REPORT OF
DEPARTMENT OF DEFENSE
ADVISORY GROUP ON ELECTRON DEVICES
WORKING GROUP C - (ELECTRO-OPTICS)

SPECIAL TECHNOLOGY AREA REVIEW ON NONLINEAR OPTICAL MATERIALS

CLEARED
FOR OPEN PUBLICATION
DEC 18 2001 9
DIRECTORATE FOR FREEDOM OF INFORMATION
AND SECURITY REVIEW
DEPARTMENT OF DEFENSE

OCTOBER 1995

OFFICE OF THE UNDER SECRETARY OF DEFENSE
ACQUISITION AND TECHNOLOGY
WASHINGTON, D.C. 20301-3140

TABLE OF CONTENTS

CONTRIBUTORS/PARTICIPANTS ii

EXECUTIVE SUMMARY 1

Important Advances in Nonlinear Optical Materials Technology 1

Observations and Concerns 2

Recommendations for Future Directions in This Technology Area 2

REPORT ON SPECIAL TECHNOLOGY AREA REVIEW (STAR) ON NONLINEAR OPTICAL MATERIALS 4

Introduction 4

Questions Directed to the Presenters 4

Advances in State of the Art 5

Impediments to Technical Advancement 6

Review of Specific Technologies 6

- Bulk Inorganic Materials 6
- Bulk Organic Materials 8
- Nonlinear Optical Materials for Photonics Applications 9

General Observations 9

TABLES and FIGURES 11

- TABLE I Second-order Nonlinear Optical Susceptibilities for Several Crystals ... 11
- TABLE II Nonlinear Coefficient, Figure of Merit, Conversion Efficiency, Burn Intensity, and Transmission Range for Nonlinear Crystals 12
- FIGURE I Figure of Merit and Transparency Range of Selected Nonlinear Crystals 13

GLOSSARY 14

CONTRIBUTORS/PARTICIPANTS

Dr. John M. MacCallum, Jr.
Executive Director, Advisory Group on Electron Devices
ODDDRE/ET, The Pentagon
Washington, DC

Dr. Thomas Hartwick
Chairman, Working Group C (Electro-Optics)
TRW
Redondo Beach, CA

Military Service Programs

Dr. Alan Craig
Air Force Programs
Air Force, AFOSR

Dr. Charles Lee
Air Force Programs
Air Force, AFOSR

Dr. Ward Trussell
Army Programs
Army, NVESD

Dr. Norm Barnes
NASA Programs
NASA, Langley Research Center

Dr. Vern Smiley
Navy Programs
Navy, NRaD

Technology Review

Fil Bartoli
$\chi^{(3)}$ Materials
Naval Research Laboratory

Robert L. Byer
Inorganic Nonlinear Materials
Stanford University

Dr. L.N. Durvasala
Nonlinear Optical Materials
ARPA

Anthony Garito
Organic Nonlinear Materials
University of Pennsylvania

Nasser Peyghambarian
Quantum Wells/Wires/Dots
University of Arizona

Report on Special Technology Area Review on Nonlinear Optical Materials

EXECUTIVE SUMMARY

Military uses of nonlinear optical materials range from **laser beamsteering and control of beam quality** to **eye-protection** and guided-wave photonic devices and components.

Materials for optical phase conjugating are **important for correcting laser beam aberrations** to near diffraction-limited beam quality, for combining a laser array into a single coherent beam and for **imaging through atmospheric turbulence**.

Materials for eye-safe optical sources and electro-optic sensor and **eye protection** are also **important for battlefield applications**.

Materials for other military applications include **guided-wave modulators and switches for photonics, optical correlators for automatic target recognition, 2-D spatial light modulators for high-speed parallel processors and metrology of surface motion and strain or air turbulence near an aerofoil surface. Nonlinear optical (NLO) techniques** are also finding new applications in the **generation and control of microwaves and millimeter waves.**

Important Advances in Nonlinear Optical Material Technology

A number of important advances for nonlinear optical material technology were reported at the STAR:

- Considerable recent progress has been made in the development of $ZnGeP_2$, which may be the material of choice for operation in the 2-5 μm range. $ZnGeP_2$ is a very promising material for infrared applications in the 2-5 μm region since it has the largest nonlinearity of any of the materials which can be used in this region.

- A doubly resonant optical parametric oscillator (OPO) has been constructed which produces 1.5 W in the 4 μm region. Using a mode-locked 1 μm source, 60% efficiency has been achieved in generating 2 μm radiation and 40% efficiency in producing radiation out to 4 μm.

