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Preparation and electrical properties of SBN thin films derived from aqueous organic gels

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Abstract

$Sr_{0.5}Ba_{0.5}Nb_2O_6$ (SBN50) thin films have been prepared using aqueous organic gel method. The differences in the decomposition between Sr–Ba–Nb nitrate precursor solutions with different pH values were investigate. By heat treatment at 700 °C for 2 h, SBN thin films with smooth and crack-free surface were derived from the precursor solution of a lower pH = 8. XRD patterns revealed the polycrystalline nature of the SBN thin films on $Pt/Ti/SiO_2/Si(100)$ substrates. Electric properties measurement indicated that the SBN films demonstrated a ferroelectric hysteresis loop. The remanent polarization (P_r) and coercive field (E_c) were 8.17 $\mu C/cm^2$ and 16.9 kV/cm, respectively.

Keywords: $Sr_{0.5}Ba_{0.5}Nb_2O_6$; Thin films; Aqueous organic gel; Electrical properties; EDTA; pH value

1. Introduction

$Sr_xBa_{1-x}Nb_2O_6$, SBN, $(0.25 < x < 0.75)$ is a ferroelectric solid solution between $BaNb_2O_6$ and $SrNb_2O_6$ which has a tetragonal tungsten bronze-type structure [1]. SBN are being extensively studied for its technological applications in electro-optic, pyroelectric, piezoelectric and photorefractive devices due to its excellent pyroelectric and linear electro-optic effects with low half-wave voltage and photorefractive sensitivity [2–4]. In addition, it has advantage with lead-free composition which is concerned with environment, safety and health.

SBN thin films have been prepared by several techniques such as pulsed laser deposition (PLD) [5], laser ablation [6] and the sol–gel process [7]. However, most of these methods are expensive and require complex equipment. In recent years, the aqueous organic gel route for synthesis of ferroelectric thin films which has become very promising offers several advantages, i.e. its low cost, homogeneous mixing at molecule level, good stoichiometric control, low processing temperature, use of an aqueous-based processing system and the ability to coat large substrate areas. In this technique, polyfunctional carboxylic acids and metal salts are used to form metal carboxylate complexes solution. The clear solution is dehydrated to yield a viscous liquid precursor which can be used for preparation of thin films by the use of spin coating techniques.

Although there have been some reports about the preparation of ferroelectric thin films of several systems such as $BaTiO_3$, $SrTiO_3$, PZT and $SrBiNb_2O_9$ by aqueous organic-gel method [8–11], systematic studies about the SBN thin films prepared by this method have not yet been reported in the literature to our knowledge.

The aim of this work was to determine the feasibility of utilizing aqueous organic gel route to produce SBN thin films on $Pt/Ti/SiO_2/Si(100)$ substrates and to investigate the differences in the decomposition between nitrate precursor solutions with different pH values. In addition, electrical properties of the obtained thin films were also studied.

2. Experimental procedure

2.1. Materials

The starting materials used were high-purity $Ba(NO_3)_2$ (>99%), $Sr(NO_3)_2$ (>99%), Nb_2O_5 (>99.99%), anhydrous citric acid (99%), ethylenediaminetetraacetic acid (EDTA)

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(99.5%) and ammonia solution (30 wt.%). Citric acid and EDTA were used as the chelating agents.

For the preparation of Ba–EDTA and Sr–EDTA complexes, the barium nitrate and strontium nitrate were separately dissolved in deionized water and mixed with aqueous EDTA acid (metal ions: EDTA mole ratio = 1:1). The required amount of ammonia solution was added to achieve pH = 7 to form transparent Ba–EDTA and Sr–EDTA complexes.

The procedure for preparation Nb–citrate complex was similar to that of the Nb–tartarate complex which was reported previously [12]. Nb_2O_5 was dissolved in HF to form $NbOF_5^{2-}$ or NbF_7^{2-} complexes by heating for 48 h. Aqueous solution of ammonium oxalate was added to the solution, keeping the oxalate ions in excess. Then ammonia solution was added with continuous stirring to form a precipitation of hydrous niobium oxide ($Nb_2O_5 \cdot nH_2O$). The precipitation was aged at 80 °C for 12 h, after which it was filtered and washed with water to make the fluoride free. The hydrous niobium oxide was then dissolved in aqueous solution of citric acid by continuous stirring and heating at 60 °C to form a transparent pale yellow Nb–citrate complex. The Nb content in the solution was determined by ICP analysis.

