Light scattering in lead magnesium niobate in the temperature region of smeared ferroelectric phase transition

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The integrated scattering of light in $PbMg_{1/3}Nb_{2/3}$ was observed to decrease with rising temperature from 20 to 400 °C, and to practically vanish at 360 °C. The temperature-dependent part of the scattering is attributed to the coexistence of ferroelectric and paraelectric phases in the region of the smeared phase transition. This part of the scattering makes an appreciable contribution to the optical density.

The light scattering accompanying phase transitions in solids have recently attracted increased interest. The significant role played by the inhomogeneities produced during the phase transition becomes more evident, as demonstrated by one of the latest studies by Ginzburg and Levanyuk.[1]

An interesting object for the study of scattering of light by structural inhomogeneities due to the phase transition is lead magnesium niobate (PMN), in which smearing of the ferroelectric phase transition was first observed and studied in[2,3]. It is proposed[2] that the smearing of the phase transition (SPT) is due to fluctuations of the composition in the sublattice of the ions occupying octahedral positions (Mg^{2+} and Nb^{5+}). Consequently, coexistence of ferroelectric and paraelectric phases should be observed in the region of the SPT temperatures. The dielectric and electric properties of PMN in the SPT region can be readily explained with the aid of the hypothesis that there exist polar regions of the ferroelectric phase, whose summary dipole moments become reoriented in the electric field.[3]

However, there are no experiments on the direct observation of the polar regions. Obviously, the coexisting phases, according to[1], can cause an appreciable integrated scattering of light.

We have investigated the scattering patterns of light of wavelength 6328 Å, using a setup based on the GS-5 goniometer, with which we could measure the angular distribution of the scattered-light intensity in the angle range from 0 to 120° with an angle accuracy ±20′. The receiving aperture of the detector (FEU-62 photomultiplier) was 1°. The temperature was stabilized accurate to ± 0.01 °C.

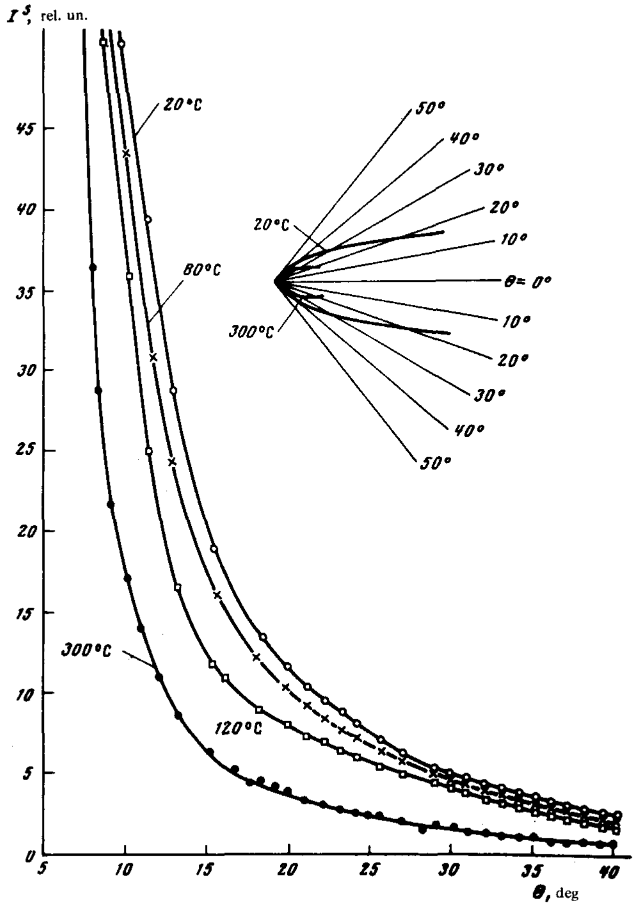

FIG. 1. Angular distribution of the scattering intensity I^S in the plane of polarization of the incident light at various temperatures. The insert shows the diagrams for two temperatures.

Samples with different orientations, in the form of rectangular plates with dimensions 3×3×0.13—0.4 mm, were prepared from PMN single crystals grown by the method of crystallization from a solution in molten PbO. The incident light was normal to the large face of the plate.

