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Mechanical Behaviour and Electrical Conductivity of Oxygen Separation Membrane under Uniaxial Compressive Loading

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***Abstract*—**The mechanical deformation and the electrical conductivity of lanthanum strontium cobalt ferrite oxide under uniaxial compression were investigated at various temperatures up to 1073 K. The material reveals a rather complex mechanical behaviour related to its ferroelasticity and completely different stress-strain curves are obtained during the 1st and 2nd loading cycles. A distinctive ferroelastic creep was observed at 293 K whilst typical ferroelastic stress-strain curve were obtained in the temperature range from 473 K to 873 K. At 1073 K, on the other hand, high-temperature creep deformation was observed instead of ferroelastic deformation. The conductivity increases with increasing compressive stress at all the temperatures. The increase in conductivity is related to both geometrical and piezoelectric effects. From 293 K to 873 K, where the material exhibits ferroelastic behaviour, the variation in the total conductivity decreases with increasing temperature. The contribution of the piezoelectric effect to the total conductivity variation also decreases with increasing temperature and the maximum in piezoconductivity has a value of about 0.75 % at 293 K for a compressive stress of 100 MPa. There is no effect of domain switching on conductivity except for the geometric effect. At 1073 K, the conductivity is simply proportional to the compressive strain.

***Keywords*—**Ferroelasticity, Piezoconductivity, oxygen separation membrane, perovskite.

I. Introduction

LANTHANUM cobaltite based perovskites (LCO) have been the focus of a large number of studies due to their potential for various electrochemical applications such as oxygen separation membrane or cathode for solid oxide fuel cells (SOFCs) [1-4]. In particular for the application as oxygen separation membrane the material has to be a very good mixed oxygen-ionic electronic conductor (MIEC), where typically the electronic conductivity is significantly higher than the ionic conductivity, hence the latter being the limiting factor for the application. A numbers of investigations have focused on the improvement of ionic conductivity or oxygen flux by doping different ions on A and/or B-site of the initial LCO [1-4]. In particular, La-Sr-Co-Fe-O (LSCF) has emerged to be one of most promising materials for the use as separation membrane since it has satisfying thermal stability and electrochemical properties, especially a rather high oxygen permeation [2, 5-7].

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Despite of numerous studies on electrochemical properties, numbers of investigations on mechanical properties are limited [8-14]. The mechanical properties such as elastic modulus and fracture properties have been investigated by means of for example resonance method and bending test. Aiming at the application limits, creep at high temperature has been also studied [13]. The lanthanum cobaltite variants are known to display ferroelastic behaviour [8,10,14-17], which is a ferroic effect observed in the mechanical behaviour [18]. In fact, ferroelastic domain switching has been observed in-situ under the application of compressive loads at room temperature [14,15]. A reported non-linear behaviours as well as hysteresis in stress-strain curves especially at low temperatures have been attributed to the ferroelasticity [8,10,17]. Furthermore, creep effects due to the ferroelasticitiy, i.e., ferroelastic creep, have been reported to occur for some lanthanum cobaltite variants under uniaxial compression [16].

On the other hand A or B-site doped LCO [19-21] and other related systems [22-24] have been intensively studied in recent years due to their attractive electronic and magnetic properties and a strong effect of stresses / strains on electrical conductivity has already been confirmed [19-24]; however these experiments have been conducted at rather low temperatures (near the Curie temperature), aiming at different applications and especially the global effect of the ferroelastic behaviour has not been considered.

The first part of this paper presents respective results and discussions on the ferroelastic deformation behaviour of LSCF under uniaxial compressive stress as a function of temperature. In the second part, the electrical conductivity of LSCF under mechanical loading and its relationship to ferroelastic deformation will be presented and discussed.

II. Mechanical Behaviour

A. Experimental Procedure

La0.58Sr0.4Co0.2Fe0.8O material prepared at IEK-1, Jülich Forschungszentrum GmbH [11], was investigated in the present experiment. Fig. 1 illustrates schematically the experimental setup. The prepared sample was placed on an alumina ceramic table between the loading rods of a mechanical testing machine (1362, Instron) that was equipped with an electrical furnace. A semi-spherical alumina ceramics was used for alignment and load transfer to the specimen and a compressive preload of 3 N was applied for specimen fixation (i.e. corresponding to a stress of ~ 0.3 MPa). For elevated

