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Quasielastic light scattering as a method for controlling the quality factor of piezoelectric crystals

© A.A. Anikiev[1], M.F. Umarov[2], A.K. Kayumzoda[3]

[1] Bauman Moscow State Technical University,
Moscow, Russia
[2] Vologda State University,
Vologda, Russia
[3] Khujand State University named after Academician Babajan Gafurov,
Khujand, Tajikistan

E-mail: aaanikyev@mail.ru

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Polarization measurements of quasi-elastic light scattering were carried out in representatives of a new family of lanthanide stibnite crystals $R_3Sb_5O_{12}$ ($R =$ Gd, Pr, Nd, Er). A connection has been established between the degree of depolarization of scattered radiation and imperfections in the structure of new compounds of the cubic symmetry group. The fraction of depolarized radiation is directly related to the acoustic quality factor of the crystals. The law of the inverse exponential relationship between the degree of depolarization of radiation scattered at right angles and the quality factor of piezoresonators based on $Pr_3Sb_5O_{12}$ and $Nb_3Sb_5O_{12}$ has been found.

Keywords: polarization, quasi-elastic scattering, quality factor, defects.

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1. Introduction

In 80–90s based on rich deposits of antimony a number of new lanthanide antimonite compounds were synthesized with the general formula $R_3Sb_5O_{12}$ ($R =$ Gd, Pr, Nd, Er), having piezoelectric and ferroelectric properties [1,2]. Interesting structural properties of new compounds being modification of fluorite structure to new branch o pseudo-fluorite, physical properties of phase transitions, order parameter in which is associated with the position of not shared E-pair of electrons in each anion vacancy, as well as change in nature of the chemical bond between atoms in region of phase transitions, which indicates possible semiconductor properties, make these compounds very important objects for further study. In practical terms, the new family of crystals as piezoelectrics and ferroelectrics can find application in radio- and acoustoelectronics, nonlinear optics. So, firstly their electromechanical parameters (elastic, piezoelectric and dielectric), their optical properties, dependence on such external factors as laser radiation, optical quality, presence o defects, admixtures and imperfections in the crystal structure are of great interest. In particular, requirements for parameters of piezoelectric crystals result in the necessity to develop methods of their prompt selection and quality control. One of the important electromechanical parameters of the piezoelectric crystals, which determines their quality, is the acoustic Q factor. It is known that Q factor of the crystal is determined by the presence in crystal lattice of the different admixtures, heterogeneities, imperfections and dislocations. The methods of vibrational spectroscopy, in particular, methods of Raman scattering are the most sensitive to defects and different violations in stoichiometry of the ideal lattice. In present paper we develop the method of analysis of polarization characteristics of light scatterings in crystals of new family of piezoelectrics and ferroelectrics — antimonites and lanthanides.

As representatives of new family of antimonites we studied crystals of praseodymium antimonite ($Pr_3Sb_5O_{12}$) and niobium antimonite ($Nb_3Sb_5O_{12}$).

2. Materials and study methods

The family of crystals with structure of antimonite $R_3Sb_5O_{12}$ ($R =$ Gd, Pr, Nd, Er) was grown by a hydrothermal method for the first time in Physical and Technical Institute after S.U. Umarov (Dushanbe), laboratory of X-ray diffraction analysis. The method, conditions and features of crystals growth are provided in detail in papers [1–3].

The cube crystals of polar dielectrics $R_3Sb_5O_{12}$ ($R =$ Gd, Pr, Nd, Er) are characterized by highest symmetry of structure and associated physical properties. Crystals of non-centrosymmetric cube class (hexatetrahedron) $\mathrm{Td}^3 = I\bar{4}3\mathrm{m}$ in polar phase being optically isotropic have only one independent piezoelectric modulus d_{14} and electrooptical coefficient — r_{41}; three independent elastic constants: C_{11}, C_{12}, C_{44}; one coefficient of thermal expansion — α and dielectric permittivity — ε. The listed independent coefficients of tensors of corresponding physical properties determined the relative easy of these crystals use in piezoelectric engineering or electronics. No studies of their vibrational spectra were performed previously.

