Use of Landau Theory for Studying of Domain and Domain Walls and Elaboration of Ferroic Lead-free NaNbO₃ Ceramics

Egidius Rwenyagila
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Directed by Professors: A. K. Tagantsev and N. Setter

Ceramics Laboratory, Materials Institute, EPFL CH-1015, Lausanne, Switzerland

Abstract

Landau theory was used to investigate some properties of domains and domain wall in ferroelectrics and antiferroelectric perovskite ferroics. First, the theory was checked for the well known ferroelectric BaTiO₃. Next, domain wall in BaTiO₃ was evaluated, a 16.3Å domain wall thickness was found which increased with temperature. Polarization distribution inside the wall was successfully derived, it has a form of kink-type tanh solution. Analytical and numerical solutions for the antiferroelectric theory show the possibility of ferroelectricity inside antiferroelectric walls that has polarization gradient. Dense ceramics of NaNbO₃ were synthesized by solid state reaction from activated Na₂CO₃ and Nb₂O₅ powders and controlled sintering. Structural, electrical and thermal characterization gave correct data corresponding to published data of perovskite-type orthorhombic NaNbO₃ single crystals. The domain structure of NaNbO₃ was studied and shows three kinds of domains two of which are antiparallel and have alternating dark and bright intensities.

Results

NaNO₃ Ceramic characterization

Dense ceramic materials, hardly reported so far, was obtained. This was achieved through powder activation and sintering optimization.

- XRD and SEM: Phase/structure of 1370°C, 2h sintered ceramics
- Microstructure of ruptured surface
- Phase transition Characteristics:
  - High temperature dielectric properties of NaNbO₃ ceramics: Frequency independent dielectric peak for orthorhombic-tetragonal phase transition [2]
  - Low temperature dielectric properties of NaNbO₃ ceramics: Dielectric peak for ferroelectric rhombohedral-antiferroelectric orthorhombic thermodynamic phase transition [3]
- Thermal behavior: Thermal gravimetric analysis of NaNbO₃ ceramics with transition points shown by arrows. Transition points correspond well to the optical data of the same NaNbO₃ [4]

NaNO₃ Domain structure

3 kinds of domains

Typical TEM images of domain patterns in antiferroelectric NaNbO₃ ceramics at room temperature.

At the domain walls alternating bright and dark contrast were observed. The observed domain structure resembles the structure of single crystal NaNbO₃ [5]

Conclusions

1. Landau theory was successfully used to investigate some of domain and domain wall properties in ferroelectric and antiferroelectric perovskite ferroics
2. Dense ceramics of NaNbO₃ were successfully synthesized and tested. Structural, electrical, thermal and domain structure properties were effectively investigated and all revealed realistic properties of antiferroelectric perovskite orthorhombic NaNbO₃

Theoretical part

Landau function of second order phase transitions:

$$\Delta G = \alpha_0(T-T_0)P^2 + \alpha_1P^4$$

- Continuous along the transition temperature $T_0$
- Ferroelectric only possible for $T < T_0$

Stability of ferroelectric phases

Simple phase stability model: Depending on relative sizes of Landau coefficients a transition is either into tetragonal $P^4 = P_0^4 > 0$ or rhombohedral phase $P^3 = P_0^3 > 0$

$$\Delta G = \alpha_0P^2 + \alpha_1P^4 + \alpha_2P^6 + \alpha_3P^8 + \alpha_4P^8 + \alpha_5P^8$$

$$P^m(T) = \frac{\alpha_0(T-T_0)}{2A_0 + \alpha_1} \frac{\alpha_1(T-T_0)}{2A_0 + \alpha_1} \Rightarrow \alpha_1 + \alpha_3 > 0$$

Ferroelectric domain wall

Domain wall thickness:

$$t_w = \frac{2\gamma}{k}$$

Polarization profile:

Tanh kink-type polarization distributions inside a ferroelectric domain wall $P_{domain} = 0$

Temperature dependence:

Wall thickness increases with $T > T_C$

Domain walls in antiferroelectrics

Domain wall energy density:

$$\Delta Q = \frac{1}{2}(T-T_c)\gamma = \frac{1}{4}k\gamma^4(\alpha_0(T-T_c) + \gamma^2) + \frac{1}{4}k\gamma^4(\alpha_0(T-T_c) + \gamma^2)$$

Sign of ferroelectricity inside antiferroelectric walls that has a polarization gradient!

Note: The order parameter is not zero everywhere inside the wall. The theoretical model for the relationship between polarization and the wall profile suggests ferroelectricity at two critical transition temperatures:

$$d < \xi$$ or $$d \geq \xi$$

Domain wall profile