PN-ABY-846
91142

ANNUAL REPORT

Covering Period 26 Jan. 1995 - 31 Jan, 1996

Submitted to the Office of the Science Advisor
U.S. Agency for International Development

Materials for Passive Radiative Cooling

Principal Investigators: G. Hodes and D. Cahen
Grantee Institution: Weizmann Institute of Science, Israel.

Collaborator: W. Estrada and M. Horn
Institution: UNI, Peru.

Grant No. TA-MOU-94-C13-219

A.I.D. Grant Project Officer: Dr. M. Rechcigl

Project Duration: Jan. 26, 1995 - Jan. 31, 1999

Executive Summary

A passive solar cooler is based on two main parts: a *selective emitter* which emits heat into space, thereby cooling the surrounding space and a *shield* which prevents heating of the cooler by either direct heat transfer (e.g., wind) or by absorption of solar energy. Thus cooling can be obtained without needing any external energy source.

This project aims to develop both the emitter (in Peru) and shield (in Israel) to the point where a commercial passive cooler can be produced, with emphasis on simple and cheap technologies.

Selective emitters have been made using a simple spray method from silicon oxynitride, using silica and ammonia. Shields have been investigated based on polyethylene sheet as substrate (one of the few practical materials for this purpose) coated with tellurium by an indirect electrochemical method. More recently, lead selenide, deposited directly on the polyethylene by a simple chemical solution method, has shown promise for the shield. This latter material is a novel one for this purpose and if as good (if not better) than Te, would be preferable due to the great simplicity of the deposition method.

Since the first year has been largely exploratory, with much time invested in techniques and equipment, each team has worked independently. During the second year, we will start to combine the output of both teams and measure actual devices.

Section I.

A. Research Objectives. To define the materials and preparation procedures for building a passive cooling device in a technologically-simple and cheap manner.

B. Research Accomplishments.

The Selective Emitter (W. Estrada and M. Horn).

Preparation and characterization of thin films of silicon oxynitride obtained by spray pyrolysis.

The first half of the year was taken up, to a large extent, with building and setting up the spray pyrolysis system. Thin films of silicon oxynitride were obtained, using this system, by spraying a solution, using air to form a mist, on to a hot substrate where a pyrolytic reaction takes place, and a coating is formed. Corning glass and aluminum foil were used as substrates. The two solutions used were (1) silicic acid ($SiO_2.xH_2O$) dissolved in ammonium hydroxide or (2) mixed silicic acid and ammonium nitride (NH_4NO_3) dissolved in ammonium hydroxide. The optimum deposition conditions for the two solutions were found to be:

(1)

Concentration of $SiO_2.xH_2O$ in the solution (13M NH_4OH): 0.05 M

Substrate temperature: 130°C

Deposition time: 30 min.

Post-deposition heat treatment: 350°C for 30 min.

(2)

As for solution (1), but with the addition of 5mM NH_4NO_3 in the solution.

The coatings deposited under the above conditions were ca. 0.5 - 1 μm thick and showed good adherence to both substrates: glass and aluminum. Electron diffraction (using transmission electron microscopy) showed that there are two phases in the coatings: SiO_2 and Si_2ON. We are currently studying which phase predominates; infrared measurements support the latter. Fig. 1 shows the infrared reflection spectra (22° incidence angle) for samples prepared under conditions (1) and (2). Both samples exhibit a high absorption peak at the region 1260-860 cm-1 (8-12 μm), and the profile of the spectra is closer to Si_2ON than to SiO_2, as can be deduced from our first report for silicon oxynitride obtained by CVD. We also observe that in the first case, the intensity is significatively higher for case (1) which is an unexpected result. This may be due to the fact that the deposition rate is lower for (2) resulting in thinner films. We are currently studying this aspect and will continue to optimise the conditions.

