

Formation Enthalpy Calculation of Oxygen Vacancy Defect in Doped Lithium Niobate Crystals*

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The relationship between temperature and oxygen vacancy concentration is deduced in this paper. Based on the data of thermal weight-loss experiment, the formation enthalpies of congruent and several doped LN crystals have been calculated. It was found that the formation enthalpy of oxygen vacancies can be decreased evidently by doping valence-changeable ions. The experimental results were discussed and a new reduction process of the photorefractive LN crystal at a relatively low temperature was proposed, and the reduced crystals showed a good effect in practical use.

Keywords Formation enthalpy calculation, Oxygen vacancy defect, Doped lithium niobate crystal

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Introduction

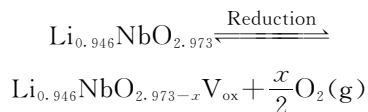
Photorefractive materials are being widely investigated for applications in holographic data storage^[1]. As one of the most popular photorefractive crystals, lithium niobate (LiNbO₃, LN) crystal has great potential as a high density holographic storage medium because it can be grown easily to a large size with excellent optical quality and has a large dynamic range. However, LN has a disadvantage, *i. e.*, its low sensitivity to photorefractivity^[2]. In practice, doping valence-changeable ions^[3] and reduction-treating can promote its sensitivity. The reduction treatment of doped LN crystals is usually carried out at a high temperature (1000 °C) and in vacuum (1.33×10^{-3} Pa) or in Ar atmosphere, but the crystals would be re-oxidized in the cooling process or cracked in fast cooling. The above problems can be solved if the reduction process is performed in non-oxidizing atmosphere and at a relatively low temperature.

The reduction of doped LN crystals can mainly be considered as a process of oxygen released from its crystal lattice, subsequently forming oxygen vacancies in the crystal^[4]. Therefore, the formation enthalpy of the oxygen vacancies indicates the difficulty of the formation of the oxygen vacancies, that is, the difficulty of the reduction process. In order to calculate the formation enthalpy of the oxygen vacancies, the

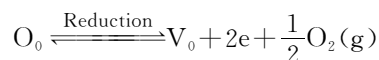
authors have deduced a formula by means of the thermodynamic analysis of the oxygen vacancy defects in LN crystals, and on the basis of thermal weight-loss experiments, the oxygen formation enthalpy of the oxygen vacancies in congruent LN and several doped LN crystals have been calculated. It was found that doping valence-changeable ions can greatly decrease the formation enthalpy of the oxygen vacancies in LN crystals. Therefore, an experimental basis for the reduction process of doped LN crystals at a relatively low temperature is provided.

Thermodynamic Analysis of Oxygen Vacancy Defects

For congruent LN crystal, the reduction process can be described as



or simply as



Where O₀ is the oxygen on lattice site; V₀ is the oxygen vacancy with two positive charges. This process means that when the temperature of the crystal is raised, for the oxygen ions on the surface site of the crystal each loses two electrons and such two oxygen atoms combine together to form an oxygen molecule, which escapes into the gas

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phase, meanwhile, the doped ions capture the free electrons and are reduced. The oxygen vacancies formed on the crystal surface diffuse inside until the equilibrium is established.

The oxygen vacancy in the LN crystal is a kind of thermodynamically stable vacancy. Its amount can be described by the concentration of oxygen vacancies $[V_o]$, which is defined as the proportion of the total number of oxygen vacancies to the total number of lattice sites (which is approximately the total number of atoms or ions in the crystal). Of course, $[V_o]$ increases with the rise of temperature of the crystal. It is not adequate to interpret this phenomenon simply by the enlargement of the vibration amplitude of atoms (or ions) with the rise of temperature of the crystal. An explicit explanation can be obtained only by means of the thermodynamic analysis of the oxygen vacancy defects.

According to thermodynamics, the stability of the oxygen vacancy defects in a crystal can be measured by its free energy, G . With a certain number of oxygen vacancies, the lower the free energy, G of the crystal, the higher the stability of the corresponding state.

