Nonlinear Optical Crystal Development at the USAF Wright Laboratory

F.K. Hopkins, N.C. Fernelius, M.C. Ohmer, and D.E. Zelmon
Wright Laboratory, Materials Directorate (WL/MLPO)
Wright-Patterson Air Force Base, Ohio 45433-7707

U.B. Ramabadran
University of Dayton Research Institute, Dayton, Ohio 45469-0178

Abstract- Wright Laboratory Materials Directorate has been the primary DoD organization developing nonlinear optical (NLO) materials. This effort has resulted in numerous successes, especially in the development of new NLO crystals for use in laser sources. These crystals significantly enhance laser performance by making possible wavelength shifting and tunability and higher power. Technical progress has been made in developing several crystals which together cover the spectral range from middle ultraviolet to the far infrared. One crystal in particular, zinc germanium phosphide, has already demonstrated average power of 3.5 watts tunable over much of the mid-infrared atmospheric window. Significant improvements have also been made with extending the transparency range and laser-damage resistance of the KTP family of compounds.

Nonlinear optics (NLO) can significantly improve the performance and character of laser sources, and it can do this as part of an all solid-state laser system. This latter point is important because chemical and gas lasers are typically problem prone due to hazardous laser gases or dyes, limited shelf and operational lifetimes, and the need for possibly unreliable media flow systems. These problems stifle the use of lasers in military systems, especially on aircraft and spacecraft, as well as in commercial systems such as for medical applications. Nonlinear optics may serve four purposes in a laser system: (1) wavelength conversion offering new discrete wavelength lines and wavelength tunability over a much broader spectral range than is possible with chemical lasers, (2) amplification, (3) Q-switches for pulsed lasers, and (4) optical phase conjugation for more ideal beam profiles and the coupling of laser beams.

The applications which have required the incorporation of NLO into laser systems are numerous. An important military application is infrared countermeasures for which it was estimated in 1993 that "there are more than $50 million worth of DIRCM research contracts currently in progress, with more government awards on the way. The potential size of this market is greater than $500 million for military aircraft alone." [1] Similar requirements for infrared laser systems exist for environmental monitoring by differential absorption LIDAR which operate in the 2 to 14 micron wavelength range [2] and for windshear detection. Additional applications requiring NLO for wavelength conversion and tunability exist for wavelengths from the vacuum-UV to the far-IR spectral regions. These include medical diagnosis and treatment, materials processing, scientific instruments, optical communications, low-light imaging, atmospheric aberration compensation for astronomy and satellite tracking, scene projectors for testing and even for entertainment, optical signal processing, data storage, underwater communications and imaging, and remote identification of biological materials.

However, available nonlinear optical materials have been unsatisfactory for many applications due to small nonlinearities, poor optical clarity, small thermal conductivities, difficulty in processing into devices, and other factors.

Wright Laboratory Program

The Air Force's Wright Laboratory Materials Directorate (WL/ML) is endeavoring to make improved NLO materials available for laser sources capable of generating tens of watts of average power over the extensive wavelength range from the far infrared (λ=12 µm) to the middle ultraviolet (λ<200 nm). Due to the applications discussed in the previous Section, greater emphasis is being given to the infrared spectral region. The categories of materials being addressed in the research and development program are listed, and their status is summarized in Figure 1. The material categories are far-infrared conversion materials, semiorganics, borates, zinc germanium phosphide, and potassium titanate phosphate and its isomorphs.

