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Structure and physical properties for a new layered pnictide-oxide: BaTi₂As₂O

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Abstract

We have successfully synthesized a new layered pnictide-oxide: BaTi₂As₂O. It shares similar characteristics with Na₂Ti₂Sb₂O. The crystal has a layered structure with a tetragonal $P4/nmm$ group ($a = 4.047(3)$ Å, $c = 7.275(4)$ Å). The resistivity shows an anomaly at 200 K, which should be ascribed to an SDW or structural transition. The SDW or structural transition is confirmed by magnetic susceptibility and heat capacity measurements. These behaviors are very similar to those observed in parent compounds of high- T_c iron-based pnictide superconductors, in which the superconductivity shows up when the anomaly due to the SDW or structural transition is suppressed. Therefore, the new layered pnictide-oxide, BaTi₂As₂O, could be a potential parent compound for superconductivity. It is found that Li⁺ doping significantly suppresses the anomaly, but no superconductivity emerges so far.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Different orders of ground states (superconductivity, spin-density wave, charge-density wave, anti- and ferromagnetism, spin liquid, etc) and the relationship among these orders are one of the central issues in condensed matter physics. The evolution from one state to another is quite interesting and it attracts many scientists. There are a lot of cases showing these amazing characteristics. It is well known that cuprates evolve from antiferromagnetism to superconductivity [1] and chalcogenides develop from charge-density wave (CDW) to superconductivity [2–5]. Recently, the discovery of 26 K superconductivity in F-doped LaFeAsO by Hosono *et al* [6] has attracted a great deal of attention. Subsequently, replacement of La by other rare-earth elements (Sm, Ce, Pr, Nd) [7–13] raises T_c up to 55 K. Other than the ZrCuSiAs-type structure, the other structure of iron-pnictide was also discovered later. The same as the cuprates, the parent compound shows antiferromagnetic order [14]. The antiferromagnetic spin-density wave (SDW) can be suppressed by doping carriers into the parent compound.

Na₂Ti₂(As, Sb)₂O was synthesized by Adam *et al* [15]: its structure consists of edge-shared $[\text{Ti}_{4/2}\text{Pn}_2\text{O}_{4/4}]^{2-}$ layers separated by double layers of Na⁺. Both Sb and As compounds show a phase transition in susceptibility and resistivity measurements. These compounds exhibit an anomalous transition in the magnetic susceptibility at $T_N = 330$ K for the As analog and $T_N = 120$ K for the Sb analog [16–20]. The behaviors observed in resistivity and magnetic susceptibility are quite similar to those observed in iron-arsenide parent compounds. Therefore, it is very interesting to study these systems, especially to dope carriers into this ‘parent compound’ to see what happens and if the superconductivity could be induced. Due to the instability of Na cations in Na₂Ti₂(As, Sb)₂O, doping carriers into Na₂Ti₂(As, Sb)₂O to suppress SDW and to introduce possible superconductivity is very difficult. We replace the double-layer Na⁺ by single-layer Ba²⁺ to obtain a new compound BaTi₂As₂O. It has a similar structure to that of Na₂Ti₂As₂O. $[\text{Ti}_{4/2}\text{Pn}_2\text{O}_{4/4}]^{2-}$ and single-layer Ba²⁺ stack alternately along the c axis. Different from the Na analog, the $[\text{Ti}_{4/2}\text{Pn}_2\text{O}_{4/4}]^{2-}$ layer in the center of the Na₂Ti₂(As, Sb)₂O unit cell shifts for $(a/2, a/2)$ in-plane to form BaTi₂As₂O. So the c axis of the Ba analog is nearly halved as shown in figure 1. The connectivity

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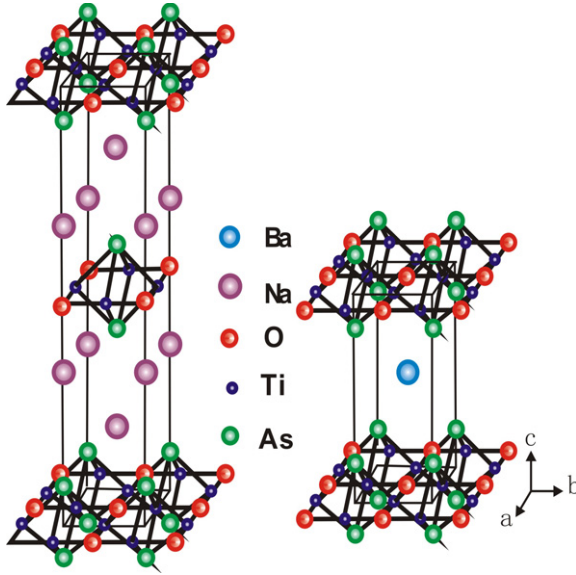


