Investigators**

APRIL 1986

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SECURITY CLASSIFICATION OF THIS PAGE

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS													
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.													
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE															
4. PERFORMING ORGANIZATION REPORT NUMBER(S) SC5422.AR		5. MONITORING ORGANIZATION REPORT NUMBER(S)													
6a. NAME OF PERFORMING ORGANIZATION Rockwell International Science Center	6b. OFFICE SYMBOL <i>(If applicable)</i>	7a. NAME OF MONITORING ORGANIZATION													
6c. ADDRESS (City, State and ZIP Code) 1049 Camino Dos Rios Thousand Oaks, CA 91360		7b. ADDRESS (City, State and ZIP Code)													
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research Engineering Sciences Program	8b. OFFICE SYMBOL <i>(If applicable)</i>	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. N00014-85-C-0140													
8c. ADDRESS (City, State and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000		10. SOURCE OF FUNDING NOS. <table border="1"><tr><td>PROGRAM ELEMENT NO.</td><td>PROJECT NO.</td><td>TASK NO.</td><td>WORK UNIT NO.</td></tr><tr><td></td><td></td><td></td><td></td></tr></table>		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.								
PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.												
11. TITLE (Include Security Classification) DIRECTED SYNTHESIS/ FABRICATION AND SURFACE MODIFICATION OF IR WINDOW MATERIALS FOR THE 8-14 MICRON REGION. (U)															
12. PERSONAL AUTHOR(S) Harker, Alan and Morgan, Peter															
13a. TYPE OF REPORT Annual Report No. 1	13b. TIME COVERED FROM 03/01/85 TO 02/28/86	14. DATE OF REPORT (Yr., Mo., Day) 1986 APRIL	15. PAGE COUNT 10												
16. SUPPLEMENTARY NOTATION Results of current work will be reported at the SPIE 30th Annual International Technical Symposium, San Diego, California, August 17-22, 1986.															
17. COSATI CODES <table border="1"><tr><td>FIELD</td><td>GROUP</td><td>SUB. GR.</td></tr><tr><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td></tr></table>		FIELD	GROUP	SUB. GR.										18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Infrared, transmitting, chalcogenides, thin films.	
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Nearly monosize particles of pure NaLaS₂ have been made by a sulfide fused salt technique. Such particles promise easier compaction and HIPing to highly dense IR window material. The increased fracture toughness of glass substrates due to the addition of a thin compressive overlayer has been measured. The fracture toughness appears to increase linearly with the total film stress and is independent of the film thickness necessary to provide that stress.															
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☒ DTIC USERS ☐		21. ABSTRACT SECURITY CLASSIFICATION Unclassified													
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE NUMBER <i>(Include Area Code)</i>	22c. OFFICE SYMBOL												



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TASK I - THE PRODUCTION OF PURE, NEARLY MONOSIZED, PARTICULATE NaLaS_2

P.E.D. Morgan .

INTRODUCTION

New materials with high transmittance in the 8 - 14 μ IR region and with high strength and thermal shock resistance are desired. In general, the first requirement needs materials with high band gaps to avoid electronic absorption effects and weak bonding with heavier atoms. The other requirements are satisfied by strong bonding and are therefore basically incompatible with the first. Two types of compromise have been attempted. In one, low coordinations with relatively strong covalent bonding such as for ZnS and ZnSiP_2 ¹ do not quite give the desired long wavelength transmittance but do have better thermal shock resistance. The other, typified by the prescient choice of CaLa_2S_4 ,²⁻⁸ is based on the use of many weaker ionic bonds with high coordinate cations and anions. In the latter case thermal shock resistance has been unsatisfactory (at least with the large grain size material), although the long wavelength properties are extremely promising, while still unoptimized.

Our work recognizes the need to produce fine grained ceramic with grain size of less than $\sim 5 \mu$, whose toughness and thermal shock resistance should be superior without degrading the transmittance. To achieve this using the new ceramic paradigm we need $< 1 \mu$ uniform particles of the material and we probably must hot-isopress (HIP) the well compacted particles at temperatures preferably $< \sim 1000^\circ\text{C}$.

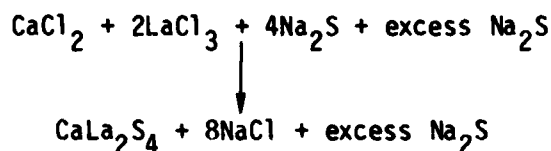
With this in mind, we used CaLa_2S_4 as a prototype to test fused salt techniques⁹⁻¹¹ to attain useful results quickly. Later we anticipated expanding the basic technique to whatever ceramic optical material(s) were the best candidate(s).



