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## A NEW 1212-TYPE PHASE: Cr-SUBSTITUTED $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ WITH $T_c$ UP TO ABOUT 110 K

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Superconductivity up to about 110 K in the  $\text{CrTiSrCaCuO}$  system was observed by resistance and ac susceptibility measurements. Powder X-ray diffraction analyses showed that a 1212-type phase, Cr-substituted  $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ , is responsible for the observed superconductivity. This is the first time that single-element substitution for  $\text{TlSr}_2\text{CaCu}_2\text{O}_7$  increases  $T_c$  of the 1212 phase to above 100 K. The Cr-substituted  $\text{TlSr}_2\text{CaCu}_2\text{O}_7$  is easily prepared and has very good quality suitable for practical applications.

After the  $\text{TlBaCaCuO}$  superconducting system was discovered,<sup>1,2</sup> two series of superconducting compounds,  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$  with double  $\text{TlO}$  layer<sup>3</sup> and  $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  with single  $\text{TlO}$  layer,<sup>4</sup> were rapidly identified. The number of  $n = 2$  with single  $\text{TlO}$  layer,  $\text{TlBa}_2\text{CaCu}_2\text{O}_7$ , has been widely called 1212-type phase. Meanwhile, the  $\text{TlSrCaCuO}$  system was found to be also superconducting at 20 K and 70 K.<sup>5</sup> In the  $\text{TlSrCaCuO}$  system there is also a 1212 phase  $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ . Although the  $\text{TlSr}_2\text{CaCu}_2\text{O}_7$  was reported to be superconducting at 70–80 K,<sup>6,7</sup> it is difficult to synthesize a pure sample, and it is often not superconducting.<sup>8,9</sup> However, when  $\text{Tl}$  is partially substituted by  $\text{Pb}$ , the  $(\text{Tl}, \text{Pb})\text{Sr}_2\text{CaCu}_2\text{O}_7$  forms easily and is superconducting at 75 K.<sup>8</sup> Meanwhile, when a rare earth (R) is introduced into the  $\text{TlSrCaCuO}$  system, the  $\text{TlSr}_2(\text{Ca}, \text{R})\text{Cu}_2\text{O}_7$  also forms easily and is superconducting around 90 K.<sup>10,11</sup> Bi-substituted 1212 phase  $(\text{Tl}, \text{Bi})\text{Sr}_2\text{CaCu}_2\text{O}_7$  was also superconducting at 75–95 K.<sup>12,13</sup> A combination substitution,  $\text{Pb}$  or  $\text{Bi}$  for  $\text{Tl}$  and  $\text{R}$  for  $\text{Ca}$ , produced  $(\text{Tl}, \text{Pb})\text{Sr}_2(\text{Ca}, \text{R})\text{Cu}_2\text{O}_7$  and  $(\text{Tl}, \text{Bi})\text{Sr}_2(\text{Ca}, \text{R})\text{Cu}_2\text{O}_7$  with even higher  $T_c$  of above 100 K.<sup>14,15</sup> Ca-free 90 K  $\text{TlSr}_2(\text{Sr}, \text{R})\text{Cu}_2\text{O}_7$  and 105 K  $(\text{Tl}, \text{Pb})\text{Sr}_2(\text{Sr}, \text{R})\text{Cu}_2\text{O}_7$  were also reported.<sup>16–19</sup> In this letter, we report a new 1212-type phase, Cr-substituted  $\text{TlSr}_2\text{CaCu}_2\text{O}_7$  with  $T_c$  up to about 110 K. This is the first time that single-element substitution for  $\text{TlSr}_2\text{CaCu}_2\text{O}_7$  enhances  $T_c$  of the 1212 phase to above 100 K. The Cr-substituted  $\text{TlSr}_2\text{CaCu}_2\text{O}_7$  is easily prepared and has very good quality suitable for practical applications. We present preparation

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of samples, resistance, ac susceptibility and thermopower measurements, and powder X-ray diffraction analyses, and we discuss location of Cr in the 1212 structure.