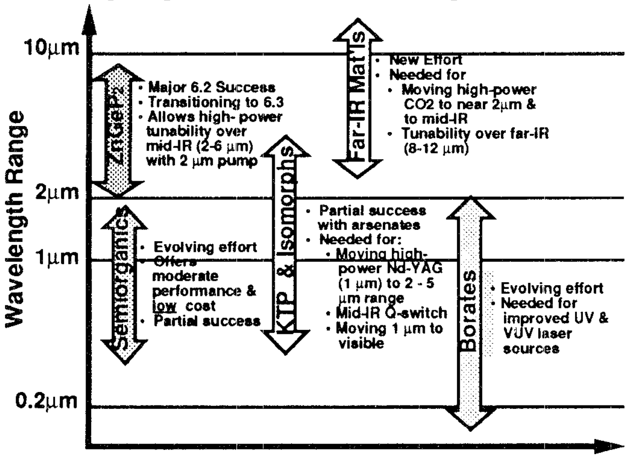

FIGURE 1. Status of NLO materials R & D

"Far-infrared conversion materials" is a new emphasis area which is needed (1) for moving the high optical power which is available from CO_2 lasers ($9 < \lambda < 11$ µm) into the mid-infrared region (2-6µm) and (2) for wavelength-tunable laser light over the far-infrared (8-12µm) atmospheric window. The presently available materials, zinc germanium phosphide ($ZnGeP_2$ or simply ZGP), silver gallium selenide ($AgGaSe_2$ or simply AGSE, and thallium arsenic selenide (Tl_3AsSe_3 or simply TAS), limit average conversion powers to a few watts. For ZGP, the limitation is due to optical absorption from 2- and 3-phonon absorption (intrinsic to the material) giving a nominal 0.5/cm absorption and to a less than ideal orientation angle which results in a reduced effective nonlinear coefficient. AGSE is principally limited by a low thermal conductivity. In addition, TAS is a relatively soft, brittle material with a low melting temperature (311°C), characteristics which severely complicate the fabrication of high-quality surfaces and surface coatings, and it has a low thermal conductivity and a moderately large walkoff angle. Finally, AGSE and TAS have only moderately sized nonlinear coefficients which are less than one third of that of ZGP.

A number of candidate materials are being investigated for the far-IR. The most promising candidates are cadmium germanium arsenide ($CdGeAs_2$), gallium selenide (GaSe), and quasi-phase-matched semiconductor structures. $CdGeAs_2$ offers an enormous nonlinearity (d_{36}=235pm/V), a wide transparency range (2.3-17 µm), and a moderately large birefringence (0.096) which result in an enormous figure of merit (d^2/n^3 = 1288 pm^2/V^2). [3] The future effort will develop a technique to grow large crystals with a reduced absorption shoulder at shorter wavelengths which is due to crystal point defects (a common problem for chalcopyrite semiconductor crystals). The second candidate, GaSe, has been well researched primarily in the former Soviet Union (over 600 publication). [4] It has a large figure of merit (d^2/n^3 = 214 pm^2/V^2) [3] for this spectral region. However, the growth of high-quality crystals will be difficult because GaSe crystals are bonded very weakly in the c-direction (like mica). Alloying may overcome this limitation. Quasi-phase-matched semiconductor structures is another promising category which utilizes the large nonlinear coefficients of well-developed semiconductors such as gallium arsenide. [5,6] The recent development of diffusion bonding techniques has made these structures possible.

Semiorganics "have the potential for combining the high optical nonlinearity and chemical flexibility of organics with the physical ruggedness of inorganics," [7] and many of the candidates in this category are intrinsically low cost because they can be aqueously grown. They are either in the form of an organic/inorganic salt or an organic ligand/metal ion complex. [8] These are useful in the near-infrared and visible spectral regions. The two most important successes from this effort so far are deuterated thiosemicarbazide cadmium chloride (d-TSCCC) and deuterated cadmium triallylthiourea chloride (d-CAT). These crystals have the best (or nearly the best) figures of merit of known materials for the following: (1) type-II third-harmonic generation of 1064nm (Nd:YAG), (2) the second harmonic generation of 972nm (a Fraunhofer line which is an efficient seawater transmission wavelength), and (3) the second harmonic generation of 868 nm (another Fraunhofer line).

Borate crystals offer the possibility of highly efficient ultraviolet laser sources which are all solid state. For example, a laser source having an output wavelength of 289 nm, pumped with 1064nm (Nd:YAG), was recently demonstrated with an overall optical efficiency of 25%. [9] It utilized lithium triborate (LiB_3O_5 or simply LBO). Continuing problems with LBO appear to still exist limiting its applications. The problems are (1) long delays in receiving crystals and (2) some crystals of poor quality due to flux inclusions. It is also reported that China has no interest in licensing the growth to US crystal growers. In the present effort, new borate compounds (not presently patented by Chinese researchers) are being investigated which will permit conversion deeper into the ultraviolet spectral region.

Zinc Germanium Phosphide

The development of zinc germanium phosphide is the most important success resulting from the program. ZGP was first explored in the US during the late 1960s and early 1970s. In fact, it was identified as the most promising NLO material for mid-infrared applications by Wright Laboratory in 1974 (then the AF Avionics Lab and AF Materials Lab). [10] However, due to changes in Air Force R&D strategy, nearly all activity in this technology area stopped until Project Forecast II in the late 1980s reemphasized it. ZGP was a logical choice for development under Project Forecast II due to its extraordinary properties: large nonlinear coefficients, wide transparency range, wide phase-matching range, good mechanical properties, and good thermal properties. These properties were reported and confirmed by early US researchers and by Russian researchers during the late 1970s and 1980s.

