Hypersonic and dielectric studies of disordered single crystals, Rb1-x(ND4)xD2Aso4, Na1/2Bi1/2TiO3 and PbMg1/3Nb2/3O3, by brillouin scattering and dielectric measurements
by Chi-Shun Tu

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics
Montana State University

Abstract:
Temperature and frequency dependent measurements of dielectric permittivity, acoustic sound velocity and damping have been carried out by using Brillouin light scattering and a capacitance and conductance component analyzer on two different types of ferroelectrics, i.e. (i) FE-AFE mixed deuteron glasses Rbl-x(ND4)xD2AsO4 (x=0, 0.10, 0.28), (ii) relaxor ferroelectrics Na1/2Bi1/2TiO3 (NBT) and PbMg1/3Nb2/3O3 (PMN).

In this study, three important results have been observed: (1)A broad and high-value maximum in dielectric permittivity has been observed in relaxors NBT and PMN, which indicates that these materials could be used for electrostrictive displacement transducers. (2) In FE-AFE mixed glasses DRADA-x, a η2μ-type quadratic coupling, squared in order parameter and linear in strain, becomes the main coupling contribution as ammonium ND4 concentration x increases from 0 to an intermediate value. The results also confirm the presence of PE/FE phase coexistence in DRADA-0.10. (3) For both FE-AFE mixed glasses and relaxor ferroelectrics, the order parameter(s) fluctuations, which are generated by the local random fields originating from short-range randomly-placed cations, are the main dynamic mechanisms for hypersonic and dielectric anomalies. In DRADA-0.10 and 0.28, these local randomly-placed ions are ND4+ and Rb+ ions. In PMN, those randomly-placed cations are Mg+2 and Nb+5 which are randomly placed at B-site positions. In NBT, those randomly-placed cations are Na+1 and Bi+3 which are placed randomly at A-site positions.

Two models, i.e. superparaelectric cluster and extrinsic bulk conductivity, also have been proposed to explain the high-temperature and low-frequency dielectric anomaly in NBT. The elastic stiffness and compliance constants are also calculated for PMN.

HYPERSONIC AND DIELECTRIC STUDIES OF DISORDERED SINGLE CRYSTALS, $Rb_{1-x}(ND_4)_xD_2AsO_4$, $Na_{1/2}Bi_{1/2}TiO_3$ AND $PbMg_{1/3}Nb_{2/3}O_3$, BY BRILLOUIN SCATTERING AND DIELECTRIC MEASUREMENTS

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APPROVAL

of a thesis submitted by

Chi-Shun Tu

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the college of Graduate Studies.

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Signature Chi-Ham Tu

Date Oct. 3, 1994

to my wife Rong-Mei (Ruth), because of whom all things are possible,

and to my son Stachus, in whom I find the reasons

VITA

The author was born Chi-Shun Tu on January 21, 1962 in Kaohsiung, Taiwan. He is the fourth child of Rou-Nu Tu (deceased) and Hsiu-Hsia Tsai Tu and has three older sisters and one younger brother. He was married to Rong-Mei (Ruth) Chien in 1988 and has one son, Stachus Igu Tu.

The author finished his undergraduate work with a B.S in physics at National Taiwan Normal University in 1985. After that time, he was in the Army for two full years to complete his obligation and then taught physics at high school for another two years. From Sept. of 1988 to June of 1990, he attended the University of Oregon in Eugene, Oregon, and graduated with a M.S. in physics. In September of 1990, he enrolled at Montana State University as a graduate teaching and research assistant until the fall of 1994, obtaining a Ph.D. in physics under Professor V. Hugo Schmidt.