The CrTiSrCaCuO samples were prepared using high-purity chemicals  $\text{Cr}_2\text{O}_3$  (or  $\text{CrO}_3$ , or  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ ),  $\text{Ti}_2\text{O}_3$ , SrO (or  $\text{SrCO}_3$ ), CaO (or  $\text{CaCO}_3$ ), and CuO. In a typical procedure, appropriate amounts of  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , CuO, and  $\text{Cr}_2\text{O}_3$  were completely mixed and ground, and heated at 900–950° C in air for about 24 hours with several intermediate grindings to obtain uniform powders. Appropriate amounts of the powders and  $\text{Ti}_2\text{O}_3$  were completely mixed and ground, and pressed into pellets with a diameter of 7 mm and a thickness of about 2–3 mm. The pellets were placed in a covered alumina crucible. The crucible with the contents was introduced into a preheated tube furnace, and heated at 1000–1050° C in flowing oxygen for 5–15 minutes. The temperature of the furnace was then decreased gradually to 850° C, and held for 8–24 hours. Finally, the temperature of the furnace decreased to below 200° C. The samples were examined by four-probe resistance and ac susceptibility measurements and by powder X-ray diffraction analyses using the methods described in Refs. 17 and 18. A few of the samples were also examined by thermopower measurement.<sup>20</sup>

Superconducting CrTiSrCaCuO samples with zero resistance temperatures above 100 K were easily prepared with a wide range of nominal compositions. As an example, Fig. 1 shows resistance-temperature curves for three samples with nominal compositions of  $\text{Cr}_{0.5}\text{Ti}_{0.5}\text{Sr}_2\text{CaCu}_2\text{O}_x$  (I),  $\text{Cr}_{0.3}\text{TiSr}_2\text{Ca}_{0.7}\text{Cu}_2\text{O}_x$  (II),

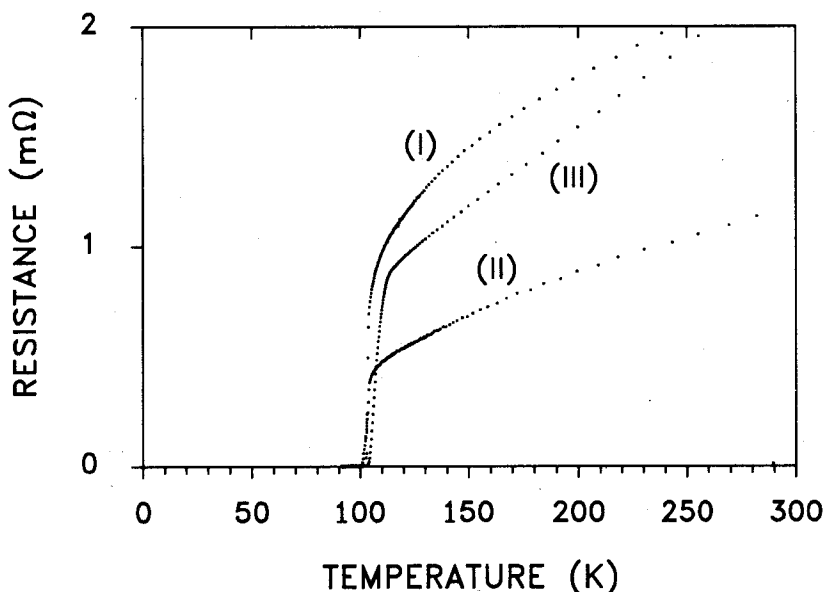


Fig. 1. Resistance-temperature curves for nominal samples  $\text{Cr}_{0.5}\text{Ti}_{0.5}\text{Sr}_2\text{CaCu}_2\text{O}_x$  (I),  $\text{Cr}_{0.3}\text{TiSr}_2\text{Ca}_{0.7}\text{Cu}_2\text{O}_x$  (II) and  $\text{Cr}_{0.5}\text{TiSr}_2\text{CaCu}_{1.5}\text{O}_x$  (III).

and  $\text{Cr}_{0.5}\text{TlSr}_2\text{CaCu}_{1.5}\text{O}_x$  (III) prepared using the typical procedure. It can be seen that all samples showed a metallic behaviour at the normal state. The onset temperature and zero-resistance temperature are 110 K and 102 K for  $\text{Cr}_{0.5}\text{Tl}_{0.5}\text{Sr}_2\text{CaCu}_2\text{O}_x$ , 107 K and 101 K for  $\text{Cr}_{0.3}\text{TlSr}_2\text{Ca}_{0.7}\text{Cu}_2\text{O}_x$ , and 112 K and 103 K for  $\text{Cr}_{0.5}\text{TlSr}_2\text{CaCu}_{1.5}\text{O}_x$ .