Silver gallium selenide, another material developed through WL, has been the only serious competitor to ZGP for 2μm-pumped optical parametric oscillator (OPO) applications. Efforts to develop it began prior to the ZGP work, and AGSE demonstrated early success for wavelength tunability through the infrared when pumped with a 2μm source. [11] More recently, OPO output powers as high as 740 mW have been demonstrated with an overall conversion efficiency of 23%. It was soon recognized, however, that the material is intrinsically limited to low average-power operation due to a low thermal conductivity (p-0.010 & s-0.011 W/cm-K) [12] which leads to a thermal gradient and subsequent thermal lensing [13].

With AGSE thus largely discredited for higher-power, mid-IR applications, ZGP (having a nonlinear coefficient more than 3 times larger and a thermal conductivity about 35 times larger [12]) is now the material of choice for 2μm-pumped OPOs with average powers greater than one watt. For example, the ARPA/Tri-Service "Mid Infrared Lasers" program is directly dependent upon ZGP. [14] In addition, it has often been used for frequency doubling the shorter CO_2-laser wavelengths having lower power. [15] Early development (6.2) of the material is now almost complete, and ZGP will soon enter advanced development (6.3).

Early-development success resulted from promising efforts in the following facets of the program: (1) the development of innovative compound synthesis and crystal growth methods, (2) crystal defect analysis and identification, (3) the development of advanced processing techniques, and (4) device demonstration.

ZGP single crystals were successfully grown in this program by a two-stage process. [16] In the first stage, elemental zinc germanium, and red phosphorus are placed in boats, sealed into heavy-walled quartz ampoules, and heated to form single-phase ZGP. A heating cycle was developed to ensure the completion of intermediate reactions in order to avoid excessive pressure build-up related to free phosphorus and zinc. Single crystals were then grown using the seeded horizontal gradient freeze technique which achieves unidirectional solidification by cooling in the presence of a controlled thermal gradient in a two-zone horizontal growth furnace. The technique has been successful in growing single crystal boules because it is characterized by extremely low thermal gradients and minimized stress across the boule. [17] A single-crystal boule and fabricated samples are illustrated in Figure 2.

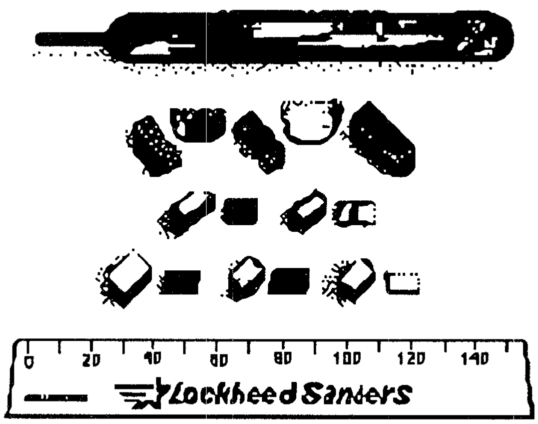

FIGURE 2. Boule and cut crystals of ZGP

In order to improve crystal yield and reduce production time, two highly innovative techniques have been developed. The first, a high-temperature transparent furnace utilizing hot mirror surfaces, as shown in Figure 3, has already been incorporated into the production process. It prevents seed loss due to melt back in this very low gradient environment because the crystal grower can visually monitor the growth. It also allows direct observation of twinning if it occurs. The twinned portion can then be melted back and single crystal growth reinitiated. The combined elimination of seed meltback and elimination of twinning has resulted in impressive yield gains. The second technique allows the rapid synthesis of ZGP compound by phosphorus injection, and it is now being further refined. The technique has been successfully applied to related semiconductors. [18]

