Induced gyrotropy in $NaBi(Mo_{1-x}W_xO_4)_2$ solid solutions

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Abstract

The dependencies of refractive indices and electrogyration parameters on tungsten concentration are obtained for the $NaBi(Mo_{1-x}W_xO_4)_2$ solid solutions with the sheelite structure. The coefficient of the transverse electrogyration effect is measured and the influence of temperature on the longitudinal electrogyration value is studied. It is shown that the refractive indices and electrogyration coefficients decrease with increasing the tungsten concentration.

Key words: Refractive index, electrogyration, solid solution, polarimetry.

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Introduction

Centrosymmetric $NaBi(MoO_4)_2$ crystals (point group 4/m) belong to structural type of sheelite and are widely used in acoustooptic devices [1]. The crystals are among those few materials which exhibit a rotation of light polarization plane induced by electric field (electrogyration) when the light propagates along the optical axes in crystal [2,3]. Since the electrogyration here is not superimposed by the electrooptic effect, the material is believed to be attractive for substituting the Faraday cells and creating the elements sensitive for electric field in optoelectronic devices. Thus searching for more efficient materials with similar properties is of interest. One of the possible ways for controlling electrogyration parameters is to synthesize solid solutions on the basis of the known materials. In particular, a complete or partial substitution of Mo by W is possible for the case of $NaBi(MoO_4)_2$ [1]. Only a slight difference in the size of $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ radicals (2.54×10^{-10} and 2.57×10^{-10}, respectively) is enabled to obtain, with the aid of Czochralski's technique, the solid solutions of $NaBi(Mo_{1-x}W_xO_4)_2$ with the tungsten concentrations ranging from $x = 0$ to 1.

Experimental results

Dependences of the ordinary (n_0) and extraordinary (n_e) refractive indices (see fig. 1) are linear on the concentration. The deviation from linearity may be explained by both experimental errors and possible differences between the tungsten concentrations in raw material and single crystals.

The value of longitudinal electrogyration effect was measured at the constant wavelength by the automated polarimeter using the technique described in [4]. It is known [2] that the value of the longitudinal effect does not depend on sample thickness and is determined by the dc voltage only:

$$\rho = \frac{\pi}{\lambda n_0}\gamma_{33}E_z\,, \qquad (1)$$

$$\varphi = \frac{\pi}{\lambda n_0}\gamma_{33}U, \qquad (2)$$

where ρ is a specific optical rotation; φ– rotation angle; λ the light wavelength in vacuum; n_0 the ordinary refractive index of crystal; γ_{33} the component of a third rank pseudotensor (or the electrogyration coefficient); E_z the external electric field; U the dc voltage. The relationship (2) is suitable for comparison electrogyration properties of crystals, because the refractive index n_0 differ for the different crystals. In our case relative changes of n_0 , which are due to concentration change are insignificant (only 4 %) and cannot affect notably the electrogyration coefficient γ_{33} calculated from the formula (1). In practice, however, the effective coefficient $\rho/E_z = \pi\gamma_{33}/(\lambda n_0)$ becomes of a primary importance, since just this coefficient defines the electrogyration sensitivity of crystal to the applied voltage value.

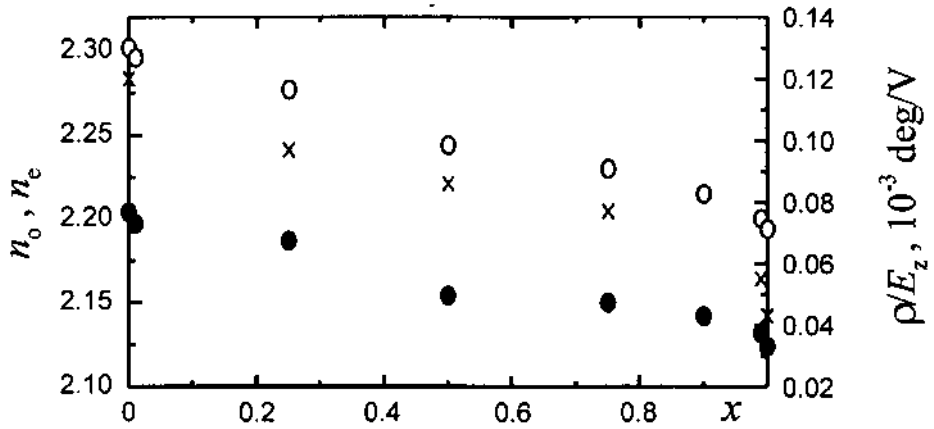

Fig.1. Concentration dependencies of the refractive indices n_0 (o) and n_e (•) and the effective electrogyration coefficient ρ/E_z(×) for the solid solutions $NaBi(Mo_{1-x}W_xO_4)_2$ at λ = 633 nm.

