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Growth and Characterization of a New Superconductor $GaBa_2Ca_3Cu_4O_{11+\delta}$

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We successfully grow a new superconductor $GaBa_2Ca_3Cu_4O_{11+\delta}$ (Ga-1234) with a transition temperature of 113 K, using the Walker-type high-pressure synthesis apparatus. X-ray diffraction measurements on the powderized samples show a mixture of the Ga-1234 phase and the $Ca_{0.85}CuO_2$ phase, and the former is dominant. Under the scanning electron microscope, plate-like crystals of the Ga-based 1234 phase with shiny surfaces can be seen. The obtained local chemical compositions revealed by energy dispersion x-ray spectroscopy are very close to the stoichiometric values. On some sub-millimeter crystal-like samples of the 1234 phase, we obtain a full Meissner shielding volume. From the temperature-dependent magnetizations, we determine the irreversibility fields and find that the system exhibits a highly anisotropic behavior.

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In recent several decades, a lot of research efforts in high-temperature superconductors (HTSs) have been devoted to searching for new superconducting materials. The synthesis of novel and high-quality HTSs is of great significance for achieving a deep insight into the fundamental nature of high-temperature superconductivity and improving the prospects of technical applications. Motivated by the discovery of superconductivity in the La–Ba–Cu–O system in 1986,[1] many structural and compositional variations have been studied in cuprate superconductors,[2–6] leading to a great richness of the cuprate family. The well-known systems include the Y,[5] Tl,[2] Bi,[6] and Hg[7–9] based compounds. Up to late 1990s, the critical temperature (T_c) was drastically enhanced from 35 K in La–Ba–Cu–O to 92 K in $YBa_2Cu_3O_{7-x}$ (YBCO),[5] and further to over 160 K (under high pressure) in $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223).[8,9]

For a typical homologous series of layered cuprate HTSs, a general formula can be written as $AE_2R_{n-1}Cu_nO_{2n+3}$[10] (A stands for heavy metals such as Tl, Hg, Bi and Pb; E and R represent alkaline-earth metals such as Ca, Ba, Sr; n is the number of CuO_2 planes per unit cell), sometimes the formula can be abbreviated as A-12($n-1$)n. In one unit cell, there are two substructures: the charge reservoir block of $(AO)(EO)_2$ and the superconductive CuO_2 layers stacking along c-axis.[11] As can be seen from the formula, with increasing n, the structure adds another layer of $RCuO_2$ unit one by one. The composition and framework of the charge reservoir layers are almost unaffected. In most such multilayered cuprates, Ca is employed as the R metal to separate the CuO_2 planes,[12] and the choice of E tends to be limited to alkaline-earth metals with relatively large ionic radii, such as Ba and Sr.[10] Thus, replacing A site cations with other elements is a widely used method to develop a new system of cuprate superconductors. In addition, in the cuprate systems with T_c above 100 K discovered so far, most of the heavy metal elements A are toxic, such as Tl, Hg and Pb. It is very useful to find some new superconducting systems without these toxic elements.

Recently, trace of superconductivity was observed in a new cuprate system Ga–Ba–Ca–Cu–O with $T_c = 82$ K.[13] In addition, the temperature dependence of magnetization shows a second superconducting transition with higher T_c at about 113 K. However, due to the quite small magnetic screening fraction ($\sim$10% in volume) of the 113 K superconducting phase, the specific compound associated with the transition at 113 K was not distinguished.

In this Letter, we report the growth and characterization of a new nontoxic cuprate superconductor $GaBa_2Ca_3Cu_4O_{11+\delta}$ with $T_c = 113$ K. The superconducting properties, crystal structure, and chemical composition are characterized by magnetization, resistivity, x-ray diffraction (XRD), and energy dispersion x-ray spectroscopy (EDS) measurements, respectively. Based on the temperature-dependent magnetizations for some crystal-like samples, we determine a rather low irreversibility line of the samples compared with other cuprate systems with similar T_c. It seems that the Ga-1234 system exhibits a highly anisotropic behavior.