- Using a Q-switched Nd:YAG laser and a KTP optical parametric oscillator, 120 mJ at 2.1 μm has been generated.

- a 10 J per pulse, 330 W average power diode pumped Nd:YAG solid state laser has been operated at a 33 Hz repetition rate with 1.2 x DL output and a 6.6% wall-plug efficiency.

Using a mosaic KTP doubler in the phase conjugated path, 5 J at 33 Hz (165 W average power) has been obtained in the green with a 60% doubling efficiency.

- Optical switching on a subpicosecond time scale has been demonstrated in a dual core silica fiber directional coupler at a switching energy of 3 nJ. The low losses of optical fibers together with the high degree of fabrication precision make the use of fiber nonlinearities of potential practical importance.

- Optical frequency shifting in the multi-THz range has been demonstrated with high efficiency at relatively low peak power.

- Nonlinear reflection modulators have been constructed using a multi-quantum-well absorptive nonlinear spacer and GaAlInAs/AlInAs quarter-wave reflecting stack. Contrast ratios of 10^3 have been obtained at a switching speed of the order of 1 ns.

Observations and Concerns

- Funding for research on new nonlinear materials and the technological development of older materials is low and is not likely to increase very much in the foreseeable future.

- Emphasis needs to be directed toward areas with more direct payoff. For example, inorganic single-crystal and nonostructures rather than organic materials.

- Programs are frequently being pursued by materials researchers without benefit of direction from device technologists, sometimes resulting in programs that are moving in unprofitable directions.

Recommendations for Future Directions in this Technology Area

- In applications requiring, for example, efficient second harmonic generation at high optical powers, **bulk inorganic crystals have no competition. Research should continue to extend the range of these materials for applications such as frequency up-converters, and optical parametric oscillators for IRCM lasers.** Funding for research, as opposed to systems level efforts is minimal.

- In photonics applications where thin-film guided-wave electro-optic devices are sought, **more emphasis should be placed on the crystalline materials where the potential for high electro-optic coefficients and hence good performance is high.** The main problem to be addressed is growth of optical-quality single-crystal thin films on glass and semiconductor substrates.

- **Organic materials** have demonstrated extraordinary second order hyperpolarizabilities; however, attempts to translate these molecular properties into useful $\psi^{(2)}$ materials have been largely unsuccessful. The potential remains enormous and this area is still an

interesting applied research topic; consequently this **work should continue but with reduced emphasis reflecting its high risk.**

- **Increasing emphasis should be placed on semiconductor quantum-wells and nanostructures for photonics applications in modulation and switching**. This field is in its infancy and holds high potential for a wide range of integrable photonics devices.

- **Research should continue into resonant and optically (or electronically)-pumped enhancement of nonlinear optical processes and optical/microwave interactions**. This area, while mainly of theoretical interest now, may suggest new ways of addressing practical problems in the future.

- **Research should continue into the area of nonlinear optical materials for eye-protection including organics.**

REPORT ON SPECIAL TECHNOLOGY AREA REVIEW (STAR) ON NONLINEAR OPTICAL MATERIALS

Introduction

On 21-22 July, 1993, Working Group C (Electro-optics) reviewed programs and progress in the area of nonlinear optical (NLO) materials technology. The review included bulk organic and inorganic nonlinear materials as well as quantum well and other engineered structures for nonlinear optoelectronics. Consideration was given to applications in eye protection/optical hardening, frequency conversion for countermeasures/eye safety, photonic device applications in communication and information processing.

Questions Directed To the Presenters

This STAR sought answers to the following specific questions:

1. What are the comparisons between different materials?
2. How easy are the materials to fabricate, what are the yields? Can these materials be scaled to sufficiently large sizes?
3. Is the material compatible with waveguide structures? Which materials are optimized for efficient cw nonlinear conversion?
4. What classes of materials provide the best opportunities for future progress?
5. What is the state of manufacturing technology and producibility programs in this area?
6. What are the systems needs which drive development in this area? How critical is this technology to meeting these needs?
7. What is the total DoD/NASA investment in this area?
8. How well coordinated are the programs funded by the various DoD and NASA offices?
9. What are the prospects for commercial applications of these materials? Could there be a mutual sharing of development or manufacturing cost? Is this dual-use technology?
10. Is the US competitive in the development of these materials? Should we rely on China and the FSU?