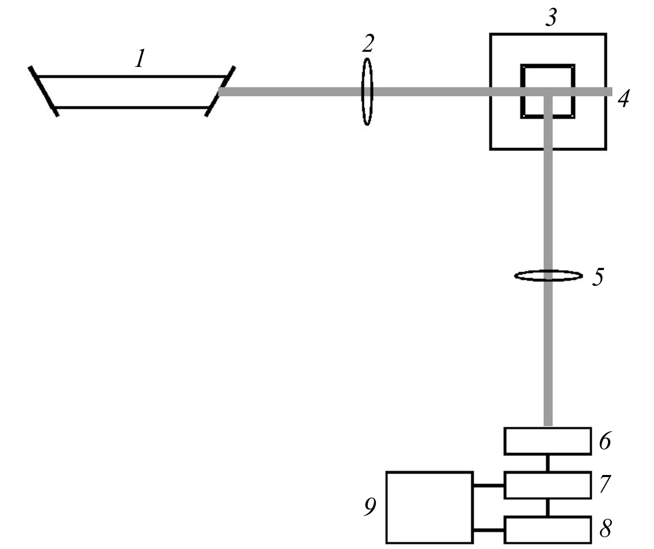

Figure 1. Functional scheme of unit to measure the depolarization degree of scattered light: *1* — helium-neon laser LG-38 ($\lambda = 632.8$ nm), *2* and *5* — focusing lens, *3* — cuvette with immersion liquid ($n = 1.50$), *4* — sample, *6* — polarizer, *7* — photomultiplier tube FEU-79, *8* — digital voltmeter, *9* — microcomputer.

The polarization characteristics of the quasielastic light scattering were measured in unit, which functional scheme is shown on Figure 1. The scattering plane xy is perpendicular to the polar axis z of the crystal — axis in the direction of symmetry center offset of lattice cell, wave vector of elastic wave, at which scattering occurs, is located in xy plane. Then, presenting scattering coefficients with appropriate polarizations as sum of contributions from all elastic waves we obtain the expression for depolarization degree [4]:

$$\rho = 1 - \left| -\frac{S_{12}}{S_{11}} \right| = \frac{a + bc^1_{44}}{c + dc^1_{44}} \quad \text{and} \quad \frac{\delta\rho^1}{\rho^1} = \frac{\delta c^*_{44}}{c^*_{44}} = Q^{-1}, \tag{1}$$

where S_{12}, S_{11} — components of scattering matrix [5], $a, b, c,\ d$ — combinations of photoelastic constants of crystals P_{11}, P_{12}, P_{44}; $\rho^1 = b - \rho$, c^1_{44} — effective elastic modulus, represented by a combination of elastic constants C_{11}, C_{12}, C_{44}, $c^*_{44} = c + dc^1_{44}$, Q^{-1} — acoustic losses caused by signal attenuation due to scattering by impurities, defects and inhomogeneities that change elastic moduli c^1_{44}.

So, the depolarization degree of scattered light directly relates to the acoustic losses and ensures determination of Q factor value by measurement of the polarization characteristics of scattered light at any set section of the crystal illuminated by focused laser beam. At that the laser spot scanning over the crystal surface ensures determination of spatial distribution of Q factor over volume without the crystal destruction.

We studied two representatives of new family of dielectric crystals — $Pr_3Sb_5O_{12}$ and $Nb_3Sb_5O_{12}$. The studied samples are parallelepipeds with size $3 \times 4 \times 6$ mm, of deep green color, transparent in visible region o spectrum. The samples do not contain visible in microscope defects or inclusions. 5 samples of praseodymium antimonite and 6 samples of niobium antimonite were prepared.