The superconducting behavior of  $\text{CrTlSrCaCuO}$  samples depends on the preparation conditions. Figure 2 shows a typical example for three samples A, B, and C, which have the same nominal composition of  $\text{Cr}_{0.25}\text{TlSr}_2\text{CaCu}_{1.75}\text{O}_x$  and are prepared under different conditions. Sample A is prepared by heating at  $1000^\circ\text{C}$  in flowing oxygen for 5 minutes followed by air cooling. Sample B is prepared using the typical procedure. Sample C is the sample B subjected to an additional step of annealing at  $750^\circ\text{C}$  in helium for 1 hour. The onset temperatures of samples A, B, and C, are 104, 106, and 112 K, respectively. Their zero-resistance temperatures are 96, 101, and 106 K, respectively. According to our experience, a longer time annealing in an oxygen atmosphere can significantly improve the quality of the samples, and a proper annealing in a non-oxygen atmosphere is necessary for the best superconducting behaviour of the samples.

The superconducting  $\text{CrTlSrCaCuO}$  samples not only are easily prepared, but also have very good quality. Most of the samples exhibit a sharp superconducting transition in resistance, ac susceptibility, and thermopower, and show a strong

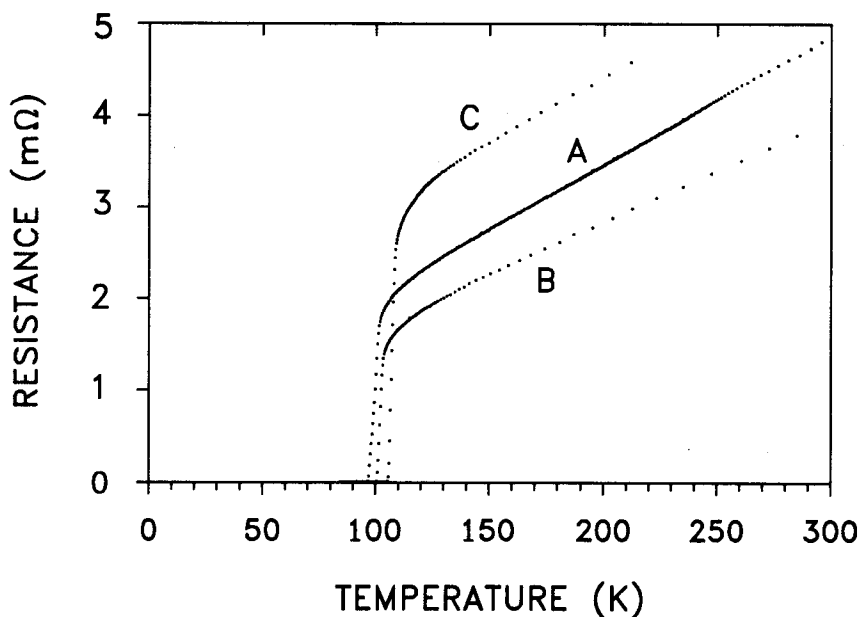


Fig. 2. Resistance-temperature curves for sample A, B and C with the same composition of  $\text{Cr}_{0.25}\text{TlSr}_2\text{CaCu}_{1.75}\text{O}_x$  prepared under different conditions. A: air cooling, B: annealed in oxygen, and C: annealed in helium.

diamagnetic signal. As an example, Fig. 3 shows temperature-dependencies of resistance, ac susceptibility and thermopower for a nominal  $\text{Cr}_{0.5}\text{TiSr}_2\text{CaCu}_{1.5}\text{O}_x$  sample. The resistance curve shows an onset temperature of 107 K and a zero-resistance temperature of 103 K. The ac susceptibility shows an onset temperature of about 103 K, which is fairly consistent with that by resistance measurement. The diamagnetic transition is very sharp, and reaches saturation at about 90 K. The saturated diamagnetic signal for the sample is comparable to those of any other superconductors with good quality, indicating a large volume of superconducting material. Thermopower  $S(\mu\text{V/K})$  of this sample increases with decreasing temperature, reaches a maximum value of about  $6 \mu\text{V/K}$  at about 115 K, and then drops sharply to zero at about 102 K. Such a behavior is generally similar to those of p-type  $\text{YBaCuO}$ ,  $\text{BiSrCaCuO}$  and  $\text{TlBaCaCuO}$  superconductors.<sup>20,22,23</sup> But, the sign of  $S(\mu\text{V/K})$  at room temperature is negative, which either indicates the excellent quality of  $\text{CrTiSrCaCuO}$  superconductor, or suggests an intrinsic property from other superconductors.

