M NaCl, 10 mM phosphate, pH 7.0) were mixed, frozen (40 s), thawed (5 min), and spotted with a capillary tube on a C_{18} TLC plate. A blue spot developed. In the absence of target, the color remained pink. For comparison, the lower limit for detecting an oligonucleotide with the use of a probe labeled with fluorescein in a sandwich hybridization system was reported to be 500 fmol [M. S. Urdea *et al.*, *Nucleic Acids Res.* **16**, 4937 (1988)].

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Superconductivity up to 126 Kelvin in Interstitially Doped $Ba_2Ca_{n-1}Cu_nO_x$ [02(n–1)n–Ba]

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A new high-temperature superconducting compound system, $Ba_2Ca_{n-1}Cu_nO_x$ [02(n–1)n–Ba] interstitially doped with calcium or (Ca,Cu) has been identified to exhibit a transition temperature up to 126 kelvin, the highest for a superconductor without a volatile toxic element. 02(n–1)n–Ba has body-centered tetragonal symmetry and an unusual charge-reservoir block. The compounds offer interesting opportunities for high-temperature superconductivity science and technology.

In the past 10 years, many high-temperature layered cuprate superconductors have been discovered (*1*). They can be represented by the generic formula $A_mE_2R_{n-1}Cu_nO_{2n+m+2}$ with a stacking sequence of m layers of (AO) inserted between two layers of (EO) on top of n layers of (CuO_2) interleaved by (n–1) layers of (R), where A, E, and R are various cations. The generic formula may be abbreviated in terms of the four-digit classification scheme (*2*) m2(n–1)n or A-m2(n–1)n–E for further subclassification. Presently, all superconductors that have transition temperatures (T_c's) above the liquid nitrogen boiling point of 77 K belong to or are derivable from the following compound families: (i) Cu-1212-Ba with R = Y or a rare-earth element, except Ce, Pr and Tb (such as $CuBa_2\ YCu_2O_7 = YBa_2Cu_3O_7$, commonly known as Y-123); (ii) A-22(n–1)n–E with A = Bi, Tl, Pb, or Hg, R = Ca, and with an appropriate E = Sr or Ba (such as $Bi_2Sr_2Ca_2Cu_3O_{10}$); and (iii) A–12(n–1)n–E with A = Tl, Hg, Au, (Cu,C), B, Al, or Ga, R = Ca, and with an appropriate E = Ba or Sr (such as $TlBa_2Ca_2Cu_3O_9$). Studies of these compounds reveal that layers in these compounds can be grouped into two (*3*), namely the charge-reservoir block of (EO)(AO)···(AO)(EO), and the active block of (CuO_2)(R)(CuO_2)···(R)(CuO_2). The charge-reservoir block provides the sources of charge-carriers for the active block which is considered the main component for the superconductivity in the compound. New high-temperature superconductor families would help further unravel the roles of the charge-reservoir block, the active block, or both.

The record T_c of high-temperature superconducting compounds is 134 K at ambient pressure (*4*) or 164 K at 30 GPa (*5*). Unfortunately, those with a T_c above 120 K contain volatile toxic elements such as Tl in Tl-2223-Ba, which superconducts at 125 K, and Hg in Hg-1223-Ba, which becomes superconducting at 134 K. This poses serious challenges to practical applications. Consequently (*6*), Cu-1212-Ba (or Y-123) remains the most viable material for high-temperature superconducting thin-film devices, in spite of its lower T_c of 93 K; and Bi-2212-Sr and Bi-2223-Sr for high-temperature superconducting conductors, operated at temperatures preferably below 77 K because of their weak flux pinning force. We report a new superconducting system, the interstitially doped $Ba_2Ca_{n-1}Cu_nO_x$ [02(n–1)n–Ba], which is synthesized under pressure and displays a T_c of 126 K for n = 3 or 117 K for n = 4. The 02(n–1)n–Ba compound system without C-inclusion exhibits a body-centered tetragonal I4 symmetry and a rather open charge-reservoir block, which offers new flexibility in modifying the compound. For instance, intercalation of carbonate, hydroxyl, or both ions into the charge-reservoir block transforms the 126 K phase into a more stable 90 K phase.