Temperature dependence of the given coefficient was measured for the two samples with the tungsten content equal to $x = 0$ and $x = 0.99$, at heating from 20 to 230 °C. To increase realibility of results, we determined the effective coefficient at every temperature, when analyzing the dependencies of the induced optical rotation angle φ on the applied voltage U, although we observed a temporal relaxation of the φ value once after turning the high-voltage source on. A linear rotation between those quantities was observed in the whole temperature range. The mentioned phenomenon was absent for thick samples (5 mm and thicker), while the relaxation times approached 20 s in the thin (near 1 mm) samples. As it is seen from fig. 2, the tungsten concentration weakly influences on the character of the temperature dependence. The electrogyration effect remains practically unchanged up to 100 °C, then decreases gradually when approaching 225 °C. This is accompanied by the increase of the conductivity which makes it impossible to measure electrogyration effect any further on. Such temperature dependence looks attractive for practical application, since the changes in effective coefficient value, which is typical for the other known material, $PbMoO_4$, are much more strong in the range between 20 and 60 °C [5], while its absolute value remains almost the same.

Under applying electric field E_z, the induced gyrotropy appears also along the direction normal to the optical axis. The

corresponding measurements are much more complicated, since the effect is superimposed with linear birefringence. We obtained the induced electrogyration coefficient $\gamma_{11} = (1.38 \pm 0.39) \times 10^{-11}$ m/V, which turned out to be somewhat larger than γ_{33}. It must be said, however, that in the latter case the experimental accuracy is not enough high.

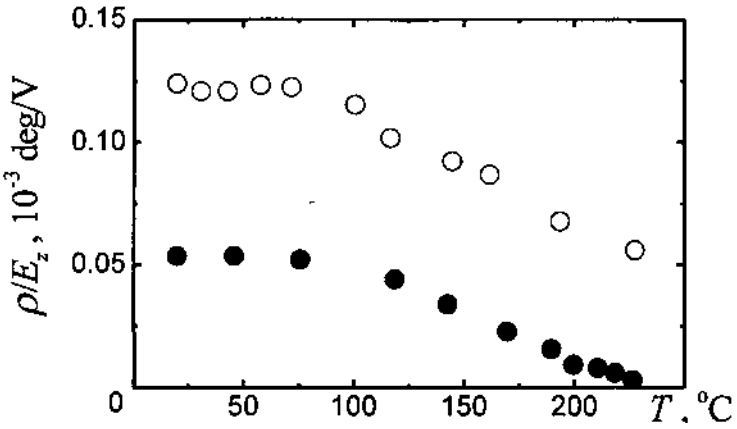

Fig.2. Temperature dependence of the optical rotation in $NaBi(MoO_4)_2$ – (o) and $NaBi(Mo_{0.01}W_{0.99}O_4)_2$ – (•) induced by electric field.

Conclusion

One can see that the substitution of Mo with W more notably reveals in electrogyration than in refractive properties. Hence, the induced optical rotation for the tungsten content $x = 0.99$ decreases more than twice, when compare with pure $NaBi(MoO_4)_2$. We suppose that this fact may be partly explained by a short-wavelength shift of the fundamental absorption edge. The localization location of the exciton absorption edge determines the induced optical activity dispersion in these crystals [6] and the absolute value of the effect at fixed wavelength. The substitution of anion complex gives rise to more essential contribution to the total decrease of the effect, since the polarizability of $[MoO_4]^{2-}$ is larger than of $[WO_4]^{2-}$ [1]. However, the most significant role in the electrogyration effect in the sheelite-type crystals belongs to cations, which determine the crystal structure too. The results obtained in this work have a reference character and may be used for both theoretical and practical calculations.

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