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Experimental and Results

A series of runs was initiated to determine conditions for precipitation and recrystallizing CaLa_2S_4 from a Na-Ca-La-S-Cl eutectic melt. Na_2S itself melts at 1175°C and NaCl at 801°C ; the eutectic in this system has not been determined as far as we know but the similar case of $\text{Na}_2\text{S}-\text{Na}_2\text{CO}_3$ (MP 856°C) has a eutectic at 755°C . It is reasonable to assume a eutectic at $< \sim 750^\circ\text{C}$ for the $\text{Na}_2\text{S}-\text{NaCl}$ system. The reaction:



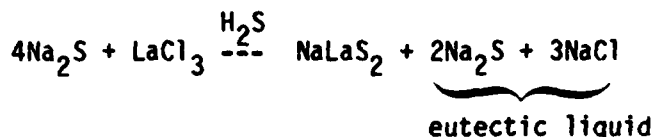
was tried with varying amounts of Ca, La and Na salts weighed out and mixed in a dry box, and fired in a 100% H_2S atmosphere in quartz glass boats in an alumina tube muffle furnace to $800 - 900^\circ\text{C}$. Slight melting was obvious at $\sim 800^\circ\text{C}$ and was pronounced at 900°C . The melts were initially extracted with cold water in which the basic $\text{Na}_2\text{S}-\text{NaCl}$ eutectic is easily soluble and the remnant powder rinsed with acetone and air dried. XRD analysis showed the presence of no CaLa_2S_4 but the obvious presence of recently discovered rock salt structure NaLaS_2 ¹² and $\text{La}_2\text{O}_2\text{S}$ contaminant. XRD analysis on the melts, before water extraction, indicated that $\text{La}_2\text{O}_2\text{S}$ was already present and was not a decomposition product of water reactions. Many runs, changing the relative amounts of Ca, La, Na, showed no sign of giving more than traces of CaLa_2S_4 , but always NaLaS_2 was a major component. The by-product $\text{La}_2\text{O}_2\text{S}$, a sign of contaminant oxygen, was greatly reduced but not eliminated by long slow heat-ups with excess H_2S .

The greater ease of formation of NaLaS_2 and the fact that it survived the water washes (and even boiling water for 30 minutes) suggested that it is a more stable compound (i.e., more negative ΔG) than CaLa_2S_4 and might be a worthy candidate, at the least for testing out the approach, and at best a real IR candidate. Having a 6:6:6 somewhat ionic coordination, it is a compromise between the types discussed earlier.



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For the next tests the almost irreducibly simple reaction:



was tried. Approximately 90% pure NaLaS_2 with ~10% $\text{La}_2\text{O}_2\text{S}$ was always produced; changes in the ratio of Na:La or extra times in H_2S did not seem to improve the purity. Indeed with large excess of Na_2S , an unknown compound, which we suspect could be something like Na_5LaS_4 , and which is unstable with water, appeared also.

The nagging problem of by-product $\text{La}_2\text{O}_2\text{S}$ was solved by replacing the H_2S stream with argon plus CS_2 . Argon was merely bubbled through CS_2 liquid in a glass jar before passing over the mixtures throughout the heating and cooling. It was reasoned that carbon might be formed but that if this occurred then the carbon would form a removable layer on top of the melt. In fact carbon was not seen and the $\text{La}_2\text{O}_2\text{S}$ contaminant was removed. Substantially pure NaLaS_2 was easily produced.

After extraction with water, no $\text{La}_2\text{O}_2\text{S}$ was seen by XRD, but in future work the eutectic melt will be dissolved by soxhleting with (m)ethanol or THF. SEM-pictures (Fig. 1) of the product indicate that indeed we can produce narrow size distributions of NaLaS_2 , resulting from the Ostwald ripening phenomenon in the melt. The particles may be showing some incipient cubic faceting and perhaps some superficial decomposition which should be eliminated by the organic extractions.

CONCLUSION

Fused salts with sulfide components seem to be suited for the production of narrow size distribution chalcogenides for IR window and other applications.



