Ferroelectric domain imaging by defect-luminescence microscopy

V. Dierolf* and C. Sandmann
Department of Physics, Lehigh University, Bethlehem, Pennsylvania 18015
S. Kim and V. Gopalan
Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802
K. Polgar
Institute for Solid State Physics and Optics, Hungarian Academy of Science, H-1112 Budapest, Hungary

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In order to study the role of defects within the domain inversion process in ferroelectric LiNbO$_3$ crystals, we investigated the optical properties of intentionally introduced Er$^{3+}$ defect complexes across a 180° domain wall produced at room temperature by electric-field poling. Using site-selective excitation-emission spectroscopy for well chosen excitation energies, we found drastic differences in the Er$^{3+}$ emission, which are due to a rearrangement of the defect complexes. We used these changes in a confocal luminescence microscope to image ferroelectric-domain structures. This powerful imaging method with a 700 nm, 50 ns spatial and temporal resolution can be used to study real-time dynamics of domain walls. © 2003 American Institute of Physics.

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Precise control of ferroelectric domains has become a very important issue for many applications, most notably, the periodical poling of materials like LiNbO$_3$, which are the basis for many powerful nonlinear optical devices, e.g., optical parametric oscillators, amplifiers, and entangled photon sources. In LiNbO$_3$ and LiTaO$_3$ it has been shown that many parameters of domain inversion and motion of domain walls are intimately connected with the intrinsic defects present in the material. The influence can be seen macroscopically by the dependences of the coercive and intrinsic fields on the stoichiometry of the sample and on the micro- and nanoscale as local strain and optical birefringence at domain walls that influence the domain shape and local reversible pinning and bending of domain walls.

Here, we study the atomic-defect/domain-wall interactions using extrinsic, intentionally doped defects and observe their behavior under domain inversion. This approach is promising when studied and fairly well-understood defect complexes (like Er$^{3+}$ in LiNbO$_3$) are employed. The Er$^{3+}$ rare-earth ion has been investigated by several groups. It has been established that, although it occupies almost exclusively the Li$^+$ sites, the Er$^{3+}$ ion exhibits multisite behavior due to differences in the required charge compensation. The latter is obtained with the help of additional (intrinsic) defects. The discrete differences among the defect sites and statistical arguments led to the assumption that charge compensation is predominantly local. This leads to the question of how charge compensators adjust to a new polarization direction. We studied this question by excitation-emission spectroscopy. The optical transitions used here are depicted in the energy level scheme in Fig. 1.

In this article, we report changes in the optical transitions of the Er$^{3+}$ probe ion complexes arising from its interactions with domain walls, and how they can be used for imaging of domain structures.

In our studies, we used two types of samples: The first was a nearly stoichiometric LiNbO$_3$ sample, which was grown by the top-seeded solution technique and doped with small amounts of Er$^{3+}$ (10$^{-2}$ mol%). The growth temperature in this technique is below the Curie temperature of LiNbO$_3$ and, therefore, the crystal grows in a single-domain state with the direction of the ferroelectric axis determined by the seed. This crystal is called the virgin state. At room temperature, random domain regions were nucleated and grown in the virgin crystal using an electric field of 2 kV/mm. The regions inside these created domains are called “poled regions” in this work. The second type of sample was a congruent-grown LiNbO$_3$ sample doped with 10$^{-1}$ mol % of Er$^{3+}$ and partially domain reversed at 21 kV/mm.

In Fig. 2, we show, for the stoichiometric sample, the contour plot of the emission data obtained at $T=10$ K using our combined excitation-emission spectroscopy technique. Details of this technique can be found in Ref. 7. In this data representation each maximum corresponds to a particular defect complex. Comparing the data taken in the virgin and poled regions, we observed changes in all spectral regions, but they are best defined for the pair of excitation ($^{4}I_{15/2}$ $\rightarrow^{4}F_{5/2}$) and emission ($^{4}S_{3/2}$ $\rightarrow^{4}I_{15/2}$) transitions depicted here.

We find that, due to domain inversion, the number of distinctly different Er$^{3+}$ environments is reduced from $\approx 11$ to essentially only three different defect complex types (labeled 1A, 2A, and 3A in Fig. 2). While these are increasing in number, others (1B, 1C, 2B, 2C, 3B) are decreasing. Further evaluation of the emission spectra [see Fig. 3(a)] reveals—besides the changes in relative defect numbers—also a small shift of the emission energies. After heating...
above 200 °C followed by cooling to 10 K, all differences between poled and unpoled regions of the sample disappear and a thermal equilibrium among the different defect arrangements is reached which resembles more closely the one we observed after the poling procedure [Fig. 3(a)]. The same center number distribution is also obtained when completely untreated as-grown samples are tempered.

