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Superconductivity and Elastic Properties of $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ with $x = 0, 0.02$ and 0.04

(Kesuperkonduksian dan Sifat Kenyal $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ dengan $x = 0, 0.02$ dan 0.04)

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ABSTRACT

The effects of mixed-valence Mn substitution at the Cu site on the superconducting and elastic properties of $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ ($x = 0$, 0.02 and 0.04) were studied. The samples were characterized by X-ray diffraction (XRD) method, temperature-dependent resistance measurements, scanning electron microscopy (SEM) and sound velocity measurements at room temperature. An elastic softening and a decrease in the critical temperature T_c was observed as Mn was substituted for Cu. The Debye temperature θ_D for $x = 0$ and 0.02 void free samples were calculated to be 459 K and 430 K, respectively. Internal lattice strain which is related to lattice parameter ratio a/c did not correlate with T_c. The electron-phonon coupling estimated using the conventional Bardeen-Cooper-Schrieffer (BCS) theory was $\lambda = 0.367$ ($x = 0$) and 0.368 ($x = 0.02$). The electron-phonon coupling in two-dimensional van Hove scenario was calculated to be $\lambda_{vH} = 0.0148$ ($x = 0$) and 0.0149 ($x = 0.02$). These results were compared with other cuprates and related superconductors. The comparison showed that other than electron-phonon coupling, the elastic moduli might play an important role in the mechanism of superconductivity in these materials.

Keywords: Debye temperature; elastic moduli; electron-phonon coupling

ABSTRAK

Kesan penggantian Mn valens bercampur di tapak Cu terhadap sifat superkonduktor dan kenyal $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ ($x = 0$, 0.02 dan 0.04) telah dikaji. Pencirian telah dijalankan melalui kaedah pembelauan sinar-X, pengukuran rintangan elektrik melawan suhu, mikroskop elektron imbasan dan pengukuran halaju bunyi pada suhu bilik. Pelembutan sifat kenyal dan penurunan suhu genting T_c telah dicerap apabila Mn menggantikan Cu. Suhu Debye θ_D untuk sampel tanpa liang $x = 0$ dan 0.02 ialah masing-masing 459 K dan 430 K. Ketegangan dalaman kekisi yang berkait dengan nisbah parameter kekisi a/c tidak berkorelasi dengan T_c. Gandingan elektron-fonon telah dianggarkan menggunakan teori Bardeen-Cooper-Schrieffer (BCS) konvensional iaitu $\lambda = 0.367$ ($x = 0$) dan $\lambda = 0.368$ ($x = 0.02$). Gandingan elektron-fonon untuk senario van Hove dua dimensi ialah $\lambda_{vH} = 0.0148$ ($x = 0$) dan 0.0149 ($x = 0.02$). Keputusan ini telah dibandingkan dengan superkonduktor kuprat dan lain-lain superkonduktor yang berkaitan. Perbandingan ini menunjukkan bahawa selain daripada gandingan elektron-fonon, sifat kenyal mungkin memainkan peranan penting dalam mekanisme kesuperkonduksian bahan ini.

Kata kunci: Gandingan elektron-fonon; modulus kekenyalan; suhu Debye

INTRODUCTION

The superconducting cuprates continue to be an interesting class of materials. Various research efforts such as substitution and addition on the cuprates have been reported (Bagiah et al. 2016; Ilham Putra et al. 2017). Among the cuprate-based high-temperature superconductors (HTSC), $La_{2-x}Sr_xCuO_4$ offers good investigation platform to obtain information in the search for superconducting mechanism in these materials. Its similarity in structural elements with $La_{1-x}Sr_xMnO_3$ which exhibits colossal magnetoresistance (CMR), and both having a perovskite structure, motivates us to explore the physical properties inherent to the CuO_6 octahedra and MnO_6 octahedra, to which the superconductivity and CMR effect is associated with, respectively.