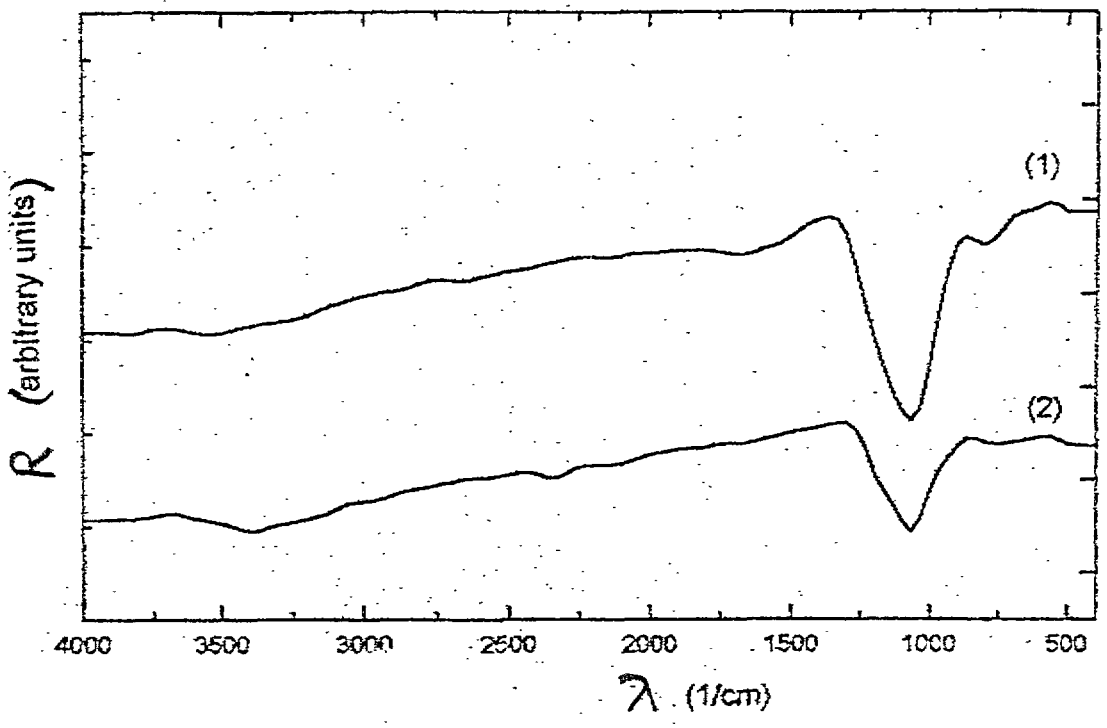

Figure 1. Infrared reflection spectrum (22° incident angle). (1) Sample deposited from solution (1) above; (2) deposited from solution (2).

The Shield (G. Hodes and D. Cahen).

The first year of the research concentrated on deposition of Te and PbSe on polyethylene foils, on optimization of the polyethylene foils themselves and to some extent, on CdTe deposition.

1. Polyethylene foils.

Thin polyethylene foils or films are the only practical substrate for the shield at present. Other materials either absorb too strongly in the window region or, as for high bandgap semiconductors, are not feasible in large areas. We studied several different types of polyethylene, both commercial and ones we prepared ourselves by polymerization.

Fig. 2 compares three different films of low density polyethylene. (A) and (B) are commercial films, differing in thickness. The 25μ film is clearly superior in its transmission; however, such thin films would be problematic in terms of strength and rigidity. Both films show an appreciable absorption at ca. 1100cm^{-1}, which is not characteristic of pure polyethylene and can be attributed to an additive which is usually added to commercial films. For this reason, we explored in-house preparation of such films where we could eliminate, or control, such additives. Fig. 2(C) shows an example of such a film (ca. 100μ thick). Its transmission in the window region is appreciably superior to the commercial film of half the thickness, due to virtual elimination of the "additive" absorption.

