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Optical second-harmonic generation in lead formate

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The optical properties of lead formate crystals are investigated, especially those affecting the usage for optical second-harmonic generation. The refractive indexes and the optical absorption are measured in the near-ultraviolet, visible, and near-infrared spectral regions. The data show that the material is suitable for the efficient generation of blue light when pumped with near-infrared laser wavelengths. Phase matching conditions for this application of lead formate are determined both experimentally and by a numerical evaluation of the index data. © *2000 American Institute of Physics.* [S0021-8979(00)09701-2]

I. INTRODUCTION

Versatile and efficient sources of blue light are of fundamental importance for various applications including optical data storage,[1,2] ophthalmologic or other medical techniques,[3] and laser displays.[4–6] In spite of the rapid development of blue laser diodes[7,8] and concurrent physical principles like optical upconversion,[9] optical second-harmonic generation[10] (SHG) still is one of the most important methods to achieve intense coherent blue light with a good optical beam quality.[11]

From symmetry aspects, SHG is only possible in crystals belonging to one of the 20 point groups which lack a center of symmetry.[12] Furthermore, to meet phase matching aspects in homogeneous crystals, refractive indexes for the fundamental and the generated harmonic wavelength must be of identical size,[13,14] optical birefringence being necessary.

Here we discuss the properties of lead formate which excellently meet the described conditions. Although described for the first time about 100 years ago,[15,16] it is a new material in the field of nonlinear optical applications.

II. CRYSTAL GROWTH AND PROPERTIES

Lead formate, $Pb(HCOO)_2$, is grown from a saturated aqueous solution at 40 °C. The material crystallizes in a rhombic disphenoid structure P 222, and a typical crystal is shown in Fig. 1.

From the angles of the shape the ratios between the lengths of the crystallographic axes can be derived. We found a relation of

$$a:b:c=0.74:1:0.85, \tag{1}$$

which is in excellent agreement with earlier published values.[15,16] One orthorhombic unit cell of the crystal contains four formula units of the compound.[17] Taking the molecular weight (297.23) and density (4.63 g/cm^3) of the material,[18] one can calculate the size of the unit cell to be $a=6.50$, $b=8.78$, and $c=7.47$ Å.

Crystals of lead formate are thermally stable up to about 115 °C where a phase transition followed by thermal decomposition takes place.[19]

III. LINEAR AND NONLINEAR OPTICAL PROPERTIES

The orthorhombic crystal structure forces the material to be optically biaxial with the axes of the indicatrix fixed to the three mutually perpendicular symmetry axes of the crystal. The only nonzero elements of the nonlinear susceptibility tensor for crystals of this symmetry (222) are d_{14}, d_{25}, and d_{36}. Thus, for efficient second-harmonic generation, only so-called critical phase matching is possible.

A. Refractive indexes

The principal refractive indexes were measured between 400 and 1100 nm using the prism method and various light sources. Applying the standard ordering for the refractive indexes of biaxial crystals, the highest index n_1 corresponds to light polarization parallel to the crystallographic c axis, n_2 to the b axis, the lowest index n_3 to the a axis.

The experimental values can be accurately described by a two parameter Sellmeier fit,

$$n_i^2-1=\frac{A_i}{\lambda_i^{-2}-\lambda^{-2}}, \tag{2}$$

with the parameters listed in Table I.

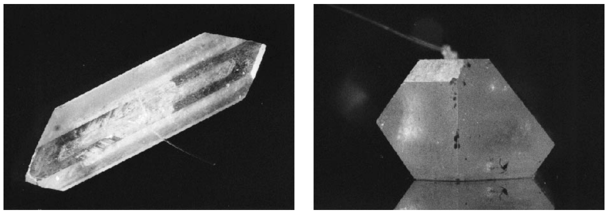

FIG. 1. Lead formate crystal, viewed along the crystallographic b (left) and c axis (right). The lower-left to upper-right diagonal in the picture on the left is the c axis (main growth direction). In the picture on the right the a axis is horizontally oriented, and the b axis vertically oriented. Crystal dimensions: $L_a \approx L_b \approx 10$ mm, $L_c \approx 40$ mm.