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temperatures a heating rate of 8 K/min was used, followed by a dwell period of more than 1 h before testing. In the mechanical test, the compressive load was raised to 903 N with a loading rate of 100 N/min (i.e. 100 MPa). After some holding period at 903 N, which were normally more than 1 min, the load was decreased to 3 N using the same rate. Whilst the loading and unloading cycle was repeated twice or three times, the applied load and the deformation of the sample were measured by the load and a displacement sensor as illustrated in Fig. 1 to obtain stress-strain curves. The testing temperatures ranged from 293 K (room temperature) to 1073 K. After the tests at each temperature, i.e., after the 2nd or 3rd cycle, the specimen was heated up at 1273 K at the same rate of 8 K/min and annealed for 1 h at 1273 K and then cooled down to room temperature before next test at a particular temperature was carried out. The deformation of the displacement sensor was separately measured and subtracted from the measured displacement (compliance correction). The equipment for the conductivity also shown in Fig. 1 will be explained in the next chapter.

B. Results

Fig. 2 represent the stress-strain curves for the 1st and 2nd loading cycle at different temperatures. The stress-strain curves display a visible anomaly related to the ferroelastic characteristic of the material. At 293 K, the stress increases nonlinearly with strain and shows significant ferroelastic creep at the applied maximum stress of 100 MPa. A ferroelastic hysteresis can be seen clearly for the 2nd loading cycle. The stress-strain curves at 473 K and 873 K illustrate a similar behaviour: in the 1st cycle, the elevated stress reaches a critical stress, where ferroelastic domains starts to switch, followed by a steeper slope due to a completion of the switching, whilst a small but clear ferroelastic hysteresis can be observed for the 2nd cycle. At 1073K, where the now cubic material is not ferroelastic anymore, the nonlinear behaviour reflects high-temperature creep [13].

It should be noted that the results were completely different when the test was sequentially conducted from 293 K to 1073 K without annealing process between the tests.

C. Discussion

The Young's modulus cannot be easily evaluated if the stress-strain curves are nonlinear. The apparent elastic characteristic was hence evaluated in several different ways. Fig. 3(a) gives the different apparent elastic moduli obtained from the stress-strain curves, where the initial modulus E_{ini} is calculated from the initial slope of the 1st loading and the unloading moduli E_{unld1} and E_{unld} from the slopes of the beginning part of the unloading curve of the 1st and the last cycles, respectively. For the 1st cycle, the initial modulus E_{ini} is about 75 GPa at 293 K, and it shows a huge decrease from 293 K to 473 K whilst it increases again. The modulus Eunld1 ranges from 80 GPa to 120 GPa, hence being much higher than Eini, and decreases from 293 K to 573 K and gradually increases from 573 K to 1073 K. The modulus values of the last cycle Eunld are very similar to Eunld1. All the values are between 20 GPa and 110 GPa, which are in a comparable range to reported moduli of the same composition [10,11,13,14] measured by different methods. The rather strong decrease observed from 293 K to 473 K might be attributed to the movement of domain walls [25] and/or a remnant effect of the ferromagnetic transition at ~ 235 K [12]. The increase in the modulus at the high temperature can be related to the rhombohedral to cubic phase transition [11], which will be accompanied by the disappearance of ferroelastic effects.