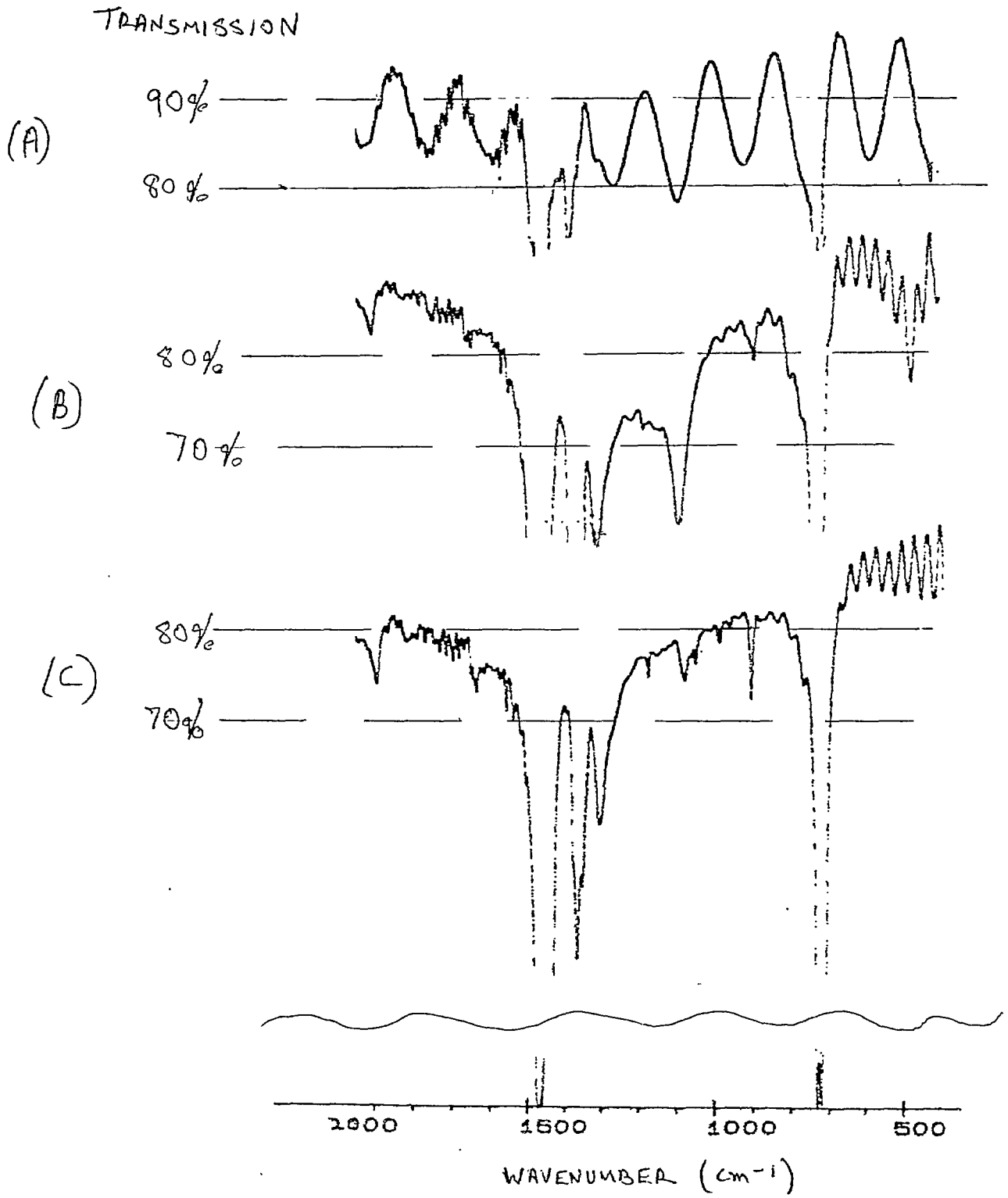

Figure 2. FTIR spectra of three polyethylene film samples. The window region is bound by the two strong absorptions at ca. 1520 and 720 cm^{-1}. (A) commercial polyethylene, 25μ thick. (B) as (A) but 50μ thick. (C) in-house prepared film, 100μ thick.

transmission in the window region is appreciably superior to the commercial film of half the thickness, due to virtual elimination of the "additive" absorption.