We searched for high-T_c compounds without volatile toxic elements by modifying the charge-reservoir block. Our examination of the existing T_c data reveals a simple empirical rule (*7*) that compounds with simpler charge-reservoir blocks, compounds whose charge-reservoir block contains Ba instead of Sr, and compounds without rare-earth elements, usually have a higher T_c. For instance, $YBa_2Cu_3O_7$ displays a $T_c \sim 93$ K, in contrast to $YBa_2Cu_4O_8$, which has a more complex charge-reservoir block and shows a lower $T_c \sim 80$ K and to $YSr_2Cu_3O_7$, which has two (SrO) layers in its charge-reservoir block and shows a lower $T_c < 60$ K. A simpler charge reservoir may be an easier way to retain the integrity of and to improve the coupling between the CuO_2 layers in the active block. The higher T_c for compounds with double BaO layers than with double SrO layers may be associated with the higher polarizability of Ba than Sr or the less possible mixing of Ba in the charge-reservoir block with Ca in the active block. The Ba-based perovskite ferroelectrics also often have a higher Curie point, below which polarization appears, than the Sr-based ones. Therefore, a desirable candidate for a high T_c without any volatile toxic element appears to be the Ba-based compound system $Ba_2Ca_{n-1}Cu_nO_x$ [02(n–1)n–Ba]. This compound system in its ideal form consists of a simple [(BaO)(BaO)] charge reservoir without any (AO) layers and an active block of n (CuO_2) layers separated by (n–1) Ca layers and is expected to display a body-centered tetragonal I4 symmetry. Compounds with similar structure were observed previously in the nonsuperconducting $(PbBa)(YSr)Cu_3O_8$ [or 0223-(PbBa) with R = (YSr)] (*8*) and the superconducting system $Sr_2Ca_{n-1}Cu_nO_{2n+2}$ [02(n–1)n–Sr] with a T_c up to ~ 85 K (*9*). The Ba-Ca-Cu-O system has also been studied previously by several groups (*10–17*) and was found to form the C-stabilized $(Cu_{1-y}C_y)Ba_2Ca_{n-1}Cu_nO_x$ [(Cu,C)–12(n–1)n–Ba]

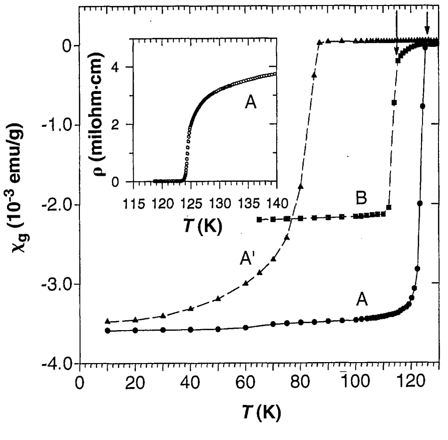

Fig. 1. Field-cooled $\chi(T)$ for A samples (0223-Ba) and a B sample (0234-Ba) as synthesized (A and B) and after exposure to humid air (A′). Inset: ρ(T); emu indicates electromagnetic units.

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with $y \sim 0.5$, which has a T_c up to 120 K and a P4 symmetry. A trace of superconductivity above 120 K was also reported (*14–17*) in a few cases and attributed to a possible modified (*16*) or an optimized (*17*) (Cu,C)-1223-Ba.

