THE DEVELOPMENT OF FERROMAGNETIC SPINELS
FOR OPTICAL ISOLATION AT 10.6 μm

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ABSTRACT

The fourth quarter of this contract was spent completing an analysis of factors which influence the optical transparency of hot-pressed CdCr_2S_4 at $10.6\text{ }\mu\text{m}$. It was found that multiphonon absorption, an intrinsic process, is the factor which limits the ultimate achievable absorption coefficient, α , at $10.6\text{ }\mu\text{m}$. Several extrinsic processes have also been found to affect the transmission of hot-pressed CdCr_2S_4 . In sufficient concentration, oxygen appearing as SO_4^{2-} or similar sulfate complexes contribute to α through an absorption band centered at $9.3\text{ }\mu\text{m}$. Cr_2O_3 , appearing as a second phase with a different index of refraction, causes scattering in concentrations as low as .01 mole percent. Despite the identification of these processes, possible uncertainties in the value of reflectivity, and surface losses, prevent the establishment of a definite lower limit on the absorption coefficient.

It was firmly established that α at $10.6\text{ }\mu\text{m}$ is decreased significantly upon cooling to 77°K . Thus, an α of $.5\text{ cm}^{-1}$, which would give a transmission of 85% in an optical isolator, still appears to be possible. CdCr_2Se_4 is suggested as an alternative material since the potential of a lower intrinsic α is a direct consequence of its lower phonon frequencies. It is proposed that CdCr_2Se_4 be emphasized in future work rather than CoCr_2S_4 .

THE DEVELOPMENT OF FERROMAGNETIC SPINELS FOR OPTICAL ISOLATION AT 10.6 μm

A. Progress to Date

During the last quarter, emphasis was placed on determining the processes which give rise to optical absorption and scattering in hot-pressed CdCr_2S_4 at 10.6 μm . Measurements of absorption coefficient, α , as a function of wavelength and temperature, and x-ray diffraction using the Debye-Scherrer method were employed for this purpose. This work has tied together results found during previous quarters and has enabled us to come to several notable conclusions regarding the minimal value of α achievable in CdCr_2S_4 .

The most important conclusion we have arrived at is that multiphonon absorption is the process responsible for setting the intrinsic lower limit of α at 10.6 μm in hot-pressed CdCr_2S_4 . Multiphonon absorption may be thought of as the transfer of energy from an incident photon to two or more phonons. Its theoretical origin is normally attributed to higher order anharmonic terms in the harmonic oscillator potential function. The existence of absorption bands at frequencies equal to the sum of fundamental phonon frequencies was demonstrated in an earlier work on two phonon absorption in CdS .¹

We have applied a similar analysis to hot-pressed CdCr_2S_4 and find extremely good agreement between the observed positions of weak absorption peaks and the theoretical two phonon frequencies. The peaks, which lie in the 12 to 16 μm range, are shown in Figure 1 while the two phonon assignments are given in Table 1.

Careful measurements of α vs. λ in hot-pressed CdCr_2S_4 at both 300°K and 77°K clearly demonstrate that the absorption structure at 12.4 μm has a tail which extends down to 10.0 μm , thus influencing the absorption coefficient at 10.6 μm . This structure is shown in Figure 2. Indeed, an excellent correlation between the absorption coefficients at 12.4 and 10.6 μm was observed for ten hot-pressed samples whose α 's were less than 7 cm^{-1} at the latter wavelength. Also, the absorption structure between 12.6 and 16 μm was found to be essentially the same in all samples tested. Thus, we are lead to believe that intrinsic multiphonon processes may be setting a lower limit to α at 10.6 μm .