Other in-house prepared films tested by us included high density polyethylene and films with copolymers. The rationale in both cases was to improve the rigidity of the films, thereby preventing convection losses due to movement of the shield caused by wind. The high density polyethylene showed unacceptable absorption in the window region. The copolymer, while slightly poorer than the normal low density samples in terms of transmission, was somewhat more rigid. While promising, we decided, because of the marginal difference to postpone this direction. We will also use the commercial film for most experiments, for reasons of ease in obtaining the films, with the intention of changing over to better quality polyethylene films when we have decided on the optimum coating.

Te coatings.

Te is one of the most ideal materials (optically speaking) for the shield. It is (theoretically, for pure, intrinsic material) transparent in the window region and should block the entire solar region. Also, because of its large dielectric constant, it has a high reflectance in the solar region. Reflectance losses in the window region are appreciable but can be lowered by antireflection coatings. While vacuum evaporation is a standard method to deposit such films, we have been considering non-vacuum techniques in preference in keeping with the demands of simplicity of preparation.

One method, the decomposition of phosphine tellurides in solution, was unsuccessful (see half-year report). We developed a method whereby H_2Te is formed electrochemically <u>in situ</u> and decomposes to a Te film on the polyethylene (H_2Te is very unstable and readily decomposes to Te and H_2). While this method gave very promising results (see half-year report and fig. 3, which shows a Te film on polyethylene, we have had problems in reproducibility. Very thin films of Te are easily formed, but thicker films are more difficult to obtain. We have recently noticed that the geometry of the placement of the polyethylene is very important as is the presence of water in the region of the polyethylene. The Te tends to deposit preferentially on the glass vessel rather than on the polyethylene. In principle this can be ameliorated by using other materials for the reaction vessel; however at this stage, glass is a much more practical material for experimental work, both in terms of availability and transparency.

Regarding the environmental aspects, H_2Te is very poisonous and there may be a problem with its use in a manufacturing facility. On the other hand, in our laboratory set-up, it is generated <u>in situ</u> in a closed system, and we found no trace of the gas in the outlet exhaust (a solution of $CuSO_4$ was used at the gas outlet, and no sign of blackening - which would be clearly visible if even traces of H_2Te were present - occured in this solution).