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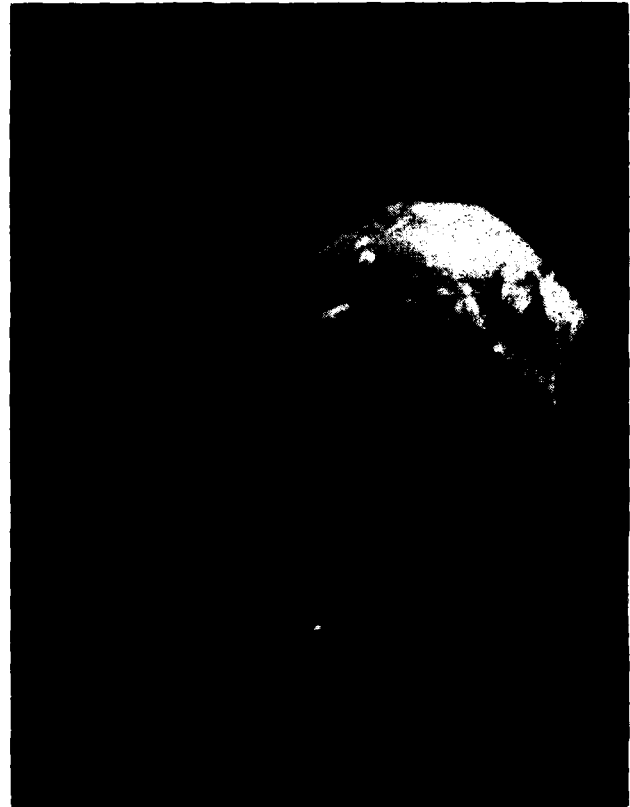


Fig. 1 SEM of particles of NaLaS_2 .



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TASK II - COMPRESSIVE THIN FILMS FOR INCREASED FRACTURE TOUGHNESS

P.H. Kobrin and A.B. Harker

Work on Task 2 has focussed on determining the effects of compressive surface layers on the measured fracture toughness of the bulk substrate. In the initial experiments single layers of Si_3N_4 , AlN , and Al_2O_3 were deposited onto glass substrates to determine if a measurable effect upon fracture toughness could be obtained. These tests were designed as a proof of principle as the substrate and film materials are not candidates for LWIR applications, and were selected for their ready availability and the fact that glass gives reproducible measurements of indent hardness and fracture toughness. The Vickers indent method was used since its application to fracture toughness and hardness determination has been well studied.¹³ In addition the compressive stress of the films was independently measured using a sensitive bending plate technique with capacitive detection.¹⁴ The goal is to have a model, perhaps empirical, that would relate the increased fracture toughness of a given substrate from a thin film of a given stress and thickness.

Single compressive layers of Si_3N_4 , Al_2O_3 , and AlN were deposited onto room temperature glass substrates to thicknesses of 500 - 10,000Å by reactive ion beam deposition.

With an uncoated substrate, there is a 1-2 decade range of loadings over which the Vickers indentation technique can be expected to yield a good measure of the materials fracture toughness, K . This range varies with different materials as does the range of crack lengths. However, within this useful range, the measured fracture toughness remains relatively constant and is in good agreement with other bulk fracture toughness tests.

With the addition of a thin compressive overlayer, the situation changes. On glass, these $< 1 \mu\text{m}$ thick films are considerably thinner than the penetration depth of the indenter (10-20 μm) or the length of the radial cracks ($< 80 \mu\text{m}$). However, the measured fracture toughness becomes a decreasing function of indenter load, that asymptotically approaches the bulk fracture tough-



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ness. The onset of cracking, the minimum load necessary to produce an observable radial crack, also increases dramatically. Thus the compressive film has a proportionally larger effect on the smaller indents.

The results of the fracture toughness measurements on glass are shown in Fig. 2. It can be seen that the increased fracture toughness, taken to be the 1.0 kg-load intercept, increases linearly with film thickness. In addition the slopes are in the order $\text{AlN} > \text{Si}_3\text{N}_4 > \text{Al}_2\text{O}_3$.