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ABSTRACT

Temperature and frequency dependent measurements of dielectric permittivity, acoustic sound velocity and damping have been carried out by using Brillouin light scattering and a capacitance and conductance component analyzer on two different types of ferroelectrics, i.e. (i) FE-AFE mixed deuteron glasses $Rb_{1-x}(ND_4)_xD_2AsO_4$ (x=0, 0.10, 0.28), (ii) relaxor ferroelectrics $Na_{1/2}Bi_{1/2}TiO_3$ (NBT) and $PbMg_{1/3}Nb_{2/3}O_3$ (PMN).

In this study, three important results have been observed: (1) A broad and high-value maximum in dielectric permittivity has been observed in relaxors NBT and PMN, which indicates that these materials could be used for electrostrictive displacement transducers. (2) In FE-AFE mixed glasses DRADA-x, a $\eta^2\mu$-type quadratic coupling, squared in order parameter and linear in strain, becomes the main coupling contribution as ammonium ND_4 concentration x increases from 0 to an intermediate value. The results also confirm the presence of PE/FE phase coexistence in DRADA-0.10. (3) For both FE-AFE mixed glasses and relaxor ferroelectrics, the order parameter(s) fluctuations, which are generated by the local random fields originating from short-range randomly-placed cations, are the main dynamic mechanisms for hypersonic and dielectric anomalies. In DRADA-0.10 and 0.28, these local randomly-placed ions are ND_4^+ and Rb^+ ions. In PMN, those randomly-placed cations are Mg^{+2} and Nb^{+5} which are randomly placed at B-site positions. In NBT, those randomly-placed cations are Na^{+1} and Bi^{+3} which are placed randomly at A-site positions.

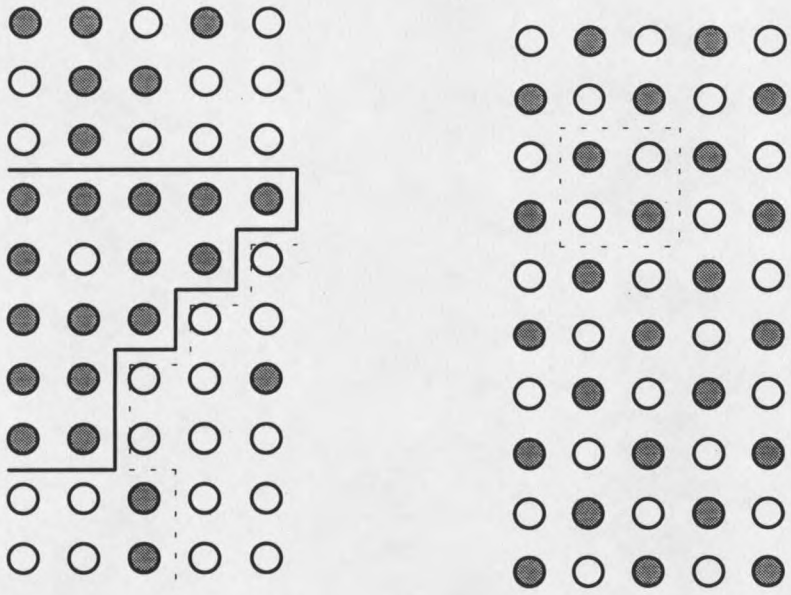
Two models, i.e. superparaelectric cluster and extrinsic bulk conductivity, also have been proposed to explain the high-temperature and low-frequency dielectric anomaly in NBT. The elastic stiffness and compliance constants are also calculated for PMN.