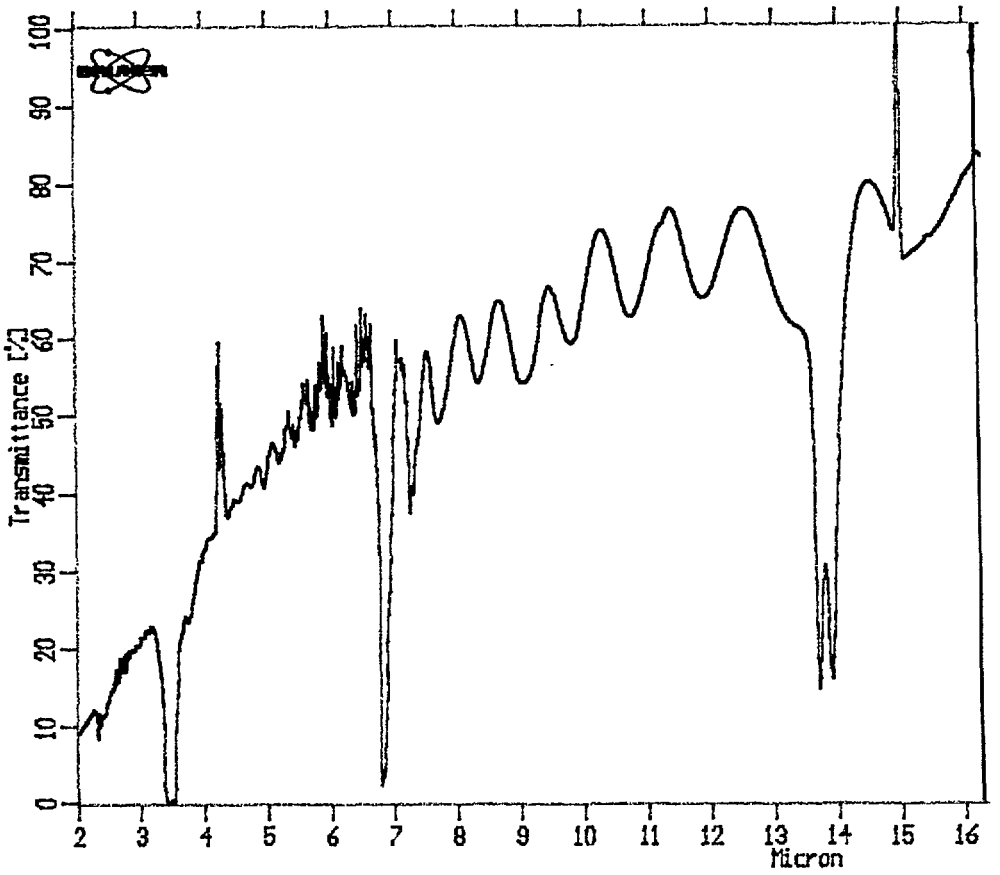

Fig. 3. FTIR transmission spectrum of Te on polyethylene.

PbSe coatings.

PbSe is a potential alternative to Te, with a low bandgap (0.27eV; 5μ), it should block the entire solar spectrum if thick enough while being transparent to the window region if undoped. Its high dielectric constant leads to high reflectivity in the solar region. This material was particularly attractive since we have experience in depositing it from aqueous solutions in different forms, in particular in controlling its optical properties in the visible and near IR region. Fig. 4 shows absorption spectra of different PbSe films chemically deposited from aqueous solutions. The leftmost spectrum is of a 50nm thick evaporated film, used as a standard. While the conditions for the individual films will not be described here, the different spectra reflect mainly different crystal sizes and size distributions in the PbSe films, leading to changes in the electronic band structure (the quantum size effect), and show clearly our ability to control optical properties.

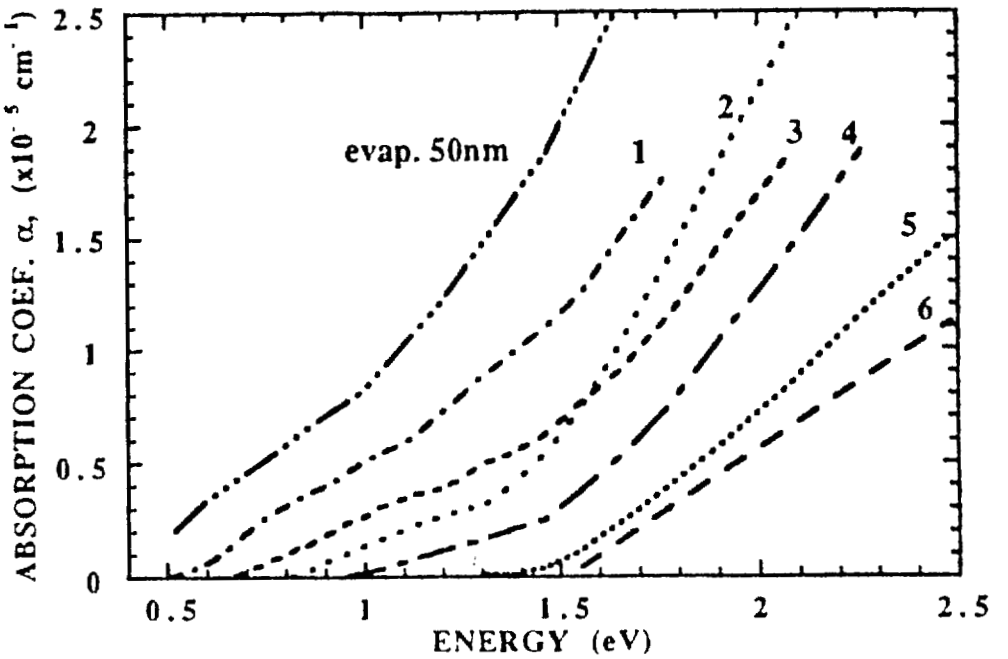

Fig. 4. Optical absorption spectra of PbSe films deposited on glass by chemical solution deposition under different deposition conditions.