Figure 1 shows the unction scheme o unit to measure the polarization characteristics of light scattered at angle of 90°.

Laser radiation *1*, polarized along the optical axis of crystal, passing through the focusing lens *2*, reaches the cuvette *3* with sample *4*. To reduce the possible effect of the surface defects on the scattering process of the untreated piezoelectric crystal the sample was loaded into the immersion liquid. The scattered light at angle 90° to incident light is gathered by lens *5* via the polarizer *6* and falls on the photoamplifier tube *7*. The amplified signal from the photodetector is supplied to digital voltmeter *8*, and one of channels of interface unit of microcomputer *9*, and intensity of scattered light was measured at room temperature.

Q factor of samples was measured by the radiotechnical resonance method at frequency of 10.1 MHz on pre-manufactured piezo-resonators s per method in [6].

3. Results and discussion

Figure 2 shows results of measurements o scattered light intensity (I) depending on the polarizer (θ) position on crystals $Pr_3Sb_5O_{12}$ with different values of Q factor.

Figure 2 shows that fraction of depolarized scattering radiation increases with decrease in Q factor Q, i.e. with increase in concentration of defects and heterogeneities of crystal structure. This is most evident at angle $\theta = 90°$, i.e. at complete crossing the polarizer relative to the incident radiation on the sample. Namely this geometry of

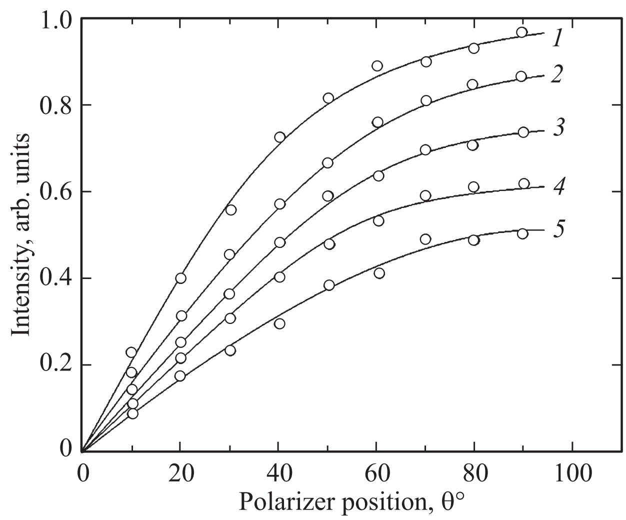

Figure 2. Graphs of intensity of scattered light (I) vs. polarizer ($\theta°$) position on crystals $Pr_3Sb_5O_{12}$ with different Q factors (Q) *1* — $0.05 \cdot 10^3$; *2* — $0.11 \cdot 10^3$; *3* — $0.92 \cdot 10^3$; *4* — $1.12 \cdot 10^3$; *5* — $1.45 \cdot 10^3$).

Coefficients of linear approximation of measured values of depolarization degree of crystals (Figure 3) as per equation (3)

Compound	Coefficient k	Coefficient b	Correlation coefficient
$Pr_3Sb_5O_{12}$	-0.197	1.514	0.999
$Nb_3Sb_5O_{12}$	-0.265	2.07	0.994

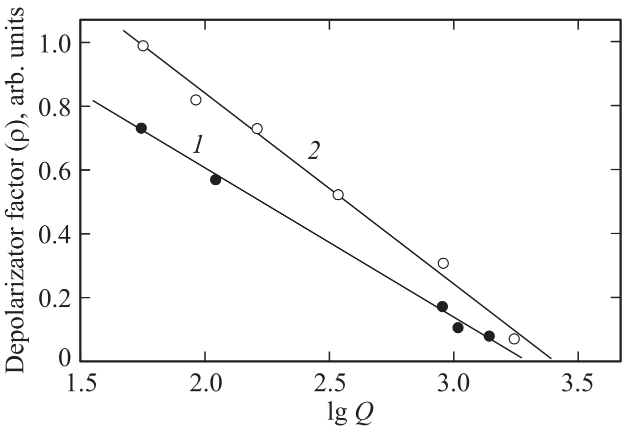

Figure 3. Graphs of depolarization degree (ρ) of quasielastic light scattering vs. Q factor of samples (Q) of crystals $Pr_3Sb_5O_{12}$ (*1*) and $Nb_3Sb_5O_{12}$ (*2*).

