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FINAL REPORT

TRIATOMIC CENTROSYMMETRIC CRYSTALS

G.W. Roland
T.J. Isaacs
K.B. Steinbruegge
R. Mazelsky
M. Rubenstein
A. Price

Sponsored by the Office of Naval Research

Contract No. N00014-71-C-0267

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A large number of sulfosalt compounds was investigated to determine the usefulness of such materials as infrared window materials, particularly at 10.6 μm. Polycrystalline synthesis were followed in a few instances by crystal-growth experiments and determination of absorption coefficients. Of the many materials examined, $TlInS_2$, $TlGaSe_2$ and $TlAsSe_3$ show most promise as window materials; in fact, the best measured absorption coefficient for Tl_3AsSe_3 ($0.016/cm^{-1}$) is the lowest ever measured on a material of this type. Particularly for Tl_3AsSe_3, it was demonstrated that absorption depends on the symmetry direction of wave propagation through the crystal.

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ABSTRACT

A large number of sulfosalt compounds was investigated to determine the usefulness of such materials as infrared window materials, particularly at 10.6 µm. Polycrystalline syntheses were followed in a few instances by crystal-growth experiments and determination of absorption coefficients. Of the materials examined, $TlInS_2$, $TlGaS_2$ and Tl_3AsSe_3 show most promise as window materials; in fact, the best measured absorption coefficient for Tl_3AsSe_3 (0.016 cm^{-1}) is the lowest ever measured on a material of this type. Particularly for Tl_3AsSe_3, it was demonstrated that absorption depends on the symmetry direction of wave propagation through the crystal.

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1. Introduction

There is considerable need at present for an optically good and mechanically strong crystal for use as a window material at the wavelength of high power CO_2 lasers, 10.6 μm. Materials which have received a great deal of attention include purely ionic crystals such as KCl and elemental and binary semiconductors such as Ge and CdTe. While a few ternary sulfides such as $CdIn_2S_4$(1) have been investigated as window materials, in general this class of compounds has heretofore been neglected; particularly this is true of selenide and telluride modifications of known ternary sulfide compounds. Theoretical considerations suggest that such compounds might have considerably enhanced optical transmission at 10.6 μm.

The aim of the present investigation was to systematically survey a large number of ternary sulfide-type compounds, select those which might show promise as 10.6 μm window materials, and attempt the crystal growth of such compounds. In addition, an effort was directed toward experimentally testing the theory that crystallographically centric compounds should show inherently less absorption at 10.6 μm than crystallographically acentric compounds. The methods and results of the study are presented in the following sections.

2. Properties of Window Materials

Of primary importance in the search for new window materials is the magnitude of the optical absorption at 10.6 μm. It is known that, to a large extent, this absorption depends on the wavelength of the low energy absorption edge, i.e., whether or not the "tail" of the absorption edge overlaps the 10.6 μm wavelength of interest. On the basis of this consideration, one would predict that selenides and tellurides would show decreased absorption at 10.6 μm, since their optical transmission ranges typically extend to 15-20 μm. This contrasts with the 8-12 μm absorption edges observed for ternary sulfide materials.

In addition, it has been predicted that a centric crystal structure is desirable from the standpoint of decreased optical absorption at 10.6 μm. In part this is due to the fact that crystals lacking a center of symmetry can exhibit nonlinear optical behavior, e.g., second harmonic generation. In window applications, so long as the possibility of phase matching is avoided, the conversion efficiency in second harmonic generation by windows made of acentric materials should be low. Nevertheless, this problem can be completely avoided by using a centrosymmetric material. In addition, the contribution to absorption due to multiphonon transitions can be important where thick windows and large optical power densities are involved. It is known that the selection rules for multiphonon processes, which involve the lattice symmetry, are much more restrictive for centric crystal structures than for acentric crystal structures.

As well as absorption, several other material properties are of fundamental importance. The electrical conductivity must be small enough so that free carrier absorption is low and the increase in concentration in charge carriers with increasing temperature does not cause thermal "run-away". Crystals must be mechanically strong, and not react with water or other atmosphere components. Finally, isotropic crystals are desirable to eliminate birefringence, although for certain noncubic crystal classes, the problem of birefringence can be eliminated by propagating the radiation along an optic axis.

3. Materials Survey

Most of the materials surveyed during this study were those known as sulfosalts and their Se and Te analogs. These can be defined as compounds having the general chemical formula $A_mB_nC_p$, where A represents a metal (usually Ag, Cu, Hg, Pb, Tl, and/or Zn); B represents As, Bi, or Sb; and C represents S, Se or Te. Well over a hundred sulfosalt minerals have been identified in ores. Many of the currently-known varieties are described in The System of Mineralogy(2) and an up-to-date compilation of chemical compositions and crystal structures is reported by Nowacki.(3) The vast preponderance of these minerals are sulfide-type, i.e., varieties in which C in the general formula represents sulfur; Se- and Te-bearing varieties are rare (in accord with the geochemical abundance of sulfur relative to that of Se and Te). We have found that synthetic Se- and Te-bearing analogs exist for many of the known minerals and further that phosphorous can occur as the B atom in the ideal chemical formula. The number of potential compounds is certainly high and indeed several new sulfosalts are identified in ores each year.