Other important conclusions reached concern the role of impurity absorption in hot-pressed CdCr_2S_4 . We have identified three impurities and evaluated their influence on the absorption coefficient at 10.6 μm . As stated in previous reports, the most important impurity in hot-pressed CdCr_2S_4 is oxygen. This light element appears in two forms, either dissolved in the CdCr_2S_4 to form a complex such as SO_4^{2-} , or as a second phase consisting of Cr_2O_3 microcrystals. In the first case, the SO_4^{2-} ion gives rise to a strong absorption band centered around 9.3 μm . Inspection of Figure 3 demonstrates that, in sufficient concentration, the SO_4^{2-} impurity band strongly influences the absorption coefficient at 10.6 μm . In fact, it is believed that the high α observed in early hot-pressings of CdCr_2S_4 was a result of a large concentration of SO_4^{2-} . However, a study of the correlation between α at 10.6 μm and at 9.3 μm shows that the two absorption coefficients do not correlate when $\alpha \leq 5 \text{ cm}^{-1}$. An example of

the latter case is shown in Figure 4. Thus, the SO_4^{2-} impurity does not appear to strongly affect the lower limit of α achievable in CdCr_2S_4 at 10.6 μm .

The effect of second phase Cr_2O_3 was investigated using doped hot-pressings of CdCr_2S_4 and Cr_2O_3 . It was found that the primary effect of Cr_2O_3 is to cause scattering and a consequent decrease in transmission which varies inversely with λ or some power of λ . Cr_2O_3 does not affect α at 10.6 μm through an absorption band at concentrations less than .01 mole percent. It was also demonstrated that Cr_2O_3 is not responsible for the structure in α seen between 12 and 16 μm , as reported by others.²

CdS can also appear as a second phase in the crystalline CdCr_2S_4 , which we produced by the liquid phase method.³ It occurs when the starting mixture of CdS and CrCl_3 does not completely react. This second phase will give rise to scattering in hot-pressed CdCr_2S_4 , but should not in itself affect α at 10.6 μm since CdS is transparent at that wavelength.

In addition to the above impurities, we have observed a structure consisting of a sharp peak at 4.2 μm which is surrounded by a broad band with a threshold of 5 μm . At 77°K, the structure sharpens in a manner indicative of an impurity. Although no correlation was found between the band and α at 10.6 μm , its presence should not be ignored and we are presently attempting to determine its origin.

We have been able to definitely establish that α at 10.6 μm is decreased upon cooling to 77°K. For example, in a good sample of hot-pressed CdCr_2S_4 , α decreased from 2.6 cm^{-1}

at 300°K to 1.8 cm^{-1} at 77°K. The magnitude of this change is consistent with, but does not prove, the interpretation that appreciable multiphonon absorption occurs at $10.6 \text{ }\mu\text{m}$. It is interesting to note that the minimum absorption coefficient observed in hot-pressed CdCr_2S_4 occurs at $7.5 \text{ }\mu\text{m}$ and has a value of $.95 \text{ cm}^{-1}$ at 77°K.

It is important to remember that the values of α have been calculated from transmission measurements and hence are strongly influenced by reflectivity corrections. This is especially critical when the absorption coefficient approaches 1 cm^{-1} , as is demonstrated in the following example. Since the relativity of CdCr_2S_4 is calculated from measured values of the index of refraction, n , an uncertainty in the value of n results in an error in the value of α . The best known value of n is 2.84 .⁴ However, if there was a 4.6% error and the value of n was, in fact, 2.97 , calculated values of α would drop from 1 cm^{-1} to $.1 \text{ cm}^{-1}$. Similar errors resulting from unknown surface scattering and surface absorption effects are also encountered. Studies to accurately determine the index of refraction and the effect of surface preparation on α are, therefore, being undertaken. Laser calorimetry, which is influenced less by reflectivity errors, also will be used to determine the lower limit on α .

B. Future Work

1. CdCr_2S_4

It is quite probable that α in CdCr_2S_4 at $10.6 \text{ }\mu\text{m}$ is determined mainly by intrinsic multiphonon processes and that these set a lower limit on α which is higher than previously

thought. However, we understand that a transmission of 85% in an isolator element is acceptable in CO_2 laser systems presently being designed for fusion applications.⁵ This would be achieved in CdCr_2S_4 with α equal to $.5 \text{ cm}^{-1}$. Such a value of α is still quite possible at 77°C . In view of the fact that most CdCr_2S_4 is so well understood compared to other materials, we propose to continue our attempts to minimize α in this material. During the next quarter, this effort will consist of studies of the effect of surface preparation on transmission to give us more accurate absolute values of α and the use of laser calorimetry at $10.6 \mu\text{m}$ to complement transmission studies. The exclusion of oxygen from starting materials and during the growth of single crystals of CdCr_2S_4 is being emphasized and will continue to be a major goal during the next quarter.