The dense bulk samples of Ga-1234 were synthesized under high pressure and high temperature by a solid-state reaction method. The precursor $BaCuO_{2.13}$ was prepared by sintering the well-ground mixture of CuO (99.995%, Alfa Aesar) and BaO_2 (99%, Aladdin) in flowing oxygen at 900 ℃ for 60 h with several intermediate grindings for purpose of homogeneity. The precursor Ca_2CuO_3 was obtained by calcining the well-ground mixture of CuO and

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$CaCO_3$ (99.99%, Alfa Aesar) in air at 950 ℃ for 20 h, and then under oxygen atmosphere at 900 ℃ for 40 h with two intermediate grindings. The starting materials of $BaCuO_{2.13}$, Ca_2CuO_3, CuO, Ga_2O_3 (99.99%, Aladdin), and an appropriate amount of Ag_2O (acting as an oxidizer, 99+%, Alfa Aesar) were weighed and mixed with the stoichiometric composition of $GaBa_2Ca_3Cu_4O_{11+\delta}$. Then, the well-ground mixture was pressed into pellets and sealed in a gold capsule. These preparation procedures were conducted with the protection of a high-purity argon atmosphere in a glove box. For the high-pressure and high-temperature synthesis process, the pellets of mixed starting materials wrapped with a gold capsule were pressed at 8 GPa and heated at 1160 ℃ for 5 h using a Walker-type[14] multianvil press (LP 1000–540/50, Max Voggenreiter), followed by cooling down to room temperature in 5 min. After that, the high pressure was released gradually.

The dc magnetization measurements were carried out on a superconducting quantum interference device with the vibrating sample magnetometer (SQUID-VSM 7T, Quantum Design). The electrical resistance was measured by the standard four-probe method using the physical property measurement system (PPMS 16T, Quantum Design). The prepared samples were characterized by powder XRD (Bruker D8 Advance) using the Cu K_α radiation at room temperature. The TOPAS 4.2 software[15] based on the Rietveld method[16] was used to analyze the diffraction patterns. The micrographs of samples were taken on a scanning electron microscope (SEM) (Phenom ProX), and the chemical composition was analyzed by EDS attached to the SEM.

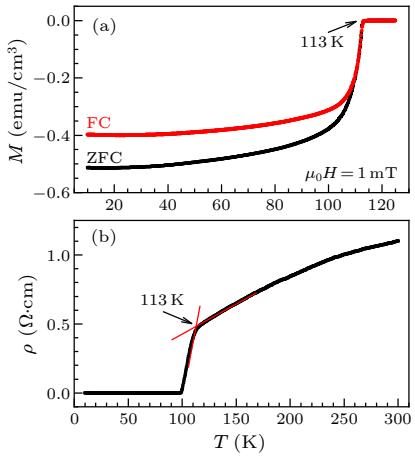

Fig. 1. (a) Temperature dependence of magnetic susceptibility for the Ga-1234 bulk sample in ZFC and FC modes under an applied magnetic field of 1 mT. (b) Temperature dependence of resistivity for the Ga-1234 bulk sample under zero magnetic field.

The superconducting properties of the as-synthesized samples are characterized by the magnetic susceptibility and resistivity measurements. Figure 1(a) depicts the temperature dependence of magnetic susceptibility measured in zero-field-cooled (ZFC) and field-cooled (FC) modes with an applied magnetic field of 1 mT. One can see that a superconducting transition occurs at around 113 K. Using the diamagnetic susceptibility measured in ZFC mode at 10 K, the magnetic shielding volume fraction ($4\pi\Delta\chi$) is calculated to be about 65%, indicating the bulk superconducting nature of the sample. The one-step superconducting transition manifests the presence of only one dominant superconducting phase in the obtained compound. We have also measured the magnetization-hysteresis-loops (MHLs) of one sample at 2, 10, 20, 30 K. The opened and rather symmetric MHLs at low temperatures indicate bulk vortex pinning. The MHL closes at about 3.8 T at 30 K, giving an irreversibility field $H_{\rm irr}(30\,{\rm K}) = 3.8$ T. Combining the subsequent XRD and EDS results of the bulk samples and characterization measurements of some sub-millimeter crystal-like samples, it can be concluded that the superconducting transition at $T_{\rm c} = 113$ K comes from the Ga-1234 phase. Figure 1(b) presents the temperature-dependent resistivity under zero magnetic field. The normal-state resistivity of the sample shows a metallic behavior. By using a linear extrapolation of the resistivity data illustrated in Fig. 1(b), the onset transition temperature is determined to be about 113 K, consistent with the magnetization measurements.