scattering is most sensitive to the quality of studied crystal. At the same time the scattering intensity in the low sensitive geometry ($\theta = 0^\circ$) can be used as a standard to control the power of the exciting radiation.

The depolarization degree is evaluated by intensity measurement of scattered radiation for four different directions of polarization I_{yx}, I_{zx}, I_{zz} and I_{yz}, where $I_{\alpha\beta}$ — intensity of scattered radiation polarized along axis β, at incident radiation with polarization along axis α, where $\alpha = y$, z and $\beta = x$, z. Using numerical values of four intensities we calculate the depolarization degree ρ:

$$\rho = \frac{I_{yx} + I_{zx}}{I_{zz} + I_{yz}}. \tag{2}$$

We measured the depolarization degree for crystals $Pr_3Sb_5O_{12}$ with preliminary measured values of Q factor $Q = 0.05;\ 0.11;\ 0.92;\ 1.12;\ 1.45 \cdot 10^3$. Same measurements were made also for crystals $Nb_3Sb_5O_{12}$ with following known Q factors: $Q = 0.06;\ 0.09;\ 0.16;\ 0.33;\ 0.89;\ 1.68 \cdot 10^3$.

Figure 3 shows graphs of depolarization degree ρ vs. Q factor Q of piezocrystals $Pr_3Sb_5O_{12}$ and $Nb_3Sb_5O_{12}$. Q factor in graph is presented in logarithmic scale.

Figure 3 shows that the depolarization degree of the quasielastic scattering actually correlates with values of Q factor of piezoelectric crystals and, dependence in studied Q factor range is close to exponential one. Approximation of the obtained empiric dependences by the linear law gives the following relationship for studied crystals

$$\rho(Q) = k \cdot \ln(Q) + b. \tag{3}$$

The linear law coefficients are given in Table for both crystals. Let's convert equation (3) to calculate Q factor of any crystal by the measured depolarization degree

$$Q(\rho) = \exp(-b/k) \cdot \exp(\rho/k). \tag{4}$$

Accordingly, the equation for Q factor calculation by measured depolarization degree, e. g., for praseodymium antimonite will be

$$Q(\rho) = 2165 \cdot \exp(-5.08 \cdot \rho). \tag{5}$$

Spread of Q factor values calculated from 11 series of sample measurements in same point of the block does not exceed $\sim 5\%$. Same measurements were also performed for several samples of $Pr_3Sb_5O_{12}$ with unknown Q factors, evaluation was performed by the obtained results. The next direct measurements by piezo resonance in JSC „Fonon" (Moscow) also confirmed that accuracy of the optical method is at least 5%. Note that the optical method for measurements does not require the manufacture of piezoelectric resonator and allows one to determine Q factor of any point of the piezoelectric crystal, limited only by the size of the spot of the focused laser beam [4].

4. Conclusion

The paper suggests non-destructive method of quality inspection of piezoelectric crystals based on measurement of depolarization degree of the quasielastic light scattering. The method determines with 5% accuracy the acoustic Q factor in any point of the piezoelectric block limited only by size of spot of focused laser beam. This makes it possible to avoid the production of piezoelectric elements, machining, polishing of crystal blocks, heating of samples, and also to increase the output of piezoelectric resonators, microgenerators or filters by identifying areas with high Q factor in the crystal block and avoiding the operation of producing the piezoelectric resonators or other elements from areas with low Q factor of the block.

Conflict of interest

The authors declare that they have no conflict of interest.

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