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Piezo-optic and elasto-optic effects in lead molibdate crystals

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ABSTRACT

Piezo-optical and elasto-optical properties of lead molibdate ($PbMoO_4$) crystals are investigated, as determined by the quantum-mechanical *ab initio* calculation of the full set of elasto-optic, piezo-optic and elastic tensor components. Indicative surfaces are built, which describe the anisotropy of these stress- and strain-optical effects and allow for its rigorous analysis. Maximum values of these properties are determined as well as the geometries of acousto-optic interaction displaying the maximum efficiency. Lead molibdate crystals are found to be characterized by a large piezo-optic efficiency, the maximum change of the optical path (per unit of mechanical stress and specimen length) being calculated to 24.9 Br, which is a much larger value than previously reported for other well-known piezo-optic materials such as $LiNbO_3$, $CaWO_4$ and GaP. It is also shown that a significant rotation (up to several tens of degrees) of the optical indicatrix about the X_3 optical axis is induced by uniaxial pressure or deformation, depending only on pressure (or deformation) direction, which has relevant implications in the design of acousto-optic cells.

1. Introduction

Despite being a well-known acousto-optic material [1–3], lead molibdate ($PbMoO_4$) has not yet been thoroughly characterized in terms of its stress- and strain-optical features. For instance, large discrepancies are found between sets of its elasto-optic coefficients (ELOC) p_{in} as reported in the literature in different studies, which are the main physical parameters governing its acousto-optic efficiency. The value of the p_{11} coefficient has been reported to be 0.24 by Coquin et al. [2] and 0.28 by Gabrielyan et al. [4]; the p_{13} coefficient spans an even larger range, from 0.255 [2] to 0.35 [4] and 0.49 [5]; the values of the p_{61} coefficient differ by a factor of 4, from 0.013 [2] to 0.05 [4]. Apart from absolute values, signs of the ELOCs have not yet been determined, which makes it impossible to accurately describe the spatial anisotropy of the elasto-optic effect (ELOE) in $PbMoO_4$ crystals, as both absolute values and signs are obviously needed for this purpose [6,7]. Moreover, the piezo-optic effect (POE) in lead molibdate, which is an essential physical parameter in the determination of the efficiency of piezo-optic light modulators and photoelastic pressure (or mechanical stress) sensors [8–11], has not yet been studied.

The aim of this paper is two-fold: i) the determination of the full set of piezo-optic π_{im} and elasto-optic p_{in} coefficients of lead molibdate $PbMoO_4$ by use of a recently developed quantum-mechanical *ab initio* theoretical approach [12,13], based on the density-functional-theory (DFT) and on the Coupled-Perturbed-Hartree-Fock/Kohn-Sham (CPHF/KS) method for the evaluation of the dielectric tensor of crystalline materials, as implemented in a developmental version of the CRYSTAL14 program [14]; ii) the careful analysis of the anisotropy of both the piezo-optic and elasto-optic effects in lead molibdate. Indicative surfaces of the POE and ELOE are here built, their maximum and minimum values found, and the acousto-optic quality coefficients determined, starting from the full fourth-rank piezo-optic and elasto-optic tensors provided by the theoretical calculations.

It is shown that lead molibdate crystals exhibit a large piezo-optic efficiency with a maximum change of the optical path of 24.9 Br (per unit of mechanical stress and specimen length), which is a larger value than in other piezo-optic materials such as $LiNbO_3$, $CaWO_4$ and GaP. The rotation of the optical indicatrix (and correspondingly of the direction along which light polarization occurs) is also found to depend considerably on the direction of an applied uniaxial pressure or strain (deformation). The angle between light polarization vector $\boldsymbol{i}$ and direction of uniaxial pressure $\boldsymbol{m}$ (or strain $\boldsymbol{n}$) can be as large as several tens of degrees, which is an effect to be accurately accounted for in designing acousto-optic cells [15].

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2. Quantum-mechanical calculation of elastic, piezo-optic and elasto-optic coefficients

The elastic, elasto-optic and piezo-optic fourth-rank tensors of $PbMoO_4$ have been computed by using the fully-automated procedures implemented into the CRYSTAL14 program [12,13,16]. The hybrid PBE0 functional is used [17], which is known to provide accurate strain-related properties of solids [18,19]. An atom-centered Gaussian-type function basis set has been adopted where oxygen atoms are described by an all-electron 8-411G(2d) basis [20] while pseudo-potentials are used to describe the core of lead [21] and molybdenum [22] atoms. The optimized equilibrium lattice parameters are a = 5.472 and c = 12.097 Å, with a ratio c/a = 2.211 and fractional coordinates of the symmetry-irreducible oxygen atom $x_O = 0.2316$, $y_O = 0.1091$ and $z_O = 0.0436$.

Lead molibdate crystals belong to the $4/m$ symmetry class of the $I4_1/a$ space group and thus have seven symmetry-independent components of the elastic stiffness and compliance tensors (C_{mn} being elastic stiffness and S_{nm} elastic compliance constants), and ten symmetry-independent components of the piezo-optic and elasto-optic tensors. The computed symmetry-irreducible elastic constants are reported in Table 1, where they are compared with available experimental determinations by Coquin et al. [2], Gabrielyan et al. [4], and Farley et al. [23].

The comparison presented in Table 1 demonstrates that almost all the calculated C_{mn} and S_{nm} elastic coefficients coincide with the corresponding experimental values with a high accuracy, with deviations between the two sets that never exceed 10%, which corresponds to the scattering of experimental data in papers [2,4,23]. Slightly larger differences between calculated and experimental values are observed only for the C_{16} and C_{66} coefficients (and correspondingly for S_{16} and S_{66}) with deviations in the range from 6 to 30% according to different sources.