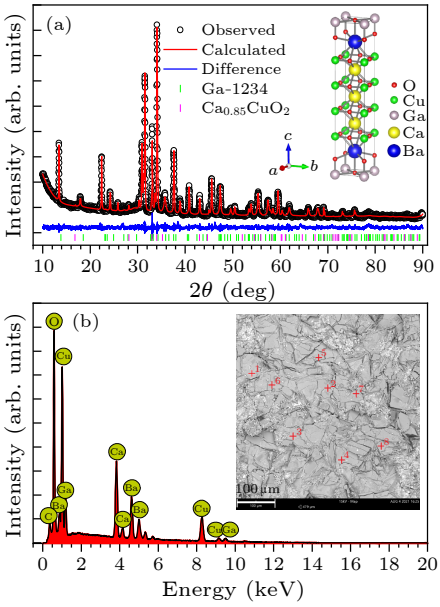

Fig. 2. (a) XRD pattern for the Ga-1234 powderized sample. The inset shows the schematic structure of Ga-1234. (b) A typical EDS spectrum for the Ga-1234 bulk sample. The inset shows the SEM morphology image of the sample.

Figure 2(a) shows the XRD pattern for the powderized sample with a nominal composition of $GaBa_2Ca_3Cu_4O_{11+\delta}$, together with the Rietveld refinement curve (the red line) of the data.[16] The refinement shows a mixture of the wanted Ga-1234 phase and the $Ca_{0.85}CuO_2$ impurity phase, and the former is dominant with a volume fraction of about 62%. It gives a tetragonal Ga-1234 phase of the $P4/mmm$ space group with lattice parameters of 3.84 Å and 19.15 Å for a and c, respectively. The main impurity phase $Ca_{0.85}CuO_2$ marked with green vertical lines takes a 38% volume fraction. Combining the

following MT and EDS measurements of the crystal-like samples with full shielding volume fraction, it can be concluded that the 113 K superconductivity is from the Ga-1234 phase, not the $Ca_{0.85}CuO_2$ impurity. In addition, we did not find any other traces of superconductivity from Fig. 1(a), so the $Ca_{0.85}CuO_2$ impurity is not superconducting. A weighed-profile R factor (R_{wp}) of 7.61% is obtained, indicating that the fitted result is reliable. The XRD result is consistent with the magnetic shielding fraction characterized by the magnetization measurement. The inset in Fig. 2(a) presents the schematic crystal structure of Ga-1234, which is isostructural to that of Hg-1234 [17] and Tl-1234, [18] with Hg or Tl replaced by Ga.

Table 1. Chemical compositions of the Ga-1234 bulk sample determined by EDS analysis. AC: atomic concentration, WC: weight concentration.

Elements	AC (at.%)	WC (wt%)
O	71.84	37.05
Cu	11.93	24.44
Ca	7.75	10.02
Ba	4.97	22.01
Ga	2.75	6.19

A local microstructure inspection of the prepared sample is performed using SEM imaging. The inset of Fig. 2(b) shows its morphology image. It displays an aggregate structure consisting of numerous crystals with shiny surfaces. The crystals are flaky and plate-like shaped, displaying the characteristic of the tetragonal crystal structure in compounds. These plate-like crystals are closely connected, with an average size of several dozens of micrometers. Then we detect the chemical compositions of these crystals using EDS analysis. A total of eight spots are measured and marked with red crosses on the morphology image. Figure 2(b) shows the EDS spectrum for spot 2, and its composition information is given in Table 1. Taking the Ga content as 1, the ratio Ga : Ba : Ca : Cu is calculated to be 1.0 : 1.81 : 2.82 : 4.34, which is very close to the expected value of 1 : 2 : 3 : 4. Moreover, the average stoichiometric composition of the eight spots is found to be $GaBa_{1.8}Ca_{2.7}Cu_{4.16}O_{11+\delta}$, confirming the formation of the Ga-1234 phase. We need to note that Ag_2O used in the synthesis is mainly for oxidization. In the small crystals with shiny surfaces under SEM, we have never detected a contamination of Ag. In addition, we did not use any reagents containing the C element to achieve the stoichiometric composition of $GaBa_2Ca_3Cu_4O_{11+\delta}$. In the preparation process, the C element is difficult to enter into the materials due to the protection of a high-purity argon atmosphere and the seal of the gold capsule. Thus, the C element detected by EDS is mainly from the conductive carbon tape used in the measurements.