Figure 1. Left: crystal structure of $\text{Na}_2\text{Ti}_2\text{As}_2\text{O}$ with anti- K_2NiF_4 type showing alternation of $[\text{Ti}_{4/2}\text{O}_{4/4}]^{2-}$ layers and double layers of Na^+ ; right: crystal structure of $\text{BaTi}_2\text{As}_2\text{O}$ with alternation of $[\text{Ti}_{4/2}\text{O}_{4/4}]^{2-}$ layer and single layer of Ba^{2+} .

of atoms in this type of $[\text{Ti}_2\text{Pn}_2\text{O}]$ layer is quite unique. It has a Ti_2O square net that is anti-structural to the $[\text{CuO}_2]$ net of the cuprate superconductors. Ti in this layer is also coordinated by four As atoms located above and below the center of the Ti_2O squares to form Ti-centered TiAs_4O_2 octahedra. These unique features can only be found in $\text{Sr}_2\text{F}_2\text{Fe}_2(\text{Se}, \text{S})_2\text{O}$ [21]. The structure of $[\text{Ti}_2\text{Pn}_2\text{O}]$ is isostructural with $[\text{Fe}_2(\text{Se}, \text{S})_2\text{O}]$ in $\text{Sr}_2\text{F}_2\text{Fe}_2(\text{Se}, \text{S})_2\text{O}$.

2. Experimental details

The polycrystalline sample of $\text{BaTi}_2\text{As}_2\text{O}$ was synthesized by the conventional solid state reaction method. $\text{BaO}(3\text{N})$, $\text{Ti}(4\text{N})$ and $\text{As}(6\text{N})$ were mixed together according to stoichiometric ratio. The mixture was ground carefully and then pressed into a pellet. The pellet was wrapped by tantalum foil and then sealed in a quartz tube. The quartz tube was heated at 850°C for 40 h. The polycrystalline samples demonstrate a dark black color. Crystal structure information was determined by x-ray diffraction. Heat capacity and magnetoresistivity was measured by a physical property measurement system (PPMS, Quantum Design). The magnetic susceptibility was measured by SQUID. The resistivity measurement was done by the standard four-probe technique.

3. Results and discussion

Figure 2 shows the x-ray diffraction pattern of $\text{BaTi}_2\text{As}_2\text{O}$. It indicates that the sample is a pure phase. It can be refined by the GASA program. The space group of $\text{BaTi}_2\text{As}_2\text{O}$ is $P4/mmm$ (no. 123) with $a = 4.045608 \text{ \AA}$; $c = 7.27228 \text{ \AA}$. The structure of $\text{BaTi}_2\text{As}_2\text{O}$ is quite similar to that of $\text{Na}_2\text{Ti}_2\text{As}_2\text{O}$. The $[\text{Ti}_{4/2}\text{Pn}_2\text{O}_{4/4}]^{2-}$ block is the same as that

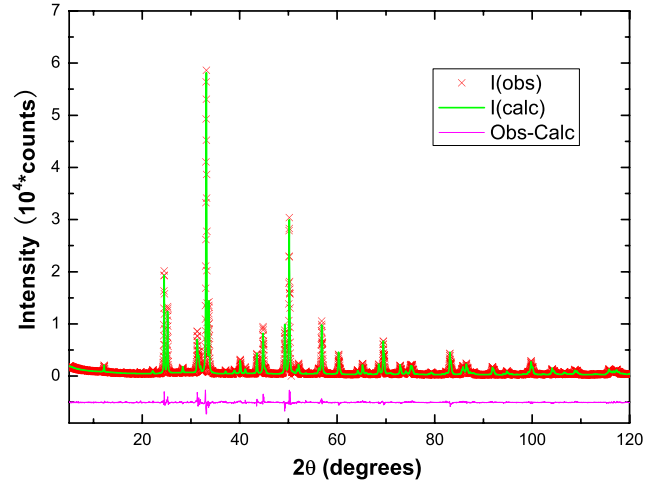


Figure 2. X-ray powder diffraction patterns at room temperature for the sample $\text{BaTi}_2\text{As}_2\text{O}$. The fork-shaped dot represents the observed data by x-ray diffraction. The solid line indicates the intensities calculated using the Rietveld method. The bottom solid curves are the differences between the observed and calculated intensities. $R_{\text{wp}} = 9.49\%$ and $R_p = 7.26\%$.