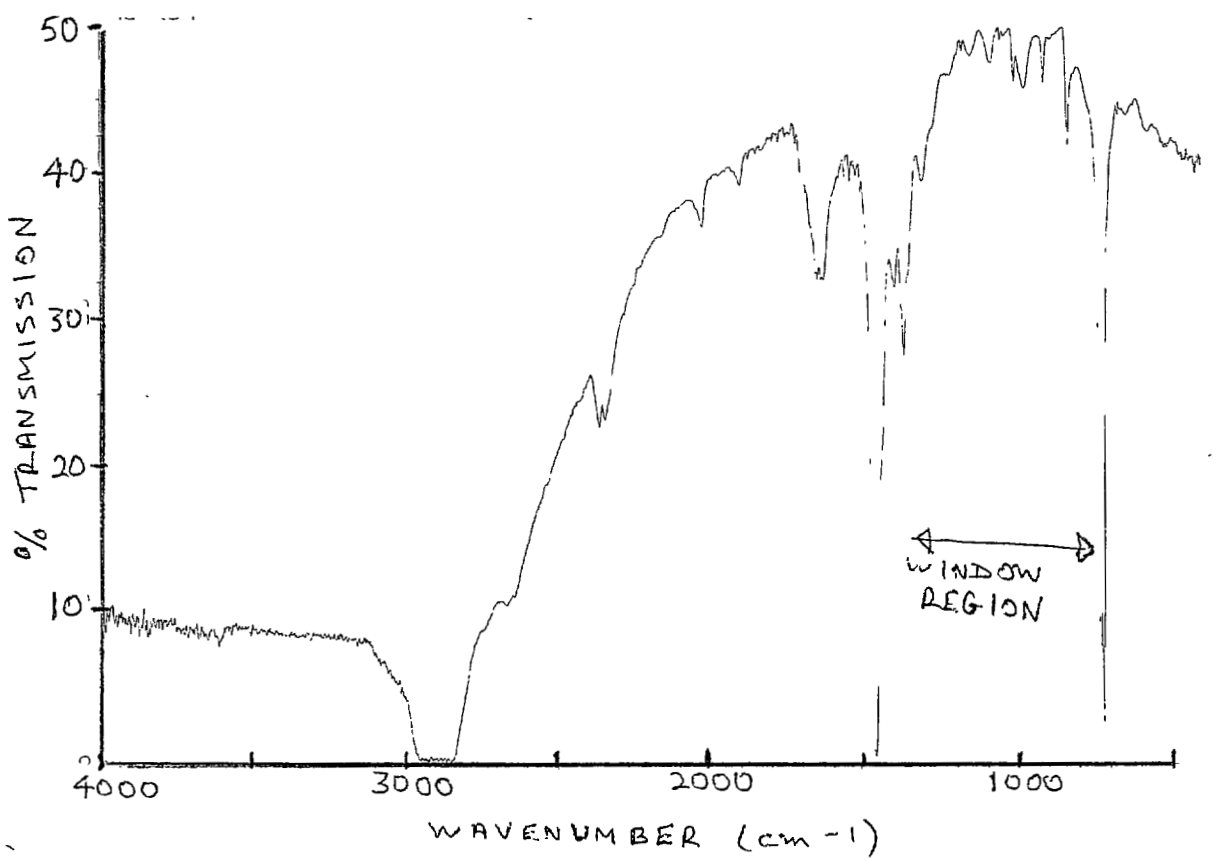

Fig. 5. FTIR transmission spectrum of PbSe film, prepared by chemical solution deposition, on polyethylene.