2.2. Preparation of Sr–Ba–Nb precursor solution

The composition of $Sr_{0.5}Ba_{0.5}Nb_2O_6$ was chosen for investigation. Stoichiometric amounts of $Ba(NO_3)_2$–EDTA, $Sr(NO_3)_2$–EDTA and Nb–citrate solutions were mixed together, followed by addition of EDTA acid in the molar ratio of EDTA acid/metal cations = 2:1. To test the effect of pH value on decomposition, the pH were adjusted to 8 and 10, respectively, with ammonia solution, and then clear transparent Sr–Ba–Nb nitrate precursor solutions had high stability and no precipitation for several months after preparation was obtained with continuous stirring.

2.3. SBN thin film process

The Sr–Ba–Nb precursor solution was heated at 80 °C to obtain a desired viscosity of 15 mPa s. Then this homogeneous solution was spin-coated onto $Pt/Ti/SiO_2/Si(100)$ substrates of 1×2 cm^2 at 4000 rpm for 20 s. After each coating, the film was dried in air at 120 °C for 30 min and was calcined at 400 °C for 1 h to remove the organic contents. The process was performed 10 times to achieve the desired film thickness. Finally, the films were annealed at 400, 500, 600 and 700 °C for 2 h, respectively. The thickness of each layer was 50 nm and final film thickness was estimated to be around 0.5 μm by ellipsometer.

For the study of the decomposition behavior of SBN precursors, each precursor solution was dried at 80 °C for 24 h and ground gently. Differential thermal analysis (DTA) and thermogravimetry (TG) were used to analyze the thermal decomposition behavior of the powdered precursors with a heating rate of 10 $°C \cdot min^{-1}$ in air up to 800 °C. The crystallization process of the prepared films was studied by X-ray diffraction. The surface morphology of the film was examined by scanning electron microcopy (SEM). Dielectric properties were measured via HP 4294 A impedance analyzer. Ferroelectric properties were obtained by using RT66 A ferroelectric tester.

3. Results and discussions

3.1. The effect of pH value and molar ratio of EDTA: metal ions

It suggests that pH value might affect the chelation between the cation and the associated carboxylate acid ion. In this work, the pH value of 8 was used during the synthesis of clear Sr–Ba–Nb precursor solution which was determined by calculation of the conditional formation constant K_{cf} of Sr–EDTA and Ba–EDTA complexes, where K_{cf} represents the modified formation constant for the following complexing reactions.

$$M^{2+} + Y^{4-} \Leftrightarrow MY^{2-} \tag{1}$$

where M^{2+} are divalent metal ions, such as Ba^{2+} and Sr^{2+}, and $Y^{4-} = (CH_2N)_2(CH_2COO)_4^{4-}$. The formation constant for reaction (1) is given by

$$K_f = [MY^{2-}]/[M^{2+}][Y^{4-}] \tag{2}$$

In aqueous solution, EDTA can remain as the compound H_4Y or disassociate increasing numbers of protons to form the species H_3Y^-, H_2Y^{2-}, HY^{3-} or Y^{4-} with the proportions of these species varying with pH values. Since the anion Y^{4-} is the ligand species in complex formation, the complexation equilibria [Eq. (1)] affected markedly by the pH is shifted to left as hydrogen ion concentration is increased due to competition for the chelating anion by hydrogen ion. K_{cf} is given as follows:

$$K_{cf} = \alpha_4 K_f \tag{3}$$

$$\frac{1}{\alpha_4} = \frac{C_{H_4Y}}{[Y^{4-}]} = 1 + \frac{[H^+]}{K_{a4}} + \frac{[H^+]^2}{K_{a3}K_{a4}} + \frac{[H^+]^3}{K_{a2}K_{a3}K_{a4}} + \frac{[H^+]^4}{K_{a1}K_{a2}K_{a3}K_{a4}}$$

where α_4 is the fraction of the total EDTA species that exists as Y^{4-}. $C_{H_4}Y$ represents the total concentration of all forms of uncomplexed EDTA. It can be given by

$$C_{H_4Y} = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^-] + [H_4Y]$$

K_{ai} ($i = 1,2,3,4$) are the dissociation constants of the variously protonated H_4Y, H_3Y^-, H_2Y^{2-} and HY^{3-} forms of

