

PHASE TRANSITIONS IN THE $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 SYSTEM

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Abstract—Two successive phase transitions, changing the crystal symmetry from rhombohedral to tetragonal, and then to cubic on a heating process, have been investigated in the $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 single crystals with the composition near the morphotropic phase boundary. The existence of the morphotropic phase boundary has been confirmed by measuring the dielectric, piezoelectric and pyroelectric constant. Anomalously large electromechanical and piezoelectric constants are observed on the morphotropic phase boundary.

1. Introduction

Lead zinc niobate, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) is a ferroelectric material with a disordered perovskite structure, which undergoes a diffuse phase transition around 140°C from rhombohedral (at room temperature) to cubic symmetry.¹⁾ Lead titanate, PbTiO_3 (PT) is also a ferroelectric with tetragonal symmetry below 490°C.^{2,3)} Single crystals of the solid solution system $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PZN-PT) can relatively easily be grown by a flux method in the whole range of composition, and the dielectric, piezoelectric, and electrooptic properties have been investigated so far.^{4,5,6)} A morphotropic phase boundary (MPB) between the tetragonal and the rhombohedral phases exists in the range from 9 to 9.5 mol% of PT content.⁴⁾ Enormously large dielectric and piezoelectric constants are found around the MPB,⁵⁾ which is similar to the case in the $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) system.⁷⁾ The values of the piezoelectric constants in PZN-PT exceed those in PZT ceramics. Investigations have been made by x-ray, dielectric, pyroelectric and piezoelectric measurements. In this paper, the description focuses on the single crystals of the (1-x) PZN-xPT solid solution close to the rhombohedral-tetragonal MPB (0.05<x<0.143).

2. Experiments

Single crystals of the solid solutions were grown from a solution in molten lead mono-oxide, the details of which have been described in the previous paper.⁸⁾ The compositions of the crystals were determined correctly to within ±0.5 mol% from both the values of the unit cell parameters and the Curie temperature, referring to the data previously reported.^{5,6)} The unit cell parameters were determined by means of an x-ray powder diffractometer, using (200), (211), (220) and (222) reflections of $\text{CuK}\alpha$ radiation. The specimens used in the dielectric measurements were rectangular (100) or (111) plates ranging from 2.5 to 5 mm on edge and from 0.3 to 1.0 mm thick. The orientations of the plates were adjusted within ±2°. Dielectric constants were measured using an automatic capacitance bridge at 1 kHz. Pyroelectric coefficients were determined by a charge-integration method with a heating rate of 0.04°C. The piezoelectric constants d_{11} and the electromechanical coupling factors k_{11} were determined at room temperature,¹⁾ according to the I.R.E. standard methods.⁸⁾ For d_{11} and k_{11} , bar-shaped specimens (1x1x6 mm for d_{31} , k_{31} , 0.3x0.3x3.5 mm for d_{33} , k_{33}) were used. Prior to the measurement the specimens were poled by applying a DC bias field of about 10 kV/cm in a cooling process from the temperature above the Curie point.

Transitions Pb

Terry C. Jones



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