Crystal-like grains can be obtained from the bulk samples. The inset of Fig. 3(a) shows the optical microscopy image of one typical grain, which possesses a cubic shape with a size up to approximately 100 μm. The inset of Fig. 3(b) displays the SEM image of the grain. As we can see, a relatively good connection exists between the crystals in the sample. The adjacent crystals tend to fuse and connect into a larger crystal. The chemical compositions of the grain are investigated using the EDS analysis. Figure 3(b) presents the EDS spectrum for spot 1, and the result is shown in Table 2. Taking the Ga content as 1, the ratio Ga : Ba : Ca : Cu is 1.0 : 1.89 : 2.84 : 4.51. In addition, the mean value of the 10 spots marked on the image is Ga : Ba : Ca : Cu = 1.0 : 1.83 : 2.76 : 4.36. Both results verify the $GaBa_2Ca_3Cu_4O_{11+\delta}$ chemical composition of the crystal-like grains. For the grain mentioned above, temperature-dependent magnetic susceptibility has also been measured under 1 mT, and the obtained data are shown in Fig. 3(a). The superconducting transition occurs at about 113 K, and the calculated Meissner shielding volume fraction using the ZFC data at 10 K is 214%. Note that the shielding volume fraction above 100% is due to the demagnetization factor. The result again confirms that the superconducting phase with T_c = 113 K is from Ga-1234. Meanwhile, it indicates that the crystal-like grains possess a high percentage of Ga-1234.

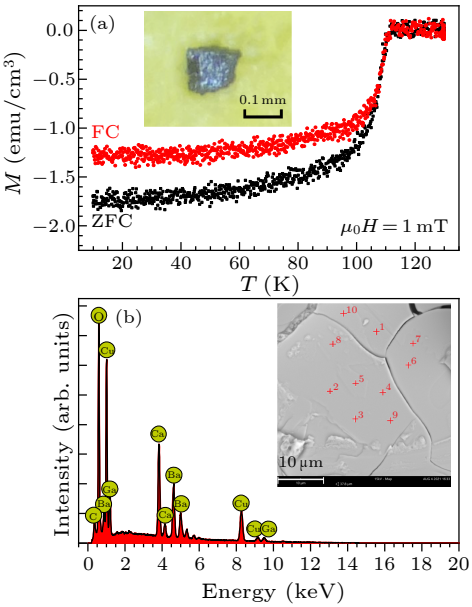

Fig. 3. (a) Temperature dependence of magnetic susceptibility for the Ga-1234 crystal-like grain in ZFC and FC modes under an applied magnetic field of 1 mT. The inset shows the optical microscopy image of the Ga-1234 crystal-like grain. (b) A typical EDS spectrum for the Ga-1234 crystal-like grain. The inset shows the SEM morphology image of the sample.

Table 2. Chemical compositions of the Ga-1234 crystal-like grain determined by EDS analysis.

Elements	AC (at.%)	WC (wt%)
O	68.55	33.43
Cu	13.44	26.03
Ca	8.46	10.34
Ba	5.62	23.53
Ga	2.98	6.33

For a type-Ⅱ superconductor, there is an irreversibility line $H_{irr}(T)$, which is the boundary between the magnetically irreversible region with finite critical current density

(J_c) and the reversible region with zero J_c. This phase line determines the upper limit for the high-field application of a superconductor. In order to investigate the $H_{irr}(T)$ of the Ga-1234 superconductor, we measured the temperature-dependent ZFC and FC magnetizations (M_{ZFC} and M_{FC}, respectively) at different magnetic fields for the Ga-1234 crystal-like grains. Figures 4(a)–4(c) present a typical data set in magnetic fields of 10 mT, 0.1 T, and 0.5 T. It can be seen that the superconducting transitions were suppressed gradually and exhibited a relatively broad behavior with the increase of the applied fields, which is due to the flux motion. The irreversibility temperature T_{irr} of the corresponding applied magnetic field can be determined from the point where the ZFC and FC magnetization curves start to separate. One can see that the T_{irr} position moves to a lower temperature with the increasing magnetic field. By carefully subtracting FC from ZFC data, the temperature-dependent magnetization difference ΔM ($= M_{ZFC} - M_{FC}$) is obtained. Thus, the temperature at which ΔM approaches zero can be taken to identify the T_{irr} value. Figure 4(d) displays the plots of ΔM versus temperature at different magnetic fields, and the estimated T_{irr} positions are marked by arrows. For example, the irreversibility fields are 0.5 T at 61 K and 0.1 T at 88 K.