An ideal 02(*n*–1)*n*–Ba compound is too unstable to form even under high pressure and the Cu-valence is too high for superconductivity to occur even if formed. By inserting Ca (and possibly O) between the two (BaO) layers in the charge-reservoir to fill the open space and to adjust the Cu valence, we succeeded in synthesizing under high pressure and identifying the interstitially doped $Ba_2Ca_{n-1+x}Cu_{n+y}O_z$ [02(*n*–1)*n*–Ba] for $0.4 < x \le 1.0$, $0 \le y \le 0.7$, and $n = 3$ or 4. We found that Ca in the charge reservoir can also be partially substituted by Cu without affecting the T_c. The formation of 02(*n*–1)*n*–Ba depends sensitively on the precursor, the processing pressure, processing temperature, and particularly the C-contaminant in the precursor and the CO_2 partial pressure present during synthesis. 0223-Ba does not form at pressures below 3.5 GPa, from C-contaminated precursor, or at temperatures above 900°C. Higher temperatures and C-contamination favor the formation of (Cu,C)-1223-Ba. $Ba_2Cu_3O_{5+x}$ was first prepared in flowing O_2 at between 650° and 860°C from cation oxides thoroughly mixed in a glove-bag filled with Ar or N_2 to avoid CO_2 and H_2O contamination from air. The presence of any unreacted BaO in $Ba_2Cu_3O_{5+x}$ will result in the absorption of CO_2, H_2O, or both from air. $Ba_2Cu_3O_{5+x}$ was then powdered and mixed with CaO to form precursors of nominal composition of $Ba_2Ca_{n-1+x}Cu_{n+y}O_z$ with $0 \le x \le 1$ and $0 \le y \le 1$ in Ar or N_2 atmosphere. In a few cases, C was purposely added to make (Cu,C)–12(*n*–1)*n*–Ba for comparison. Compacted pellets of these precursors were calcinated in flowing O_2 between 650° and 900°C for 40 to 48 hours, with two intermittent pulverizations and compactions. The pellets were subsequently powdered, mixed with AgO as an oxidizer, whose amount depends on the O-content in $Ba_2Cu_3O_{5+x}$ and can be zero when x is large, wrapped in Au foil, and heated in a multianvil Walker module (*18*) from Rockland Research under 5 to 6 GPa at 800° to 1000°C for 0.5 to 24 hours, with MgO as pressure medium. A Ca-doped $LaCrO_3$ furnace, instead of the graphite