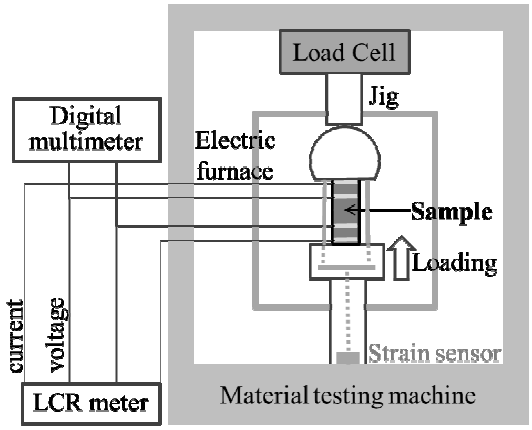


Fig. 1 Experimental setup for compressive test at elevated temperature

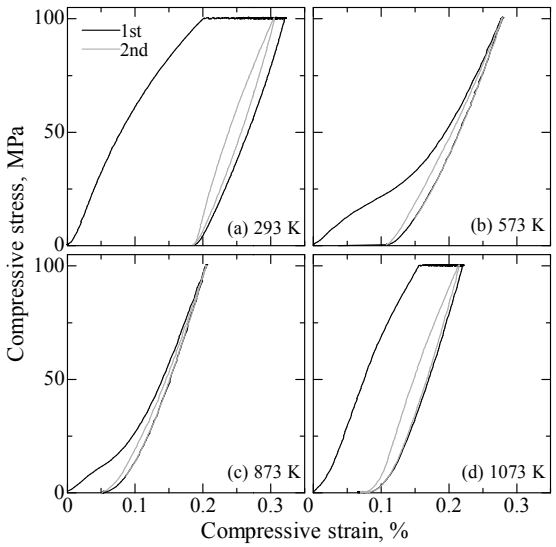


Fig. 2 Stress-strain curves measured at
(a) 293 K, (b) 473 K, (c) 873 K, and (d) 1073 K

Fig. 3(b) shows the maximum and minimum critical stresses σ_c, where the strain shows a progressive increase due to the domain switching, obtained from the stress-strain curves. Only a minimum value could be estimated at 293 K, whereas only a maximum value could be determined at 1073 K. The estimated average critical stress is higher than 80 MPa at 293 K, and it monotonically decreases with increasing temperature up to 1073 K. The decrease from 293 K to 473 K seems to be most significant. A decrease in critical stress at elevated temperatures has been reported for ferroelastic materials, which has been explained by a reduced energy barrier for domain

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switching at high temperature [26].

Fig. 4 shows the deformations at 293 K and at 1073 K under a constant load of 100 MPa. The sample compressed with 100 MPa at 293 K shows a huge deformation during 1 h. Such an effect is known as ferroelastic creep due to domain switching [16,27,28], which saturates for longer holding time, since the amount of switchable domains is limited. It should be noted that ferroelastic strain was already observed for holding times of only 1 min at stresses exceeding 30 MPa. The sample compressed at 1073 K with a constant stress of 100 MPa also reveals an increasing deformation with time, although the absolute value is smaller than at 293 K. Unlike the deformation at 293 K, it still increases even after 1 h without any signs of saturation and can therefore be attributed to the primary region of the reported high temperature creep [13].

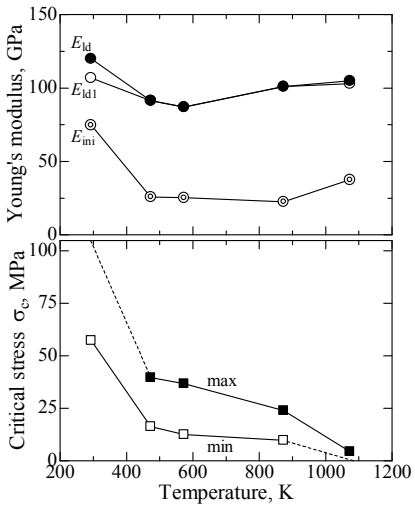


Fig. 3 Temperature dependence of (a) apparent elastic moduli and (b) critical stress

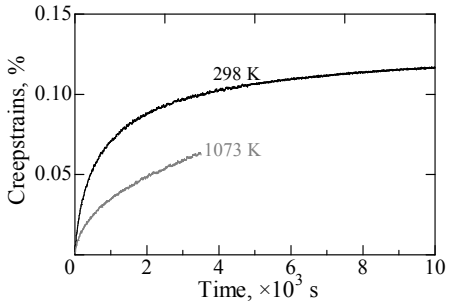


Fig. 4 Ferroelastic creep strain at 293 K and high-temperature creep strain at 1073 K

III. Electrical Conductivity

A. Experimental Procedure

The same experimental setup was used for the present measurement of the electrical conductivity as shown in Fig. 1. The four-terminal method was employed and the electrical conductivity was measured simultaneously during the compressive test in the previous chapter. A direct electric current I of about 40 mA was applied during the compression test and the voltage V was measured by a LCR meter (Hioki E.E., 3532-50). The voltage was also measured by a digital multimeter (Agilent technologies, U1251B). The electrical conductivity σ was simply calculated by: $\sigma = L\Delta I / A\Delta V$, where L is the span between the voltage electrodes and A is the cross-section area of the specimen. Note, deformations related to thermal or chemical expansions at higher temperatures are not considered in the calculation. The conductivity was measured in the direction parallel to the compressive loading as illustrated in Fig. 1.

