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New Phase Boundary Originating from Coexistence of Ferroelectrics and Relaxor in Lead-free Piezoelectric KNN-based Composites

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Abstract

Lead–based piezoelectric materials have been used in various commercial high–tech applications such as sensors, actuators and ultrasonic transducers. According to European environmental legislation, leadwith high toxity brings harmfuleffects on the environment and human. Recently, in order to replace lead–based piezoelectric materials, lead–free ones were strongly developed. Several kinds of lead–free piezoceramics have been extensively investigated, such as $BaTiO_3$–based, $(Bi_{1/2}Na_{1/2})TiO_3$–based and $(K_{0.5}Na_{0.5})NbO_3$–based (KNN) materials. Among them, KNN and its compounds have been considered as one of promising candidates because of their excellent dielectric and piezoelectric properties. The unique advantages of KNN ceramics such as a high Curie temperature ($T_C \approx 420^oC$) and a high piezoelectricity, represents a promising candidate for replacement of lead–based materials. From that, many studies focused on addition, substitution, modification chemical elements to improve the properties for KNN–based materials defined the concept of polymorphic phase transition (PPT) at room temperature, and morphotropic phase boundary (MPB). The PPT compositions in KNN–based materials have improved the piezoelectric properties; however, remain the temperature sensitive problem since the phase boundary corresponding to R−O or O−T possesses the PPT characteristic depending on not only the compositions but also the temperatures. To prevent this problem, many studies paid their attentions on MPB. The MPB is the nearly vertical phase boundary separating rhombohedral (R), tetragonal (T), and/or monoclinic (M) ferroelectric phases and nearly temperature independent. There are many studies for MPB, mentioned about the improvement in piezoelectric properties and the temperature stability of d_{33}. However, the explanation for these behaviors still remains a challenge. Recently, some studies suggested ferroelectric−relaxor phase boundary with the crystal structure transit from non cubic phase (orthorhombic or tetragonal) to pseudocubic (PC) phase. Though the enhancement of piezoelectric constant and/or electromechanical strain

can be observed, the temperature stability of piezoelectric properties was not considered.

In order to saperate and maintain the phase in materials, the composite method was mentioned in this work, by mixing the calcined powders of two phase components. For tetragonal phase stabilization, $SrTiO_3$ is a promising candidate which can improve not only the sinterability but also piezoelectric properties of KNN ceramics. Tetragonal phase was stabilized and maintained good properties for the modification content of 0.06 mol. Such high amount of $SrTiO_3$ causes the higher sintering temperature and significantly reduces T_C. Then Li^+ was doped into KNN–4ST to solve problems. On the other hand, we found the stabilized PC phase with relaxor features in $BaZrO_3$–modified KNN ceramics.

Finally, the ferroelectric/relaxor piezocomposites were compounded by T–phase KNN–4ST–4Li and PC–phase KNN–8BZ in different T–phase fraction *f*. The phase boundary was found at the composites of 70 mol% of T phase and 30 mol% of PC phase with the enhanced piezoelectric constant d_{33} and coupling factor k_p values of 210 pC/N and 34%, respectively. Besides, the enhanced strain properties at $f = 0.7$ composites are related with the coexistence of ferroelectric domain, tetragonal micro domains and pola nanoregions, which originates from the relatively contribution of the ferroelectric and relaxor components in composites. Moreover, the low variation (≤ 10%) of d_{33} in the temperature range of 25°C –225° performs good temperature stalility of the piezoelectric constant, corresponding with phase transition in temperature dependent XRD patterns.

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Chapter 1: Introduction

1.1. Back ground

Lead–based piezoelectric materials have been used in various applications for sensors and actuators, based on their mutual conversion between mechanical energy and electrical energy [1-3]. However, it seems that the high toxicity of lead (Pb) in wastes of those devices causes serious problems to environment and human body. Some laws and regulations were legislated to prohibit the use of lead, including European Union passed the Restriction of Hazardous Substances (RoHS) law in 2003, Household Electronic Products Recycling Law in Japan, and Electronic Information Product Pollution Control Management Regulation in China in 2006 [4]. Hence, lead–free materials have been intensively investigated to replace lead–based piezoelectric material. Several groups of lead–free piezoceramics have been extensively investigated, such as $BaTiO_3$ [5,6], $(Bi_{1/2}Na_{1/2})TiO_3$ [7,8], and $(K_{0.5}Na_{0.5})NbO_3$ (KNN) [9-11]. Among them, potassium sodium niobate $K_{0.5}Na_{0.5}NbO_3$ (KNN) has drawn much attention due to their relatively high Curie temperature, excellent dielectric and piezoelectric properties. Several promising achievements was recently reported in KNN–based ceramics with constructing new phase boundaries such as polymorphic phase transition (PPT) [12] and morphotropic phase boundary (MPB) [13]. While PPT leads to the temperature sensitive problem since the characteristic depends on bothcompositionand temperature, the nearly vertical phase boundary MPB independing on temperature can solve that proplem. Liu *et al.* (2018) introduced a way of forming MPB by shifting diffused phase transitions closer to create a partially overlapped phase transition over a broad temperature range [14]. In this work, we suggest another approximation to form an MPB by mixing two end members with different crystal symmetries at room temperature. In the formation of rhombohedral (R)–tetragonal (T) MPB, most of studies believed that the R phase in KNN ceramics can