11. What are the critical investments which should be made in this area?

Advances in State of the Art

A number of advances were discussed during the STAR. These include:

1. An important enhancement to the utility of lasers is the ability to change the output to new wavelengths using nonlinear frequency conversion. $AgGaSe_2$ is a well developed material and deserves consideration for OPO operation in the 2-5 μm region; with 2.06 μm pumping, OPO performance has been reported at the 2 W average power level. Considerable recent progress has been made in the development of $ZnGeP_2$, which may be the material of choice for operation in the 2-5 μm range. Recently, large crystals have been grown which have loss of 0.25 cm^{-1} at 2 μm. While this loss is relatively high compared to other nonlinear materials, the high thermal conductivity and low thermal lensing provide some compensation. A doubly resonant OPO has been constructed which produces 1.5 W in the 4 μm region. Using a mode-locked 1 μm source, Spectra Technology has demonstrated 60% efficiency in generating 2 μm radiation and 40% efficiency in producing radiation out to 4 μm.

2. Using a Q-switched Nd:YAG laser and a KTP optical parametric oscillator, the Night Vision and Electro-Optical Division of the Army Center for Night Vision and Electro-Optics has generated 120 mJ at 2.1 μm.

3. Under ARPA's Diode Pumped Solid State Laser (DAPKL) program, a 10 J per pulse, 330 W average power diode pumped Nd:YAG solid state laser has been operated by TRW at a 33 Hz repetition rate with 1.2 x DL output and a 6.6% wall-plug efficiency. The high beam quality is obtained by placing a phase conjugator after the first pass through the amplifier chain. Using a mosaic KTP doubler in the phase conjugated path, 5 J at 33 Hz (165 W average power) has been obtained in the green with a 60% doubling efficiency. With improvements in several of the components, the laser should be able to achieve close to its design goal of 1 kW average power and near-diffraction limited operation at 100 pps repetition rate and 9.3% wall-plug efficiency; over 500 W is expected in the green.

4. Optical switching on a subpicosecond time scale has been demonstrated in a dual core silica fiber directional coupler at a switching energy of 3 nJ. Measurements of pulse reshaping effects showed that the response time was on the order of femtoseconds. The low losses of optical fibers together with the high degree of fabrication precision make the use of fiber nonlinearities of potential practical importance.

5. Optical switching and frequency shifting using GaAlAs waveguides has been studied for a number of years. Recently, optical frequency shifting in the multi-THz range has been demonstrated with high efficiency at relatively low peak

power. Since it is possible to include amplification in the semiconductor device, the new frequency shifted signal can have substantial gain compared to the original signal at the input frequency.

6. Nonlinear reflection modulators have been constructed using a multi-quantum-well absorptive nonlinear spacer and GaAlInAs/AlInAs quarter-wave reflecting stack. Contrast ratios of 10^3 have been obtained at a switching speed of the order of 1 ns.

Impediments to Technical Advancement

There are several important impediments to progress in nonlinear materials and devices:

1. Funding for research on new nonlinear materials and the technological development of older materials is low and is not likely to increase very much in the foreseeable future.

2. There is undue emphasis on fundamental research, in physical organic chemistry for example, which results in good research, many publications have been produced but few concrete applications have resulted. Emphasis needs to be directed toward areas with more direct payoff. For example inorganic single-crystal and nanostructures rather than organic materials.

3. Programs are frequently being pursued by materials researchers without benefit of direction from device technologists, sometimes resulting in programs that are moving in unprofitable directions. One example of the manifestation of this problem is for organic materials where a disproportionate effort is concentrated upon third order materials. These are not very interesting from an applications standpoint since their nonlinear optical properties are unremarkable.

Review of Specific Technologies

Bulk Inorganic Materials

Most applications of bulk inorganic materials involve second order frequency conversion processes such as harmonic generation, sum and difference frequency generation, and optical parametric oscillation. For these purposes, it is important to consider some of the following relevant issues:

For availability:

- reliable crystal growth techniques

For high conversion efficiency:

- optical nonlinearity;
- birefringence and optical dispersion;
- moderate to high transparency; and
- optical homogeneity

For ease of fabrication:

- mechanical strength;
- chemical stability; and
- polishing and coating technology

For high average power:

- low absorption;
- temperature phase matching bandwidth;
- fracture toughness; and
- thermoelastomechanical properties

For lifetime and system compatibility:

- damage threshold;
- nonlinear absorption;
- nonlinear index; and
- brittleness

These same considerations also apply to bulk organic materials.

Some second order nonlinear materials are listed in Tables I and II along with their nonlinear coefficients and, in the case of Table II, a number of other important parameters including transparency range. Figure 1 graphically shows size of nonlinearity and transparency range for various infrared nonlinear materials.