In La_2CuO_4 it is known that the CuO plane is instrumental for superconductivity. Previous experimental results indicated that the substitution for non-Cu site (including Ba, Sr, Ca, Bi, Pb, K, Na and other rare-earth elements i.e. Ln) have a weak influence on T_c. However, for the substitution at Cu site, a few percent of magnetic ions (i.e. Cr, Mn, Fe, Co, Ni) or non-magnetic ions (i.e. Al, Zn, Mg, Ga) can suppress the superconductivity completely. Therefore, probing the effect of chemical substitution at the Cu site would show what property is directly affected along with superconductivity. Many studies had been made on $La_{1.85}Sr_{0.15}Cu_{1-x}A_xO_4$ (A = Cr, Mn, Fe, Ni, Co, Zn, Al, Mg, Ga) system (Bulut et al. 1989; Kochelaev et al. 1994; Xu et al. 1999a, 1999b). Suppression of superconductivity by substitution of 3d

or sp elements was attributed to magnetic pair-breaking effect (Bulut et al. 1989).

Substitution with magnetic ions increases nearest-neighbor spin correlation, while non-magnetic ions decreases spin correlation energy (Ishikawa et al. 1992). In order to compensate for the increase in valence due to trivalent ions substitution, which leads to strong decrease of carrier concentration, double substitution method was widely employed (Ishikawa et al. 1992; Xu et al. 1998; Xu et al. 1999b).

Sound velocity measurement is a very sensitive probe in detecting superconducting phase transition and lattice instabilities. In this work, we investigated the superconductivity and elastic property in mixed valence Mn doped $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ (x = 0, 0.02 and 0.04). The double substitution method is employed in order to maintain the valence balance. The carrier concentration is expected to remain unchanged and the Mn^{3+}/Mn^{4+} ratio is fixed at 1:1. The influence on superconductivity and magnetism had been investigated (Wang et al. 2006). It was found that for $x \leq 0.02$, superconductivity phase co-exists with paramagnetic (PM) phase, between $0.04 \leq x \leq 0.06$ superconductivity phase co-exists with ferromagnetic (FM) phase, and for $0.08 \leq x \leq 0.15$ more Mn ions get together to form FM clusters. In this work, we extended further the investigation to include the effect on the elastic property due to mixed valence Mn substitution at the Cu site. The objectives were to investigate the effects of Mn on the elastic properties and electron-phonon coupling constant of $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$.

EXPERIMENTAL DETAILS

Samples of $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ were prepared by the conventional solid-state reaction method. Starting materials of La_2O_3, $SrCO_3$, CuO and MnO_2 with purity of ≥ 99.9% were used. The mixed powders were ground thoroughly, calcined at 900°C for a period of 36 h with intermediate grinding. The calcined materials were pressed into pellets of 13 mm diameter and 2.5 mm thickness. The pellets were sintered in air at 1150°C for 24 h.

The electrical resistance measurements were carried out using the d.c. four-point probe method with silver paint contacts. The phase was characterized by X-ray powder diffraction (XRD) technique using Bruker AXS D8 Advance Diffractometer with CuK_α radiation. The microstructure of the samples was recorded using a Philips XL 30 scanning electron microscope (SEM). Longitudinal and shear velocity measurements were performed at room temperature by employing the pulse-echo-overlap method utilizing a Matec Model 7700-based system in the MHz range frequency. The sample was bonded to the longitudinal and shear transducer using Nonaq stopcock grease and Sonotech shear gel ultrasonic couplant, respectively. Sound velocity measurements were made on two samples (x = 0 and 0.02) where ultrasonic echoes were observed.

RESULTS AND DISCUSSION

Analysis of XRD patterns (Figure 1) confirmed that all the samples are single phase $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ having tetragonal lattice with space group *I*4/*mmm*. The lattice parameters, internal lattice strain *a*/*c* and unit volume are listed in Table 1. While lattice parameter *a* did not change in a certain manner, *c* showed a decrease with increase in substitution level *x*. Previous studies on other 3D transition metal substitution in this system showed increase in *a* and decrease in *c* with increasing *x*, which leads to increase in *a*/*c* (Mao et al. 1998; Wang et al. 2006; Xu et al. 2004; Zhang & Zhang 2003). The *a*/*c* ratio which indicates internal lattice strain has been attributed to characterize the Jahn-Teller distortion of oxygen octahedron around Cu^{2+} (Xu et al. 2004). The lattice parameters *a* and *c* obtained in this study are in good agreement with those reported previously.