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (U_{iso}) for $\text{Ba}_2\text{Ti}_2\text{As}_2\text{O}$. Rietveld refinements proceeded smoothly for all compositions using profile function $\#3$ of the GSAS Rietveld refinement program [27].

Atom	Wyck site	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$
Ba	1d	1/2	1/2	1/2	0.0205(3)
Ti	2f	1/2	0	0	0.0081(6)
As	2g	0	0	0.7560(1)	0.0072(4)
O	1c	1/2	1/2	0	0.0025(3)

in $\text{Na}_2\text{Ti}_2(\text{As}, \text{Sb})_2\text{O}$. The double layers of Na^+ is replaced by a single layer of Ba^{2+} , which causes a decrease in the distance between $[\text{Ti}_{4/2}\text{As}_2\text{O}_{4/4}]^{2-}$ layers from $d = 7.655 \text{ \AA}$ for the Na analog to 7.274 \AA for the Ba analog. Table 1 gives the structural parameters from the refinement.

Figure 3 shows the temperature-dependent magnetic susceptibility. It shows a weak temperature dependence above 200 K, and clearly shows an anomaly at 200 K and a sharp decrease in susceptibility. This feature can also be observed in the Na analog and iron-arsenide parent compounds. In the iron-arsenide system, this anomaly is ascribed to the SDW/structural transition. Ozawa *et al* [17] pointed out that the anomaly of the Na analog was an indication of a new kind of two-dimensional CDW/SDW behavior. Therefore, the anomaly of magnetic susceptibility suggests a possible SDW/CDW behavior. But at low temperature the Ba analog shows a much stronger Curie–Weiss behavior than the Na analog.

Figure 4(a) shows the temperature dependence of resistivity for $\text{BaTi}_2\text{As}_2\text{O}$. An anomaly is clearly observed. At 200 K, resistivity shows an upturn and then decreases with decreasing temperature, being quite similar to that observed in CaFe_2As_2 [13] and cobalt-doped BaFe_2As_2 [22, 23]. Chu *et al* [23] has given an explanation for the upturn of cobalt doping BaFe_2As_2 . As we know, a gap opens when an SDW/CDW

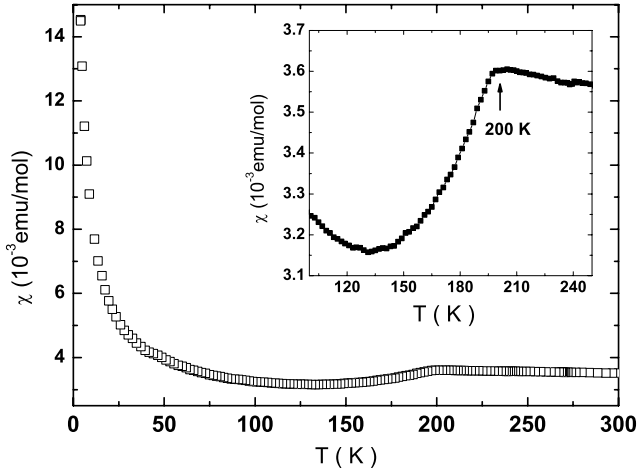


Figure 3. Temperature-dependent susceptibility measured under 1 T for the sample BaTi₂As₂O. The inset figure shows that the data zoom in near the phase transition.

occurs. The order of the charge/spin causes a decrease of the carriers and a reduction in the scattering chance. The balance between two influences leads to different behaviors below the SDW/CDW transition temperature. Figure 4(b) shows the isothermal magnetoresistance. A large magnetoresistance appears below the SDW/CDW transition at 200 K and it increases with decreasing temperature. At 14 T, it goes up to 20% at 4 K. The significant magnetoresistance may arise from the enhanced magnetic scattering by magnetic field. Such behavior is widely observed in parent compounds of pnictide superconductors. It gives an indication for SDW ordering at 200 K in BaTi₂As₂O.