Important materials which have been recently undergoing development include LBO, BBO, and $ZnGeP_2$. LBO and BBO were first grown in China and much of the supply of these crystals still comes from China. These are the materials of choice for generating radiation in the UV range and for visible and near-IR parametric oscillators. In fact, these materials are responsible for the rebirth of the optical parametric oscillator which for many years has been viewed as an impractical device.

$ZnGeP_2$ is a very promising material for infrared applications in the 2-5 μm region since it has the largest nonlinearity of any of the materials which can be used in this region. Much of the current effort on this material is oriented toward reducing absorption loss.

Intra-laser-cavity doubling and the use of external cavities are enabling the development of efficient, low average power doubling systems consistent with the output powers of small cw solid state lasers and even diode lasers. The development of higher quality nonlinear materials, improved beam quality lasers, and the use of electronic cavity control to optimize

output have been significant aspects of this technological advance. Continuous green powers of as high as 10 W have been achieved.

The use of quasiphasematching techniques is also undergoing a renaissance. The phase mismatch due to chromatic dispersion can be compensated by periodically reversing the orientation of the nonlinear polarization tensor of a crystal. This reversal can be accomplished in easily poled materials such as $LiNb0_3$ with an external electric field. The direction of propagation, hence the direction of polarization, of the optical fields can be chosen to optimize the nonlinear coefficient; this is often not the case with birefringent phasematching. A periodically poled $LiNbO_3$ crystal of 1.3 mm length has produced 1.7 W in the green. In materials such as GaAs, where the polarization direction cannot be changed with an external DC field, stacks of alternating polarization crystals are being fabricated using diffusion bonding. Because GaAs is not birefringnent, this is the only method for achieving phasematching.

Bulk Organic Materials

Only organic and polymeric materials with nonlinear optical properties originating from the hyperpolarizabilities of the constituent molecules are discussed here. Materials such as liquid crystals and photorefractive materials are not discussed here.

Molecules (chromophores) with hyperpolarizabilities β and γ will generate $\chi^{(2)}$ and $\chi^{(3)}$, respectively, in bulk materials. The $\chi^{(2)}$ effect can only be observed if the chromophores are oriented in one direction in the bulk; thus, these materials require special processing.

For the third order susceptibility, the hyperpolarizability based on non-resonant transitions is typically too small for practical applications. The largest non-resonant $\chi^{(3)}$ currently is around 10^9 esu. Resonant $\chi^{(3)}$'s, however, reach 10^{-7} esu, and this may be a large enough value to be useful for laser hardening/sensor protection applications. Research activities currently are focusing on understanding the structure property relationships that can increase the γ of the chromophores.

Chromophores with β can be converted into $\chi^{(2)}$ bulk materials in several different ways. $\chi^{(2)}$ organic materials can be classified into three categories based on the processing methods. They are: 1) single crystals, 2) deposited thin films, and 3) poled polymers. Many chromophores have β values that, if properly converted into suitable $\chi^{(2)}$ materials, can be considered for electro-optical modulation in addition to frequency conversion. Chromophores with larger β values per unit molecular weight are always desirable.

Single crystal organics which have large $\chi^{(2)}$ could be useful for frequency conversion of laser radiation. However, researchers in the United States interested in applying these techniques are mostly employing inorganic crystals instead of organics. A major concern in this area is material stability under high power operation.

Deposited thin films have the advantage of coverage over large areas. However, the time to generate a film thickness suitable for waveguiding can be impractical.

Poled polymer films are the easiest to process and are best for low cost device fabrication. With appropriate solubility, they can be spin-coated and electrically poled to generate $\chi^{(2)}$ films. Channel waveguides have been fabricated in these materials using lithographic techniques or reactive ion etching. Their nonlinear susceptibilities are, however, inherently lower compared to those fabricated from single crystals and deposited thin films because of chromophore number density consideration. The major interest in this class of materials is for electro-optic modulation and optical switching. Electro-optic coefficients as large as 40-60 pm/V have been reported, but these early material samples suffer from temporal instability of the $\chi^{(2)}$ process due to loss of chromophore orientation. Recent progress has produced materials with long term $\chi^{(2)}$ stability and with electro-optic coefficients as high as 16 pm/V at 1.3 μm. Several systems with larger Pockel's coefficients are currently being evaluated.

One advantage of organic electro-optical materials is their low dielectric constant. This makes this class of materials ideal for high frequency (10-100 GHz) modulation. Recent research has demonstrated 60 GHz modulation using poled polymers.

