Technical note

Linear and nonlinear optical susceptibilities of orthorhombic rare earth molybdates RE$_2$(MoO$_4$)$_3$

D. Xue, K. Betzler*, H. Hesse, D. Lammers

Fachbereich Physik, Universität Osnabrück, D-49069 Osnabrück, Germany

Abstract

The dielectric responses (i.e. the refractive indices and the second order nonlinear susceptibilities) of all orthorhombic rare earth molybdates have been studied on the basis of the relationship between dielectric responses and the average atomic number of constituent atoms of crystals. Both the linear and second order nonlinear optical responses at 1.064 μm decrease with increasing atomic number from La to Lu. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: A. Oxides; A. Optical materials; D. Crystal structure; A. Optical properties

1. Introduction

In recent years, acentric orthorhombic rare earth molybdates RE$_2$(MoO$_4$)$_3$ (REMO, where RE represents the respective rare earth element) have attracted considerable attention [1–3], since one member of this crystal group, Gd$_2$(MoO$_4$)$_3$ has been shown to be an efficient frequency doubling medium for laser–diode pumping [4,5]. Nd^{3+}:Gd$_2$(MoO$_4$)$_3$ turned out to be a promising candidate for multi-color generation and self-frequency doubling or self-frequency mixing [6].

For the application of these materials, a sound knowledge of the optical properties—both linear and nonlinear—is of fundamental importance. These properties have been calculated for selected members of the REMO group from structural data using the chemical bond method [2]. In this letter, we present an extension of the former results to the whole set of REMO crystals. The extension is based on the fact that the dielectric properties of closely related compounds are linearly correlated to the average atomic number of the constituent atoms Z_{av} [7].

2. Fundamentals

Quantitatively, the linear dielectric constant of a solid, ϵ, may be expressed in terms of the polarizability of its constituent atoms, α_i, as following:

$$\epsilon = 1 + \frac{\sum N_i \alpha_i / \epsilon_0}{1 - \sum \gamma N_i \alpha_i / \epsilon_0} \tag{1}$$

where N_i is the number of atoms of species i per unit volume, ϵ_0 is the free-space permittivity, and γ is the Lorentz factor. Since α_i may be considered to be linearly related to the atomic number Z, the dielectric constant for a certain group of solids with similar crystal structure [8] can be written as

$$\epsilon = (a_1 - b_1 Z_{av})^{-1} \text{ or } \epsilon = a'_1 - b'_1 Z_{av} \tag{2}$$

where a_1 and b_1 or a'_1 and b'_1, respectively, are constant for each group of solids. Z_{av} is defined as the mean of the atomic numbers of the constituent atoms. For the case of, e.g. an A$_{1-x}$B$_x$C type compound, $Z_{av} = [(1-x)Z_A + xZ_B + Z_C]/2$.

On the basis of the optical properties of all constituent chemical bonds, the nonlinear optical tensor coefficients d_{ij} of a crystal material can be expressed as [9,10]

$$d_{ij} = \sum_\mu \frac{G_{ij}^\mu}{d^\mu q^\mu} \left\{ N_b^\mu (0.5) \frac{(Z_A^\mu)^* + n(Z_B^\mu)^*}{(Z_A^\mu)^* - n(Z_B^\mu)^*} f_i^\mu (\chi_b^\mu)^2 \right.$$
$$\left. + \frac{N_b^\mu s(2s-1)(r_0^\mu)^2}{(r_0^\mu - r_c^\mu)^2} f_c^\mu (\chi_b^\mu)^2 \rho^\mu \right\} \tag{3}$$

* Corresponding author. Tel.: +49-541-969-2636; fax: +49-541-969-3512.

