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Recent Developments in Nonlinear Optical Materials

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1. Introduction

Advances in nonlinear frequency conversion involve developments in laser pump sources, and nonlinear optical materials and techniques. There is a renewed interest in the development of nonlinear optical materials that has resulted from advances in the other areas, and from applications requiring tunable coherent radiation. Recent materials developments have included improvements in available size and optical quality of established nonlinear materials and the development of new materials that extend the conditions under which nonlinear frequency conversion can be used. There is a large amount of earlier materials work that is the subject of reviews [1]. The current effort in nonlinear optical materials development is also extensive, and the discussion here is limited to bulk inorganic materials used in second order nonlinear frequency conversion processes. Silver gallium selenide, lithium niobate and barium borate are discussed to provide examples.

There are about two dozen nonlinear optical materials that are commercially available. In choosing a nonlinear material or selecting new materials for development, it is necessary to consider an number of factors. Linear as well as nonlinear optical properties are important. A material must be transmitting, it must be phasematchable, and it must have good crystalline quality. Different figures of merit have be developed for various conditions. The quantity (d_{eff}^2/n^3) is a simple figure of merit for comparing nonlinearity. Here d_{eff} is the effective nonlinear coefficient for the material for a specified phasematching geometry and direction of propagation, and n is the refractive index. A high nonlinear coefficient alone is not a satisfactory criterion for an acceptable material. The intensity threshold for optical damage must be considered, and nonlinear absorption and intensity dependent changes in the refractive index can also limit nonlinear frequency conversion. Chemical stability and mechanical strength may be of concern. Thermal properties are important for high average power applications. Other properties that may be of concern are birefringent walkoff of pump and generated beams or temporal walkoff of short pulses due to group velocity mismatch. Material losses caused by absorption or scattering are important in high finesse resonant cavity techniques. And perhaps most important is the availability of the nonlinear optical material.

2. Silver Gallium Selenide

Nonlinear materials for applications between 4 and 10 μm in the infrared have been difficult to obtain. Materials which were available for use in this range had problems with low damage threshold, poor optical quality, or very limited availability. The use of $AgGaSe_2$ for nonlinear frequency conversion was first proposed in 1972 [2], and it is only recently that high optical quality crystals of large size have been produced. It can be phasematched for second harmonic generation for fundamental wavelengths between 3.1 and 13 μm. The transparency range extends from 0.8 to 17 μm with some multiphonon absorption at wavelengths longer than 13 μm. The nonlinear optical coefficient is $d_{36} = 43 \times 10^{-12}$ m/V. $AgGaSe_2$ has performed well in second harmonic generation and sum generation of the third harmonic of carbon dioxide laser radiation. $AgGaSe_2$ is now being grown in high quality boules yielding angle phasematched crystals of lengths up to 3.5 cm, and it is becoming available as a commercial product.

Some material development problems remain for silver gallium selenide. Post growth heat treatment in the presence of excess Ag_2Se is required to reduce the scattering in as-grown

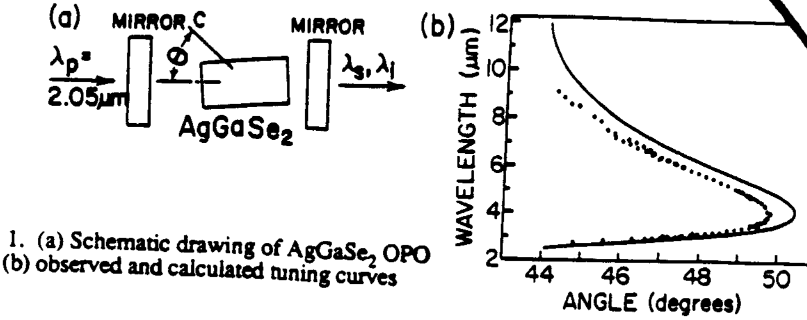

Fig. 1. (a) Schematic drawing of AgGaSe$_2$ OPO and (b) observed and calculated tuning curves

material. Adjustment of the heat treatment process is being investigated for higher yields and more complete elimination of the scattering. Scattering loss coefficients as low as 0.01 cm^{-1} have been achieved but values of 0.03 cm^{-1} are more typical in material now being produced. The residual scattering centers are small voids. Development of a surface treatment procedure that would increase damage threshold would be beneficial. The surface damage threshold is 13 MW/cm^2 for pulse durations of approximately 50 ns. The damage threshold for bulk optical damage is 10 times higher than that for surface damage. The bulk material also has excellent average power capabilities; average intensities of 200 kW/cm^2 have been transmitted in the bulk material without damage.