It is worth mentioning that the sign of the C_{16} coefficient depends on the particular choice for the right-handed coordinate system. If right-handed crystal physics coordinate system X, Y, Z is chosen in such a way that the deviation of the magnetic axes from $+X$ and $+Y$ is counterclockwise, then the C_{16} coefficient will have negative sign [23]. According to this conventional orientation, the C_{16} elastic coefficient has been reported to be negative for all the 4 crystals with scheelite structure studied by Farley et al. [23]: $CaMoO_4$, $SrMoO_4$, $PbMoO_4$ and $CaWO_4$. Piezo-optic coefficients (POC) π_{im} and elasto-optic coefficients p_{in} have also been computed by assuming the same coordinate system, so as to ensure consistency of all computed quantities. Computed values of these coefficients are given in Table 2, where elasto-optic ones are also compared with previous experimental determinations [2,4].

The computed absolute values of the p_{in} coefficients in Table 2 are relatively close to the experimental ones reported by Coquin et al. [2] while they significantly differ from those by Gabrielyan et al. [4] overall. The main difference between experimental [2] and computed elasto-optic coefficients is again represented by the signs of some coefficients (p_{45}, p_{16} and p_{61}). Let us stress that signs in [2] correspond to a different choice of the orientation of the right-handed coordinate system (i.e. a rotation by 180° about the $+Z$ axis of the coordinate system given in [23]). An explicit account of the dependence of rotating, shear or rotating-shear piezo-optic and elasto-optic coefficients π_{im} and p_{in} on the choice of right-handed coordinate systems is given in detail in [24]. In Table 2 we also report the first determination of the full set of piezo-optic coefficients of $PbMoO_4$.

Table 1
Coefficients of elastic stiffness C_{mn} (in 10^9 N/m^2 = 1 GPa) and elastic compliance S_{nm} (in 10^{-12} m^2/N = 1 Brewster = 1 Br) for $PbMoO_4$ crystal.

C_{mn}	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	C_{16}
This work	112.14	67.94	51.35	94.09	27.14	38.31	−12.82
[2]	109.2	68.3	52.8	91.7	26.7	33.7	13.6
[4]	108.0	63.2	50.7	95.2	26.4	35.4	15.8
[23]	109.0	68.0	53.0	92.0	26.7	33.7	−14.0
S_{nm}	S_{11}	S_{12}	S_{13}	S_{33}	S_{44}	S_{66}	S_{16}
This work	18.07	−10.01	−4.40	15.43	36.85	32.39	9.39
[23]	21.0	−12.4	−4.9	16.6	37.5	40.6	13.5

3. Results analysis

On the basis of the full and consistent quantum-mechanical determination of all of the elastic, elasto-optic and piezo-optic coefficients reported in Tables 1 and 2, this section is devoted to the investigation of the maximum piezo-optic efficiency of lead molibdate, to the detailed analysis of its piezo-optic and elasto-optic effect anisotropy, and to the determination of the maximum values of the acousto-optic quality coefficient for $PbMoO_4$ crystals.

3.1. Change of optical path induced by mechanical pressure

Given that five piezo-optic coefficients π_{im} of lead molibdate are large (π_{12}, π_{13}, π_{44}, π_{66}, and especially π_{33}, whose value exceeds 3 Br), it is expected that also the optical path change $\delta\Delta_k$ under the action of a mechanical stress will be large, as well as the efficiency of photoelastic light modulation. The optical path changes $\delta\Delta_k$ can be computed from the following well-known equation [24,25]:

$$\delta\Delta_k = -\frac{1}{2}\pi_{im}\sigma_m d_k n_i^3 + S_{km}\sigma_m d_k (n_i - 1), \tag{1}$$

where σ_m is the mechanical stress value, d_k the specimen thickness, n_i the refractive index, and i, k, m indices denote light polarization, light propagation and uniaxial pressure action directions, respectively. Let us rewrite Eq. (1) so as to introduce the optical path change per mechanical stress unit and specimen length unit:

$$\frac{\delta\Delta_k}{\sigma_m d_k} = -\frac{1}{2}\pi_{im} n_i^3 + S_{km}(n_i - 1), \tag{2}$$

which is an important parameter in the evaluation of the efficiency of piezo-optic pressure sensors and piezo-optic light modulators [8–11]. Let us evaluate the value (to be given in Br) of this quantity for the experiment conditions $m = 3$, $i = 3$, $k = 2$ that is, when the large π_{33} POC is acting:

$$\frac{\delta\Delta_2}{\sigma_3 d_2} = -\frac{1}{2}\pi_{33} n_3^3 + S_{23}(n_3 - 1) = -19,3\ (77,5\%) - 5,6\ (22,5\%) = -24,9\ \text{Br}. \tag{3}$$

Here, we have taken into account that $S_{23} = S_{13}$, we have used S_{km} and π_{im} coefficients as computed in this work (see Tables 1 and 2), and we have used $n_1 = n_2 = n_o = 2.386$ and $n_3 = n_e = 2.262$ for $\lambda = 632.8$ nm from [2]. The negative sign of the result in Eq. (3) implies that the optical path of the light beam passing through the specimen decreases under the action of a positive specimen tension σ_m. Percentage values within brackets in Eq. (3) represent the piezo-optic (77.5%) and the elastic deformation (22.5%) contributions to the specimen optical path change in the direction of light propagation. Other $\delta\Delta_k/(\sigma_m d_k)$ values, due to the other large POCs π_{12} and π_{13} are considerably lower than the result in Eq. (3) being equal to −15.3 and −17.9 Br, with piezo-optic contributions

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