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Oxygen vacancy dependent structural phases in $KNbO_3$

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ABSTRACT

By considering the fact that oxygen vacancies are always the integral part of oxides when prepared at high temperature, variation in oxygen vacancy concentration was introduced in $KNbO_3$ by varying calcinations temperature of precursors. A similar kind of variation was also introduced in $KNbO_3$ by varying La^{3+} doping concentration. Our analysis shows that the phase formation in $KNbO_3$ greatly responds to the variation in concentration of oxygen vacancy. It was found that, when $KNbO_3$ bears more oxygen vacancies orthorhombic phase formation at room temperature becomes favorite otherwise cubic phase is favored. The result seems to be highly important to look insight into the mechanism of paraelectric-ferroelectric phase transition.

1. Introduction

Perovskites such as $BaTiO_3$, $PbTiO_3$ and $KNbO_3$ are proven to be highly attracting candidates for dielectric, piezoelectric, ferroelectric memory cell and photoluminescence applications [1–3]. All they bear paraelectric cubic phase above the Curie temperature and with the fall in temperature undergo paraelectric-ferroelectric phase transition [4]. In this context, Devonshire's theory seems to be highly fundamental [4].

According to Devonshire's theory, the phase transition temperature is one for which three minima, one at polarization $P = 0$ and other two at $P = \pm P_s$ (spontaneous polarization) on Gibb's free energy– polarization (P) plot (Fig. 1) are all of equal depth. The paraelectric-ferroelectric phase transition occurs when depth of two $P = \pm P_s$ is more than $P = 0$. This condition is temperature dependent and the transition occurs when temperature decreases below the Curie temperature. The three minima however arise when P_s is non-zero. If P_s is zero, then all three minima coincide at $P = 0$; the condition may be assigned to the pure and perfectly unstrained cubic phased crystal. However, such kinds of ferroelectric perovskites crystals are practically impossible as some kinds of defects are always there [5–7]. It is to be noted that the internal strain in the perovskites is mainly due to distortions in oxygen octahedral [4]. The distortion in octahedra may be a consequence of presence of defects such as oxygen vacancy, impurity ions and dislocations.

Oxygen vacancies are the integral part of the perovskite compounds [3,5]. Their concentration is assumed to be more when the compounds are prepared by high temperature synthesis techniques [5–7]. As the formation of oxygen vacancy is greatly affected by calcinations temperature and doping impurities [7], the concentration of oxygen vacancy can be varied easily. Since the oxygen vacancy shows prominent effects for trapping the charge carriers [8], changing the remnant polarization and coercive field [9], enhancing the lattice parameters and dielectric tunability [10], pinning and tailoring the domain walls [11] and producing distortion in octahedral cage [12], its contribution for producing the strain in the crystal is expected to be significant. Accordingly, we believe that the paraelectric-ferroelectric phase transition is partially dependent on the concentration of oxygen vacancy. The effect of oxygen vacancy for phase transition however is not found in the literature and hence presented here in the present letter.

2. Material and methods

Undoped $KNbO_3$, and La^{3+} doped compounds i.e., $K_{1-x}NbO_3{:}La_x$ ($x = 0.005$, 0.01, 0.015 and 0.02) were synthesized by a modified polymerized complex method which is similar to the method used for the preparation of undoped $KNbO_3$ nanoparticles given in the supplementary file of ref. [13]. Analytical grade source chemicals Nb_2O_5, K_2CO_3, and $La(NO_3)_3{\cdot}6H_2O$ were used for the synthesis. For La^{3+}doped $KNbO_3$ compounds $La(NO_3)_3{\cdot}6H_2O$ was mixed stoichiometrically with K_2CO_3. The doped compounds were prepared by calcining their respective precursor at 800 °C for 6 h, whereas undoped $KNbO_3$ compounds were prepared by calcining the precursors at temperatures 800, 750, 700 and 650 °C for the

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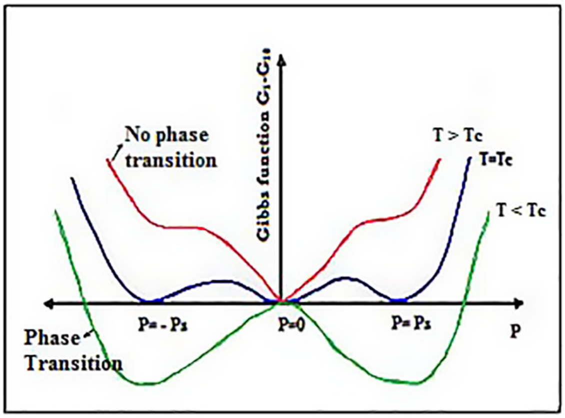

Fig. 1. Schematic representation of change in Gibb's function with polarization for first order phase transition [4].

same period. All these compounds were characterized by X- ray diffraction (XRD) patterns. The XRD data of all these compounds at room temperature were recorded by using X-ray diffractometer (D8 ADVANCE, BRUKER, GERMANY) employing Cu-Kα radiation (1.5406 Å) in 2θ range 15–80°.