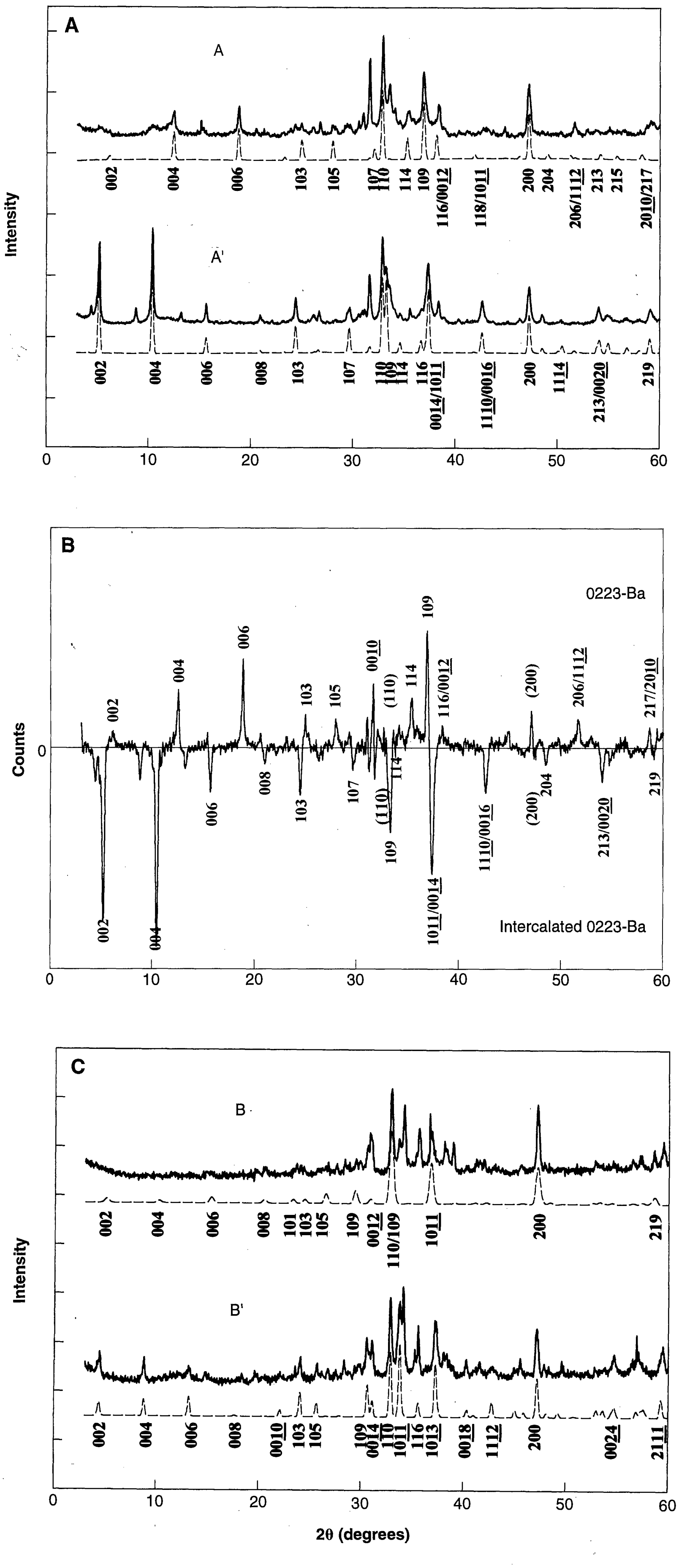

Fig. 2. XRD patterns (**A**) for the A sample as synthesized (A) and after exposure to humid air (A′); (**B**) for XRD(A)–XRD(A′); and (**C**) for the B sample as synthesized (B) and after exposure to humid air (B′). The dashed curves are computer simulation patterns based on the proposed interstitially doped 0223-Ba and 0234-Ba model (Fig. 3).

furnace commonly employed, was used to avoid accidental C-contamination at high temperature. Even with such precautions, a small amount of (Cu,C)-1223-Ba was detected in some of the 0223-Ba samples. The pressure was determined with the load-versus-pressure curve provided by Rockland Research and the temperature by a D-type thermocouple located next to the sample inside the high-pressure cell.

The samples were characterized in their as synthesized and some in their postannealed states. The T_c was determined resistively by the standard four-probe technique and magnetically by a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The structure was determined by a Rigaku D-MAX/BIII powder diffractometer. The composition was measured by an energy dispersive spectrometer for x-ray analysis (EDX) attached to a transmission electron microscope (TEM) and a scanning electron microscope (SEM), a wave-dispersive spectrometer (WDS), and an electron energy-loss spectrometer (EELS) attached to the TEM.

The magnetic susceptibility (χ) results of our samples (Fig. 1) exhibit a sharp transition with their onset T_c clustering around two regions, 121 to 126 K and 117 to 118 K, corresponding to two groups of samples, A samples and B samples, respectively. The superconducting volume fraction of these samples reached $\geq$40%, as determined magnetically in the field-cooled mode without the demagnetization correction. Resistivity (ρ) becomes zero at temperatures up to 124 K for the A samples (Fig. 1, inset). After exposure to humid air for 24 hours, the sharp superconducting transition shifts down to ~90 K for the A samples (Fig. 1) but only to ~116 K for the B samples.

The x-ray diffraction (XRD) patterns of all samples show one major phase for each sample group together with some mono and binary oxides (Fig. 2, A and C). In some samples, (Cu,C)-1223-Ba also appeared as a minor phase. The main peak of fine Ag dispersions, resulting from reacted AgO, was weak and overlapped with the 38.12° peak of the 0223-Ba phase. Large changes in the XRD patterns for these samples after exposure to humid air for 24 hours are also evident in Fig. 2, A and C. The differential XRD pattern of one A sample before and after being exposed to air was also taken to extract the diffraction patterns (excluding the hk0 lines) of these two superconducting phases (Fig. 2B), by removing those peaks associated with impurities. These two major phases in A and B samples as synthesized can thus easily be described in terms of a body-centered tetragonal (I4) structure with lattice parameters of a = 0.385 nm and c = 2.82 nm, and a = 0.385 nm and c = 3.48 nm, respectively. The I4 structural symmetry is evident from the systematic absence of the diffraction lines with $h+k+l$ = odd (Fig. 2). The lattice parameters of phases in A and B samples after exposure to air become a = 0.385 nm and c = 3.37 nm, and a = 0.385 nm and c = 4.03 nm, respectively, with the I4 symmetry unchanged.