CHAPTER 1

INTRODUCTION

Introduction to Disordered Crystals

If the composition in a crystal is not completely uniform (compositional heterogeneity) down to the unit cell scale or has cation fluctuations statistically or dynamically, then the crystal is usually called "disordered".[1] In terms of symmetry, "disordered" means that there is no long-range translational symmetry inside the crystal. Among disordered materials, many experiments have concentrated on two different systems, i.e. ferroelectric (FE)-antiferroelectric (AFE) mixed crystals with the general formula $A_{1-x}(NH_4)_xH_2BO_4$ [A=Rb, K, Cs and Tl, B=P and As][2-11] and complex relaxor ferroelectrics with formula $(A'_xA''_{1-x})^{+2}B^{+4}O_3^{-2}$ or $A^{+2}(B'_xB''_{1-x})^{+4}O_3^{-2}$.[1,12,13] In these systems, local random fields originating from randomly-placed cations (or ions) play an important role for physical properties such as acoustic (sound velocity and damping) and dielectric anomalies. Since local random fields can suppress the long-range electric ordering and produce the order parameter fluctuations, a normal sharp phase transition usually is not observed in these materials. "Diffuse" (non-sharp peak) phase transition is the typical anomalous characteristic of these disordered materials. The two-dimensional distributions of ions (or cations) for both ordered and disordered states are given schematically in Fig. 1.



(a) (b)

$(A_1A_2)BO_3$, $A(B_1B_2)O_3$, $A_x(NH_4)_{1-x}H_2BO_4$ and $A_x(ND_4)_{1-x}D_2BO_4$

Disordered State	Ordered State
—A_1(●), B_1(●) or A(●) rich region	Uniform composition
····A_2(O), B_2(O) or $NH(D)_4$(O) rich region	Full translational symmetry

Figure 1. Two-dimensional illustrations of ordered and disordered states for both FE-AFE mixed glasses $A_x(NH_4)_{1-x}H_2BO_4$ [or $A_x(ND_4)_{1-x}D_2BO_4$] and complex relaxor ferroelectric systems $(A_1A_2)BO_3$, $A(B_1B_2)O_3$.

For relaxor ferroelectrics, one can use thermal treatments such as annealing, quenching and ratio of cations to control ordering.[1] In FE-AFE mixed proton glasses, the crystal ordering depends on ammonium concentration.[2-7] From experimental results, some general differences have been found between ordered and disordered ferroelectrics:

(1) Ordered (normal):

a) Sharp dielectric phase transition at T_c

b) Stable remanent polarization

c) No strong dielectric frequency dependence at phase transition

d) Stable birefringence

e) No local random fields

f) Usually no intermediate phase between high- and low-symmetries

(2) Disordered:

a) Diffuse dielectric transition which doesn't correspond to any specific change of symmetry (or phase)

b) No stable remanent polarization

c) Strong frequency dependence at diffuse transition

d) No stable birefringence

e) Strong local random fields

f) Usually associated with a sequence of phase transitions, i.e. one (or more) intermediate phase occurred between high- and low-symmetries

In this study, five different single crystals have been measured, i.e. FE-AFE mixed deuteron glasses, $Rb_x(ND_4)_{1-x}D_2AsO_4$ with x=0, 0.10 and 0.28 and complex relaxor ferroelectrics, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Na_{1/2}Bi_{1/2}TiO_3$ (NBT). The introductions to these two different systems are given below.

Relaxor Ferroelectrics (RF)

Perovskite is the name of the mineral calcium titanate ($CaTiO_3$). Most of the useful piezoelectric (ferroelectric) crystals, such as barium titanate ($BaTiO_3$), lead titanate ($PbTiO_3$), lead zirconate titanate ($PbZr_{1-x}Ti_xO_3$), lead lanthanum zirconate titanate (PLZT), sodium bismuth titanate $Na_{1/2}Bi_{1/2}TiO_3$ and lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ etc., have perovskite-type structure, i.e. ABO_3-type unit cell.[13] Here "O" is oxygen, "A" represents a cation with a larger ionic radius, and "B" a cation with a

smaller ionic radius. Fig. 2 shows a typical cubic ABO_3 perovskite-type structure in the paraelectric phase and possible directions of distortion in the ferroelectric phase.[14]