In the investigated temperature interval 20—400 °C we observed an intense temperature-dependent scattering of light. The coefficient of scattering through an angle 90° at room temperature was $\sim 4\times10^{-4}$ cm^{-1}. No significant difference between the scattering patterns of samples with different orientations was observed. Figure 1 shows the scattering patterns in the polarization plane of the incident beam at different temperatures (the insert in the figure illustrates the corresponding scattering diagrams). The patterns and the typical temperature dependence of the scattering of light through 20°, shown in Fig. 2, point to a considerable decrease of the scattering with increasing temperature, and to a practical cessation of the scattering at temperatures above ~360 °C. The transmission of the sample in the forward direction increases in this case ($\theta = 0°$ on Fig. 1). We attribute this large faction of temperature-dependent light scattering to scattering by the polar regions, by their boundaries with the paraphase, by the domain walls, and by the adjacent volumes of the paraelectric phase, the refractive index of which is altered by the electric and mechanical stresses. The strong temperature dependence of the refractive index (n) of PMN, which is observed according to data of[4] in the SPT region, also stops at 360 °C, this being interpreted as the result of the completion of the phase transition, in good agreement with our results.

The small difference between the refractive indices of the polar and nonpolar phases (2.52 and 2.55, respectively) allows us to apply the Rayleigh-Gans scattering theory[5] to the temperature-dependent component. In our case, for light scattered by spherical particles and emerging through the face of the sample at an angle θ between the direction of the incident and scattered light, the following relation holds:

$$I^s = C(T) I_0 [\sqrt{9\pi/2u^3}\, J_{3/2}(u)]^2, \tag{1}$$

where I^S is the intensity of the light emerging at the angle θ, I_0 is the intensity of the incident light, $C(T)$ is a certain function that does not depend on the angle θ at a constant temperature T, $u = 2x\sin(\theta/2n)$, $x = ka$, $k = 2\pi n/\lambda$ is the wave vector in the medium, λ is the wavelength of the light, a is the radius of the scattering particle, and J is a Bessel function of order $\frac{3}{2}$.

There is no doubt that the scattering of light in PMN in the SPT temperature region is much more complicated than the phenomena described by the theory of Rayleigh and Gans. Nevertheless, we have used expression (1) to estimate the dimensions of the temperature-dependent scattering regions, assuming them to be spherical. At 120 °C, in samples of thickness less than 0.17 mm, at which, according to[5], the condition for single scattering is satisfied, the average radius is $\sim 4\times10^{-7}$ m, which is in good agreement with the present notions concerning the dimensions of the polar regions. A comparison of the diagrams for the temperature-dependent part of the scattering indicates that the dimension of the scattering region decreases with increasing temperature.

It should be noted that the scattering of light in the SPT range can lead to anomalies of the optical density. Thus, a maximum of the optical density on the edge of the absorption band was observed in[6] in the region of

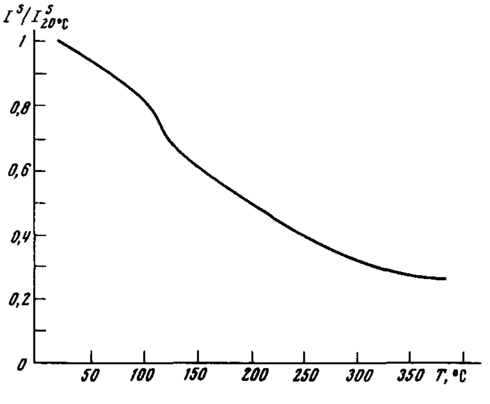

FIG. 2. Temperature dependence of the scatter-light intensity (referred to the value at 20 °C), $I^S/I^S_{20°C}$, emerging at an angle 20° to the direction of the incident beam.

the average Curie temperature of PMN, and was attributed by the authors to scattering. Indeed, when determining the absorption coefficient by the method of different thicknesses, the use of a receiver with an aperture, say, 7° result in the attenuation coefficient due to the scattering, which amounts to 0.6 cm^{-1} according to our data, to be contained in the measured absorption coefficient 2–5 cm^{-1}. The contribution of the scattering to the optical density may turn out to be even larger as the fundamental absorption band is approached.

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