Figure 5 shows the heat capacity for the sample BaTi₂As₂O. A clear anomaly is observed at 200 K in specific heat, indicating a bulk phase transition at 200 K due to the SDW/CDW transition. In the low temperature region the specific heat follows the form $C_p = \gamma T + \beta T^3$. The Debye temperature can be estimated from the equation $\beta = (12\pi^4 n k_B)/(5\Theta_D^3)$, where n is the number of atoms per formula unit. From the plot of C_p/T versus T^2 data between 3.9 and 25 K, we determine the Sommerfeld coefficient $\gamma = 15.3 \text{ mJ K}^{-2} \text{ mol}^{-1}$, $\beta = 0.79 \text{ mJ K}^{-4} \text{ mol}^{-1}$ and Debye temperature $\Theta_D = 223 \text{ K}$ for BaTi₂As₂O.

4. Doping carriers

We confirm the SDW/CDW transition at 200 K in different ways. As demonstrated in the iron-pnictides, doping carriers into the system can suppress the SDW transition and introduce superconductivity. We have tried to introduce holes by replacing Ba by K and Na, and to introduce electrons by doping La, Sm, Bi and Al into the system. But no changes can be observed in the resistivity. It may be due to the extremely high stability of the BaTi₂As₂O crystal structure, and any doping is very hard and not successful. Therefore, we turn our attention to doping the element to occupy the interstitial space in the crystal structure. It is well known that Li⁺ has a rather small radius, and can be doped into interstitial sites for several

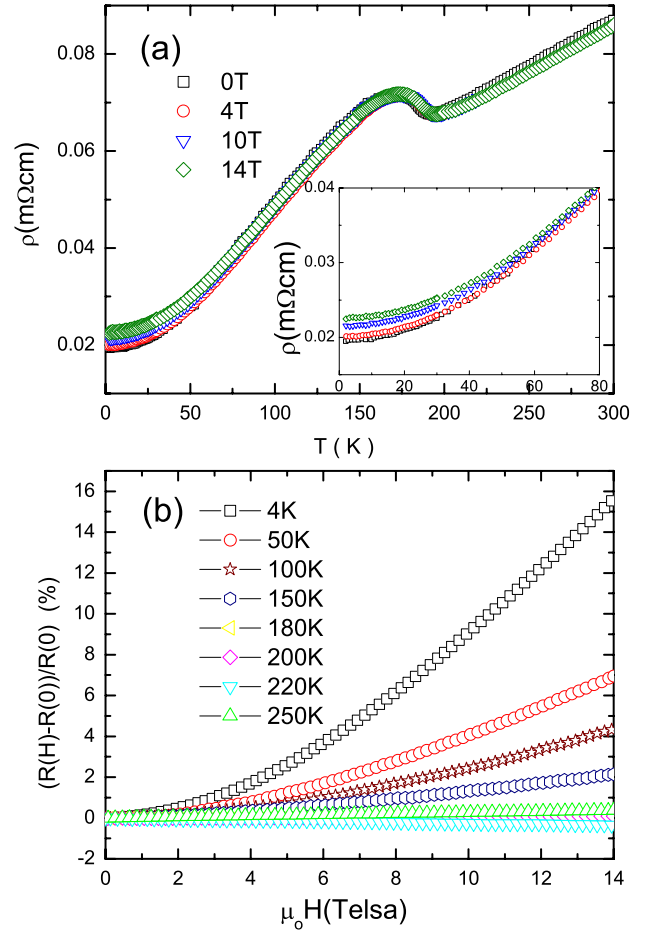


Figure 4. (a) Temperature dependence of resistivity at different fields and the inset shows the low temperature part of the $R-T$ curve at different magnetic fields. (b) Isothermal magnetoresistance at different temperatures for the sample BaTi₂As₂O.