Powder X-ray diffraction analyses (with  $\text{Cu K}\alpha$  radiation) for a number of  $\text{CrTiSrCaCuO}$  samples showed that a 1212-type phase, Cr-substituted  $\text{TiSr}_2\text{-CaCu}_2\text{O}_7$ , is responsible for the observed 110 K superconductivity. As an example, Fig. 4 shows the X-ray diffraction pattern for a nominal  $\text{Cr}_{0.25}\text{TiSr}_2\text{CaCu}_{1.75}\text{O}_x$

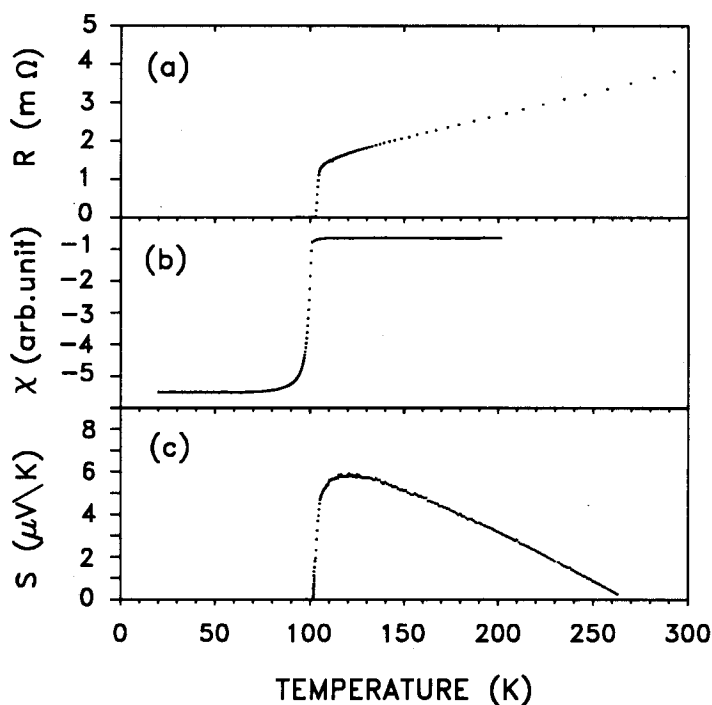


Fig. 3. Temperature dependencies of (a) resistance, (b) ac susceptibility, and (c) thermopower for a nominal sample  $\text{Cr}_{0.5}\text{TiSr}_2\text{CaCu}_{1.5}\text{O}_x$ .

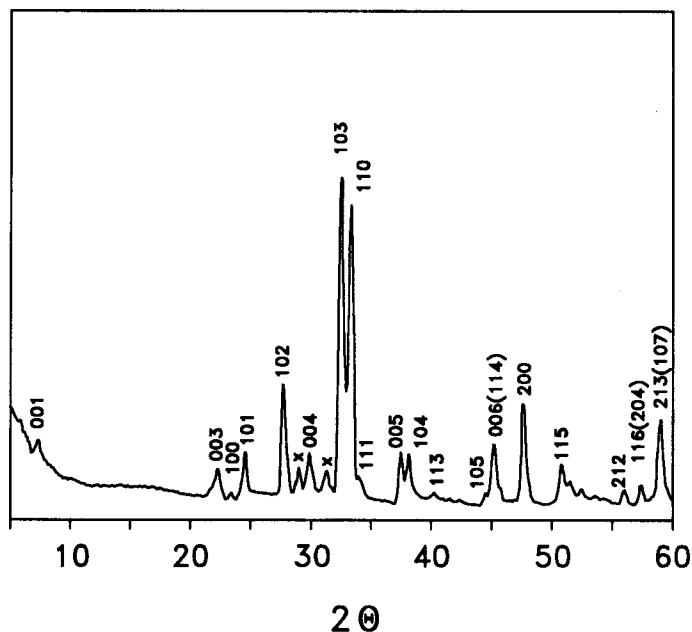


Fig. 4. Powder X-ray diffraction pattern for a sample  $\text{Cr}_{0.25}\text{TlSr}_2\text{CaCu}_{1.75}\text{O}_x$ .  $x$ : unidentified.