Suppose the total number of atoms (or ions) in a crystal is N , the total number of oxygen vacancies is n , the enthalpy change induced by the formation of one oxygen vacancy is ΔH_f , the change of vibrational entropy is ΔS_v , then the configurational entropy after the formation of oxygen vacancies is given by

$$S_m = k \ln \frac{(N+n)!}{N!n!} =$$

$$k[(N+n)\ln(N+n) - N\ln N - n\ln n]^{[5]} \quad (1)$$

where k is Boltzmann constant.

According to Gibbs-Helmholtz equation and the principle of minimum free energy, we obtain

$$\Delta H_f - T\Delta S_v + kT \ln \frac{n}{N} = 0 \quad (2)$$

$$\ln \frac{n}{N} = -\frac{\Delta H_f}{kT} + \frac{\Delta S_v}{k} \quad (3)$$

If 1 mol of oxygen vacancies is formed, then

$$\ln \frac{n}{N} = -\frac{\Delta \tilde{H}_f}{RT} + \frac{\Delta \tilde{S}_v}{R} \quad (4)$$

where $\Delta \tilde{H}_f$ and $\Delta \tilde{S}_v$ denote the formation enthalpy and the change of vibrational entropy, respectively, when 1 mol of oxygen vacancies is formed.

Considering the definition of the concentration

of oxygen vacancies, we can obtain

$$[V_o] = \frac{n}{N} = \exp\left(\frac{\Delta \tilde{S}_v}{R}\right) \exp\left(-\frac{\Delta \tilde{H}_f}{RT}\right) \quad (5)$$

At a certain partial pressure of oxygen, if the concentration of oxygen vacancies in the LN crystal at room temperature is supposed to be zero, the relative concentration of oxygen vacancies $[V'_o]$ is related with temperature T and formation enthalpy $\Delta \tilde{H}_f$:

$$[V'_o] = A \exp\left(-\frac{\Delta \tilde{H}_f}{RT}\right) \quad (6)$$

where A is a constant functionally including the change of vibrational entropy.

Taking the logarithm of equation (6), we have

$$\lg[V'_o] = \frac{-\Delta \tilde{H}_f}{2.303RT} + \lg A \quad (7)$$

Then we can obtain the formation enthalpy of oxygen vacancies $\Delta \tilde{H}_f$ via the linear relationship between $\lg[V'_o]$ and $1/T$.

Results and Discussion

The samples used in our experiments are congruent LN, Na : LN (0.1%Na), Sr : LN (0.1%Sr), Ti : LN (0.1%Ti), Fe : LN (0.1%Fe), Ce : LN (0.1%Ce), Eu : LN (0.1%Eu), Eu : Ce : LN (0.1% of Eu and Ce respectively), Fe : Ce : LN (0.1% of Fe and Ce respectively). Pulverizing the sample to powder, which can get through a 200 mesh sieve, it was annealed at 800 °C in air for 20 h and cooled slowly to room temperature. LN crystal does not volatile at a temperature below its melting point. Li₂O volatile only in trace amount and its volatility can be neglected in comparison. Therefore the weight loss of the sample under a certain temperature can be considered to be the weight of escaping oxygen, and the concentration of oxygen vacancies can be obtained by means of the weight loss of the sample.

The weight-loss experiments were carried out on a TAS-100 thermoanalyzer (Japan), the precision of which is 0.01 mg. We set the partial pressure of oxygen at 2.13×10^4 Pa and kept the temperature constantly at different temperatures. The equilibrium is considered to be set when the sample weight is not changing within 1 h. The concentrations of oxygen vacancies $[V'_o]$ at various temperatures can be calculated. By plotting $\lg[V'_o]$ against $1/T$, the linear relationship between $\lg[V'_o]$ and $1/T$ is obtained (Fig. 1). Finding the slopes of the corresponding curves $\Delta \tilde{H}_f/(2.303R)$

by least square fitting, thereupon we can calculate the formation enthalpies of various doped LN

crystals. The results are given in Table 1.