Table 1
Conditional formation constant K_{cf} of Ba–EDTA and Sr–EDTA complexes at different pHs

pH	α_4	Ba–EDTA	Sr–EDTA
2	4.1×10^{-14}	2.36×10^{-6}	1.75×10^{-5}
3	6.3×10^{-11}	3.62×10^{-3}	2.68×10^{-2}
4	3.6×10^{-9}	2.07×10^{-1}	1.53
5	3.5×10^{-7}	2.01×10	1.49×10^{2}
6	2.2×10^{-5}	1.27×10^{3}	9.37×10^{3}
7	4.8×10^{-4}	2.76×10^{4}	2.04×10^{5}
8	5.4×10^{-3}	3.11×10^{5}	2.30×10^{6}
9	5.2×10^{-2}	2.99×10^{6}	2.22×10^{7}
10	3.5×10^{-1}	2.01×10^{7}	1.49×10^{8}
11	8.5×10^{-1}	4.89×10^{7}	3.62×10^{8}
12	9.8×10^{-1}	5.64×10^{7}	4.17×10^{8}

EDTA in aqueous solution, with the values of 1.0×10^{-2}, 2.2×10^{-3}, 6.9×10^{-7} and 5.5×10^{-11}, respectively [13]. Moreover, the formation constants for Ba–EDTA and Sr–EDTA chelates are 5.75×10^{7} and 4.26×10^{8}, respectively [14], and the values of K_{cf} for various pH values can be calculated according to Eq. (3) and are shown in Table 1. The data show that with the increase of the pH, both the value of α_4 and K_{cf} increase indicating that more EDTA is ionized and more carboxylic groups can be available to chelate the metallic ions in the solution at higher pH conditions. When the pH value is above 8, the conditional formation constant is high enough to form stable metal EDTA complexes. In addition, Narendar has reported that the citrato–niobium bond is unstable at $\mathrm{pH} < 5$, and the precipitation of niobium hydrate is observed [15]. Consequently, the stable Sr–Ba–Nb precursor solutions should be synthesized at $\mathrm{pH} > 8$ to ensure complete chelation of all the cations according to the above results.

Fig. 1 shows the DTA and TG curves for the two powdered precursors obtained at different pHs. Both of the TG-DTA curves involve three primary stages. The first stage weight loss corresponding to a broad endothermic event occurs between 50 and 200 °C, which can be attributed to the loss of free and bound water from the gels. The second stage weight loss between 280 and 400 °C corresponds to an exothermic peak. This can be attributed to the decomposition of the metal carboxylate precursors and liberation of NO_2, CO_2 and H_2O. The third weight loss between 500 and 600 °C corresponding to another exothermic peak may be due to the oxidation of the residual organic groups in the precursors. No further weight loss up to 800 °C and no clear exothermic peak corresponding to SBN crystallization were found; it is probably masked with the strongest exothermic event around ~ 550 °C.

For the Sr–Ba–Nb precursor obtained at higher pH values, a much sharper exothermic peak and a weight loss of volatile materials were observed. The sharp decomposition of the precursor at pH = 10 leads to generation of a large amount of heat and gaseous reaction products. This is due to the addition of excess of ammonia. The ammonia can react with the NO_3 groups from the nitrate precursor to form ammonium nitrate which is strongly oxidizing and greatly accelerates the decomposition of the powdered precursor on heating, producing strongly exothermic reactions. These reactions can result in the destruction of the films derived from the precursor. Consequently, the addition of excess of ammonia is deleterious and to be avoided in the synthesis of SBN thin films by using the aqueous organic gel routes. The optimum pH value for the formation of clear homogeneous Sr–Ba–Nb precursor solution is 8.