Infrared parametric oscillation has been demonstrated in AgGaSe$_2$ using a 2.05-μm, Q-switched holmium laser as a pump source [3]. This application of the material illustrates the broad spectral range over which it is useful. The output was continuously tunable between 2.65 and 9.0 μm. The 2-cm long parametric oscillator crystal was angle tuned between 45° and 50°. The experimental setup and observed wavelength tuning curve are shown in Fig. 1. Threshold for parametric oscillation was 4 mJ which was approximately one-fourth of the pump energy at which crystal surface damage was observed. The peak efficiency was 16% of the pump energy converted into signal and idler. The tuning range was limited by the mirror reflectivity in the singly resonant oscillator. Improved performance is possible with the 3.5-cm-long crystals now available.

3. Lithium Niobate

Even though lithium niobate has been used as a nonlinear optical material since the mid 1960s, development is continuing to improve and extend its properties. It has a relatively high nonlinear optical coefficient $d_{31} = 6.57 \times 10^{-12}$ m/V, compared to d_{36}(KDP) = 0.41×10^{-12} m/V, and it has high transmission in the near infrared, and good physical properties. It is grown by the Czochralski technique which yields large crystals of good quality. LiNbO$_3$ will 90° phasematch for harmonic generation of fundamental wavelengths near 1.06 μm, thus providing greater angular acceptance and eliminating the problem of birefringent walkoff. Photorefractive damage of LiNbO$_3$, however, has limited its use at high intensity in the visible. Recently two methods for reducing the photorefractive damage have been demonstrated. Doping the material with 5 mole percent of MgO substantially reduces the photorefractive damage that occurs at high intensity [4]. In the second method the material is returned to stoichiometric composition by lithium in-diffusion [5]. This raises the phasematching temperature for fundamental wavelengths near 1.06 μm to 234 C which is well above the annealing point. Preliminary observations have shown that even below the annealing temperature photorefractive damage cleans up after a few seconds. In addition the lithium-diffused stoichiometric material has excellent optical uniformity.

The use of MgO:LiNbO$_3$ has been demonstrated in an external resonant cavity second harmonic generator which provided stable harmonic conversion of a diode-pumped Nd:YAG laser output [6]. The external resonant cavity (Fig. 2) was formed by depositing highly reflecting dielectric coatings on the polished spherical surfaces of the nonlinear crystal. Temperature-tuned 90° phasematching was used, and the resonant frequency of the monolithic cavity was tuned electro-optically by applying a voltage transversely across the MgO:LiNbO$_3$

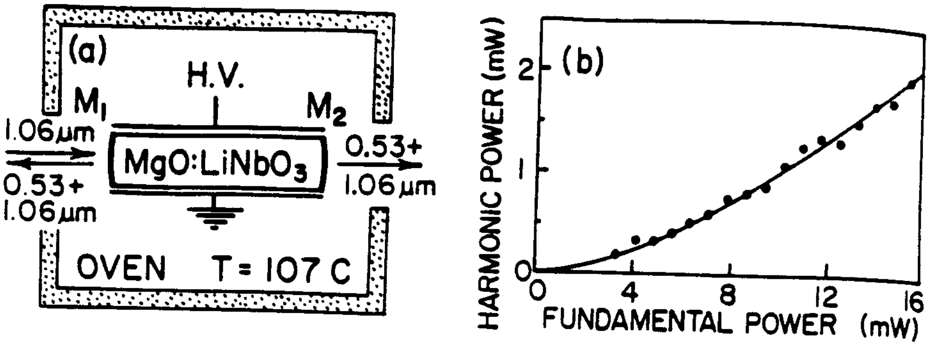

Fig. 2. External resonant cavity second harmonic generation with MgO:LiNbO$_3$; (a) schematic of setup and (b) observed harmonic power dependence on incident fundamental power

