Peculiarities of the Electron Diffraction from Nanostructured Objects in High-Symmetry Projections

S. K. Maksimov, R. Herrero, and B. P. Sobolev

Abstract—The crystals of M$_{1-x}$R$_x$F$_{2+x}$ (where M = Ca, Ba, Cd and R is a rare earth element, Ga, or In) are susceptible to phase separation on a nanometer scale (nanostructurization), which determines to a considerable degree the properties of these materials. The patterns of electron diffraction from such nanostructured crystals exhibit reflections corresponding to unknown structural features, but these reflections may completely disappear when the sample is tilted within <1°. It is shown that suppression of the nonmatrix reflections is related to peculiarities of the electron diffraction from such objects rather than to any structural features. © 2004 MAIK "Nauka/Interperiodica".

Calcium fluoride (CaF$_2$) is the most important material for far-UV range optics. However, the mechanism of optical absorption in this spectral range for CaF$_2$ crystals is still incompletely clear [1]. Fluorides of the M$_{1-x}$R$_x$F$_{2+x}$ system, where M = Ca, Ba, Cd, and R is a rare earth element, Ga, or In, are promising materials for many applications. For example, Cd$_{1-x}$In$_x$F$_{2+x}$ has no competitors as a medium for three-dimensional holography [1].

The ratio of cations and anions in M$_{1-x}$R$_x$F$_{2+x}$ is not equal to the ratio of allowed positions in the cationic and anionic sublattices. The structure of these ionic crystals contains, besides ions of the component elements, a certain amount of point defects [1]. Interactions in the subsystems of defects and components lead to the phenomenon of composition-defect separation [1–3] over a ~10 nm scale and the formation of defect regions with an unknown structure, one that is defective with respect to the matrix structure. At the same time, the lattices of the matrix and these defect regions have close parameters and exhibit coherent matching. Such crystal structures are referred to as nanostructured [1–3]. At least a part of MF$_2$ may exist in the form of a partly disordered phase of the MF$_{2-\delta}$F$_\delta$ type, where F and F' refer to fluorine ions located at the regular positions (1/4, 1/4, 1/4) and in interstitials, respectively, and $\delta$ is the fraction of interstitial fluorine ions [1], which may also account for nanostructurization.

In electron diffraction patterns, the defect regions are manifested by the characteristic systems of reflections, which are absent in the projections corresponding precisely to the [001], [011], and [111] directions (referred to below as exact high-symmetry projections, or simply exact projections) but appear upon deviations from these directions within $\pm 1°$ [4]. The electron diffraction patterns with two or more subsystems of reflections (composite diffraction patterns, CDPs) correspond to heterophase objects [5]. In particular, the electron diffraction patterns of twinned crystals also exhibit different subsystems of reflections [5]. Within the framework of the kinematic approach, suppression of the nonmatrix reflections during variation of the inclination axes is explained by deviations of the reflection sphere from the corresponding planes of the reciprocal lattice [5]. An exact projection in the matrix lattice may not correspond to the reflecting position for the lattice of inclusions as a result of mismatch between these lattices [5]. For an object with twins in one projection (e.g., [011]), the reflections of some twins are localized in the projection plane, while those of the other twins (e.g., [111]) fall completely within the twinned Laue diffraction zones [5]. The reflections from these Laue zones appear on the diffraction patterns for deviations within $\pm 1°–4°$ from the exact high-symmetry directions, but disappear on the exact projections [5]. Elucidation of the nature (twin versus defect region) of the objects responsible for nonmatrix reflections is a task of primary importance in electron diffraction. The possibility of misorientation between the crystal lattices of the matrix and defect regions is also of fundamental importance for explaining the phenomenon of nanostructurization [1], which requires elucidating factors accounting for the suppression of nonmatrix reflections.

In this context, we have performed an electron-microscopic investigation of the commercial crystals of CaF$_2$ and the single crystals of Ba$_{0.75}$La$_{0.25}$F$_{2.25}$ and Ba$_{0.69}$La$_{0.31}$F$_{2.31}$ grown using the Bridgman method.
The crystals were studied in the initial state and upon annealing at 1173 K in a fluorine-containing atmosphere [1, 2]. The samples were prepared by cleavage; the cleaved sections exhibited transparent regions with a width of $\sim 0.5 \, \text{mm}$ at the edge. The measurements were performed with a Philips CM-30 electron microscope.

The difference between the radii of $\text{Ba}^{2+}$ and $\text{La}^{3+}$ ions is much greater than, for example, that between the radii of $\text{Cd}^{2+}$ and $\text{In}^{3+}$ ions. This must lead to a significant difference between the lattice parameters of the matrix and defect regions and should facilitate the observation of diffraction reflections from the latter regions. Since the amplitudes of electron scattering for Ba and La atoms are virtually equal, it is possible to exclude from consideration the effects related to differences in the atomic scattering amplitudes. The results obtained for the as-grown and annealed crystals have proved to be identical.

The CDPs of $\text{CaF}_2$ observed for an $0.5^\circ$–$1^\circ$ deviation from the exact projections $[011]_m$, $[111]_m$, and $[112]_m$ exhibited reflections from the fluorite matrix with $a = 0.545 \, \text{nm}$ and from the defect regions (Fig. 1(I)). For $\text{CaF}_2$, the reflections indexed as $002_d$ (here and below, the subscripts “m” and “d” refer to the matrix and defect regions, respectively) formed a rectangle. The form of the network of reflections cannot be explained by different inclinations of the twinning planes, since it is the same in the exact projection. Therefore, despite the fact that the reflections from defect regions are close to those from twins, these reflections represent inclusions of the second phase with a slightly distorted cubic lattice. With neglect of the distortion, the ratios of the lattice parameters of the matrix and defect regions are as follows:

- $a_d/a_m = \sqrt{3}/2$ for $\{111\}_m \parallel \{001\}_d$ and $\{211\}_m \parallel \{110\}_d$.
- $d_{002d} = d_{111m}$, $3d_{111m} = 4d_{002d}$, $3d_{211m} = 2d_{110d}$, $3d_{221m} = 2d_{111d}$, $13d_{110m} = 5d_{110d}$ (the latter value is determined to within 0.07%).

This provides for a three-dimensional matching of the lattices with virtually zero misfit stresses.

On the passage to the exact projections $[011]_m$, $[111]_m$, and $[112]_m$, the intensity of reflections from defect regions decreased, although the CDPs of the exact projections strictly corresponded to the same volumes of the crystal as the CDPs of inclined projections.