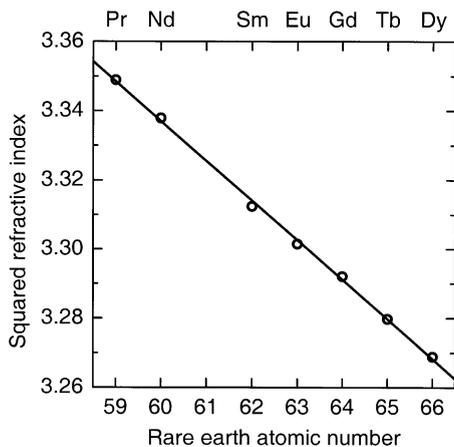*E-mail address:* klaus.betzler@uni-osnabrueck.de (K. Betzler).

Fig. 1. Squared refractive indices of selected rare earth molybdates REMO (RE = Pr, Nd, Sm, Eu, Gd, Tb, Dy and MO = $(MoO_4)_3$) as a function of the rare earth atomic number. The data points indicate values calculated from structural data (see Ref. [2]). The line represents a linear fit.

Fig. 2. Nonlinear optical tensor coefficients d_{ij} of selected rare earth molybdates REMO (RE = Pr, Nd, Sm, Eu, Gd, Tb, Dy and MO = $(MoO_4)_3$) as a function of the rare earth atomic number. The data points indicate values calculated from structural data (see Ref. [2]). Lines are appropriate linear fits. Tensor coefficients d_{ij} in 10^{-9} esu.

where ρ^μ is the difference in the atomic sizes, r_c^μ is the core radius. q^μ is the bond charge of the μ-th bond, and G_{ij}^μ is the geometrical contribution of chemical bonds of type μ. All of the above parameters can be deduced from the detailed chemical bonding structures of all constituent atoms [9,10]. For a group of solids with a similar crystal structure, the parameters in Eq. (3) only change with different constituent atoms, the dependence on the mean of the atomic numbers can be approximated—again linearly—by $d_{ij} = a_2 - b_2 Z_{av}$ where a_2 and b_2 are constants for each group of solids.

If the amount or type of only one of the constituent atoms of a compound varies, Z_{av} depends linearly on the effective Z of this atom. The linear dependencies of the susceptibilities on Z_{av} then can be simplified and referred to as linear dependencies on the effective atomic number of this constituent.

3. Results and discussion

Due to their crystal symmetry, rare earth molybdates in the low temperature orthorhombic phase exhibit three different fundamental refractive indices, n_x, n_y, n_z. In Ref. [2] data for the 'isotropic' index (i.e. the mean value of the three fundamental indices) at 1.064 μm for PrMO, NdMO, SmMO, EuMO, TbMO and DyMO have been calculated. Although they were not explicitly given there, experimental data are available for GdMO [11]. The squares of these 'isotropic' refractive indices are plotted in Fig. 1 as a function of the rare earth atomic number, the linear relation between susceptibility and average atomic number is quite evident. A similar dependence was found for the variation of the unit cell volume as a function of the atomic number [12].
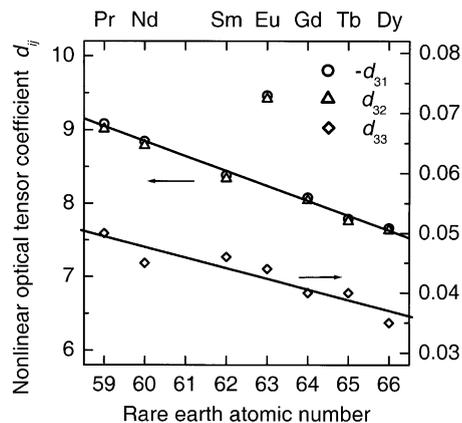
This assures that the susceptibility is connected to the geometry due to the fact that the electronic energies depend directly on the unit cell size. Taking the found linear dependence, the susceptibilities of all other REMO crystals—which could not be calculated due to the absence of structural data—now can be derived (Table 1).