crystal. Feedback control was obtained by deriving the applied voltage from the from the magnitude of the reflected pump wave. The harmonic output was a stable single longitudinal and lowest order transverse mode. A conversion efficiency of 13% was obtained with 15-mW pump power. The measured finesse of the harmonic cavity was 450, indicating that losses for a round trip in the 25-mm crystal were 0.8% when the 0.6% transmission of the coatings was taken into account. The very low transmission loss, good optical quality, and increased resistance to photorefractive damage of the MgO:LiNbO$_3$ material were important properties in this application. Optimization of mirror reflectivities could eliminate the back reflected and transmitted fundamental, increasing harmonic conversion. Preliminary indications are that the lithium-diffused stoichiometric LiNbO$_3$ will perform even better.

4. Barium Borate

The use of barium borate (BaB$_2$O$_4$ or BBO) as a nonlinear optical material is a recent development [7]. BBO is particularly useful for generation of ultraviolet radiation as short as 200 nm by sum frequency and harmonic generation [8]. The second through fifth harmonics of 1.06-µm Nd laser radiation can be generated with high efficiency in BBO, and the material appears to have potential for high average power applications [9]. BBO is highly transmitting between 200 nm and 2.2 µm. The nonlinear coefficient is $d_{22} = \pm 1.7 \times 10^{-12}$ m/V. The material is being grown at the Fujian Institute of Research on the Structure of Matter in the Peoples Republic of China, and some is exported for sale. Several other groups have started investigation of the growth of this material.

The melting point of BaB$_2$O$_4$ is 1095 ± 3 C. The crystal has two solid phases. The low temperature phase which occurs when crystallization takes place below 925 ± 2 C is non-centrosymmetric with large second order nonlinear susceptibility. A top seeded solution growth technique is required to produce quality crystals of the low temperature phase. The crystals tend to grow in flat boules which limits the length of material that can be harvested in the phasematched direction. Growth of BBO, particularly inclusion free material, is difficult.

Several crystals of excellent quality supplied by the Fujian Institute of Research on the Structure of Matter were used to generate harmonics of Q-switched Nd:YAG laser output. The performance of BaB$_2$O$_4$ in the generation of second, third and fourth harmonics compared favorably with that of KDP and ADP crystals. The setup for cascaded harmonic generation to 213 nm is shown in Fig. 3. When pumped with a 540-mJ unstable resonator Q-switched Nd:YAG laser, 5th harmonic energy of 20 mJ was produced. This value could be improved by avoiding excessive depletion of the fundamental which was summed with the fourth harmonic. The 5th harmonic at 213 nm is at a wavelength which can be phasematched for cascaded conversion to the 15th harmonic by 3rd harmonic generation in Ne gas [10].

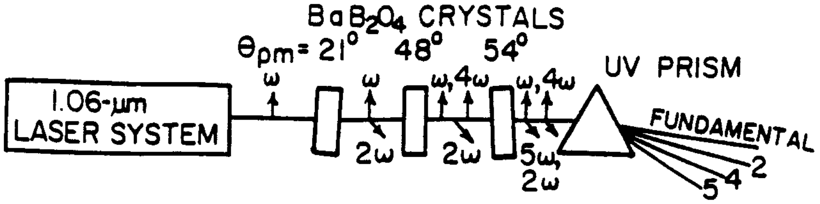

Fig. 3. Schematic representation of setup for fifth harmonic generation of Nd laser radiation in BaB_2O_4

Summary

A limited number of examples were used to illustrate some of the recent developments in nonlinear optical materials. There is a large amount of work on other materials that has not been mentioned. The examples given here are representative of materials development for new spectral regions and for a variety of nonlinear conversion techniques. With one laser and these three materials, it would be possible to generate continuously tunable coherent radiation from 200 nm to 17 μm. The problems of material growth are not trivial, but with continued effort considerable progress is being made.

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