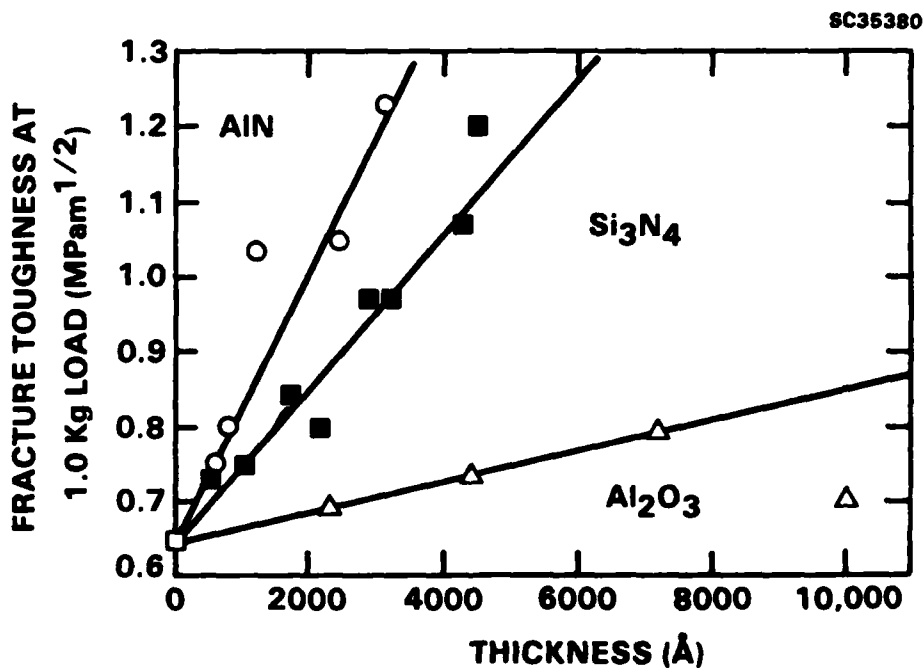


Fig. 2 Increased toughness of glass with films.

Stress measurements made with the bending plate technique gave values of 15×10^9 dyne/cm² for Si_3N_4 and 2×10^9 dyne/cm² for Al_2O_3 . An example is shown in Fig. 3. The AlN stress measurements proved to be erratic due to oxygen contamination. Comparing results we find that the Si_3N_4 films have 6.5 to 7.5 times more stress than the Al_2O_3 films while the fracture toughness of the Si_3N_4 coated glass increases 5 to 6 times faster with thickness.



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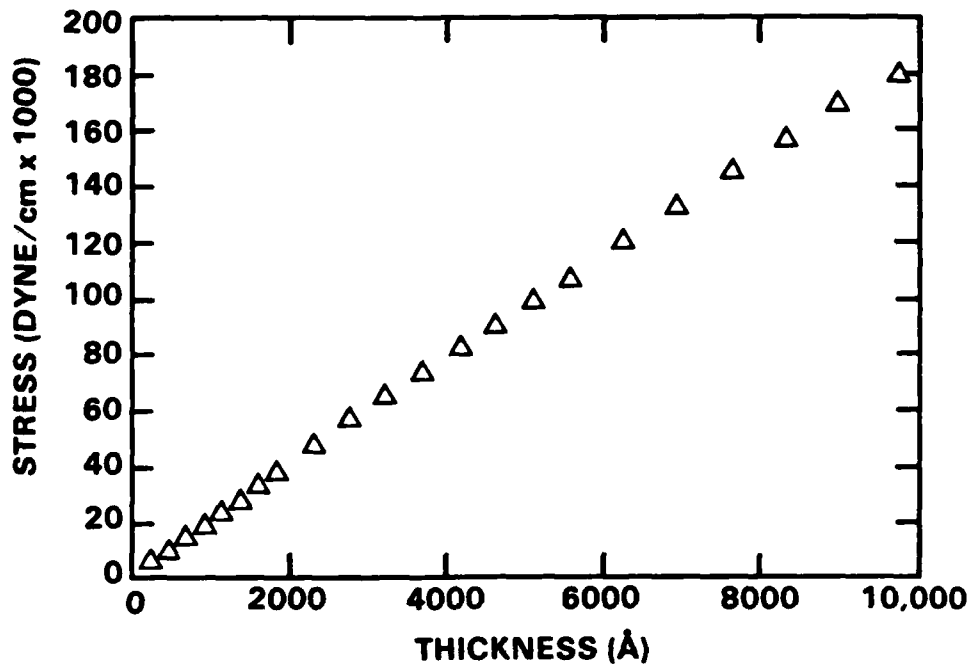


Fig. 3 Stress induced by an ion beam sputtered Al_2O_3 coating.

Thus the fracture toughness appears to increase linearly with the total film stress but is independent of the film thickness necessary to provide that stress. This is in disagreement with the fracture mechanics based model of Lawn and Fuller¹⁵ which has been used to model the decreased fracture toughness of ion irradiated glass. In that model the change in fracture toughness is proportional to the total stress divided by the square root of the layer thickness.

Attempts to extend these studies to spectroscopic grade ZnS (Cleartrans) which is a LWIR material proved futile as the indentation technique does not work well with the size grains present in the Cleartrans. Further studies on the smaller grained, yellow ZnS are therefore planned.

Results of current work will be reported at the SPIE 30th Annual International Technical Symposium, San Diego, California, August 17-22, 1986.



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