The B and C atoms in the general sulfosalt formula $A_mB_nC_p$ are always closely associated in the crystal structures, forming finite groups, rings, chains, or nets of BC_3 trigonal pyramids or BC_4 tetrahedra (with or without additional C ions). Nowacki has classified all known sulfosalt minerals according to which of these structural units is present. Perhaps a more convenient (but related) classification is by ϕ number, where

$$\phi = \frac{\text{Number of C atoms}}{\text{Number of B atoms}}$$

For Ag_3AsS_3, $\phi = 3$. For Tl_3AsS_4, $\phi = 4$, etc. Compounds with $\phi = 4$ typically contain, for example, isolated BS_3 pyramids with excess sulfur, or isolated BS_4 tetrahedra. The classification has been discussed in some detail by Nowacki.

In investigations at Westinghouse Research(4) we noted that the ϕ number of a sulfosalt can to some extent be used to indicate the probability that a given compound will be centric or acentric in a crystallographic sense. Table 1 shows the percent of centricity versus ϕ for 64 sulfosalt minerals for which the structures are known. This table indicates that compounds having centrosymmetric crystal structures occur with much higher frequency for compounds with low ϕ numbers rather than for compounds with high ϕ numbers, say above 3. As discussed above, a centrosymmetric structure appears to be a desirable feature of a 10.6 μm crystal window, and we therefore concentrated on compounds with $\phi < 3$.

Table 1

The Percent of Centricity Versus ϕ
for Sulfosalt Minerals

Value of ϕ	Percent of known minerals that have Centric Structures
> 4	Insufficient Data
4	0
3 to 4	20
3	50
2 to 3	70
2	74
1 to 2	100
1	55

3.1 Criteria for Selecting Promising Materials

In an extensive materials survey such as that undertaken during this program, it is necessary to have easily-applied criteria so that little unproductive effort is wasted on unsuitable materials. This is particularly true when selecting materials for lengthy crystal growth experiments. In general, the following sequence of events was followed for each material examined:

1) The material was prepared as a polycrystalline ingot and examined visually for homogeneity followed by microscope examination of polished specimens. Samples that were glassy or polyphase were rejected on the grounds that crystals could probably not be obtained by Bridgeman growth, the

best technique for growing large crystals of sulfide-type materials.

2) Wherever possible, a fragment of single crystal from a polycrystalline ingot was selected for determining the optical transmission range. In only a few instances could this be done.

3) The electrical conductivity of the material was determined with a volt-ohmmeter.

4) X-ray powder diffraction patterns were taken to help identify the crystal symmetry. For a few compounds, single crystal photographs were taken using a Buerger precession camera.

The large majority of compositions examined failed one or more of the above tests and were summarily rejected as window-material candidates. In a few cases, compounds were deemed sufficiently promising that crystal growth experiments were undertaken. The physical and optical properties of the crystals are described in sections subsequent to the description of experimental techniques below.

3.2 Preparation of Polycrystalline Ingots

In all cases, charges for preparation of polycrystalline ingots were prepared from carefully weighed stoichiometric amounts of the elements. Elemental reactants were purchased from the American Smelting and Refining Company (ASARCO) and were 99.999 + weight percent pure as determined by the suppliers spectrographic analyses. The weighed mixtures were sealed under vacuum in quartz-glass containers and heated above the melting point of the particular compound being examined. Mixing was assumed by opening the furnace several times and vigorously shaking the ampoules. The charge was then cooled slowly to room temperature, either by shutting off power to the furnace or by opening the furnace and allowing the charge to air cool. The product was then examined as described above.

3.3 Crystal Growth

Experience at Westinghouse Research in growing proustite and pyrargyrite(5,6) has shown that the essential features for crystal growth of congruently-melting sulfosalt materials are: (1) carefully prepared reactant material that precisely matches the composition of the desired crystal, (2) a slow growth rate (10 to 20 mm/day), and (3) a steep (5 to 15°C/mm) temperature gradient. The slow growth rate and steep temperature gradient are necessary to eliminate constitutional supercooling. We have optimized the growth facilities to provide the necessary steep temperature profiles and slow growth rates.

Reactant material is prepared directly from the deoxidized high-purity elements, thus eliminating additional preparation steps and the use of compounds of uncertain stoichiometry. The elements are weighed in desired proportions and sealed under vacuum in a quartz ampoule. Usually about 50 grams of each reactant are prepared per batch. The elemental mixture is slowly heated to some temperature above the melting point, the liquid mixed by vigorously shaking the quartz container, and the liquid allowed to crystallize slowly and cool to room temperature. Portions of the prepared reactant are sealed under about 0.8 atm of pure argon pressure in quartz "crystal-growing" tubes which contain a necked-in portion near the bottom to initiate single-crystal growth. The tube is allowed to drop slowly through a two-zone furnace and the melt crystallizes as it drops into the lower (cooler) furnace. The two-zone furnace is specially constructed to give the required steep temperature gradient.

The grown crystal is allowed to anneal at the temperature of the lower furnace (usually set at about half the melting temperature) and then cooled to room temperature over a period of two to three days. Usually no problem occurred with regard to cracking of the crystals.

3.4 Optical Measurements

Routine measurements of optical absorption were made from near the electronic absorption edge ($\lesssim$ 1 μm) out to 10.6 μm by comparing samples of different lengths in absorption spectrophotometers. This technique allows one to eliminate qualitatively the contribution from surface reflection to the total measured loss. For optical losses below about 3%, a calorimetric technique is preferable.