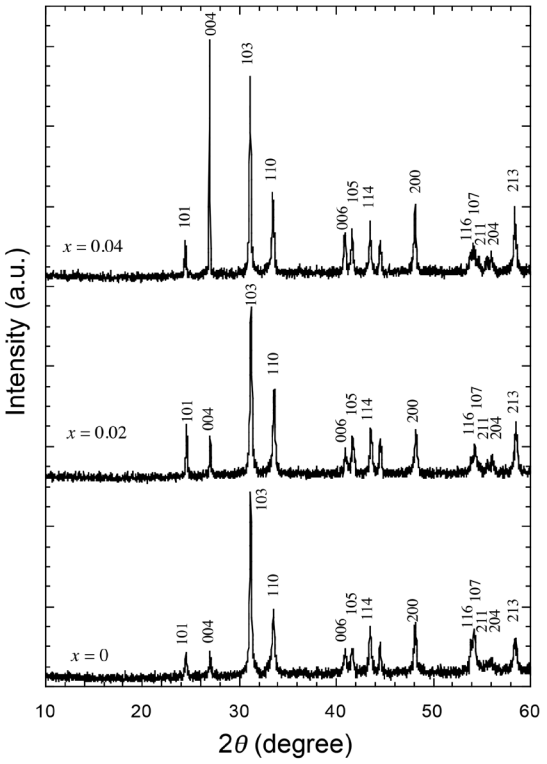


FIGURE 1. X-ray powder diffraction patterns of $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ (x = 0, 0.02, 0.04)

TABLE 1. Lattice parameters *a* and *c*, ratio *a*/*c* and unit cell volume for $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ with x = 0, 0.02 and 0.04

	a (Å)	*c* (Å)	*a*/*c*	*V* (Å^3)
0	3.7815	13.2310	0.2858	189.20
0.02	3.7783	13.2293	0.2856	188.86
0.04	3.7813	13.2262	0.2859	189.11

Figure 2 shows the temperature dependence of resistance for $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ (x = 0, 0.02, 0.04). The x = 0 sample showed a metallic normal state behavior for a broad temperature range with a slight upturn of resistance before undergoing a sharp superconducting transition at T_c = 36 K. The superconducting transition was observed at T_c = 27 K and 22 K for x = 0.02 and x = 0.04, respectively. Similar to x = 0, both the doped samples display metallic behavior over a broad temperature region with a slight upturn of resistance prior to superconducting transition. All samples showed resistance upturn just above T_c. This upturn appeared because the charge carriers tend to be localized at low temperatures. This localization behavior which is evidenced by the variable-range-hopping-type resistivity is similar to that observed in the lower doped $(La_{1-x}Sr_x)_2CuO_4$ system (Takagi et al. 1989). XRD patterns showed that all samples are single phase. This rules out any secondary phase as causing the resistance upturn.

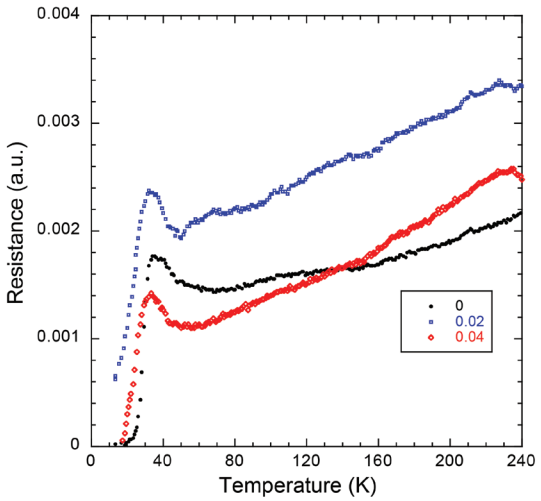
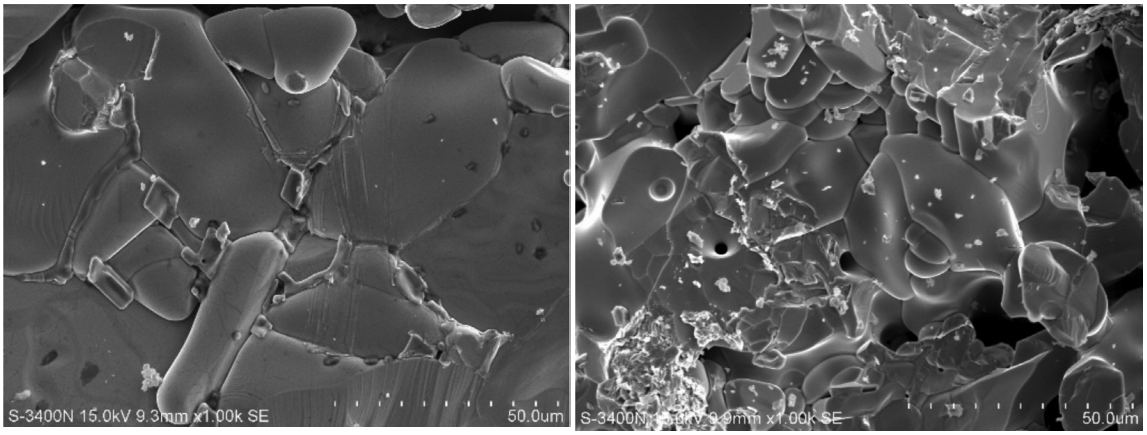
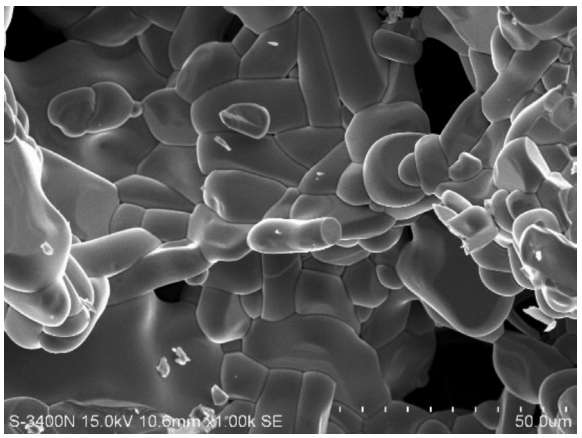