In spite of chelation of all the metal cations in the Sr–Ba–Nb precursor solution, white precipitations identified as barium or strontium ethylenetetracetate hydrate were formed during dehydration. Using excess EDTA in the Sr–Ba–Nb precursor solution can circumvent the precipitation

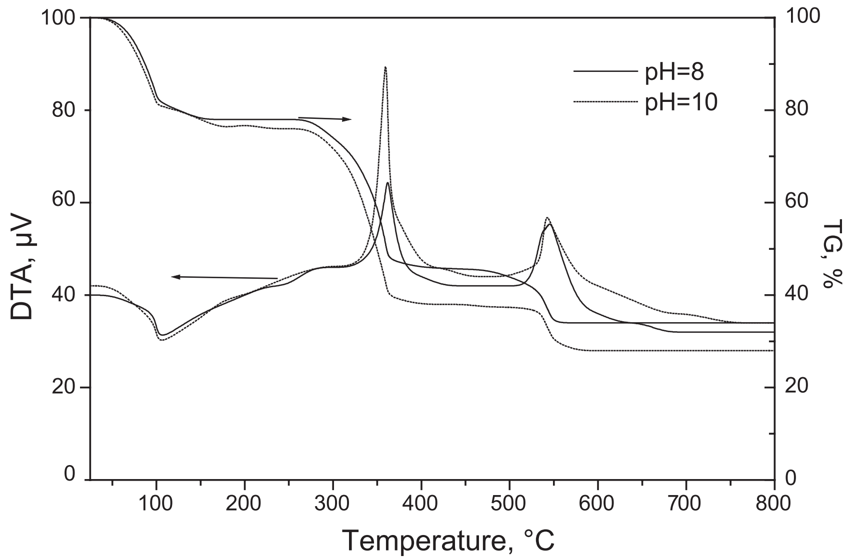

Fig. 1. TG/DTA curves of the Sr–Ba–Nb precursors obtained at different pH values.

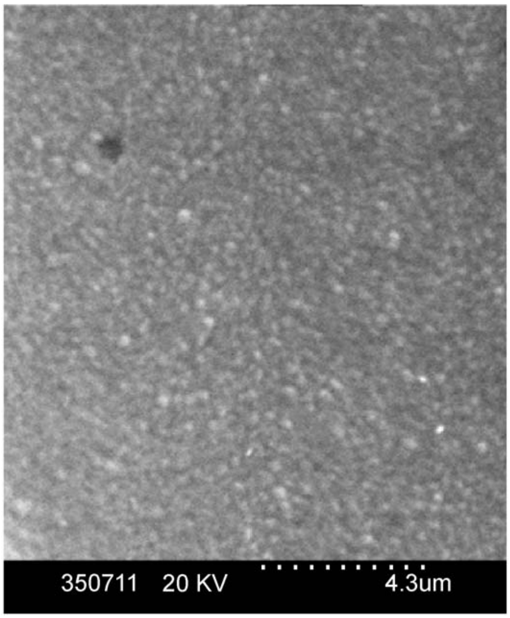

Fig. 2. SEM micrograph of surface morphology of SBN thin films derived from the precursor solution at pH = 8.

problem. Consequently, the optimum ratio of EDTA/metal ions is 2:1.

SEM micrograph of surface morphology of SBN thin film derived from the precursor solutions at pH = 8 was shown in Fig. 2. The film's surface looked smooth and densely packed. While for the precursor solution at pH = 10, films with cracks were obtained. The observation is consistent with the above analysis.

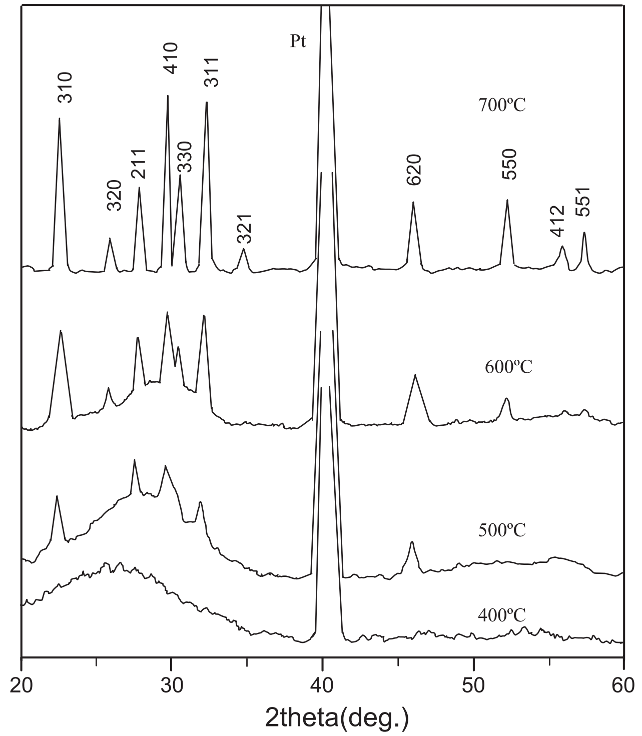

Fig. 3. X-ray diffractograms of the films annealed at different temperatures.