10.6 μm Calorimetric Absorption Loss Measurements

A 10.6 μm laser-calorimeter has been assembled, calibrated and used to determine the optical absorption loss in infrared window materials. The 10.6 μm laser beam is generated in a 1.8 meter long x 2.5 cm ID water cooled discharge tube contain a flowing mixture of $10CO_2$-$10N_2$-80He at about 5 to 10 torr. The gas discharge is maintained using a ballasted 12 kV 0.5 amp direct current power supply. Under normal operating conditions the discharge current is 0.06 to 0.11 amp. Annular cooled electrodes have been fitted to the tube to provide a uniform discharge and the tube has Brewster angle KCl windows on the ends to insure beam polarization. Several combinations of external 10.6 μm reflecting mirrors are available which permit continuous output powers over 100 watts to be obtained. For the work being reported,the resonant cavity was formed using a 21 meter radius of curvature copper mirror at one end of the discharge tube and a flat gold coated stainless steel mirror with a 3 mm diameter hole centered on the beam axis as the output mirror. An Hex #1 Universal Shutter is located between the discharge tube and the output mirror to permit the output laser beam to be turned on and off at will. Various size apertures are available which allow us to reduce the beam power and divergence as required. The laser and calorimeter system is mounted on two 3.3 meter long by 2 cm diameter Invar rods which serve to reduce the effects of temperature variations in the laboratory. For the absorption loss measurements the laser parameters were adjusted to provide a stable (i.e., fluctuations less than 5%) 10.6 μm output beam of 7 watts with a diameter of about 4 mm.

The test samples measured were cylindrical single crystals of KCl and Tl_3AsSe_3(TAS). The KCl sample was finished to 9.45 mm dia x 4.88 mm thick and the TAS sample was finished to 9.50 mm dia x 3.61 mm thick. The faces on each sample were finished flat to about 1 wave at 0.5 μm and unfortunately, the surfaces were visibly scratched.

The samples were mounted in a Micarta ring 4 cm ID and held on three Teflon points having a contact area with the sample of about 1.8 mm^2 each. One of the Teflon tips is recessed to hold the Veco 35A1 beam thermistor which was used in conjunction with a bridge circuit and chart recorder to determine temperature rise due to laser heating. The thermistor was coated with a thin coating of Wakefield Thermal Compound to insure good thermal contact with the sample. The thermistor and bridge combination was designed to give a potential of 14 millivolt/°C and temperature changes as low 0.01°C can be determined with this system.

3.5 Results of Materials Survey

The results of the materials survey are presented below in tabular form.

Table 2

Compositions Examined during this Investigation

Composition	Remarks
	$\phi = 3.5$
$In_4Ga_2S_9$	Incomplete reaction at 900°C
	$\phi = 3$
Tl_2GeS_3	Polyphase
Tl_2VS_3	Single phase, nonconducting, cubic
$Ag_5Pb_2S_6$	Polyphase, conducting
$InSbS_3$	Polyphase
$InSbSe_3$	Polyphase
$InSbTe_3$	Polyphase
$InAsS_3$	Incomplete reaction at 900°C
$InAsSe_3$	Polyphase
$InAsTe_3$	Polyphase
In_4SbSe_3	Polyphase
$Pb_3Bi_2S_6$	Polyphase

	$\phi = 2.5$
$Tl_2As_2Te_5$	Conducting glass
	$\phi = 2$
$TlBiSe_2$	Single phase, conducting
$TlBiS_2$	Single phase, conducting
$TlAsS_2$	Glass
$TlAsSe_2$	Glass
$TlAsTe_2$	Glass
$TlSbS_2$	Polyphase
$TlSbSe_2$	Single phase, nonconducting
$TlInS_2$	Single phase, nonconducting
$TlInSe_2$	Single phase, conducting
$TlGaS_2$	Incomplete reaction at 900°C
$TlGaSe_2$	Single phase, nonconducting
Tl_2PbS_2	Polyphase
$TlGaTe_2$	Single phase, conducting
$AgAsS_2$	Glass
$AgAsSe_2$	Polyphase
$AgBiS_2$	Single phase, conducting
$AgSbS_2$	Single phase, nonconducting
$AgPbSb_3S_6$	Single phase, nonconducting
$AgSbSe_2$	Single phase, conducting
$AgInSe_2$	Single phase, conducting
Ag_3TlS_2	Single phase, nonconducting
$AgTlS_2$	Single phase, nonconducting
$AgGaSe_2$	Single phase, conducting
$AgGaTe_2$	Single phase, conducting
In_3SbTe_2	Polyphase
In_3SbSe_2	Polyphase
$InBiSe_2$	Polyphase
Cu_3TlS_2	Single phase, conducting
Cu_3AgS_2	Single phase, conducting
$KGaS_2$	Very soft, single phase

$\underline{\phi = 1}$

$InAs_3Se_3$	Polyphase
AgTlS	Very low melting point

Solid Solution Series

Nine compositions in the system $AgBiS_2$-$AgSbS_2$ were tried and four of these were single phase and nonconducting. Two were selected for crystal growth experiments, described below.

Compositions in the series GeP_xTe_y were prepared with $x = 1$ and 2 and $y = 3$ and 4. These appear single phase and nonconducting.

For convenience the compounds have been grouped by ϕ number. A few compounds are included that are not strictly sulfosalts according to the definition in Section 3.1; these were investigated however because of their crystal-chemical similarity to this class of compounds. Observations of pertinence to the search for new window materials are reported in the "Remarks" section of the table.