FIGURE 2. Temperature dependence of resistance of $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ (x = 0, 0.02, 0.04)

Figure 3(a), 3(b) and 3(c) shows SEM micrograph for x = 0, 0.02 and 0.04, respectively. Sample with x = 0 showed a highly dense structure consisting of rectangular-shaped grains of varying sizes. The microstructure of sample x = 0.02 and 0.04 is strikingly different than x = 0 in term of porosity. Both samples consist of smaller irregularly shaped grains having voids and pores. Although there were changes in the microstructure, the normal state properties (metallic) did not change for all three samples.



(a) (b)



(c)

FIGURE 3. Scanning electron micrograph of $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ with (a) x = 0, (b) 0.02 and (c) 0.04

The polycrystalline ceramics can be treated as an isotropic elastic material. This medium would have independent elastic moduli; longitudinal modulus L, shear modulus G, bulk modulus B and Young's modulus Y, which can be written as $L = \rho v_L^2$, $G = \rho v_S^2$ and $B = \rho v_L^2 - \frac{4}{3}\rho v_S^2$, $Y = 3GB/(B + G/3)$, where ρ is the mass density, v_s is the shear sound velocity and v_L is the longitudinal velocity. The acoustic Debye temperature can be calculated from the sound velocities using $\theta_D = \left(\frac{h}{k}\right)\left(\frac{3N}{4\pi V}\right)^{1/3} v_m$, where h is the Planck's constant, N is the number of mass-point, V is the atomic volume and v_m is the mean velocity given by $\frac{3}{v_m^3} = \frac{1}{v_L^3} + \frac{2}{v_S^3}$.

The Debye temperature θ_D calculated based on the measured sound velocities (at ~300 K) for $x = 0$ and 0.02 void free samples are 459 K and 430 K, respectively. The longitudinal (v_L) and shear (v_s) velocities, the related elastic moduli, and Debye temperature θ_D are presented in Table 2. Increase in Mn substitution level from $x = 0$ to 0.02, led to decrease in T_c and θ_D. The Debye temperature θ_D of $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ system is at the upper limit of the range of acoustic θ_D reported for various cuprate high temperature superconductors, which is in 250-500 K range (Abd-Shukor 2002).