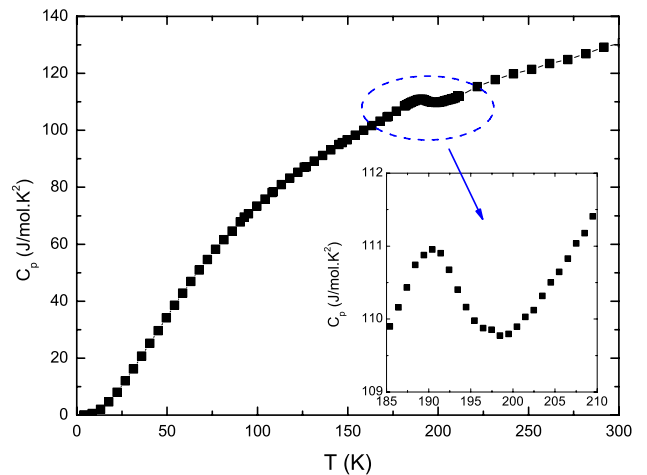


Figure 5. Temperature dependence of specific heat for the sample BaTi₂As₂O. The inset shows the anomaly of specific heat around the phase transition.

materials [24–26]. We choose Li as the possible candidate for introducing carriers into the system to suppress the SDW/CDW transition and to achieve superconductivity.

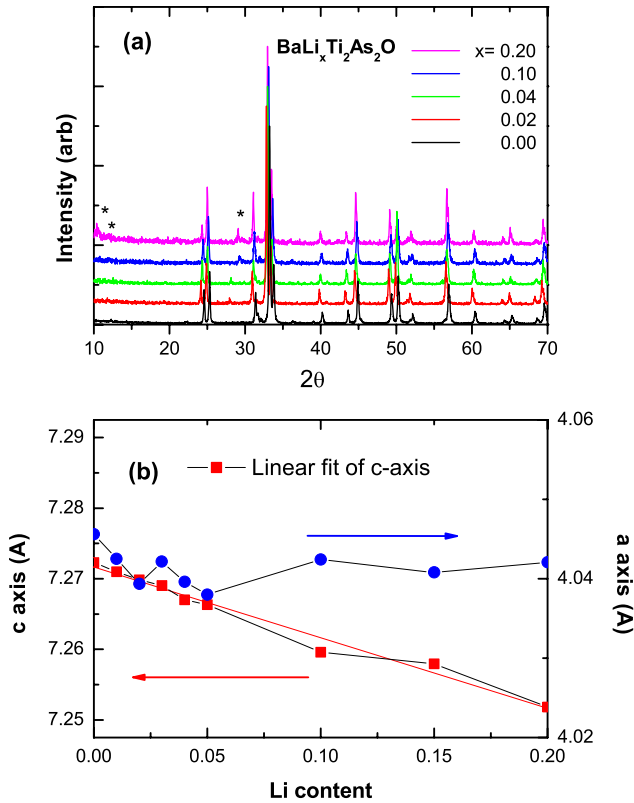


Figure 6. (a) X-ray diffraction patterns of the samples $\text{BaLi}_x\text{Ti}_2\text{As}_2\text{O}$ with different doping levels: $x = 0.00, 0.02, 0.04, 0.10$ and 0.20 , ‘*’ marks the impurity phase. (b) The a -axis and c -axis lattice parameters as a function of x .

Li-doped samples were synthesized by conventional solid state reaction almost the same as $\text{BaTi}_2\text{As}_2\text{O}$. Starting material LiAs was obtained by reacting Li pieces with As powders at 500°C for 10 h in a sealed tantalum tube. LiAs , BaO , Ti and As powders were mixed in the chemical stoichiometry ratio, then ground and pressed into pellets. The pellet was baked at 800°C for 40 h.

The samples with different doping content were checked by x-ray diffraction as shown in figure 6. The c -axis lattice parameter systematically decreases with increasing Li doping up to $x = 0.2$. But the a -axis lattice parameter remains almost constant. The interstitial Li^+ ions may enhance the attracting force between negative $[\text{Ti}_{4/2}\text{As}_2\text{O}_{4/4}]^{2-}$ planes and reduce the distance of the $[\text{Ti}_{4/2}\text{As}_2\text{O}_{4/4}]^{2-}$ plane. Further doping lithium into $\text{BaTi}_2\text{As}_2\text{O}$ failed.