3.6 Crystal Growth Experiments

At least twenty-five crystal-growth experiments were undertaken on compounds selected from Table 2. In many cases, we were unable to obtain single crystals--only a polycrystalline aggregate resulted, although often containing relatively large crystallites (> 2 mm). While in certain cases we can ascribe our failure to obtain single crystals to reasons such as twin formation, in other cases the cause of failure is obscure. Slight deviations from stoichiometry at elevated temperature are possible causes; probably only a complete study of the phase diagrams in the appropriate chemical systems would resolve the difficulties. Growth experiments on the various compounds are described in detail below.

<u>$AgSbS_2$</u> is of hardness between 3 and 5.5, and melts at approximately 580°C. We tried growing it at a gradient of 11°C/mm and at rates from 13 to 15 mm/day. This material is dimorphic, with the high-temperature form being cubic (NaCl structure), and the low-temperature form being monoclinic.(7) The inversion, while sluggish, was too rapid for growth of a large single crystal using a melt technique.

Experiments conducted on <u>$AgBiS_2$</u> indicated that its inversion was sluggish enough to permit the growth of large single crystals. Unfortunately, this material is conducting and therefore not useful as windows. As $AgSbS_2$ is not conducting, and as there probably is solid solution between these compounds, we tried growing two intermediate compositions in this series (<u>$AgSb_{.7}Bi_{.3}S_2$</u> and <u>$AgSb_{.3}Bi_{.7}S_2$</u>). Both of these materials melt at approximately 700°C. They were grown using a gradient of 11°C/mm, and at rates of 15.3 and 11.8 mm/day for $AgSb_{.7}Bi_{.3}S_2$ and $AgSb_{.3}Bi_{.7}S_2$ respectively. Good quality single crystals were not obtained; transmission tests showed that the samples were polycrystalline.

<u>$TlSbSe_2$</u> has been reported as having a centro-symmetric orthorhombic structure.(8) This compound has one excellent cleavage and is somewhat platy. Its hardness is between 3 and 5.5. It melts at approximately 450°C, and was grown at a gradient of 10°C/mm at a rate of 12 and 13.3 mm/day. We did not obtain a single crystal.

Chalcothallite (Cu_3TlS_2) was found to be conducting, so we made its silver analogue, <u>Ag_3TlS_2</u>. It melts at approximately 300°C, and was grown at a gradient of 10°C/mm and a rate of 14.6 mm/day. We obtained a polycrystalline aggregate rather than a single crystal from this experiment. This material has no obvious cleavages, and has a hardness between 3 and 5.5

Another material which we tried to grow as a large single crystal is $\underline{AgPbSb_3S_6}$. The compound melts at approximately 400°C. Two growth runs were tried, one at a rate of 10 mm/day, the other at 12 mm/day. Both runs had a gradient of 10°C/mm. Neither run produced the desired result, and the "crystals" fell apart. The compound has a good cleavage, and is fairly soft with hardness under 3.

We have recently grown two materials which show promise for use as windows. These are $\underline{TlInS_2}$ and $\underline{TlGaSe_2}$. The first mentioned has an orange-red color and transmits to 15.6 nm. The second material has a dark red color and transmits to 14 nm. No absorption bands at 10μm were observed for either material.

Both of these compounds have been made elsewhere, with their symmetry given as tetragonal (TlSe-type). Two forms of $TlInS_2$ have been reported,(9-11) one of which (β-$TlInS_2$) corresponds to the material which we made. We have not made the α-form. According to the literature it has a bluish-blackish color, and is tetragonal, space group I4/mcm (which is the same as the β-form). A study of polymorphism in this compound, and possible polymorphism in $TlGaSe_2$ and $TlGaS_2$ should be undertaken to provide us with information necessary to the understanding of their growth as large single crystals of high optical quality.

The melting point of $TlInS_2$ was determined to be approximately 760°C and that of $TlGaSe_2$ approximately 780°C. We grew large single crystals of these materials using a temperature gradient of 15°C/mm for each, and growth rates of 11.1 mm/day for $TlInS_2$ and 17.5 mm/day for $TlGaSe_2$.

Both of these compounds show one excellent cleavage, and tend to be somewhat platy. Both are rather soft with hardnesses under 3 in the Moh scale.

Small single crystals of $TlGaSe_2$ and $TlInS_2$ were studied using the x-ray precession technique. We have ascertained that $TlGaSe_2$ is monoclinic with lattice parameters $a = b = 7.56$ Å, $c = 30.9$ Å and $\beta \simeq 94^\circ$. $TlInS_2$ appears to be tetragonal with lattice parameters $a = 7.7$ Å, $c = 29.8$ Å. Zero-level photographs indicate a primitive lattice rather than the body-centered lattice reported in the literature.

Piezoelectric tests on both of these materials were negative, which, while not proof positive of a center of symmetry, is an indication of possible centro symmetric structures.

We also tried making related compounds and found that $TlGaTe_2$ and $TlInSe_2$ are conducting and therefore cannot be used as window materials. We were unable to synthesize $TlGaS_2$ using techniques mentioned earlier in this report because of its high melting point.

Another new material which grows as a large single crystal and is not conducting is Tl_2VS_3. X-ray powder diffraction patterns taken of the reactang show a body-centered cubic symmetry. No prominent cleavage planes were seen. The material is rather soft with hardness under 3. The melting point is approximately 500°C, and the crystal was grown with a gradient of 10°C/mm at a rate of 13.8 mm/day. Absorption measurements showed relatively high absorption at 10.6 μm (> 1.0 cm^{-1}) but improved crystal quality would probably result in reduced absorption.