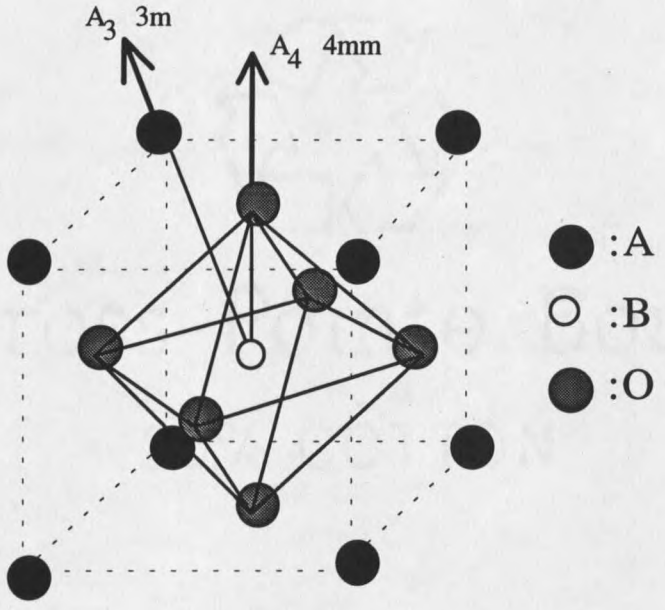


Figure 2. A perovskite cubic unit cell. The point group usually is m3m for a paraelectric cubic ABO_3 perovskite-type structure. Solid lines indicate the BO_6 octahedron. A_4 indicates one of three 4-fold rotation axes and 4mm is the usual corresponding point group in the tetragonal ferroelectric phase. A_3 indicates one of four 3-fold rotation axes and 3m is the usual corresponding point group in the trigonal ferroelectric phase.

Many of the complex relaxor ferroelectrics with perovskite-type structure are compounds with either $A^{+2}B^{+4}O_3^{-2}$ or $A^{+1}B^{+5}O_3^{-2}$-type formula. In the perovskite family, there are many compounds with the formula $A^{+3}B^{+3}O_3^{-2}$, but among them no ferroelectrics have been discovered.[13]

The perovskite structure is essentially a three-dimensional network of BO_6 octahedra (see Fig. 2). It may also be regarded as a cubic close-packed arrangement of A and B ions with B ions filling the octahedral interstitial positions.[13] The packing situation of this structure may be characterized by a tolerance factor t, which is defined by the following equations:[13]

$$R_A + R_O = t\sqrt{2}(R_B + R_O) \quad (1)$$

or

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad (2)$$

where R_A, R_B and R_o are the ionic radii of A, B and O ions, respectively. When t is equal to 1, the packing is said to be ideal. When t is larger than 1, there is too large a space available for the B ion, and therefore this ion can "move" inside its octahedron. In general, to form a stable perovskite structure, one requires that $0.9<t<1.1$. Besides the ionic radii, other factors, such as polarizability and character of bonds, must also be taken into account.[13]

The term "complex relaxor ferroelectrics" generally refers to the complex perovskites in which the charge classifications of $(A'_xA''_{1-x})^{+2}B^{+4}O_3^{-2}$ or $A^{+2}(B'_xB''_{1-x})^{+4}O_3^{-2}$ etc. are satisfied and unlike-valence cations belonging to a given site (A or B) are present in the correct ratio for charge balance, but are situated randomly on these cation sites. For example, sodium bismuth titanate $Na_{1/2}Bi_{1/2}TiO_3$ has two unlike valence cations Na^+ and Bi^{+3} distributed in the A site and lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ has two unlike valence cations Mg^{+2} and Nb^{+5} distributed in the B site.[1,15,16] These randomly different cation charges give rise to random electric fields and cause random elastic distortion fields in microregions. These random fields tend to make the phase transitions "diffuse" instead of sharp as in normal ferroelectrics, and complicate the task of determining structure and state of electric order. The electric properties of relaxor ferroelectrics also depends on the cation ordering degree. The degree of ordering inside a crystal depend on several things such as method of crystal growth, cation valence, and thermal treatment (e.g. quenching and annealing). In certain compounds,