Fig. 5 shows the FTIR spectrum of our best sample of PbSe/polyethylene up to now. Transmission in the window region is ca. 50% (compared to ca.80% for the polyethylene substrate). The decrease in transmission starting at ca. $2000cm^{-1}$ is due to bandgap absorption of the PbSe (Eg = 0.28eV; ca. 5μ). The 10% transmission over the 3100-4000 range is probably due to pinholes and other inhomogeneities in the film (which would explain the lack of wavelength dependence). While PbSe may seem a potentially better choice for the shield than Te, we need more data and better samples before we can be sure of this. It does have the advantage of simpler preparation, since it does not require the separate step of gas generation.

CdTe electrodeposition.

While we decided that electrodeposition techniques will probably be inferior (practically speaking) to chemically deposited ones, due to the conductivity requirements of the substrate, we have studied electrodeposition of CdTe in a form that allows control of the optical properties, and sum up the results here.

CdTe was electrodeposited, using pulse plating, from a dimethylsulfoxide solution containing cadmium perchlorate, Te and tributylphosphine. The most important factor influencing the optical properties of the CdTe films was the ratio between the plating pulse duration (t_c) and the "off" (actually slightly anodic, to dissolve elemental Cd and Te) pulse (t_a). Fig. 6 shows the optical transmission spectra of 4 different films, with various t_c/t_a ratios and a standard evaporated film (the rightmost film), together with the estimated bandgaps of the films. The differences are due to the different crystal sizes in the nanocrystalline films.

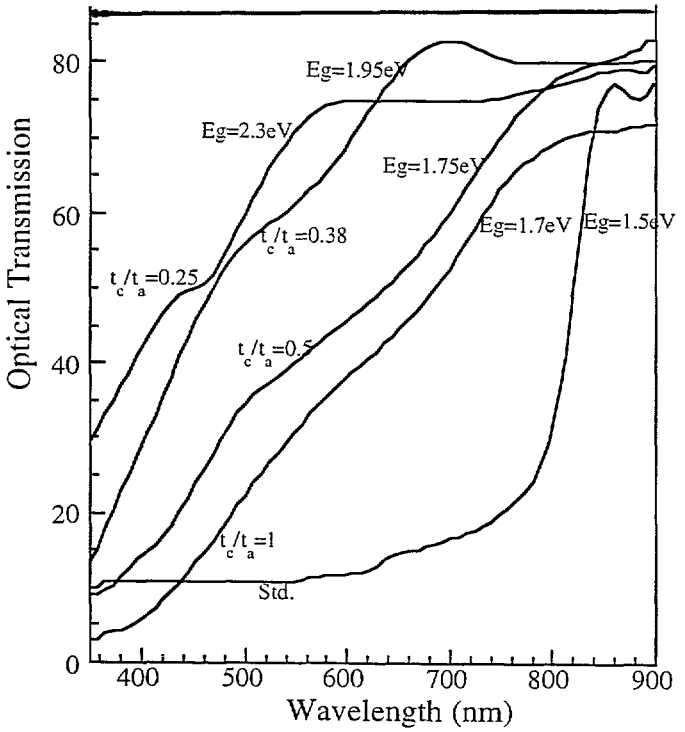

Fig. 6. Pulse electroplated CdTe on conducting glass.

C. Scientific Impact of Collaboration. At this early stage, the two teams have worked independently.

D. Description of Project Impact. The anticipated use of the results is the economic production of passive cooling devices.

E. Strengthening of Developing Country Institutions. A spray pyrolysis facility for deposition of the emitter material (and which can be readily adapted to the deposition of a wide range of different materials) has been set up in the Peruvian Laboratory.

F. Future Work. This first year of the project was largely involved with setting up equipment and techniques and exploratory research. In the proposal, we suggested PbS as a possible shield material. This material was found to absorb a considerable amount of the window radiation; PbSe, on the contrary, was found to be much more transparent, and therefore we have concentrated our efforts on that material instead.

Section II

A. Managerial Issues: None

B. Budget: No changes.

C. Special Concerns: None.

D. Collaboration, Travel, Training and Publications: Collaboration by fax and email at this stage,

E. Request for A.I.D. or BOSTID Actions: None.