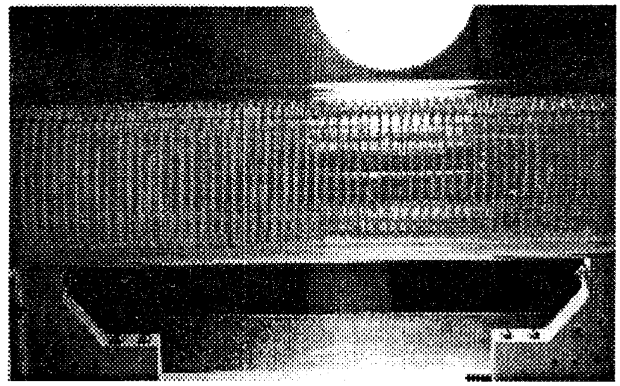

FIGURE 3. High-temperature, transparent furnace

The second facet of the ZGP success was in crystal defect analysis and identification. A typical transmission spectra for an as-grown ZGP crystal is shown as curve 1 in Figure 4 which clearly reveals an absorption shoulder which extends from the band edge to a wavelength of approximately 2.5μm. Such a shoulder, which severely limits the usefulness of the crystal when using a 2μm laser pump source, is common for these types of semiconductors, and it is caused by a crystal point defect. The defect was analyzed by the following techniques: transmission spectroscopy (polarized, temperature varied) [19], photoluminescence (polarized) [20], Hall measurements [21], electron paramagnetic resonance [22], cathodal luminescence [19], ENDOR [23], optical epr [24], and magic angle spinning NMR [25]. From this characterization, it was found that the absorption shoulder is directly related to a native acceptor (i.e., it is not related to impurities). The early characterization indicated that the acceptor is deep, it is highly polarization sensitive, and it is due to a zinc vacancy or a zinc ion on a germanium site. Therefore, it originally appeared that disordering of the zinc and germanium was probably the principal cause. [26] However, the latest ENDOR results have uniquely defined the defect as the zinc vacancy. In fact, recent investigations show no evidence of disorder or non-stoichiometric related anti-sites. Even in Zn-rich material it appears that a zinc-rich cubic phase of Zn_3P_2 forms dilutely still allowing V_{Zn} to remain the dominant defect.

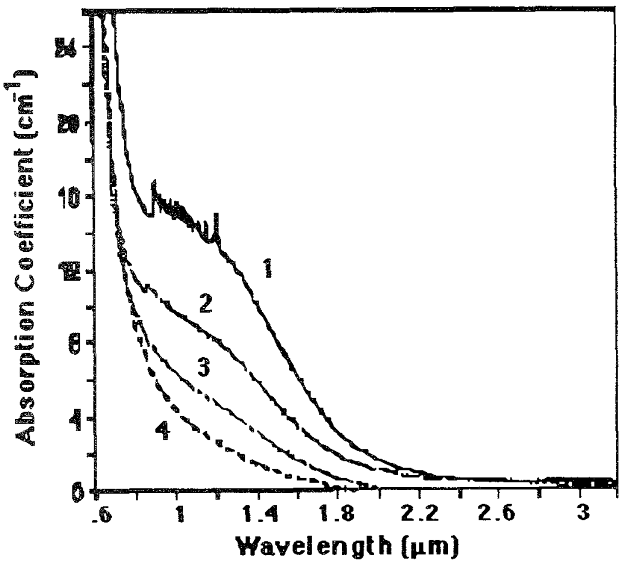

FIGURE 4. Transmission spectra for ZGP crystals. Curve 1 for as-grown sample, Curve 2 for sample with optimized stoichiometry, Curve 3 for crystal receiving post-growth annealing, and curve 4 for crystal irradiated with e-beam.

The third facet of the ZGP success was in the development of improved processing methods which have been partially guided by the defect analysis efforts. As displayed in Figure 5, thermal annealing and radiation treatment procedures have been developed which improve transparency. The mechanism for improvement with thermal annealing is most likely due either to a reduction in zinc vacancies or to an introduction of phosphorus vacancies (resulting in donors which can electrically compensate the zinc-vacancy acceptor or perhaps resulting from a mechanism similar to chemically complexing with hydrogen at the vacancy which would eliminate the electrical activity of the Zn vacancy). Electron-beam and gamma-ray irradiation of crystals appear to create donor sites, deeper in the energy gap, which compensate the native acceptors. [27] Another area of enhanced processing concerns improvements to surface finishing and antireflective-coating techniques.

