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EVOLUTION OF REGULAR HETEROPHASE STRUCTURE NEAR TRANSITION POINT

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Abstract. The kinetics of formation and development of heterophase structure was investigated in a wide range of heating/cooling rates in single crystals of GMO and BNNO, with controlled spatial distribution of defects.

INTRODUCTION

It is well-known that the appearance of regular heterophase structure in the vicinity of ferroelectric and ferroelastic phase transition points is attributed to long-range interactions between isolated volumes of new phase. Moreover, in real objects the essential influence of structural defects on phase transformation is observed. In the last case the regularity of the structures, if any, is due to the existence of a periodical distribution of defects. The instantaneous patterns of the heterophase structures depend strongly on the heating/cooling rates and temperature gradients.

Different experimental methods can be used for in situ investigation of the kinetics of heterophase evolution near the transition point. It seems that the elastic light scattering is the most suitable method of investigation of regular structure evolution. The time dependence of total scattered light intensity contains information about the evolution of individual phase volumes (density of emerging centers per volume and their growth velocity). In addition the change of sizes and orientation of the growing clusters (appearing as a result of coalescence of the new phase) can be extracted from the transitory angular dependence of the scattered light intensity.

We studied high-quality crystals of improper ferroelectric-ferroelastic gadolinium molybdate \(Gd_2(MoO_4)_3\) (GMO) as an example of a system in which long-range interactions prevail. The role of the periodical spatial distribution of defects was investigated in barium sodium niobate \(Ba_2NaNb_5O_{15}\) (BNNO) crystals with controlled orientation of growth layers.

EXPERIMENT

The optical scheme of the setup is demonstrated in Figure 1. The weak power density beam of an He-Ne laser \((\lambda = 0.63 \mu m, W = 1 mW)\) with controlled orientation of polarization was used as a probe. The diameter of the light spot on the sample...
FIGURE 1: Optical scheme of the setup for in situ registration of angular dependence of scattered light. 1 - He-Ne laser, 2 - λ/4 phase plate, 3 - polarizer, 4,7 - lenses, 5 - sample in furnace, 6 - angle modulator, 8 - detector. Above - geometry of experiments.

surface was about 1 mm. The heating/cooling rates and temperature gradients in the investigated samples were controlled during the experiment. For the analysis of complicated diffraction patterns we used scanning in two directions (perpendicular to each other): transverse and longitudinal (Figure 1). Use of the angle modulator and lens allows the registration of the sequence of signals proportional to light intensity scattered at different angles by one and the same part of the detector. The time of complete measurement in the angle range up to 60 degrees is about 10 ms (angle resolution 0.1 degree). For the comparison of local and integral data, direct observation of the structure in the near field was also carried out.

The light scattering data measured during phase transitions needs two qualitatively different approaches for its mathematical treatment. The total intensity of scattered light is directly proportional to the fraction of growing phase and the diffraction pattern (angular dependence of scattered light) is determined by the correlation function of scattering centers (clusters of new phase). The existence of a quasi-periodical structure of regions with different optical characteristics leads to the appearance of maxima in the angular dependence of the scattered light. Analysis of the sequence of instantaneous angular dependence data allows the determination of the time dependence of the heterostructure period during cooling/heating.

GADOLINIUM MOLYBDENUM

The plates of GMO were cut perpendicular to the (010) axis (typical thickness about 0.7 mm, area - 20 mm²). It was shown that in this geometry only interphase boundaries are observed in transmitted light. A temperature gradient of about 1.5 K/mm was held at 30 degrees to the c axis. Near the transition point the appearance of a heterostructure consisting of lamellar phase volumes is obtained. Their width changes due to the temperature gradient. As a result the angular dependence of the scattered light intensity is significantly changed during cooling.
FIGURE 2: Evolution during cooling near $T_c$ in GMO: a) instantaneous angular dependence of scattered light, b) increase of average period of lamellar structure.

(Figure 2a). From the experimental data the evolution of the heterostructure period with time/temperature was obtained (Figure 2b). It is interesting to point out the step-like change of the period during cooling. The average value of the sideways velocity of lamella growth is 0.18 $\mu$m/s.

BARIAUM SODIUM NIOBATE

The influence of the spatial periodical distribution of defects was studied in BNNO single crystals with controlled growth layers. The samples contain the growth layers clearly visible at any temperature (even for $T > T_c$). The polar axis lies in the plane of these layers. Such orientation avoids the appearance of regular domain structure, and all regular differences from a periodical pattern due to the growth layers can be attributed to the regular heterophase structure. The polished faces of the samples were oriented normally to crystal axes (typical sizes $2 \times 4 \times 4$ $\text{mm}^3$). The temperature gradient (about $5\text{K/mm}$) was held in the polar direction.

During heating/cooling the heterophase region was scanned by the laser beam (polarization parallel to the polar axis) (Figure 1). Experimental data obtained under these conditions are presented in Figure 3. It is seen that a pronounced broadening of the diffraction pattern is observed as a result of spatial inhomogeneity of the refractive index due to its variation near $T_c^{7,8}$ (Figure 3a). The diffraction patterns in para- and ferrophases are stable with periodicity defined by the growth layers (Figure 3b). In contrast, the pattern for the transition region is changing with time and its parameters are extremely sensitive to heating/cooling rates and temperature gradients. The observed period considerably exceeds the layer period. We suggest that this effect is due to the existence of a heterophase structure.

CONCLUSIONS

The comparative study of two limiting situations for the evolution of a heterophase near the transition point was examined. It was shown that the kinetic parameters can be determined from in situ measurements of light scattering. The long-range
elastic interaction in GMO leads to the formation of a periodical heterophase structure and determines its orientation and period. In BNNO the geometry of the heterostructure is defined by the periodical spatial distribution of the structural defects. The applied technique makes it possible to investigate quantitatively the kinetics of formation and the evolution of the heterophase structure in a wide range of cooling/heating rates and temperature gradients. The method can be used for studying the heterophase evolution in detail during various phase transitions.

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