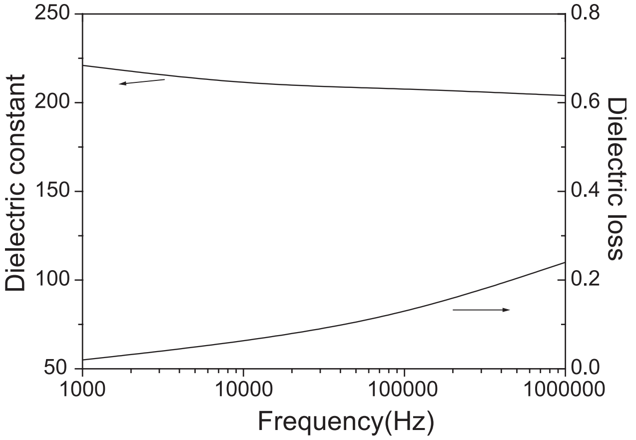

Fig. 4. Dielectric constant and loss tangent as a function of frequency for SBN50 thin film annealed at 700 °C.

3.2. Phase transformation and electrical properties

Fig. 3 shows the XRD patterns of SBN films samples annealed in air at different temperatures from 400 to 700 °C for 2 h. A clear transition from amorphous state to crystalline state could be noticed. The film was amorphous in structure, as shown by the broad continuum at 400 °C, which required to be calcined at elevated temperature to yield SBN phase. We detected the first appearance of tetragonal tungsten bronze phase SBN in the sample heated at 500 °C. As the temperature is increased, the intensities of the diffraction peaks are strengthened which indicates the improved crystallinity. The films are polycrystalline, showing no *c*-axis-preferred orientation, but rather random orientation. Lattice parameters calculated for the film heat-treated at 700 °C were $a = b = 12.4656$ nm and $c = 3.9527$ nm. These values are close to the bulk material ($a = b = 12.4652$ nm and $c = 3.9521$ nm).

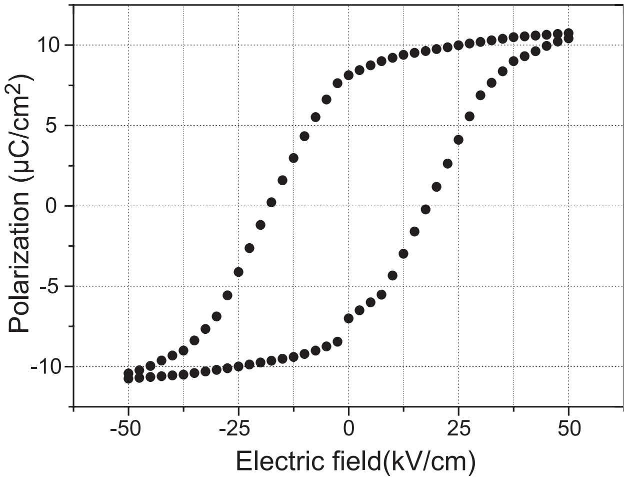

Fig. 5. P-E hysteresis loop of SBN50 thin film.

Table 2
Comparison between the electrical properties of SBN thin films obtained by aqueous organic gel and other processing methods

Reference	Materials	Synthesis methods	ε_r	Pr (μC/cm^2)	E_c (kV/cm)
Present work	$Sr_{0.5}Ba_{0.5}Nb_2O_9$	aqueous organic gel	221	8.17	16.9
Sakamoto et al. [7]	$Sr_{0.5}Ba_{0.5}Nb_2O_9$	sol–gel	79	1.9	180
Nishio et al. [16]	$Sr_{0.3}Ba_{0.7}Nb_2O_9$	sol–gel	–	5.1	1.2
Kakimoto et al. [17]	$Sr_{0.3}Ba_{0.7}Nb_2O_9$	PLD	1200	12.8	3.1
Cheng et al. [5]	$Sr_{0.5}Ba_{0.5}Nb_2O_9$	PLD	210	–	–

Fig. 4 shows the variation of dielectric constant and tan δ for SBN50 films as a function of frequency. Dielectric constant values of 221 and 210, and dielectric loss values of 0.02 and 0.06 were obtained for the SBN thin films at measuring frequencies of 1 and 10 kHz, respectively.