sample. The diffraction peaks, except two small peaks at  $2\theta$  of about  $28.8^\circ$  and  $31.3^\circ$ , can be well indexed based on a tetragonal unit cell (space group  $P4/mmm$ ) with  $a = 3.813 \text{ \AA}$  and  $c = 12.026 \text{ \AA}$ . The indexed diffraction data are listed in Table 1. Powder X-ray diffraction analyses for some serial samples, including  $\text{Cr}_y\text{Tl}_{1-y}\text{Sr}_2\text{CaCu}_2\text{O}_x$ ,  $\text{Cr}_y\text{TlSr}_2\text{Ca}_{1-y}\text{Cu}_2\text{O}_x$ , and  $\text{Cr}_y\text{TlSr}_2\text{CaCu}_{2-y}\text{O}_x$ , showed a notable common feature: with the increase of Cr content in the samples,  $a$ -axis of the 1212 phase increases and  $c$ -axis decreases. Table 2 lists  $a$ -axis and  $c$ -axis for the 1212 phase in serial samples of  $\text{Cr}_y\text{TlSr}_2\text{CaCu}_{2-y}\text{O}_x$  as an example.

In the point of view of chemical property, Cr in the Cr-substituted  $\text{TlSr}_2\text{CaCu}_2\text{O}_7$  is most probably at  $3+$  valence state. This is also supported by experimental results that rather pure 1212 phase samples could be synthesized with  $\text{Cr}_2\text{O}_3$ ,  $\text{Tl}_2\text{O}_3$ ,  $\text{SrO}$ ,  $\text{CaO}$ , and  $\text{CuO}$  in a sealed container. The determination of the location of  $\text{Cr}^{3+}$  in the 1212 structure is rather complicated. Firstly,  $\text{Cr}^{3+}$  may locate in Tl site. The Tl-based 1212 phase is an analogue of the famous 123 phase  $\text{RBa}_2\text{Cu}_3\text{O}_7$ ; the TlO plane in the 1212 structure corresponds to the CuO chain in 123 structure. Cr was reported to locate in the CuO chain rather than in the CuO plane in the 123 structure.<sup>24</sup> Therefore,  $\text{Cr}^{3+}$  in the 1212 phase may be in the Tl site. Secondly, Cr and Cu are both  $3d$  elements, and have similar electron configurations ( $3d^54s^1$ , half filled  $3d$  electron shell, for Cr;  $3d^{10}4s^1$ , fully filled  $3d$  electron shell, for Cu) and similar ionic radii. Cr may substitute for Cu. However, substitution of the smaller  $\text{Cr}^{3+}$ , either for Tl or for Cu, would not increase  $a$ -axis of the 1212 phase.

Table 1. Diffraction data for the 1212 phase in a nominal  $\text{Cr}_{0.25}\text{TlSr}_2\text{CaCu}_{1.75}\text{O}_x$  sample.

<i>h</i>	<i>k</i>	<i>l</i>	$d_{\text{obs}}(\text{\AA})$	$d_{\text{cal}}(\text{\AA})$	Int.
0	0	1	12.0634	12.0257	7
0	0	3	4.0172	4.0086	11
1	0	0	3.8132	3.8133	3
1	0	1	3.6293	3.6349	16
1	0	2	3.2173	3.2203	37
0	0	4	3.0052	3.0064	12
1	0	3	2.7610	2.7629	100
1	1	0	2.6963	2.6964	90
1	1	1	2.6347	2.6310	4
0	0	5	2.4028	2.4051	16
1	0	4	2.3603	2.3609	16
1	1	3	2.2391	2.2373	4
1	0	5	2.0348	2.0343	2
1	1	4	2.0091	2.0073	(23)
0	0	6	2.0049	2.0043	(23)
2	0	0	1.9056	1.9066	35
1	1	5	1.7964	1.7949	14
2	1	2	1.6414	1.6406	6
2	0	4	1.6098	1.6101	(6)
1	1	6	1.6085	1.6086	(6)
2	1	3	1.5686	1.5692	(28)
1	0	7	1.5661	1.5663	(28)

Table 2. Lattice parameters *a* and *c* of the 1212 in the nominal samples  $\text{Cr}_y\text{TlSr}_2\text{CaCu}_{2-y}\text{O}_x$ .