Nonlinear Optical Materials for Photonics Applications

Optical switching, modulation and frequency shifting play important roles in optical communication and information processing. For all-optical communication, nonlinear optics is essential. For these applications, the nonlinear process should be compatible with typical semiconductor diode laser output. Thus, efficient low peak power and very low average power processes are desirable. The use of waveguides enhances the nonlinear processes through high intensities and long interaction lengths.

Bulk nonlinearities in waveguiding structures have been studied for a number of years. Often bandgap resonant enhancement is used to increase the efficiency of the inherent nonlinear properties of semiconductors. Quantum confined structures, such as quantum wells, quantum wires and quantum dots, have been used to improve density-of-states factors and to increase the size of transition matrix elements.

Some other areas in which research has been carried out include: 1) the use of novel holographic techniques involving SBN fibers and spatial spatial light modulators to achieve very high storage densities, 2) the use of cascaded $\chi^{(2)}$ processes to produce enhanced $\chi^{(3)}$ effects, and 3) the use of two-photon resonant enhancement to increase the size of $\chi^{(3)}$ without increasing linear absorption.

General Observations

1. In attempting to compare different NLO materials, there are many parameters, some of whose importance is often dependent upon specific requirements. Important parameters include: susceptibility, nonlinear figure of merit, absorption constant, thermal conductivity, heat capacity, temperature dependence of

refractive index and phase matching angle, damage threshold dependence on pulse length, average power handling capability, walk-off angle, phase matching acceptance angle, phase matching bandwidth, two-photon absorption, transparency range, and mechanical, thermal, and chemical stability.

2. Of the three classes of NLO materials we have defined in the report, the bulk inorganic materials have been most widely applied. They are the workhorses of frequency conversion including application to second harmonic generation, sum and difference generation, and optical parametric oscillation. They play and should continue to play an important role for applications, such as countermeasures, for which direct laser sources may be nonexistent or unacceptable.

3. The commercially available bulk inorganic materials include LBO, BBO, KTP, KDP, $LiNbO_2$, $KNbO_3$, $AgGaSe_2$, $AgGaS_2$, and $ZnGeP_2$. The DoD has been instrumental in funding much of the research and development of these materials. Many require little improvement while others, such as $ZnGeP_2$, require substantial further development.

4. Doubling inside cavities and quasiphasematching can reduce the power levels required for nonlinear conversion; quasiphasematching also allows the use of materials which are not birefringent such as the III-V semiconductors.

5. To improve output beam quality of high power lasers, stimulated Brillouin scattering in gases and liquids is used for phase conjugation. The most common Brillouin materials are high pressure CH_4 and fluorocarbons. Because of future restrictions on the use of fluorocarbons, replacement materials will need to be found.

6. Organic nonlinear materials hold great promise because of their high nonlinear susceptibilities $\chi^{(2)}$ and $\chi^{(3)}$. At present, a number of these materials have high absorption loss constant, α, so that one commonly used figure of merit, $\chi^{(n)}/\alpha$, is unacceptably low. With further research and development it may be that some of these materials will prove practical.

7. Because guided wave nonlinear optical devices can play an important role in optical information technology and, in fact, are essential for all-optical communication, it is important that the opportunities and limitations of these techniques be explored thoroughly. To date, there are no practical applications for these technologies.

Table I Second-order nonlinear optical susceptibilities for several crystals

Material	Point group	d_{ij} (10^{-9} esu)
Quartz	$32 = D_3$	$d_{11} = 0.96$ $d_{14} = 0.02$
$Ba_2NaNb_5O_{15}$	$mm2 = C_{2v}$	$d_{31} = -35$ $d_{32} = -35$ $d_{33} = -48$
$LiNbO_3$	$3m = C_{3v}$	$d_{22} = 7.4$ $d_{31} = 14$ $d_{33} = 98$
$BaTiO_3$	$4mm = C_{4v}$	$d_{15} = -41$ $d_{31} = -43$ $d_{33} = -16$
$NH_4H_2PO_4$ (ADP)	$\bar{4}2m = D_{2d}$	$d_{14} = 1.2$ $d_{36} = 1.2$
KH_2PO_4 (KDP)	$\bar{4}2m = D_{2d}$	$d_{14} = 1.2$ $d_{36} = 1.1$
$LiIO_3$	$6 = C_6$	$d_{35} = -13$ $d_{36} = -10$
CdSe	$6mm = C_{6v}$	$d_{15} = 74$ $d_{31} = 68$ $d_{33} = 130$
KD_2PO_4 (KD*P)	$\bar{4}2m = D_{2d}$	$d_{36} = 1.26$ $d_{14} = 1.26$
CdS	$6mm = C_{6v}$	$d_{33} = 86$ $d_{31} = 90$ $d_{36} = 100$
Ag_3AsS_3 (proustite)	$3m = C_{3v}$	$d_{22} = 68$ $d_{31} = 36$
$CdGeAs_2$	$\bar{4}2m = D_{2d}$	$d_{36} = 1090$
$AgGaSe_2$	$\bar{4}2m = D_{2d}$	$d_{36} = 81$
$AgSbS_3$ (pyrargyrite)	$3m = C_{3v}$	$d_{31} = 30$ $d_{22} = 32$
β-BaB_2O_4 (beta barium borate)		$d_{11} = 4.6$