Tl_3AsSe_3. Although this compound was identified and grown as single crystals prior to the start of this contract, we made several new growth runs for the purpose of evaluating its potential as a window material. The results obtained from optical measurements are described below.

4. Absorption Measurements

Measurements of the optical absorption at a wavelength of 10.6 µm were undertaken with two purposes in mind. Foremost, of course, was to determine what promise a given compound showed for window applications at 10.6 µm. Of nearly equal importance however, were absorption measurements undertaken to test a theory based on theoretical considerations by Nicolai(12) that minimal optical absorption is obtained with crystals which have symmetry with respect to optical modes and with preferred orientations of the crystals. These latter absorption measurements were all performed using the calorimetric techniques described in Section 4.2.

4.1 Spectrophotometer Measurements

Measurements of optical absorption using a spectrophotometer were performed on crystals of three chemical compositions: Tl_3AsSe_3, $TlInS_2$ and $TlGaSe_2$. Their crystal growth was described above.

The newly determined curves relating optical absorption versus wavelength for Tl_3AsSe_3 were similar to those previously determined;(4) the data are shown in Figs. 1 and 2. Measurements of the absorption using samples of different path length showed that absorption was less than about 3.0% cm^{-1}, about the limit of resolution using this technique. Additional calorimetric measurements are reported below.

Optical absorption curves for $TlGaSe_2$ and $TlInS_2$ in the infrared have not previously been reported. The curves we have determined

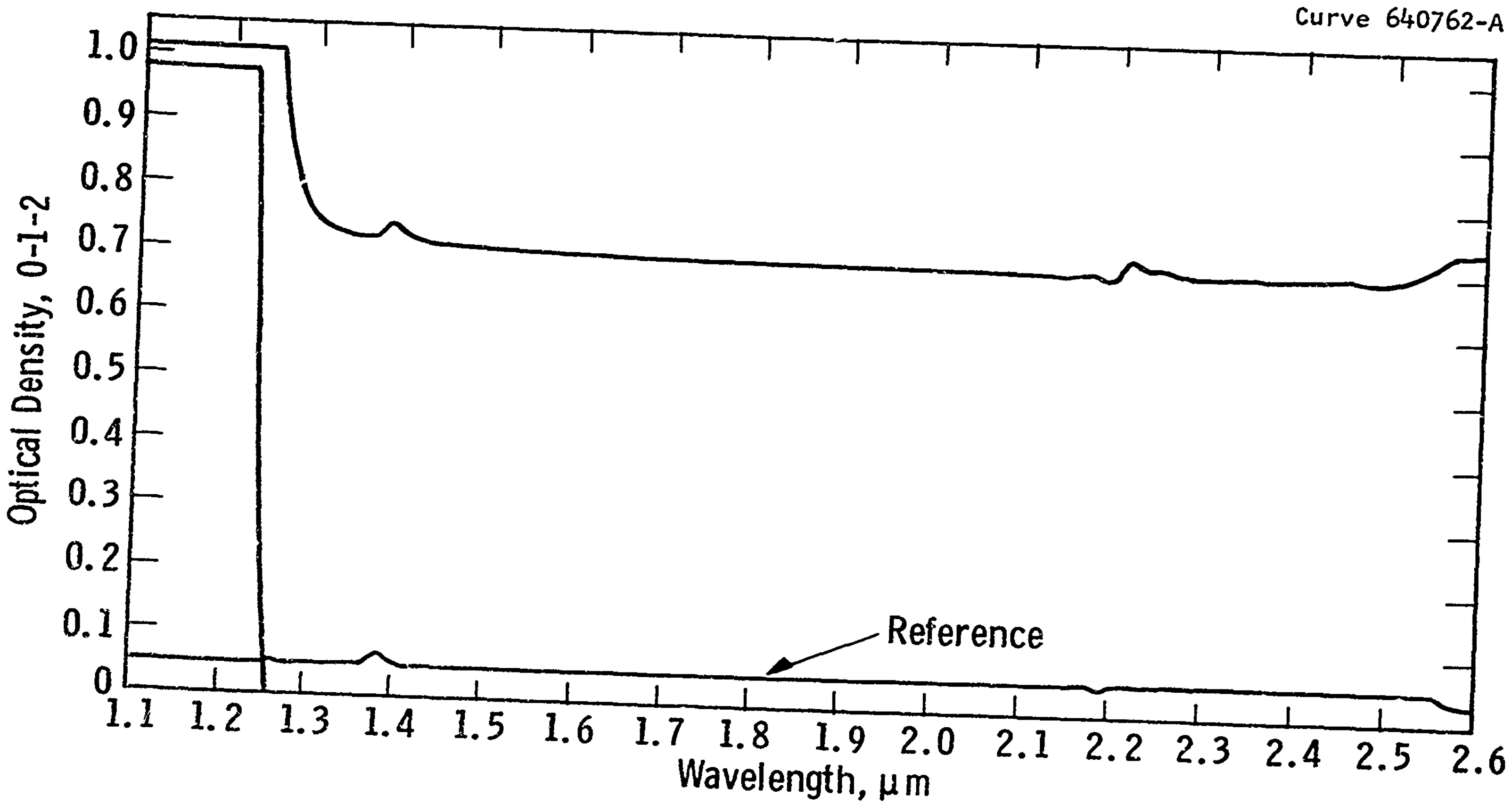

Fig. 1 —Optical density of Tl_3AsSe_3 in the 1.1μm-2.6μm region. Sample thickness 0.545 cm. Curve uncorrected for reflection losses