3. Result and discussion

Fig. 2a shows the XRD patterns of the synthesized undoped $KNbO_3$ compounds prepared at various temperatures. It is seen that the compound prepared at 800 °C stabilizes in orthorhombic phase at room temperature with the lattice parameters **a** = 3.968 Å, **b** = 5.663 Å and **c** = 5.676 Å, calculated by least squares fit method. The XRD pattern coincides with the JCPDS profile (file no.710946) of orthorhombic $KNbO_3$.

Interestingly, it is also found that, with the decrease in calcined temperature of precursors the orthorhombic nature diminishes gradually. This conclusion was made due to decrease in resolution of (0 2 2) and (2 0 0) peaks of orthorhombic cell at 2θ ~ 45° as observed in Fig. 2b. Finally, for 650 °C calcinations temperature the compound stabilizes in cubic phase (Fig. 2a); correspondingly Fig. 2b shows only one peak at 2θ ~ 45° position i.e., (2 0 0).

In fact, the high temperature phase of all these compounds was cubic [4]. While cooling the samples during the synthesis it was expected that they all undergo cubic-tetragonal-orthorhombic phase transition so that the room temperature phase will be orthorhombic. The first three samples follow the line of expectation however, the last sample remains cubic. This indicates that the 650 °C calcined sample is violating the Devonshire's theory of phase transition.

Devonshire's theory of phase transition is based on the concept of strain in the crystal. The strain in perovskite crystals is due to the distortions in oxygen octahedra which might be contributed by oxygen vacancies. Thus, the role of oxygen vacancy seems to be significant in this matter. The stabilization of the last sample in cubic phase at room temperature indicates that, this compound bears insufficient oxygen vacancies to produce the necessary strain required for the phase transition. This may be due to lower calcinations temperature. The peaks patterns in Fig. 2a show that, with the increase in calcinations temperature the phase became orthorhombic. This was due to increase in concentration of oxygen vacancies beyond a certain value; result in a cubic-tetragonal-orthorhombic phase transition. The estimation of oxygen vacancy concentration required to induce a phase transition in $KNbO_3$ is difficult at present, but will be an issue of future interest.

To cross examine the role of oxygen vacancy for phase stabilization, a series of La^{3+} doped $KNbO_3$ samples were grown. Fig. 3a shows the XRD patterns of these compounds. It was found that doped compounds $K_{0.995}NbO_3{:}La_{0.005}$ and $K_{0.99}NbO_3{:}La_{0.01}$ stabilize in orthorhombic phase, whereas $K_{0.985}NbO_3{:}La_{0.015}$ stabilizes in cubic phase. The XRD patterns of these three compounds do not

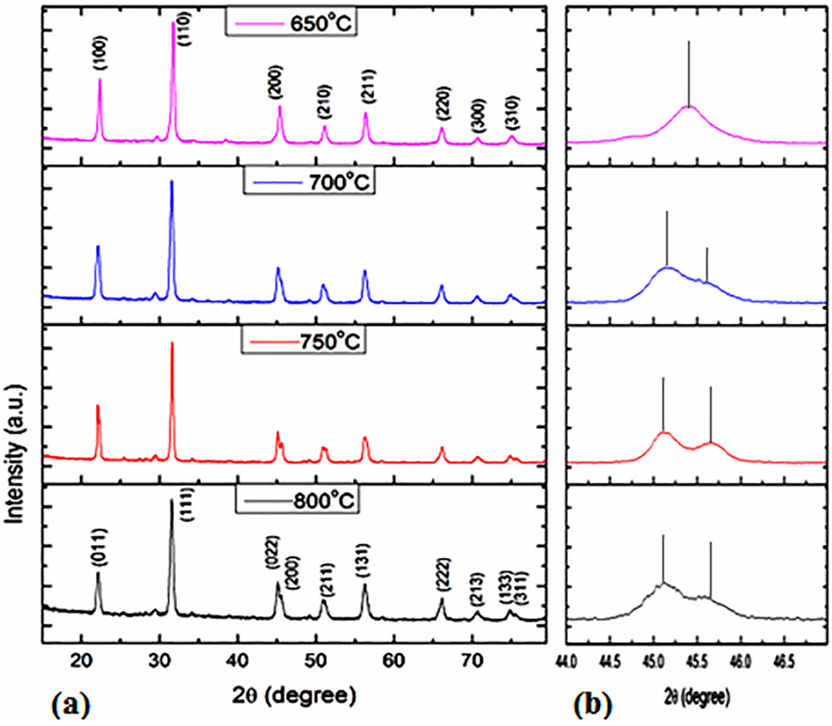

Fig. 2. (a) XRD patterns of $KNbO_3$ compounds prepared at calcined temperatures 800, 750,700 and 650 °C and (b) resolved XRD peaks in the range 2θ = 44 to 47°.