Notes: Values are obtained from a variety of sources. One of the more complete tabulations is that of S. Singh in *Handbook of Lasers*, Chemical Rubber Company, Cleveland, Ohio 1971.

To convert to the MKS system using the convention that $P = dE^2$, multiply each entry by $4\pi\epsilon_0/3 \times 10^4 = 3.71 \times 10^{-15}$ to obtain d in units of C/V^2.

To convert to the MKS system using the convention that $P = \epsilon_0 dE^2$, multiply each entry by $4\pi/3 \times 10^4 = 4.189 \times 10^{-4}$ to obtain d in units of m/V.

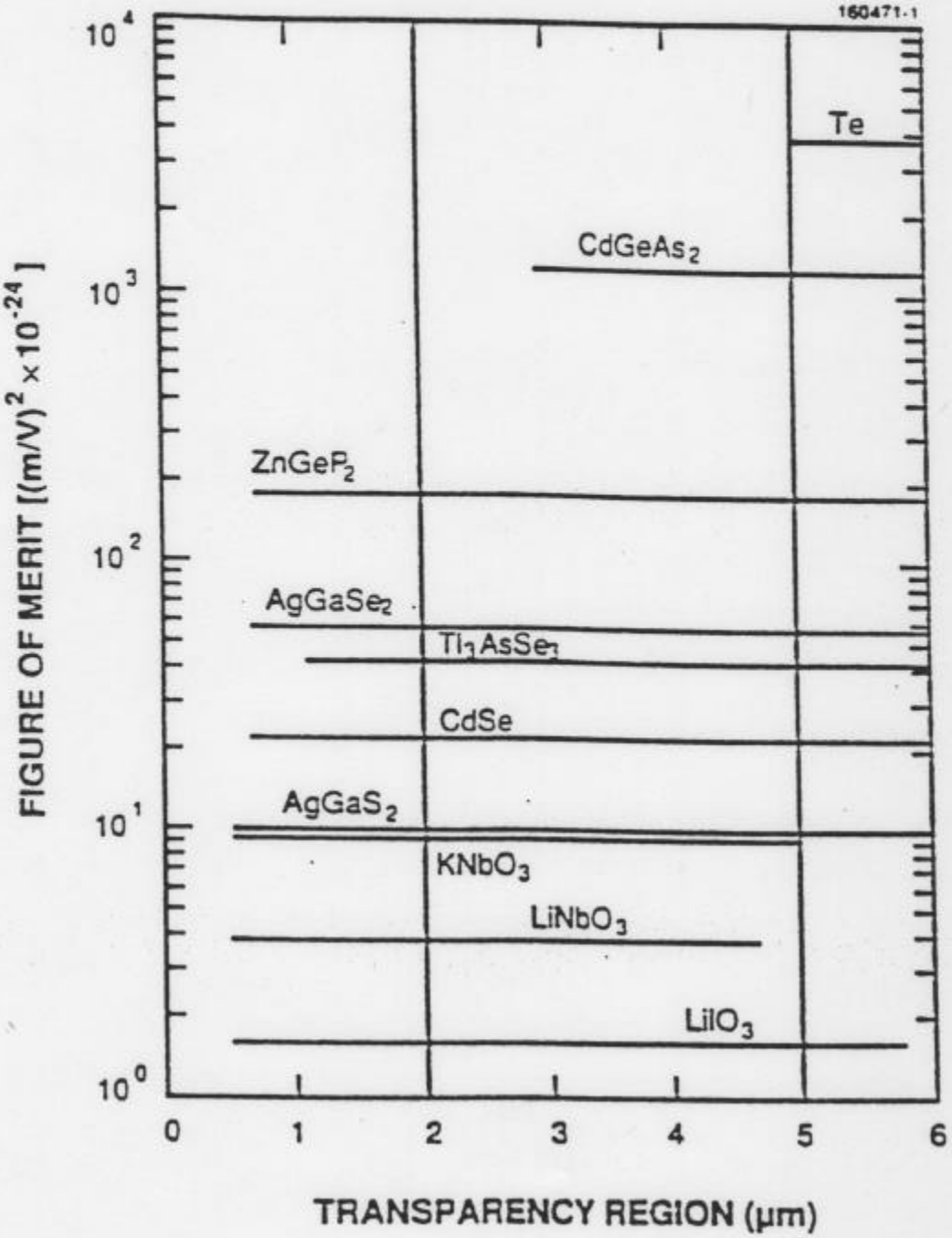
In any system of units, $\chi^{(2)} = 2d$ by convention.