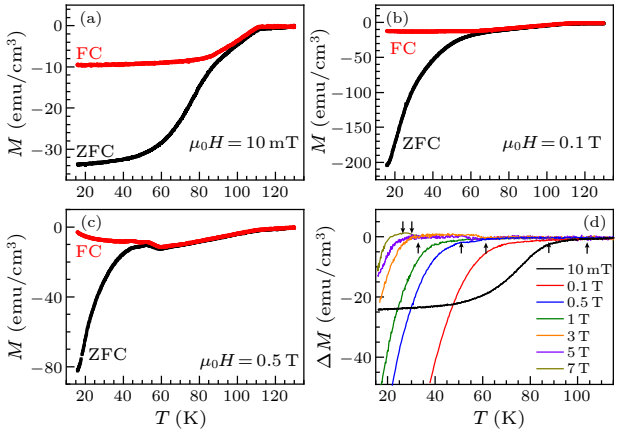

Fig. 4. Temperature dependence of magnetic susceptibility for the Ga-1234 crystal-like grain in ZFC and FC modes under applied magnetic fields of (a) 10 mT, (b) 0.1 T, and (c) 0.5 T. (d) Temperature dependence of magnetization difference ΔM ($= M_{ZFC} - M_{FC}$) at H = 10 mT, 0.1 T, 0.5 T, 1 T, 3 T, 5 T, 7 T.

Figure 5 shows a comparison of the irreversibility lines for Ga-1234 crystal-like grains and other cuprate superconductors, including (Cu,C)-1234 polycrystal,[19] YBCO single crystal,[20] Hg-1223 single crystal,[21] and Bi-2223 single crystal.[22] The nontoxic (Cu,C)-1234 polycrystal exhibits the highest irreversibility line among all superconductors. Therefore, it offers great potential for practical applications. The YBCO single crystal has a high irreversibility field of about 10 T at 77 K. The H_{irr} of Hg-1223 single crystal is higher than that of YBCO for $T > 90$ K. However, the toxic element Hg strongly limits its applications. For the Bi-2223 single crystal, which has a transition temperature exceeding 100 K, the irreversibility line is strongly depressed due to its high anisotropy and short coherence length.[22] One can see that the Ga-1234 crystal-like grain shows a pretty low irreversibility line under high magnetic fields, which is slightly higher than that of Bi-2223 and lower than that of Hg-1223. The low irreversibility fields seem to indicate, as in Bi-2223, that Ga-1234 is a highly anisotropic superconductor with strong two-dimensional nature. Further, the insulating Ga-O layers, which can greatly weaken the Josephson coupling between the superconducting CuO_2 blocks along the c-axis, may be the crucial factor responsible for the high anisotropy.

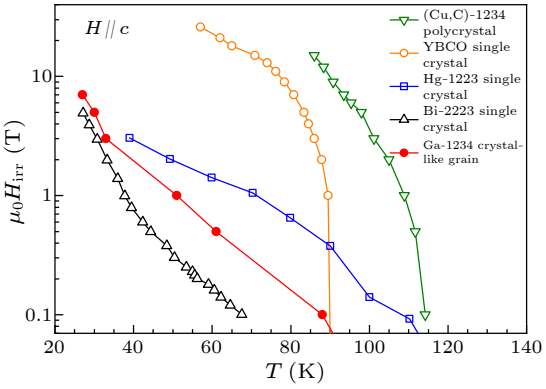

Fig. 5. Irreversibility lines for Ga-1234 crystal-like grain (this work), (Cu,C)-1234 polycrystal,[19] YBCO single crystal,[20] Hg-1223 single crystal,[21] and Bi-2223 single crystal.[22]

In conclusion, we have successfully synthesized the new nontoxic superconductor $GaBa_2Ca_3Cu_4O_{11+\delta}$ under high pressure and high temperature. Bulk superconductivity of $T_c = 113$ K is observed from the dc susceptibility and resistivity measurements. The XRD and EDS results of the bulk samples and characterization measurements of the crystal-like grains confirm that the 113 K superconducting transition comes from Ga-1234. From the temperature-dependent magnetizations on the crystal-like grains, we determine the irreversibility fields. The small H_{irr} values indicate that Ga-1234 is a highly anisotropic superconductor with strong two-dimensionality. However, the crystal exhibits a layered structure with a shiny surface, thus it could be a good sample system for fundamental research. The discovery of the Ga-1234 superconductor provides a new platform for the study of cuprate materials and physical properties. Furthermore, in order to avoid the influence of the defects and grain boundaries in samples, more efforts are necessary to prepare high-quality single crystals with larger sizes by optimizing the high-pressure conditions.

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