Figure 7 shows the temperature dependence of resistivity for the samples $\text{BaLi}_x\text{Ti}_2\text{As}_2\text{O}$ with different doping levels. It clearly shows that the anomaly in resistivity has been gradually suppressed by doping. For the samples with $x = 0.01, 0.02$ and 0.03 , the temperature corresponding to the SDW/CDW transition goes to 175 K, 150 K and 60 K, respectively. With increasing Li doping, the SDW/CDW transition is continuously suppressed. For the sample with $x = 0.20$, the anomaly in resistivity is nearly destroyed, but no superconductivity emerges.

A new layered pnictide-oxide, $\text{BaTi}_2\text{As}_2\text{O}$, is discovered. It is interesting that its structure is quite similar to that

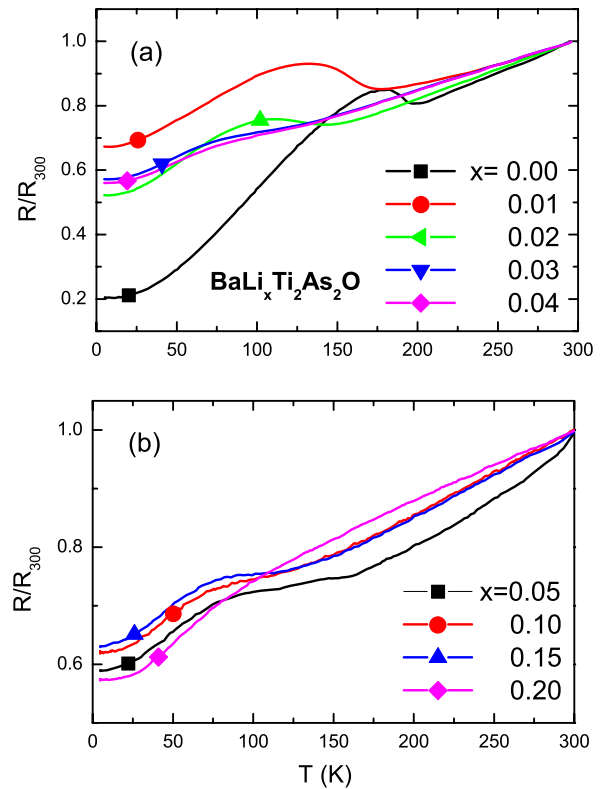


Figure 7. Temperature dependence of resistivity for the samples $\text{BaLi}_x\text{Ti}_2\text{As}_2\text{O}$ with different doping levels. (a): $x = 0.00, 0.01, 0.02, 0.03$ and 0.04 . (b): $x = 0.05, 0.10, 0.15$ and 0.20 .

of the high- T_c cuprate superconductors, while its behaviors obtained from resistivity, susceptibility, magnetoresistance and specific heat measurements are very similar to that of the parent compounds for the second family of high- T_c iron-based pnictide superconductors. Therefore, the $\text{BaTi}_2\text{As}_2\text{O}$ could be considered as a possible potential parent compound for superconductivity. It is significant to study its physical properties to understand the occurrence of high- T_c superconductors. To understand the anomaly observed in resistivity, susceptibility and specific heat, the neutron measurements is necessary to determine its magnetic structure.

5. Conclusions

We have successfully synthesized a new layered pnictide-oxide $\text{BaTi}_2\text{As}_2\text{O}$. It has a layered structure consisting of a single-layer Ba^{2+} and TiAsO layer. Different from that of $\text{NaTi}_2\text{As}_2\text{O}$, the $[\text{Ti}_{4/2}\text{As}_2\text{O}_{4/4}]^{2-}$ layer shifts $(a/2, a/2)$. The resistivity, magnetic susceptibility and heat capacity all show an anomaly at 200 K, which is ascribed to a possible SDW/CDW transition. These features are similar to those observed in the iron-arsenide parent compounds, since superconductivity in cuprates and iron-arsenides is somehow an outcome of suppressing antiferromagnetism by different doping. Since $\text{BaTi}_2\text{As}_2\text{O}$ has a quite similar crystal structure to that of cuprate superconductors and shares physical properties with those of iron-arsenide parent compounds, it is a potential parent compound for superconductors. It should be

significant to understand the superconductivity in cuprates and iron pnictides. Although SDW/CDW is gradually suppressed by doping Li^+ into interstitial sites, no superconductivity emerges. Further study for searching for superconductivity is underway.

Acknowledgments

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