Table 1 Formation enthalpies of oxygen vacancies in undoped and doped LN crystals

| Crystal | LN | Na : LN | Sr : LN | Ti : LN | Fe : LN | Eu : LN | Ce : LN | Eu : Ce : LN | Fe : Ce : LN |
|---|-------|---------|---------|---------|---------|---------|---------|--------------|--------------|
| $\Delta\tilde{H}_f / (\text{kJ} \cdot \text{mol}^{-1})$ | 40.17 | 41.68 | 49.07 | 36.14 | 26.12 | 15.98 | 10.38 | 10.21 | 15.80 |

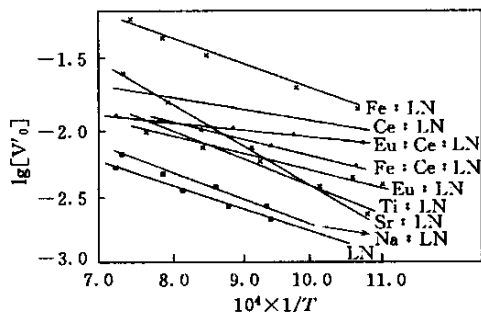
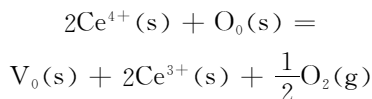


Fig. 1 The relationship between temperature and oxygen vacancies concentration in doped and congruent LN crystals.

From the experimental results we can see that the doping of LN crystals with valence-changeable ions greatly reduces the formation enthalpy of oxygen vacancies, $\Delta\tilde{H}_f$. This is due to the fact that the high- and low-valence ions in doped LN crystal interchange in the reduction process. Taking Ce : LN crystal for example, the reduction process may be described as



where the $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ transformation promotes the formation of oxygen vacancies. That means that at the same temperature, the oxygen vacancies are more in the LN crystal doped with valence-changeable ions than in the congruent LN crystal. Therefore we can reduce the doped LN crystals with valence-changeable ions at a relatively low temperature and obtain a suitable concentration of low valence ions and a profitable sensitivity to photorefractivity. We put Ce : LN and Eu : Ce : LN crystal slices in Li_2CO_3 powder, reduced them at 550 °C for 24 h and cooled them slowly to room temperature, no abnormality such as crack was observed. These slices were used in holography, multi-wave coupling, real time correlation storage and phase conjugation, and good results were obtained. It may be concluded that the reduction of doped $E_{\text{Fe}-\text{O}}$ crystals with valence-changeable ions is feasible.

From the experimental facts that the doping of LN crystal decreases the formation enthalpy of oxygen vacancies, we can also judge which sites in the LN crystal lattice the doped RE ions would occupy. As reported in the literature^[6], the strength series of bonds Li—O, Nb—O, Na—O, Sr—O, Ti—O, Fe—O, Ce—O, Eu—O is $E_{\text{Nb}-\text{O}} > E_{\text{Ti}-\text{O}} > E_{\text{Ce}-\text{O}} > E_{\text{Fe}-\text{O}} > E_{\text{Eu}-\text{O}} > E_{\text{Sr}-\text{O}} > E_{\text{Li}-\text{O}} > E_{\text{Na}-\text{O}}$. Therefore, only when Ti^{4+} , Ce^{4+} , Eu^{3+} ions have substituted or mainly substituted for the Nb^{5+} ions (to form negatively charged vacancies Ce'_{Nb} , Ti'_{Nb} , Eu''_{Nb} , Fe''_{Nb}), can the oxygen ions around Ce'_{Nb} , Fe'_{Nb} , Ti'_{Nb} in the crystal lattice escape easily.

Conclusion

From the thermodynamic point of view, we have deduced the calculation formula of the formation enthalpy $\Delta\tilde{H}_f$ of oxygen vacancies in LN crystals. Meanwhile, the $\Delta\tilde{H}_f$'s have been calculated for congruent LN and several doped LN crystals. The results denote that doping LN crystals with valence-changeable elements can greatly decrease the $\Delta\tilde{H}_f$. Therefore the reduction process of doped LN crystals with valence-changeable ions can be completed at a relatively low temperature and good practical effects have been achieved. In this way, all the problems such as the complexity of reduction process, re-oxidation and cracking of the crystal in cooling process have been solved to a great extent.

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