B. Results

Fig. 5 shows the development of the conductivity σ during the compression test. The conductivity increases with increasing compressive strain at all temperatures. The increasing and decreasing conductivity behaviours are similar to the behaviour of the stress for the temperature range 293 K to 873 K shown in Fig. 2, although the conductivity value after the loading/unloading cycle is higher than the initial value. There is a conductivity hysteresis at 293 K and 473 K. The values of the conductivity are relatively scattered especially at 873 K since the measured voltage and also its variation with the strain were rather small. The effect of the strain caused by ferroelastic creep at 293 K is clearly visible in the conductivity, whereas the strain due to high-temperature creep at 1073 K is not reflected in the conductivity. The increase in the conductivity is approximately 1 % under the action of the compressive stress of 100 MPa, whereas the effect on the strain is smaller than 0.4 % for all temperatures.

Fig. 6 illustrates how the conductivity depends on the applied compressive stress. The conductivity and the stress have an almost linear relationship despite the anomaly in the stress - strain curves in Fig. 2. The conductivity dependency is almost identical at each temperature except for the beginning of the 1st loading. The clear conductivity hysteresis can be seen at 293 K and also 1073 K unlike the case of the conductivity – strain behaviours Fig. 5.

C. Discussion

The conductivity increases with increasing compressive stress / strain at all temperatures. Some of this increase can be related to the change in geometry by the compressive stress since it will lead to a shortening of the specimen and an enlargement of its cross-sectional area. However, the variation in conductivity is larger than that in the strain. The variation in the conductivity $\Delta\sigma$ can therefore only partially be attributed to the change in geometry, defined as $\Delta\sigma_g$, and the main contribution will be related to a piezoelectric effect, being defined as $\Delta\sigma_p$. The contribution of the geometry change to the conductivity can be taken into account as: $\sigma = (L + \delta L)\Delta I / (A + \delta A)\Delta V$, where the change in the length δL (< 0) is simply determined by the strain and the change in the cross-section area δA (> 0) can be calculated from δL and the materials' Poisson's ratio ($\nu = 0.3$ [29]).

Fig. 7 presents the variation of $\Delta\sigma$ as and $\Delta\sigma_p$ with stress during the loading of the 1st cycle and the unloading of the 2nd cycle, where the values are normalised by the conductivity before the respective loading, σ_0. Both the total variation and

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piezoelectric effect decrease with increasing temperature up to 873 K and show only a small increase at 1073 K. There is a good agreement in the behaviour for all loading and unloading cases for the piezoelectric effect (not all shown here). The contribution of the piezoelectric effect to the total conductivity change is larger at lower temperatures, e.g. 80 % at 293 K, and it decreases to lower than 50 % at 873 K. The geometric effect $\Delta\sigma_g$, which is equal to the difference of total and piezoelectric variations, has a peak at 473 K and shows a monotonic decrease with increasing temperature up to 1073 K as can already be seen in the behaviour of the maximum strains in Fig. 2.

Although there has been no study quoting a direct effect of an uniaxial stress on the electrical conductivity (piezoconductivity) or resistivity (piezoresistivity) of LSCF at membrane and SOFC operation relevant elevated temperatures as presented here, effects of stress or strain on electrical resistivity of lanthanum oxide perovskites have been investigated at and below room temperature [19-21]. Although most of those investigations intended to obtain a giant piezoresistivity by applying large stresses / strains near the Curie temperature T_c, some variation in the resistivity with applied stress / strain has been also observed at temperatures above T_c, where the materials exhibit paramagnetic characteristics, and the fraction is comparable to the results reported in the present study. The LSCF variant used in the current experiment has a Curie temperature T_c of around 235 K and the phase transition temperature from rhombohedral to cubic is between 973 K and 1073 K [11]. The stress influences T_c and its effect on the resistivity is strongest around T_c as described above [19-23]; the piezoelectric effect observed in this study could be large at the room temperature and decrease with temperature. Considering the temperature dependence of the piezoelectric effect between 293 K and 873 K, the activation energy for the hole-conduction could be slightly decreased by the compressive stress, which may be related to the change in the bandwidth W. The reason for the slight increase of the piezoelectric effect at 1073 K, on the other hand, is not clear but the stress might have an influence on the transition temperature, in a similarly as for the effect on T_c, which requires more detailed future studies at elevated temperatures.