In the simplest form, according to the Bardeen-Cooper-Schrieffer (BCS) theory, $T_c = 1.13\theta_D e^{-1/\lambda}$, where λ is the electron-phonon coupling constant. The van Hove scenario takes into account the singularity in the density of states at the Fermi level of a two-dimensional system. In this scenario, the transition temperature can be written as $T_c = 27.2\theta_D e^{-1/\sqrt{\lambda_{vH}}}$, where λ_{vH} is the van Hove electron-phonon coupling constant (Getino et al. 1992). The electron-phonon coupling constant estimated using the conventional BCS theory for $x = 0$ and 0.02 was $\lambda \sim 0.367$ and 0.368, respectively. The electron-phonon coupling estimated from the two-dimensional van Hove scenario for $x = 0$ and 0.02 was $\lambda_{vH} \sim 0.0148$ and 0.0149, respectively. The electron-phonon coupling from both mechanisms did not show significant variation as Mn was substituted. The electron-phonon coupling constants λ and λ_{vH} depend both on Θ_D and T_c. In our samples there was only slight change in λ and λ_{vH} due to the simultaneous change in both Θ_D and T_c which kept the electron-phonon coupling constants invariant. This result showed that the electron-phonon coupling is not the only factor in determining T_c.

The electron-phonon coupling constant for $EuBa_2Cu_3O_{6.98}$ (θ_D = 457 K, T_c = 90 K) using the conventional BCS theory and van Hove scenario is $\lambda = 0.57$ and $\lambda_{vH} = 0.041$, respectively. While those for $ErBa_2Cu_3O_{6.9}$ (θ_D = 375 K, T_c = 94 K) is λ = 0.66 and λ_{vH} = 0.046, respectively (Abd-Shukor 2007). The results are similar with this work on the $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ in terms of the order of magnitude of λ and λ_{vH}. However, in our samples the Debye temperature increased with increasing T_c and this is consistent with previous reports on various families of the HTSC (Ledbetter 1994). The electron-phonon coupling constant for other related superconductors are shown in Table 2. The Debye temperature of our La-based void free samples (T_c = 38 and 27 K) are comparable with $YBa_2Cu_3O_{7-d}$ with T_c = 91 K (Nikiforov et al. 2016). However, the electron-phonon coupling is higher for the $YBa_2Cu_3O_{7-d}$ (λ = 0.6 and λ_{vH} = 0.0426).

In conclusion, the effect of mixed valence Mn substitution at the Cu site in $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ on superconductivity, structure and elastic property has been investigated. As Mn content was increased the critical temperature T_c and Debye temperature θ_D decreased. The calculated θ_D from the sound velocity measurements (at ~300 K) is 459 K and 430 K, respectively. The Debye

TABLE 2. Transition temperature T_c, longitudinal velocity (v_L), shear velocity (v_s), shear modulus (G), bulk modulus (B), Young's modulus (Y), Debye temperature (θ_D) (void free), Bardeen-Cooper-Schrieffer (BCS) electron-phonon coupling (λ), van Hove electron-phonon coupling (λ_{vH}) of $La_{1.85-1.5x}Sr_{0.15+1.5x}Cu_{1-x}Mn_xO_4$ with $x = 0$ and 0.02 and other related superconductors. (Numbers in parenthesis are experimental values)

Sample	T_c (K)	v_L (m s^{-1})	v_S (m s^{-1})	G (GPa)	B (GPa)	Y (GPa)	θ_D (K)	λ	λ_{vH}	Ref.
$x = 0$	38	5690 (5160)	3230 (2930)	72.6 (49.3)	129 (87.7)	183 (125)	459 (417)	0.367	0.0148	This work
$x = 0.02$	27	5170 (4470)	3030 (2620)	63.8 (35.6)	101 (56.4)	158 (88.2)	430 (372)	0.368	0.0149	This work
$FeTe_{0.5}Se_{0.5}$	13.5	3550	1970	22.8	46.4	62.2	334	0.300	0.024	Abd-Shukor et al. 2017
$YBa_2Cu_3O_{7-d}$	91	4537	2895	50.1	56.4	116.0	426	0.600	0.0426	Nikiforov et al. 2016
$MgCNi_3$	8	6270	3100	61.5	171.1	168.2	460	0.25	0.018	Abd-Shukor 2013
LaOFeP	4	7980	4800	99.0	69.1	169.1	491	0.202	0.0152	Abd-Shukor & Kong 2011
LiFeAs	18	8250	4820	58.0	92.8	144.0	509	0.289	0.0152	Abd-Shukor & Kong 2011
MgB_2	39	9030	5390	74.2	96.6	177.2	819	0.31	0.024	Ichitsubo et al. 2002

temperature showed lattice softening with the reduction of T_c and this is generally observed in the cuprate superconductors. This finding is important in the search for superconducting mechanism in these materials.

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