<i>y</i>	<i>a</i> (\AA)	<i>c</i> (\AA)
0.0	3.783	12.12
0.1	3.804	12.06
0.2	3.809	12.06
0.3	3.811	12.00
0.4	3.819	12.01
0.5	3.817	12.02
0.6	3.819	12.01
1.0	3.814	12.00

The location of Cr in the 1212 structure was determined on samples with nominal compositions  $\text{Cr}_{0.25}\text{TlSr}_2\text{CaCu}_{1.75}\text{O}_x$  and  $\text{Cr}_{0.5}\text{TlSr}_2\text{CaCu}_{1.5}\text{O}_x$ . These specimens were examined by electron microanalysis and structures were determined by Reitveld analysis of powder X-ray diffraction data.<sup>25</sup> The former sample yields a 1212 superconductor with unit cell dimensions  $a = 3.8159(2) \text{ \AA}$  and  $c = 12.0111(9) \text{ \AA}$ , and an approximate composition  $\text{Tl}_{1.00}\text{Sr}_{2.00}(\text{Ca}_{0.83}\text{Cr}_{0.17})$



$\text{Cu}_{2.00}\text{O}_x$ . This sample also contains a small amount of a second unidentified Ca-rich phase. The second sample yields a 1212 superconductor with similar unit cell dimensions  $a = 3.8176(6) \text{ \AA}$  and  $c = 12.0312(25) \text{ \AA}$ , and an approximate composition  $(\text{Tl}_{0.97}\text{Cr}_{0.03})\text{Sr}_{2.00}(\text{Ca}_{0.86}\text{Cr}_{0.14})\text{Cu}_{2.00}\text{O}_x$ . It is interesting that  $\text{Cr}^{3+}$  substitutes primarily for  $\text{Ca}^{2+}$ , playing the role of a rare earth, while substitution for  $\text{Tl}^{3+}$  is minor. There is no evidence for Cr substitution in Cu sites. This result well explained why  $\text{Cr}^{3+}$ -substitution increases  $a$ -axis and decreases  $c$ -axis of the 1212 phase. On one hand, substitution of smaller  $\text{Cr}^{3+}$  for larger "spacer" ion  $\text{Ca}^{2+}$  results in the decrease of  $c$ -axis. On the other hand, according to the concept of "average Cu valence", stoichiometric  $\text{TlSr}_2\text{CaCu}_2\text{O}_7$  has a average Cu valence of 2.5+, or is overdoped by holes; substitution of higher valence  $\text{Cr}^{3+}$  for lower valence  $\text{Ca}^{2+}$  would decrease the average valence of Cu, and thus expand  $a$ -axis of the 1212 phase (and stabilize the 1212 phase). A similar effect of rare earths on lattice parameters  $a$  and  $c$  has been reported for  $\text{TlBa}_2(\text{Ca},\text{R})\text{Cu}_2\text{O}_7$ .<sup>26</sup>

The existing data showed that substitution of  $\text{R}^{3+}$  for  $\text{Ca}^{2+}$  in  $\text{TlSr}_2\text{CaCu}_2\text{O}_7$  can only reach  $T_c$  of about 90 K,<sup>10,11</sup> and double substitutions, Pb (or Bi) for Tl, and R for Ca, are necessary for the 1212 phase to exhibit superconductivity above 100 K.<sup>14,15</sup> The single substitution of  $\text{Cr}^{3+}$  for  $\text{Ca}^{2+}$  does increase  $T_c$  of the 1212 phase to above 100 K. This may simply suggest a special capability of  $\text{Cr}^{3+}$  in enhancing  $T_c$  of the 1212 phase. However, it is also possible that the single element of Cr plays a role of double substitutions:  $\text{Cr}^{3+}$  substitutes for both  $\text{Tl}^{3+}$  and  $\text{Ca}^{2+}$ , resulting in enhancement of  $T_c$ . Furthermore, substitution of trace Cr for Cu cannot be ruled out. The CuO plane is believed to be responsible for high  $T_c$  superconductivity, and replacement of Cu is most sensitive to superconductivity. A trace amount of Cr going to the Cu site may enhance  $T_c$  to above 100 K. Nevertheless, the discovery of the 110 K Cr-substituted  $\text{TlSr}_2\text{CaCu}_2\text{O}_7$  not only provides a new superconductor suitable for practical applications, but also opens a new and fruitful line of elemental substitution. In this regard, most promising is that R in some existing R-bearing superconductors may be replaced by the inexpensive Cr, perhaps with enhancement of  $T_c$ .

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