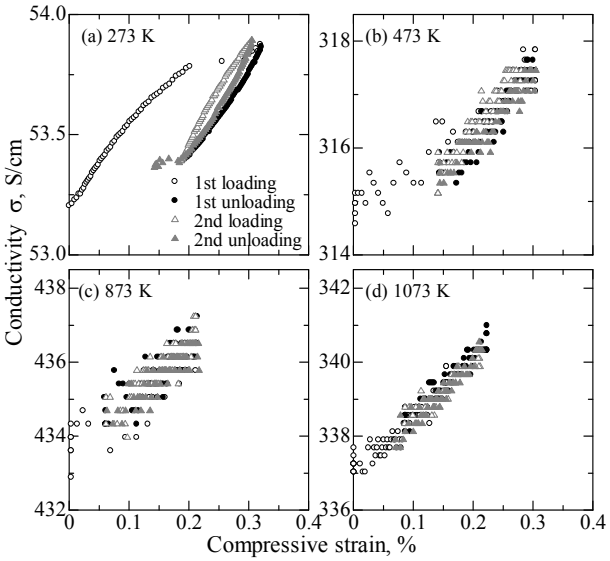


Fig. 5 Conductivity change with compressive strain at (a) 293 K, (b) 473 K, (c) 873 K, and (d) 1073 K

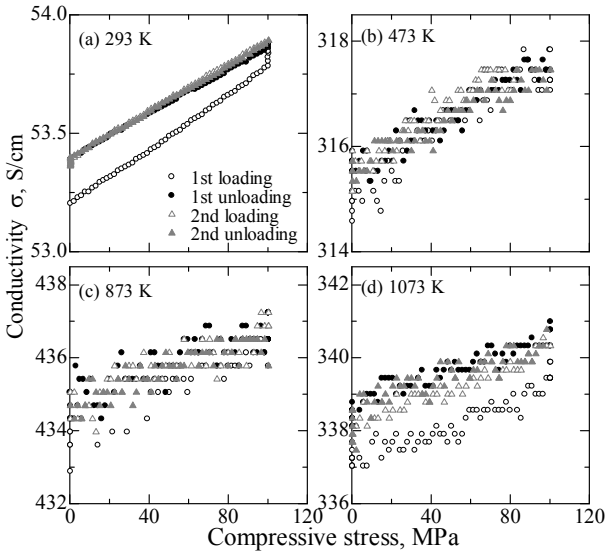


Fig. 6 Conductivity change with compressive stress at (a) 293 K, (b) 473 K, (c) 873 K, and (d) 1073 K

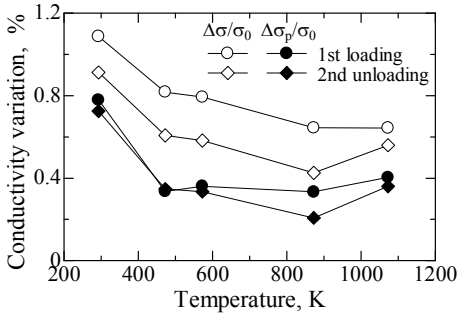


Fig. 7 Temperature dependence of variations of total conductivity $\Delta\sigma$ and piezoconductivity $\Delta\sigma_p$ with 100 MPa of compressive stress

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IV. Conclusion

In the present study, the mechanical behaviour and the electrical conductivity of LSCF were examined under the uniaxial compressive loading at elevated temperature up to 1073 K.

The material reveals a rather complex mechanical behaviour related to its ferroelasticity and completely different stress-strain curves are obtained during the 1st and 2nd loading cycle. A distinctive ferroelastic creep was observed at 293 K, whilst typical ferroelastic stress-strain curve were obtained in the temperature range 473 K to 873 K. At 1073 K, on the other hand, high-temperature creep deformation was observed instead of ferroelastic deformation. The apparent elastic modulus was evaluated from various parts of the stress-strain curves; the modulus determined by the last unloading curve was ranged between 85 GPa and 120 GPa. The obtained critical stress monotonically decreases from about 80 MPa to zero with increasing temperature, corresponding to the behaviour of the remnant strain.

The conductivity increases with increasing compressive stress at all temperatures. The increase in conductivity can be related to both geometrical and piezoelectric effects. From 293 K to 873 K, where the material exhibits ferroelastic behaviour, the variation in the total conductivity decreases with increasing temperature. The contribution of the piezoelectric effect to the total conductivity variation also decreases with increasing temperature and the maximum in piezoconductivity has a value of about 0.75 % at 293 K for a compressive stress of 100 MPa. There is no effect of domain switching on conductivity except for the geometric effect. At 1073 K, where the ferroelastic characteristic almost disappears and the high-temperature creep behaviour appears, the conductivity is simply proportional to the compressive strain.