be stabilized by $AZrO_3$ (A = Ba, Ca, Sr ...) modification. However, some studies recently suggested the stabilization of relaxor based on the orthorhombic (O)–pseudocubic (PC) phase transition in $AZrO_3$–modified KNN. Therefore, there are still arguments on the definition of the stabilized phase in KNN ceramics by modifying Zr–based compounds. In this thesis, the stabilized phase in $BaZrO_3$–modified KNN is defined as PC phase relating with the ferroelectric–to–relaxor transition. By using a T phase and a PC phase components to produce the composites, we obtain the new T–PC phase boundary with the enhanced piezoelectric properties and temperature stability in KNN−based composites. Moreover, the improvement of strain behaviors in the composites can be originated from a new phase boundary with ferroelectric−relaxor coexistance.

1.2. Aim and scope of research

Research aim:

The principle aim of this thesis work is improving the piezoelectric properties, and their temperature insensibility in lead–free KNN–based piezoelectric materials using the composite method, based on the phase coexistance. In order to serve that main goal, the following issues will be resolved:

- Stabilize the tetragonal phase in KNN ceramics.
- Define the pseudocubic phase and relaxor stabilization in$BaZrO_3$–modified KNN.
- Produce the compostites using two components, one in ferroelectric tetragonal phase and one in relaxor pseudocubic phase, then investigate the enhanced piezoelectric properties and temperature stability near MPB region, based on the high temperature crystal structure XRD.
- Propose a model of ferroelectric−relaxor coexistance, and explain the improvement of strain behaviors in the composites.

Research scope:

The solid solution $0.92(Na_{0.5}K_{0.5})NbO_3–(0.08–x)(Bi_{0.5}Li_{0.5})TiO_3–xBaZrO_3$ ternary system was investigated to study the features of morphotropic phase boundary.

The tetragonal phase is stabilized in $(1–x)(Na_{0.5}K_{0.5})NbO_3 – xSrTiO_3$ piezoceramics at room temperature with the amount of $SrTiO_3$ modification higher than 0.05 mol%. However, when $SrTiO_3$ content further increases, the Curie temperature and piezoelectric properties are reduced. Therefore, $0.96(K_{0.5}Na_{0.5})_{1-y}Li_yNbO_3–0.04SrTiO_3$ piezoceramics system was also investigated.

Two systems of $(K_{0.5}Na_{0.5})(Nb_{1-x}Zr_x)O_3$ and $(1–y)(Na_{0.5}K_{0.5})NbO_3$ are compared to investigate the relaxor behaviors and clarify the stabilized phase in KNN–based ceramics. The pseudocubic phase can be found in KNN–100*y*BZ around room temperature with $y \geq 0.08$, corresponding with the relaxor stabilization.

Finally, two components of ferroelectric tetragonal KNN–4ST−4L and relaxor pseudocubic KNN–8BZ are mixed in different KNN–4ST−4L content fractions *f*. The crystal structure, microstructure, and other properties such as dielectric permittivity, ferroelectric polarization, bipolar strain, piezoelectric responses, etc. were carried out as well as the temperature stability.

1.3. Outline of the thesis

The thesis consists of five Chapters.

The background, research objectives and outline of this thesis are given in Chapter 1. Chapter 2 consists of two parts. The first part provides the basics ferroelectrics and their related properties applicable to the objectives of this research. The second

partmentionsabout the review of literature on lead–based piezoelectrics, lead–free piezoelectrics (BT –barium titanate, BNT –bismuth sodium titanate and KNN –sodium potasium niobate), phase boundaries and relaxor ferroelectricity in KNN–based materials. Chapter 3 presents the experimental procedure with particular compositions, detailed fabricating conditions and characterization techniques that had been used in this research work.

Chapter 4 is the main content in this study and includes five parts. An example of tetragonal–rhobohedral morphotropic phase boundary in $0.92(Na_{0.5}K_{0.5})NbO_3$–$(0.08–x)(Bi_{0.5}Li_{0.5})TiO_3$–$xBaZrO_3$ ternary system using convetional solid solution is considered in the first part. Next two parts investigate the effects of $SrTiO_3$ and Li+ modification on the tetragonal stabilization of KNN–based ceramics. The forth part determines the orthorombic–pseudocubic polymorphic phase transition and ferroelectric–relaxor crossover in $BaZrO_3$–modified KNN ceramics. The last part studies new phase boundary in the composites of ferroelectric tetragonal $0.96(K_{0.5}Na_{0.5})_{0.96}Li_{0.04}NbO_3$–$0.04SrTiO_3$ and relaxor pseudocubic $0.92Na_{0.5}K_{0.5}NbO_3$–$0.08BaZrO_3$.

Finally, Chapter 5 presents the summary of this research work.