The fourth facet of the ZGP success was the demonstration of OPOs utilizing the material which validated the overall success of the program and provided guidance to the materials R&D effort. An OPO has been demonstrated with an output of over 2.5 watts at a frequency of 4 KHz, a pump wavelength of 2.05µm, and extremely-high output efficiencies of almost 50% overall and about 65% slope efficiency (see Figure 5). [28] An output power of 3.5 watts has more recently been demonstrated. These demonstrations have highlighted the crystal's advantage with its large thermal conductivity because the crystal's absorption coefficient in these tests was 0.26/cm at 2.05µm which is larger than its competitor $AgGaSe_2$. In fact, it appears reasonably certain that the rollover seen in Figure 5 is not due to thermal effects but rather to reconversion of signal.

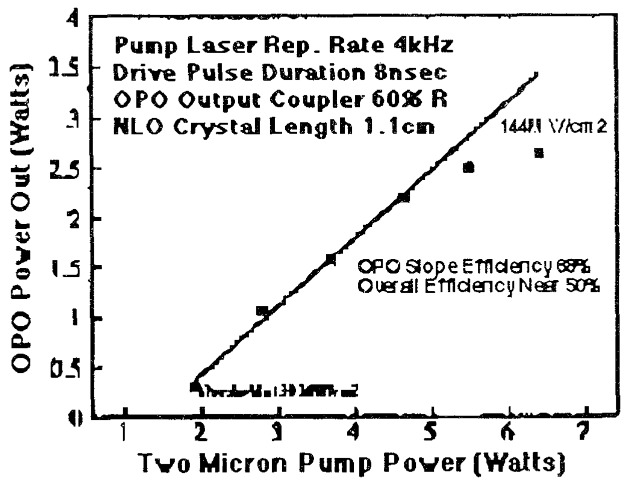

FIGURE 5. Output power versus 2-µm pump power for OPO utilizing a ZGP crystal

Future efforts with this material will be to establish a reliable process which produces large single crystals with high transparency (<0.15/cm at 2.05µm) and a high degree of homogeneity.

Potassium Titanyl Phosphate and Isomorphs

The final category of materials is the KTP family of compounds. KTP ($KTiOPO_4$) has superior properties for several NLO applications. Its high nonlinear optical coefficients, high optical damage threshold, wide acceptance angles and thermally stable phase matching properties make it useful for high-power wavelength conversion applications (SHG & OPO). [29] Its large linear electrooptic coefficients and low dielectric constants make it attractive as well for other applications such as modulators and Q switches. However, the application and availability of the crystal has been limited until recently partially due to a series of patents held by DuPont, but the patents have begun to expire. [30]

Wright Laboratory (WL) was responsible for steadily pushing forward the state of the art for the crystal growth of KTP, developing both the flux and hydrothermal growth techniques. [31,32,33] The effort today is contained in three areas of R&D. These are (1) the exploration and early development of isomorphs of KTP which extends the useable wavelength range to beyond 5μm, (2) the growth of KTP with a reduced susceptibility to grey tracking, and (3) the exploration and early development of alloys of KTP which permit noncritical phase matching at selected wavelengths. WL is principally pursuing the first two areas.

The first area concerns isomorphs of KTP which are useable to wavelengths beyond 5μm. [34] As illustrated in Figure 6, KTP is limited to wavelengths less than 3μm for high power applications. The new materials with extended wavelength range permit the high power from Nd:YAG at $\lambda=1\mu m$ to be converted to wavelengths out to 5μm. In addition due to a low electrical conductivity, they make possible improved Q-switches for the mid-infrared. The most promising candidates announced are $KTiOAsO_4$ (KTA), $RbTiOAsO_4$ (RTA), and $CsTiOAsO_4$ (CTA) (shown in Figure 6). However, even these may be somewhat limited to lower output power because the arsenate compounds are characterized by a small absorption in the 4 - 5μm range. Therefore, other KTP-like compounds (e.g., $KTiOSbO_4$ and $KTiONbO_4$) are also being investigated.

In addition, the nonlinear optical (NLO) crystal, $KTiOPO_4$ (or KTP), has been industry's workhorse for wavelength conversion in military and commercial laser systems operating in the visible and near-infrared spectral regions. Yet, laser damage, caused by a defect referred to as "grey tracks," has limited the use of the material in high-average-power laser systems. From an investigation of the causes for the grey track effect and its relationship to the chemistry and crystal growth processes, an improved crystal growth technique has been developed which reliably produces large-aperture crystals at low cost with a significantly improved damage threshold. In fact, using a standardized laser test system capable of inducing damage in all other types of commercially available KTP, the new material could not be damaged even at a power density of 3 J/cm^2, using radiation of 532nm, 20nsec pulse width and 10,000 shots. [35] This break-through development will soon lead to the availability of low-cost, large-aperture KTP from Crystal Associates with a greatly improved damage threshold.