Fig. 5 shows a typical polarization-electric field (P-E) hysteresis loop (measured at room temperature, 1 kHz) for a SBN thin film. The remnant polarization (P_r) and the coercive field (E_c) were 8.17 μC/cm^2 and 16.9 kV/cm, respectively.

These values are comparable with SBN thin films having similar compositions and obtained by different processing methods. Table 2 shows the dielectric constant, P_r and E_c observed in the present work and in the literatures. Sakamoto et al. [7] prepared SBN films by sol–gel method; however, the reported electrical properties are not good. The value of dielectric constant for the SBN thin film is improved by using aqueous organic gel method, which is higher than that prepared by sol–gel method. Better results are reported by Kakimoto et al. [17] for SBN films; however, the films were heat-treated in oxygen atmosphere. These results suggest that altering the processing method may improve the electrical properties of SBN films.

4. Conclusions

Polycrystalline ferroelectric $Sr_{0.5}Ba_{0.5}Nb_2O_6$ thin films have been obtained by the aqueous organic gel method. XRD and SEM have been used to characterize the films, and the results have shown that smooth and crack-free SBN thin films with a single tetragonal tungsten bronze phase were deposited on Pt/Ti/SiO_2/Si(100) substrates. The SBN thin films showed good P-E hysteresis loop and high dielectric constant.

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References

[1] Y. Xu, Ferroelectric Materials and Their Applications, North Holland, Amsterdam, 1991, p. 254.
[2] M.D. Ewbank, R.R. Neurgaonkar, W.K. Cory, J. Feinberg, J. Appl. Phys. 62 (1987) 374–375.
[3] R.B. Maciolek, S.T. Liu, J. Electron. Mater. 2 (1973) 191–193.
[4] R.R. Neurgaonkar, M.H. Kalisher, T.C. Lim, E.J. Staples, K.I. Keester, Mater. Res. Bull. 15 (1980) 1235–1237.
[5] H.F. Cheng, G.S. Chiou, K.S. Liu, I.N. Lin, Appl. Surf. Sci. 113–114 (1997) 217–221.
[6] K. Kakimoto, H. Kakemoto, A. Baba, J. Eur. Ceram. Soc. 21 (2001) 1569–1572.
[7] W. Sakamoto, T. Yogo, K. Kikuta, J. Am. Ceram. Soc. 79 (1996) 2283–2288.
[8] E.J.H. Lee, F.M. Pontes, E.R. Leite, E. Longo, J. Mater. Sci. Lett. 19 (2000) 1457–1459.
[9] M.S.J. Nues, E.R. Leite, F.M. Ponte, Mater. Lett. 49 (2001) 365–370.
[10] F.M. Ponte, E.R. Leite, E.J.H. Lee, J. Eur. Ceram. Soc. 21 (2001) 419–426.
[11] S.M. Zanetti, E.B. Araujo, E.R. Leite, Mater. Lett. 40 (1999) 33–38.
[12] S.M. Zanetti, A.E. Longo, J.A. Varela, E.R. Leite, Mater. Lett. 31 (1997) 173–175.
[13] R.N. Das, P. Pramanik, Mater. Lett. 46 (2000) 7–9.
[14] G.D. Christian, Analytical Chemistry, Wiley, New York, 1986, p. 226.
[15] M.A. Earl, Critical Stability Constants, vol. 5, Plenum, New York, 1974, p. 75.
[16] K. Nishio, Y. Watanabe, T. Tsuchiya, J. Sol-Gel Sci. Technol. 26 (2003) 245–250.
[17] K. Kakimoto, H. Kakemoto, A. Baba, J. Mater. Sci. 37 (2002) 3045–3051.