Table II Nonlinear coefficient, figure of merit, conversion efficiency, burn intensity, and transmission range for nonlinear crystals.

Material (point group pump wavelength)	$d \times 10^{12}$ (m/V) (References)	n_o n_e	$n_e - n_o$	θ_m	ϱ	$d_{eff} \times 10^{12}$	$d^2_{eff}/n^2_o n_3 \times 10^{24}$	$l(\varrho)_{eff}$ (cm)	$\Gamma^2 l^2$ (1 W)	$\Gamma^2 l^2$ (1 MW/cm²)	I_{burn} (MW/cm²)	Transmission range (μm)
Te(32) $\lambda_p = 5.3$ μm	$d_{11} = 1089$[a,d]	6.25 4.80	−1.45	14°	0.10	$1065(d\cos^2\theta_m)$	10175	0.011	2.66×10^{-4}	0.50	40–60	4–25
$CdGeAs_2$ (42 m) $\lambda_p = 5.3$ μm	$d_{36} = 453$[a,e]	3.51 3.59	+0.086	II 55° I 35°	0.021 0.021	341 $(d\sin\theta)$ 406 $(d\sin 2\theta)$	2688 3811	0.34	1.4×10^{-3} 1.7×10^{-3}	0.12 0.147	20–40	2.4–17
GaAs ($\bar{4}3$ m)* (10.6 μm)	$d_{36} = 151$[a]	3.30	0	—	—	—	635	$l_{coh} = 107$ μm	—	—	60	0.9, 1.4 –17
GaP ($\bar{4}3$ m) (10.6 μm)	$d_{36} = 58.1$[a]	3.00	0	—	—	—	125	—	—	—	—	—
$ZnGeP_2$ ($\bar{4}2$ m) $\lambda_p = 1.83$ μm	$d_{36} = 138$[a,c]	3.11 3.15	+0.038	II 90° I 62°	0.0 0.01	d_{36} 114 $(d\sin 2\theta)$	625 426	$l = 1$ cm 0.59	2.9×10^{-3} 6.1×10^{-3}	0.71 0.17	> 4	0.7–12
GaSe ($\bar{6}$ m2) $\lambda_p = 5.3$ μm	$d_{22} = 88.5$[a,h]	2.807 2.456	−0.351	12°40′	0.001	$86.3(d_{22}\cos\theta)$	341	$l = 1$ cm	4.8×10^{-4}	0.045	30	0.65–18
Tl_3AsSe_3 (3 m) $\lambda_p = 5.3$ μm	$d_+ = 66$[a,e]	3.34 3.15	−0.182	22°	0.03	d_+	131	0.184	4.2×10^{-3}	7.4×10^{-3}	32	1.2–18
$AgGaSe_2$ ($\bar{4}2$ m) $\lambda_p = 1.83$ μm	$d_{36} = 65$[a]	2.62 2.58	−0.32	I 55° I 90°	0.01 0.0	53 $(d\sin\theta)$ d_{36}	161 242	0.71 $l = 1$ cm	2.14×10^{-3} 7.68×10^{-3}	0.08 0.271	> 10	0.73–17
CdSe (6 mm) $\lambda_p = 1.83$ μm	$d_{31} = 29.5$[a]	2.45 2.47	+0.019	90°	0.0	d_{31}	58	$l = 2$ cm	3.1×10^{-3}	0.22	60	0.75–25
$AgGaS_2$ ($\bar{4}2$ m) $\lambda_p = 1.06$	$d_{36} = 24.2$[a,f]	2.42 2.36	−0.054	I 58° I 90°	0.17 0.0	20.5 $(d\sin\theta)$ d_{36}	30.4 42.3	0.14 $l = 1$ cm	8.3×10^{-4} 9.2×10^{-3}	0.047 0.18	12–25	0.60–13
Ag_3SbS_3 (3 m) $\lambda_p = 5.3$ μm	$d_+ = 20.1$[a,d]	2.86	−0.19	29°	0.042	d_+	21.3	0.11	3.5×10^{-6}	1.2×10^{-3}	14–50	0.60–14
Ag_3AsS_3 (3 m) $\lambda_p = 5.3$ μm	$d_+ = 19$	2.76 2.54	−0.223	22.5°	0.059	d_+	22	0.60	1.46×10^{-6}	1.0×10^{-3}	12–40	0.60–13
$LiIO_3$(6) $\lambda_p = 0.694$ μm	$d_{31} = 6.8$[a]	1.85 1.72	−0.135	23°	0.071	2.75 $(d\sin\theta)$	1.54	0.008	4.6×10^{-6}	4.5×10^{-3}	125	0.31–5.5
$LiNbO_3$ (3 m) $\lambda_p = 0.532$	$d_{31} = 5.95$[a]	2.24 2.16	−0.081	90°	0.0	d_{31}	3.51	$l = 5$ cm	1.9×10^{-3}	1.15	80–300	0.35–4.5
ADP ($\bar{4}2$ m) $\lambda_p = 0.266$	$d_{36} = 0.86$[a,d]	1.53 1.48	−0.0458	90°	0.0	d_{36}	0.23	$l = 5$ cm	6.6×10^{-3}	0.297	> 500	0.20–1.1
KDP ($\bar{4}2$ m) $\lambda_p = 0.266$	$d_{36} = 0.71$[a]	1.51 1.47	−0.0417	90°	0.0	d_{36}	0.11	$l = 5$ cm	4.6×10^{-3}	0.21	> 500	0.22–11
SiO_2 (32) (1.06 μm)	$d_{11} = 0.46$[a,e]	1.55 1.56	+0.0095	—	—	d_{11}	0.015	$l_{coh} = 14$ μ	—	—	> 1000	0.18–35