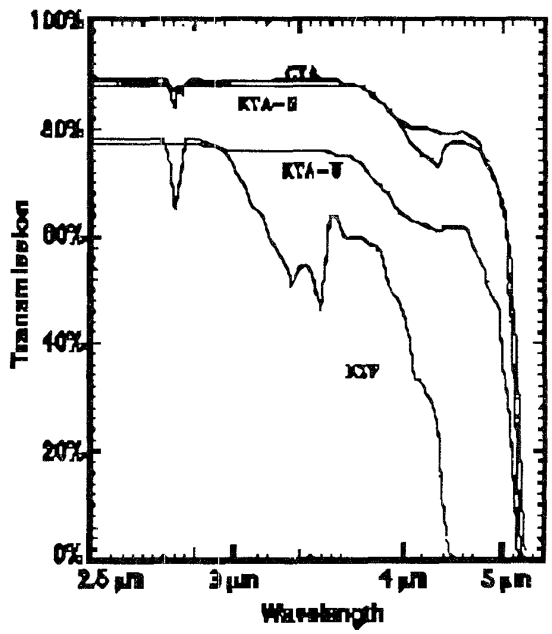

FIGURE 6. Transmission spectra of KTP, KTA, and CTA crystals

Conclusion

Nonlinear optical crystals are needed for laser sources which are in turn required for a number of applications. These applications include infrared countermeasures and environmental monitoring. As a result of Wright Laboratory's NLO materials program, crystals with greatly enhanced properties are becoming available and thus beginning to make these applications possible.

The program's organizational structure in Wright Laboratory has two key elements which are responsible for its many successes. These elements are found in each of the material areas described. Using ZGP as a typical example, they are as follows.

The first element is an integrated product team which is materials managed yet focussed by application goals. The development team has included crystal growers, material characterization specialists, and laser researchers who have cooperated on a continuing basis during the past seven years. The program management was by material scientists and engineers who understand the basics of growing and processing crystals (Materials Directorate at WL)). Yet, the final goals were set, and laser system testing performed, by the users (AF Wright Lab/EL and AA, AF Phillips Lab/LI, Naval Research Lab, NASA Langley Research Center, Army NVESD, and others).

The second element is the interlacing of federal inhouse research together with industrially-based early development (i.e., tackling the fundamental scientific problems arising during the course of development by an inhouse research team). Development of ZGP, for example, is being or has been pursued with AF funding at Lockheed Sanders, Westinghouse, Cleveland Crystals, and Inrad. However, these development efforts by themselves proved insufficient to optimize the crystal growth technique and optical properties; fundamental material problems existed. Research issues therefore have been pursued concurrent, and in collaboration, with the industrial programs, principally at Wright Lab in cooperation with other federal laboratories: Rome, Phillips, Seiler, Naval Research, and NASA. These laboratory efforts have permitted innovative crystal growth and processing techniques to be explored and the crystals' defects to be analyzed and controlled, and the research has been structured in such a manner that the complete technology will ultimately reside in the commercial sector.

Three additional characteristics are present as well in nearly all materials R&D programs. They are:
(1) generalized 6.1 research gave birth to the successful efforts *(comment: the promising characteristics of ZGP were identified as part of a much broader search for new materials)*,
(2) 6.2 and 6.3 development is indispensable for making the technology available to the device and system communities *(comment: development is truly a separate activity from research, and it cannot be disregarded; too often, system planners cite the millions of dollars which are spent on materials research and wonder why resulting materials are not incorporated into devices and systems)*, and
(3) both of these efforts require time *(comment: for ZGP, approximately two decades passed between commencement of 6.1 and the beginning of 6.2 and an additional decade will pass between the beginning of 6.2 and the incorporation of the crystal into systems).*

Acknowledgment

We acknowledge the inspired efforts of the many scientists and engineers who have made this program a success. They are David Fischer, Robert Nelson, and others from WL/MLPO, Tom Pollak and Peter Schunemann from Lockheed Sanders, Gabe Loiacono, Dick Stolzenberger, and Dominic Loiacono from Crystal Associates, Gretchen Kennedy and Gary Catella from Cleveland Crystals, Narsingh Singh from Westinghouse, and many others.

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