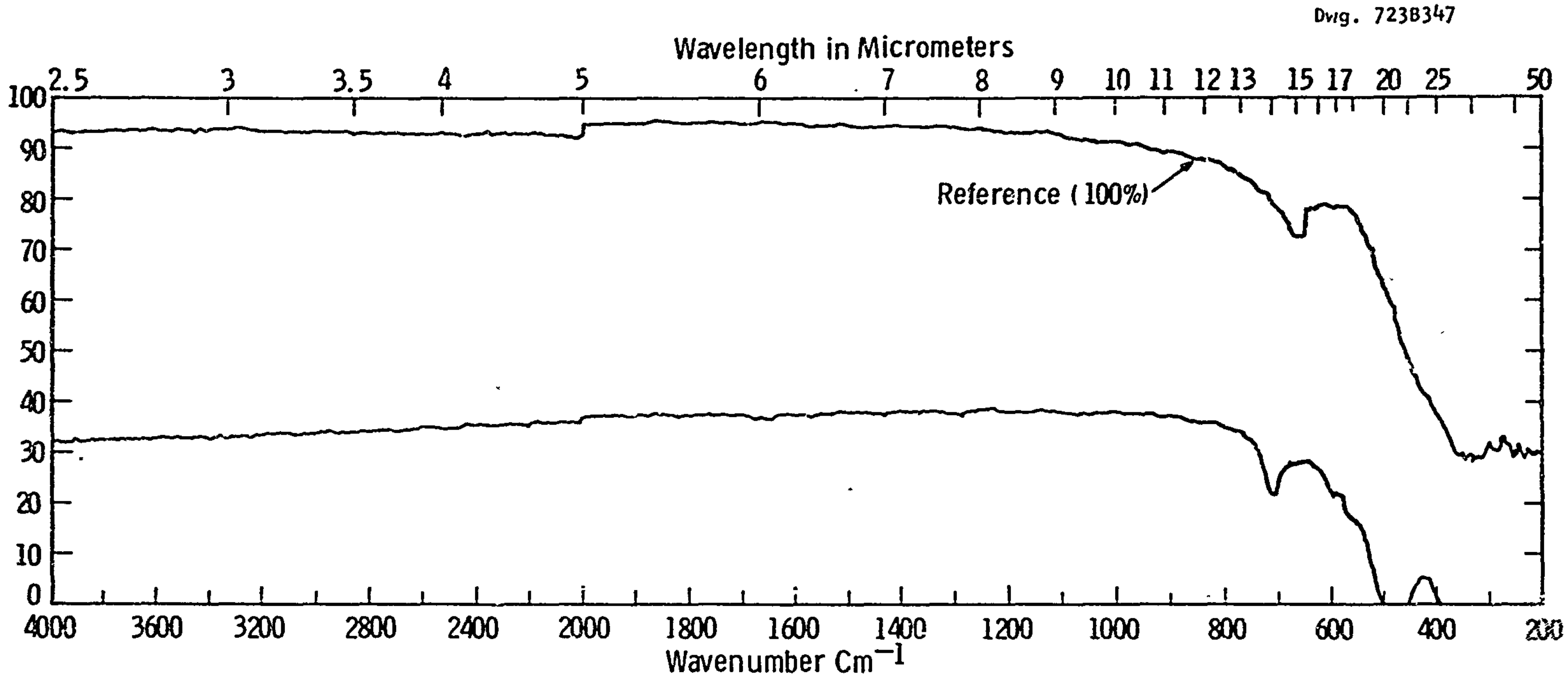

Fig. 2— Optical transmission of $T\ell_3 As Se_3$ in the 2.5 μm → 20 μm region. Curve uncorrected for reflection losses. Sample thickness 0.63 cm

(Figs. 3 and 4) show that $TlInS_2$ transmits to beyond 15 μm and that $TlGaSe_2$ transmits to beyond 14 μm. No absorption bands are present at 10.6 μm. Particularly for the sulfide material, the lack of absorption bands at 10.6 μm is surprising since such bands are present in nearly all other such materials.

4.2 Calorimetric Measurements

Calorimetric measurements on Tl_3AsSe_3 were undertaken to verify the theory of absorption with respect to preferred crystal orientation as noted above. Two sets of measurements have been made. The first set was performed on Westinghouse-grown Tl_3AsSe_3 crystals by Alan Thompson, Bell and Howell Corp. The measurements were conducted on samples which in one case were cut and polished with the c axis (polar) normal the polished surfaces, and in the second case, lay in the polished surfaces. The measurement data are presented in Table 3.