[a] *M.M.Choy, R.L.Byer*: Phys. Rev. B 14, 1693 (1976)
[b] *J.Jerphagon, S.K.Kurtz*: Phys. Rev. B 1, 1739 (1970)
[c] *J.Jerphagnon, S.K.Kurtz*: J. Appl. Phys. 41, 1667 (1970)
[d] *A.H.M.Ross, G.D.Boyd, R.H.Schmidt*: Appl. Phys. Lett. 17, 57 (1970)
[e] *G.D.Boyd, H.Kaspar, J.H.McFee*: IEEE J. QE-7, 563 (1971)
[f] *D.S.Chemla, R.F.Begley, R.L.Byer*: IEEE J. QE-10, 71 (1974)
[h] *G.B.Abdullaev, L.A.Kulevskii, A.M Prokhorov, A.D.Savel'ev, E.Yu Salev, V.V.Smirnov*: JETP Lett. 16, 90 (1972)

Figure 1
Figure of merit and transparency range of selected nonlinear crystals.



GLOSSARY

$AgGaS_2$	Silver Gallium Sulfide
$AgGaSe_2$	Silver Gallium Selenide
AlInAs	Aluminum Indium Arsenide
ARPA	Advanced Research Projects Agency
BBO	β Barium Borate
CH_4	Methane
DAPKL	Diode Array-Pumped Kilowatt Laser
DoD	Department of Defense
esu	Electrostatic units
FSU	Former Soviet Union
GaAs	Gallium Arsenide
GaAlAs	Gallium Aluminum Arsenide
GaAlInAs	Gallium Aluminum Indium Arsenide
GHz	Gigahertz
InAs	Indium Arsenide
IRCM	Infrared Counter Measures
KDP	Potassium DiRydrogen Phosphate
$KNbO_3$	Potassium Niobate
KTP	Potassium Titanyl Phosphate
LBO	Lithium Triborate
$LiNbO_3$	Lithium Niobate
NASA	National Aeronautics and Space Administration
Nd:YAG	Neodynium Yttrium Aluminum Garnet
nJ	Nanojoule
NLO	Non-linear Optical
OPO	Optical Parametric Oscillators
pm/V	Picometers per volt
SBN	Strontium Barium Niobate
THz	Terahertz
$ZnGeP_2$	Zinc Germanium Phosphide