The spectroscopic results for the congruent sample are qualitatively the same. Although the defect distribution for this composition is quite different in the as-grown sample, we again found a strong decrease of defects which emit at the higher-energy side of the spectrum (type A), and an increase of those with low-energy emission (B and C). This is shown for the defect types (1A,1B, and 1C) in Fig. 3(b). This indicates that a similar center redistribution takes place. Finer details, like the spectral shifts just discussed, cannot be determined due to the increased inhomogeneous spectral-line broadening. In both types of samples, changes in the number distribution of different defect complexes can also be detected quite easily at room temperature, despite the considerable homogeneous line broadening.

In earlier papers, we classified the Er$^{3+}$ sites with respect to their symmetry and other properties, like shifts under the application of external perturbation (see Fig. 2). Center categories 1, 2, and 3 can be distinguished in all spectral regions and exhibit different symmetries; all of type 1 are axial C$_3$ and types 2, 3 are nonaxial with an increasing deviation from C$_3$. This suggested that they differ in the location of the primary closest charge compensators. Within the same type (1, 2, or 3), the differences in the subcategories A, B, and C are more subtle and are obscured in most spectral regions. Only in the depicted spectral region do they become so clearly distinct. A comparison with the shifts under external perturbations [see arrows in Fig. 2(b)] suggests that these categories are due to variations of the crystal or electric field along the $z$ axis caused by a secondary-charge compensation or different ion arrangement within the primary one. The observations reported here indicate that under domain inversion, centers of subcategories B and C are converted into A. This may be caused by a rearrangement of the charge-compensating defect. A similar behavior has been observed for OH$^-$ in LiNbO$_3$ (Ref. 15) for which it has been proposed (within an Nb-antisite intrinsic defect model$^{16}$) that Li vacancies and Nb located in the usually unoccupied oxygen octahedron are created out of the Nb antisite. Assuming a similar rearrangement, in our case, requires minimal mobility of the lattice ions. In this model, the small shift in emission energy
observed for center type A can be associated with the fact that the charge compensation has changed its position relative to the $\text{Er}^{3+}$ site, causing a change in sign of their electric-field interaction relative to the ferroelectric axis. Based on measurements of the Stark shift under the application of external fields, the change in electric field can be estimated to be of the order of $10^7 \text{V/m}$. On the other hand it cannot be excluded that the charge compensation rearranges itself more drastically along with the $\text{Er}^{3+}$ ion, requiring at least a limited local ion mobility. The observation that a similar defect distribution is achieved by tempering at moderate temperatures, for which Li vacancies have some mobility, may be an indication in that direction. Further clarification of the microscopic structure awaits investigations involving ligand sensitive techniques (like magnetic resonance) and quantitative, theoretical modeling of the complexes. The observed spectral changes can still be used for imaging of domain structures.

In order to show the feasibility of this technique, we used a confocal luminescence microscope$^{17}$ in which a single-mode fiber end replaces the required pinhole.$^{18}$ For high spatial resolution (better than 700 nm) and good repeatability, we use in this application, a two-step excitation scheme (see Fig. 1) to select certain defect complexes using a very stable, tunable-external-cavity semiconductor laser at 980 nm. An example of the images obtained is shown in Fig. 4. For Fig. 4 about $10^7$ emission spectra for centers of type I have been recorded at room temperature with a rate of 20/s. Even for the rather broad spectral features observed under these conditions, we obtained a very good contrast (1:30) by evaluating the complete emission spectra and depicting the value of their first moments. For this sample, the poling process was stopped before the complete sample was inverted and, hence, the characteristic self-organized hexagonal domains are seen. Signal-to-noise ratio and the contrast can be seen in the line scan depicted in Fig. 4(b). Still better contrast can be obtained by taking higher moments into account. Due to the fact that our imaging technique is based on evaluating the spectral information, it is insensitive to intensity fluctuation and is free of topographic artifacts. The influence of the domain wall extends over more than 2.5 $\mu$m, consistent with what has been seen with other methods (near-field scanning optical microscopy and atomic force microscopy). Hence, our spatial resolution is sufficient to study details of the defect/domain-wall interaction. This shows that domain imaging using defect luminescence has the potential to become a powerful tool. It is noninvasive and can be done not only on the surface but also inside the sample, allowing three-dimensional imaging. In order to further increase spatial resolution, the approach can readily be applied to near field microscopy as well. In both confocal and near field modes, the luminescence changes can be monitored as a function of time and, hence, in-situ investigations of the domain inversion are possible. Regarding a better understanding of the defect/domain-wall interaction, the main advantage of our approach is that the obtained images are directly connected with the defects. Moreover, the presence of different defect types yields the added advantage that such studies can be performed selectively for different defect configurations which can be selected by simply choosing the appropriate wavelength of the excitation laser.

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