Table 3

Calorimetric Measurements on Tl_3AsSe_3

Crystal No.	Orientation	Absorption Coeff.
204554-31-1	c axis in plane	
	E vector of radiation $\parallel$ c axis	.044
	E vector of radiation $\perp$ c axis	.062
204554-36-7	c axis normal plane	.55

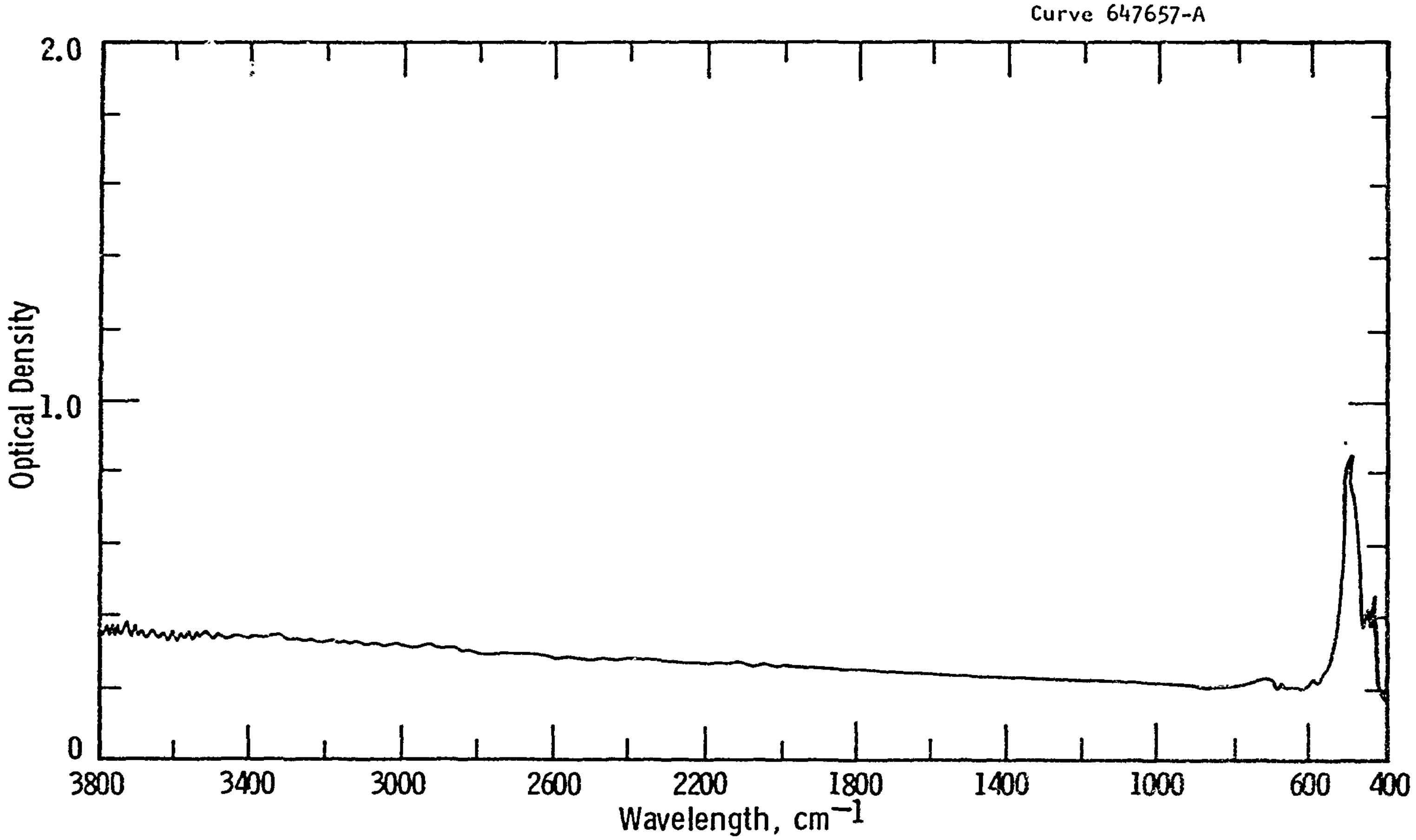

Fig. 3—Optical density of single crystal $TlGaSe_2$. Curve uncorrected for reflection losses. Sample thickness approximately 1mm.