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References

[1] Teraoka Y, Zhang HM, Furukawa S, Yamazoe N. Chem Lett 1985; 11:1743.
[2] Stevenson JW, Armstrong TR, Carneim RD, Pederson LR, Weber WJ. J Electrochem Soc 1996; 143:2722.
[3] Kharton VV, Kovalevsky AV, Tikhonovich VN, NaumovichEN, Viskup AP. Solid State Ionics 1998; 110:53.
[4] Sunarso J, Baumann S, Serra JM, Meulenberg WA, Liu S, Lin YS, Diniz da Costa JC. J Membr Sci 2008; 320:13.
[5] Mai A, Haanappel VAC, Uhlenbruck S, Tietz F, Stöver D. Solid State Ionics 2005;176:1341.
[6] Mineshige A, Izutsu J, Nakamura M, Nigaki K, Abe J, Kobune M, Fujii S, Yazawa T. Solid State Ionics 2005;176:1145.
[7] Li K, Tan X, Liu Y. J Membr Sci 2006; 272:1.
[8] Kleveland K, Orlovskaya N, Grande T, Moe AMM, Einarsrud MA, Breder K, Gogotsi G. J Am Ceram Soc 2001;84:2029.
[9] Orlovskaya N, Lugocy M, Pathak S, Steinmetz D, Lloyd J, Fegely L, Radovic M, Payzant EA, Lara-Curzio E, Allard LF, Kuebler J. J Power Sources 2008;182:230.
[10] Huang BX, Malzbender J, Steinbrech RW. Wessel E, Penkalla HJ, Singheiser L. J Membr Sci 2010; 349:183.
[11] Huang BX, Malzbender J, Steinbrech RW. J Mater Sci 2011; 26:1388.
[12] Kimura Y, Kushi T, Hashimoto S, Amezawa K, Kawada T. J Am Ceram Soc 2012; 95:2608.
[13] Huang BX, Steinbrech RW, Baumann S, Malzbender J. Acta Mater 2012;60:2479.
[14] Huang BX, Thermo-mechanical properties of mixed ion-electron conducting membrane. Faculty of Mechanical Engineering, RWTH Aachen, 2010; Huang BX, J Malzbender, Steinbrech RW. Solid State Ionics submitted.
[15] Orlovskaya N, Browning N, Nicholls A. Acta Mater 2003; 51:5063.
[16] Lugovy M, Slyunyayev V, Orlovskaya N, Verbylo D, Reece MJ. Phys Rev B 2008; 78:024107.
[17] Vullum PE, Holmestad R, Lein HL, Mastin J, Einarsrud MA, Grande T. Adv Mater 2007;19:4399.
[18] K Aizu. Phys Rev B 1970; 2:754.
[19] Lengsdorf R, Ait-Tahar M, Saxena S, Ellerby M, Khomskii DI, Micklitz H, Lorentz T,Abd-Elmeguid MM. Phys Rev B 2004;69:140403.
[20] Rata AD, Herklotz A, Nenkov K, Schultz L, Dörr K. Phys Rev B 2008;100:076401.
[21] Zhu QX, Wang W, Zhao XQ, Li XM, Wang Y, Luo HS, Chan HLW, Zheng R. J Appl Phys 2012;111:103702.
[22] Sharma V, Hossu MR, Lee WH, Koymen AR, Priya S. J Mater Sci 2007;42:9841.
[23] Sharma V, Hossu MR, Lee WH, Koymen AR, Priya S. Appl Phys Lett 2006;89:202902.
[24] Tiele C, Dörr K, Fähler S, Schultz L, Meyer DC, Levin AA, Paufler P. Appl Phys Lett 2005;87:262502.
[25] Sheng WX, Fang CJ, Hui K, Jun CZ, Wei L. J Alloys Comp 2011; 509:5029.
[26] Leist T, Webber KG, Granzow T, Aulbach E, Suffner J, Rödel J. J Appl. Phys. 2011;109:054109.
[27] Fett T, Thun G. J Mater Sci Lett. 1998; 17:1929.
[28] Forrester JS, Kisi EH. J Eur Ceram Soc 2004; 24:595.
[29] Huang BX, Steinbrech RW, Baumann S, Malzbender J. Acta Mater 2012;60:2479.