Further, we also can derive the nonlinear optical tensor coefficients d_{31}, d_{32}, and d_{33} at 1.064 μm of all REMO crystals on the basis of the linear correlation between these three tensor coefficients and the rare earth atomic number. Data for those REMO crystals, where structural data are

Table 1
Deduced refractive indices n and nonlinear optical tensor coefficients d_{31}, d_{32}, and d_{33} at 1.064 μm. Units of d_{ij} tensor elements are in 10^{-9} esu

Refractive index	Nonlinear optical tensor coefficients			
	n	d_{31}	d_{32}	d_{33}
$La_2(MoO_4)_3$	1.836	−9.46	9.38	0.053
$Ce_2(MoO_4)_3$	1.833	−9.25	9.18	0.051
$Pr_2(MoO_4)_3$	1.830	−9.05	8.98	0.050
$Nd_2(MoO_4)_3$	1.827	−8.85	8.79	0.048
$Pm_2(MoO_4)_3$	1.824	−8.64	8.59	0.046
$Sm_2(MoO_4)_3$	1.820	−8.44	8.39	0.044
$Eu_2(MoO_4)_3$	1.817	−8.24	8.19	0.042
$Gd_2(MoO_4)_3$	1.814	−8.04	8.00	0.041
$Tb_2(MoO_4)_3$	1.811	−7.83	7.80	0.039
$Dy_2(MoO_4)_3$	1.808	−7.63	7.60	0.037
$Ho_2(MoO_4)_3$	1.805	−7.45	7.40	0.035
$Er_2(MoO_4)_3$	1.801	−7.22	7.21	0.033
$Tm_2(MoO_4)_3$	1.798	−7.02	7.01	0.032
$Yb_2(MoO_4)_3$	1.795	−6.82	6.81	0.030
$Lu_2(MoO_4)_3$	1.792	−6.61	6.61	0.028

available, were quantitatively calculated recently [2], these calculated values are plotted in summary in Fig. 2.

Figs. 1 and 2 show that the absolute values of both the linear and nonlinear optical susceptibilities of the REMO series of crystals decrease with increasing atomic number of the rare earth element. This agrees well with the conclusion that a major part of the nonlinear optical properties of these REMO crystals arises from the REO_7 constituent groups [2].

In Fig. 2, one obvious deviation from the stated linear correlation is evident: the slightly larger d_{31} and d_{32} tensor coefficients for EuMO. As already discussed [2], the covalent radius of the Eu atom is the largest among all lanthanide elements, and the calculational procedure applied to get the numerical results is rather sensitive to that parameter. The differing data are an important hint that all parameters have to be considered very carefully before the discussed linear interpolation should be applied. The linear susceptibility does not seem to be too sensitive to structural details, whereas for the nonlinear susceptibility deviations in the structural data—even slight ones—may play an important role.

The data for the linear and nonlinear optical susceptibilities at 1.064 μm derived by applying the linearization schemes discussed are summarized in Table 1 for all orthorhombic rare earth molybdates.

Unfortunately, up to now only few experimental data for the optical susceptibilities of the discussed crystals are available. Thus, only the magnitude and the general trend can be verified by a comparison to experimental data. Miller et al. [13] found for GdMO: $d_{31} = -9.34$ and $d_{32} = 9.28$, and for TbMO: $d_{31} = -7.13$ and $d_{32} = 7.05$; Bonneville and Auzel [12] for GdMO: $d_{31} = -9.6$ and $d_{32} = 9.5$, and for TbMO: $d_{31} = -7.4$ and $d_{32} = 7.2$ (all values in 10^{-9} esu). All data compare well—concerning magnitude and trend—with our calculated values.

4. Conclusions

In the current work, linear and second order nonlinear optical susceptibilities of all orthorhombic rare earth molybdates are described. Their linear correlations to the average atomic number of the constituent atoms Z_{av} could be shown. From the above results, we can assume that the presented method probably can be applied as a useful tool in predicting the dielectric constants and second order nonlinear optical tensor coefficients of complex crystals belonging to the same crystal series.

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