Our hot pressing procedures will be refined through the use of RF heating to replace our present resistance furnace. It is clear that successful hot pressing of the spinels requires a fine grained starting material which necessitates careful sieving of the ground crystals. This procedure will be implemented during the next quarter. Damage tests on hot pressed material, using a well characterized high power pulsed CO_2 laser will also be emphasized.

2. CdCr_2Se_4

Our discovery of the importance of multiphonon processes at $10.6 \mu\text{m}$ in CdCr_2S_4 has lead us to re-evaluate the use of the spinels for isolators at that wavelength. In these materials the position of the reststrahl absorption is determined primarily by the anion. For example, the reststrahl peaks of

CoCr_2S_4 lie very near to those of CdCr_2S_4 , shifted only slightly to shorter wavelengths because Co is somewhat lighter than Cd. This, of course, results in two phonon absorption at slightly shorter wavelengths. Thus, CoCr_2S_4 is expected to have a slightly higher absorption coefficient at $10.6 \mu\text{m}$ than CdCr_2S_4 if multiphonon absorption is important. On the other hand, CdCr_2Se_4 has reststrahl peaks at longer wavelengths than CdCr_2S_4 as a consequence to the heavier anion. Its multiphonon structure occurs between 19 and $20 \mu\text{m}$, considerably further from $10.6 \mu\text{m}$ than in CdCr_2S_4 . Thus, it is expected that multiphonon absorption will not be as significant at $10.6 \mu\text{m}$ in CdCr_2Se_4 as it is in CoCr_2S and CdCr_2S .

We, therefore, propose to discontinue work on CoCr_2S_4 and emphasize CdCr_2Se_4 as the best possible candidate for an isolator at $10.6 \mu\text{m}$. This change in emphasis will not require any major change in materials preparation or characterization, because of the similarity of the physical properties of CdCr_2S_4 and CdCr_2Se_4 . Also, the magnetic properties of the two compounds are almost identical at $10.6 \mu\text{m}$, hence isolator design would not be affected by this change in material.

C. Personnel

In June, we were joined by Dr. Achim Bubenzer who accepted the position of research associate. Dr. Bubenzer has a strong background in crystallography and will be responsible for the preparation of materials and x-ray analysis. During the month of May, Mr. Robert Freese, a graduate student in optics, worked half time on the measurement of α in CdCr_2S_4 at 300°K and 77°K .

He continued his work full time in the months of June and July. Mr. Luigi Colombo, a graduate student in materials science, worked full time during the months of June and July as did Mr. John Stulak, a graduate student in optics. Their effort was devoted primarily to materials preparation. The principal investigator, Kenneth J. Teegarden, spent 30% of his time on the contract during May, and 100% during June and July.

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Absorption Band Designation	Phonon Transitions	$\frac{1}{\lambda}$ Theory	$\frac{1}{\lambda}$ Measured
A	2 LO_1	779.8 cm^{-1}	800 cm^{-1}
B	$\text{TO}_1 + \text{TO}_2$	698.5	700
C	$\text{LO}_2 + \text{TO}_1$	724.1	725
D	$\text{LO}_2 + \text{TO}_2$	668.8	670
E	2 TO_2	643.2	640

$$\text{TO}_1 = 376.9 \text{ cm}^{-1}$$

$$\text{TO}_2 = 321.6$$

$$\text{LO}_1 = 389.9$$

$$\text{LO}_2 = 347.2$$

TABLE 1. Two Phonon Absorption in Hot-Pressed CdCr_2S_4

Figure 1. Two phonon absorption peak.

Figure 2. multiphonon tail extending down to 10.0μm.

Figure 3. Strong influence of $9.3\mu\text{m}$ impurity band on transmission at $10.6\mu\text{m}$

Figure 4. Minimal influence of 9.3 μm impurity band on transmission at 10.6 μm.