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TABLE I. Parameters for the Sellmeier description of the refractive indexes of lead formate. Usual ordering of the indexes is used (subscript 1 denotes the highest, and subscript 3 the lowest index value).

Index	A_i	λ_i
n_1	8.231×10^{13} m^{-2}	1.688×10^{-7} m
n_2	9.582×10^{13} m^{-2}	1.536×10^{-7} m
n_3	8.605×10^{13} m^{-2}	1.546×10^{-7} m

Using this Sellmeier description, the complete wavelength dependence of the three refractive indexes can be calculated; this dependence is sketched in Fig. 2.

B. Optical absorption

For optical applications in general, and especially for SHG, the material considered must be transparent in the wavelength region of interest. To check this, we measured the optical absorption of lead formate using a grating spectrometer for the visible and ultraviolet spectral regions and a Fourier transform spectrometer for the infrared region.

The measured results, plotted in Fig. 3, show a transparency region spanning from approximately 300 to 2200 nm. The steep rise below 300 nm is caused by the fundamental electronic absorption of the material; the absorption bands in the infrared region should be due to intramolecular vibrational excitations in the $(\mathrm{HCOO})^-$ system.

C. Phase matching angle

The tensor of the nonlinear optical susceptibility for lead formate can be written as

$$d=\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix}, \tag{3}$$

with only three nonzero elements. We determined the size of these elements using a modified Maker fringe technique.[20] As expected from Kleinman's rule,[21] they are all in the same order of magnitude, approximately $(1.1\pm0.5)\times10^{-12}$ m/V (the comparably large uncertainty of our measured d values is due to a partly minor optical quality of the samples used for the fringe measurements). The nonlinear susceptibility turns out to be about twice that of the standard material potassium dihydrogen phosphate (KDP) where $d_{36}\approx0.46\times10^{-12}$ m/V.[22]

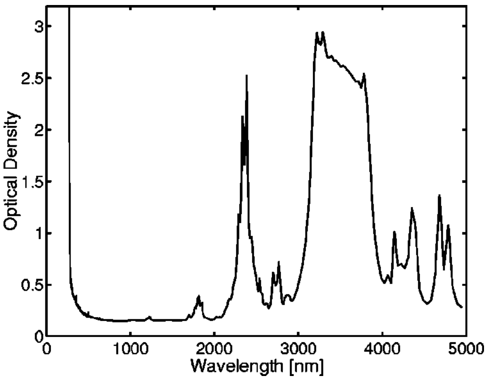

FIG. 3. Optical density of lead formate measured on a 2 mm thick platelet for light polarized in the n_1 direction (the crystallographic c axis). For the other polarizations only slight differences were found. The data are *not* corrected for reflection, therefore the seemingly nonzero absorption in the transparent region.

With the already discussed ordering of the dielectric axes, phase matching is possible for d_{25} and d_{36}, respectively. The latter uses the largest birefringence present in the material, thus is the most interesting one for the generation of blue light. For this configuration, where the fundamental beam uses a mixed refractive index between the two larger ones (n_1,n_2) and the harmonic beam uses the smallest one (n_3), we calculated the phase matching angles as a function of the fundamental wavelength utilizing the Sellmeier description for the refractive indexes. As a check of the calculations we also measured this angle experimentally using several wavelengths of a titanium sapphire laser. The results are shown in Fig. 4.

The valid effective tensor element is reduced to $d_{\mathrm{eff}}=d_{36}\sin\Phi\cos\Phi$, yielding a reasonable efficiency between 770 and 890 nm for this configuration.