Curve 647658-A

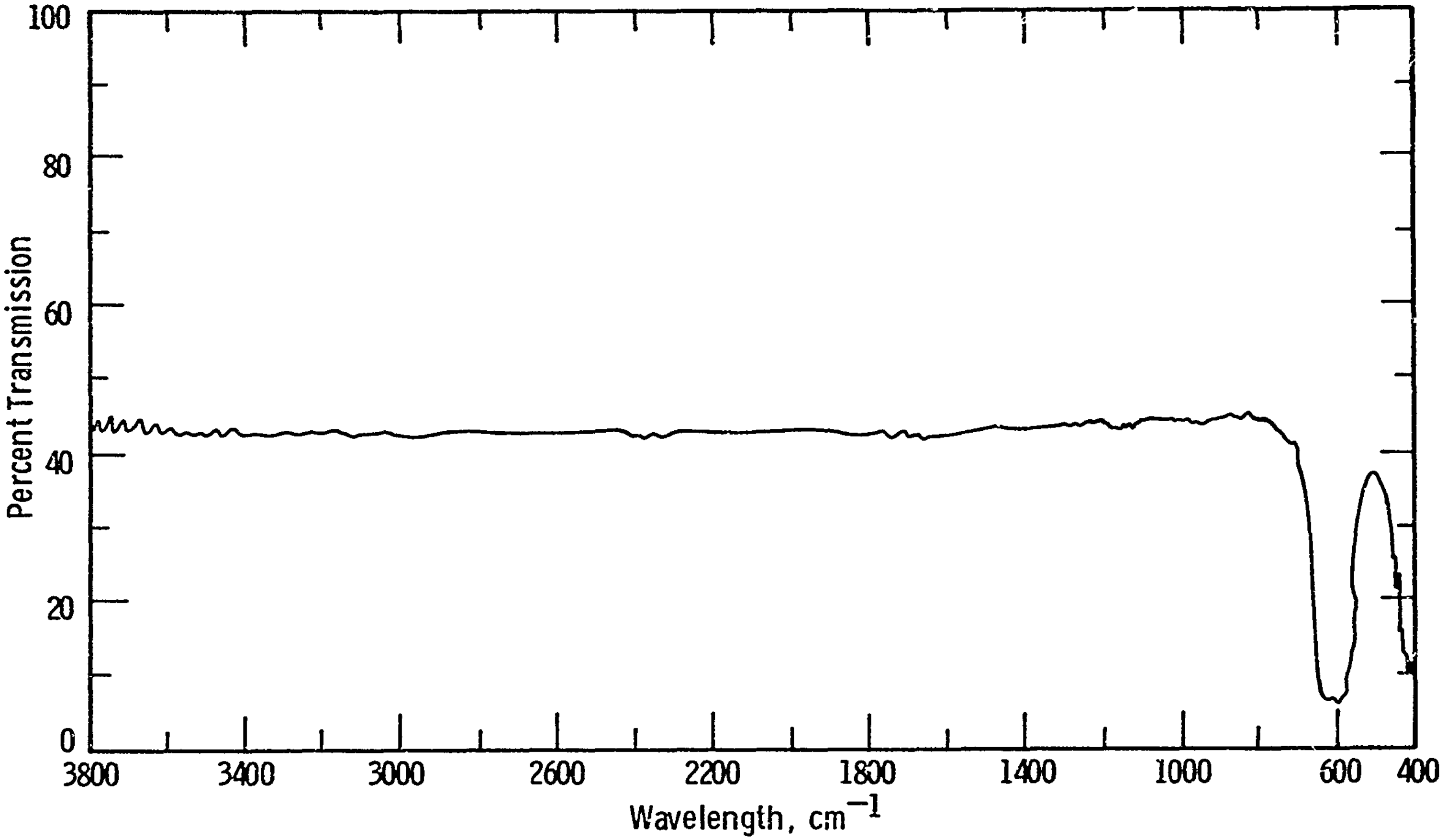

Fig. 4—Optical transmission of $Tl InS_2$. Curve uncorrected for reflection losses. Sample thickness approximately 1mm.

Subsequent to the data reported in Table 3, we have constructed a calorimeter at Westinghouse and have initiated calorimetric studies on both Tl_3AsSe_3 and KCl. The experimental work to date with the Westinghouse calorimetry system has been accomplished with the sample located in air, shielded from air drafts. Laser exposure times were adjusted so that the total temperature rise of the sample was less than 1°C (i.e., laser on time ∿ 4-10 seconds). Cooling of the sample during the heating cycle was corrected for using standard calorimetric techniques and amounted to less than a 10% correction.

Table 4

Material	Absorption Coef. (cm^{-1})
KCl	0.0052 (a_1 axis propagation, $E \| a_2$)
Tl_3AsSe_3	0.035, 0.032, 0.032, 0.016 (c axis propagation)

Table 4 is a summary of the absorption coefficients measured for the two samples. Since the 10.6 μm laser beam was much smaller than the sample, small areas of the sample could be studied. In the case of the KCl the measured absorption coefficient was largely independent of position of the laser beam on the samples (i.e., within 10%). With the Tl_3AsSe_3 sample however, one quadrant of the sample appears to have lower absorption by a factor of two than the rest of the sample. It is possible that scattering in the crystalline sample is affecting the values measured and more work will be required to separate this effect but it is certain that this crystalline sample is not of uniform quality.

The fact that the surface preparation of the samples was poor leads us to believe that surface absorption may be a large contributor to the observed heating of the sample. This could not be separated from the results at this time. The values of absorption loss at 10.6 μm reported in Table 4 should thus be considered upper values for the bulk material.

4.3 Discussion

It was an anticipation of this program that crystals of chemically related compounds, both centric and acentric, could be grown to test the dependence of absorption on crystal symmetry. This unfortunately proved an optimistic goal. In lieu of such crystals, we concentrated on determining the optical absorption along different directions in Tl_3AsSe_3. Particularly for the crystal polished with the crystal a axis parallel the polished face there is a clear dependence of absorption with symmetry direction. The comparison of the a axis and c axis directions is clouded, however, because different crystals were used to prepare the slices.

6. Conclusions

Of the various sulfosalt compounds investigated, we conclude that the most potential for window materials is shown by Tl_3AsSe_3 and the new family of materials including $TlInS_2$ and $TlGaSe_2$. Particularly intriguing are the calorimetric measurements on Tl_3AsSe_3 which show an absorption coefficient of .016, the lowest ever observed for a sulfosalt material. We anticipate that material prepared using high standards of purity and a better grade of surface polish will show even lower absorption at 10.6 µm. We also conclude that the absorption measurements on Tl_3AsSe_3 show a dependence of absorption on symmetry direction and we recommend that the dependence of absorption on symmetry direction be determined for other potential window materials such as CdSe and GaS.

Additional study should be conducted on crystal growth of $TlGaSe_2$' $TlInS_2$, and Tl_2VS_3 as well as additional as yet unsynthesized members of this group of materials.

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