For longer wavelengths configurations with ''oblique'' beam direction have to be used. For this general case of an arbitrary beam direction there is no simple comprehensive description. The phase matching conditions must be calcu-

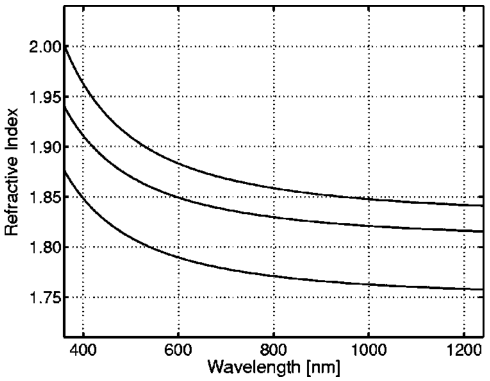

FIG. 2. Refractive indexes of lead formate, and the Sellmeier fit to the experimental values. Upper curve: n_1, light polarization parallel to the crystallographic c axis; middle curve: n_2, b axis; lower curve: n_3, a axis.

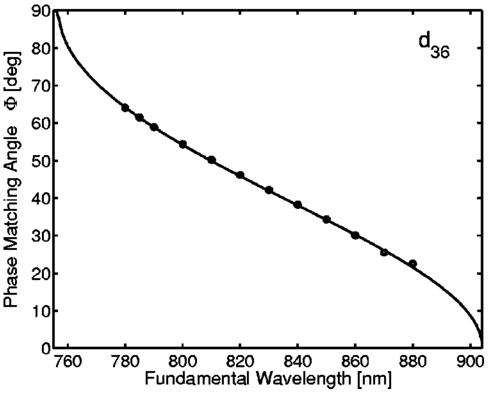

FIG. 4. Phase matching angle for the generation of blue light in lead formate. The angle given is measured between the direction of the fundamental beam and the crystallographic c axis.

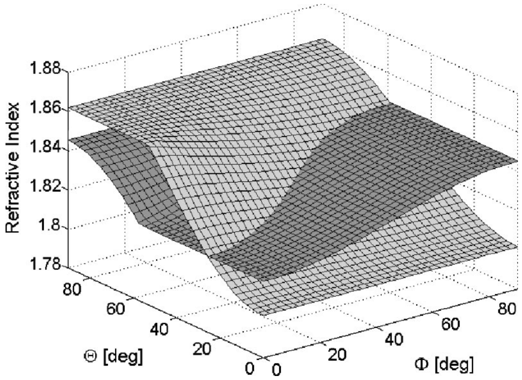

FIG. 5. Index surfaces for the larger of the two refractive indexes at the fundamental wavelength of 1064 nm (dark gray) and the smaller of the two at the harmonic wavelength (light gray). The phase matching angles are defined by the intersection curve between the two surfaces. Φ is measured to the *a-c* plane, and Θ is the elevation from the *a-b* plane of the crystal. The distinct kink in both surfaces (at Φ=0, Θ≈58°) marks the direction of one optical axis of the crystal.

lated specifically for each desired wavelength. An example is given in Fig. 5 for a fundamental wavelength of 1064 nm (a Nd:YAG laser). The set of phase matching angles is defined by the intersecting line between the index functions for the refractive indexes involved. To get the most efficient direction one has to calculate the doubling efficiency along that curve using the exact absolute or relative magnitude and the relative sign of each tensor element.

D. Damage threshold

Up to the maximum pulse energies available with our equipment (about 0.5 mJ focused on a spot of 0.1 mm diameter at a repetition rate of 1 kHz) no damage of the crystal could be detected. Furthermore, long term measurements proved that no observable degradation in the generated second-harmonic intensity takes place. Thus also so-called optical or photorefractive damage, as experienced, for instance, in lithium niobate,[23] does not seem to occur, even in the blue and green spectral regions considered.

IV. CONCLUSION

The linear and nonlinear optical properties of lead formate, $Pb(HCOO)_2$, show that this material is a promising candidate for nonlinear optical applications. It can be utilized for second-harmonic generation at fundamental wavelengths between 770 and 2500 nm with tensor elements that are about twice as large as, for instance, those in KDP.

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