The WDS and EDX data on grains from the as synthesized samples, show a cation ratio of Ba:Ca:Cu = $2{:}2+x{:}3+y$ for the A samples and $2{:}3+x{:}4+y$ for the B samples, both with rather large ranges of interstitial dopings, that is, $0.4 \leq x \leq 1.0$ and $0 \leq y \leq 0.7$. No C was detected in these grains to our resolution of ~0.04 mol per formula by EDX and EELS. These results, together with the XRD data, suggest that the A and B samples can be represented by $Ba_2Ca_{n-1+x}Cu_{n+y}O_z$ with n = 3 and 4, respectively, and belong to the body-centered tetragonal 02(n–1)n–(Ba) system doped interstitially by (Ca,Cu). An atomic arrangement (not including the interstitial O sites) proposed for the interstitially doped 0223-Ba is displayed in Fig. 3. Computer-simulation diffraction patterns (Fig. 2) based on this model account well for the observed XRD pattern. Such a model does not consist of the rock-salt [for the A–22(n–1)n–E and A–12(n–1)n–E families] or the fluorite [for the 1T′ phase] slab layer in the charge-reservoir block. Instead, the cation dopant [that is, (Ca,Cu)] most likely occupies the 4d positions in the lattices to satisfy the I4 symmetry and the observed lattice parameter c, simultaneously. This rather open structure enables the easy intercalation of the OH^-, CO_3^{2-}, or both ions to the charge-reservoir block, leading to the observed decrease of T_c in 02(n–1)n–Ba. Experiments also showed that the T_c's of 0223-B and 0234-Ba behave differently from that of (Cu,C)-1223-Ba with doping after various identical annealings under thermal equilibrium (Fig. 4). All these suggest that the superconducting, interstitially doped 02(n–1)n–Ba represents a genuine new compound family. Unfortunately, the compound crystalinity degrades under a 200-eV electron-beam irradiation from a TEM. The local environment of the interstitial (Ca,Cu)-dopant and the O sites are yet to be determined.

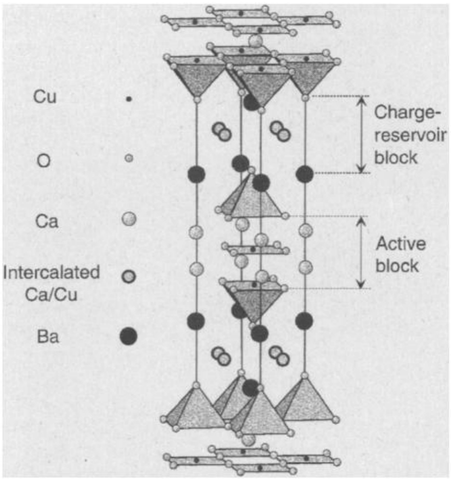

Fig. 3. The proposed schematic atomic arrangement of interstitially doped 0223-Ba, excluding O in the charge-reservoir block.

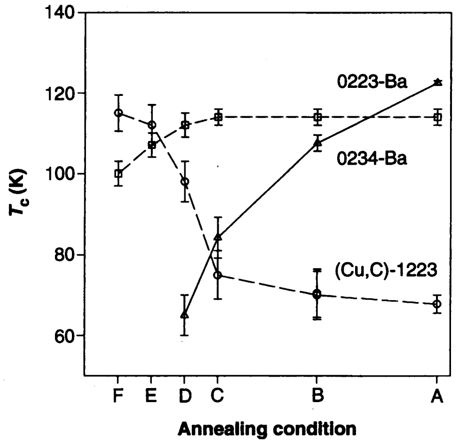

Fig. 4. Effects of annealing under different thermal equilibrium conditions on the T_c of 0223-Ba, (Cu,C)-1223, and 0234-Ba. Annealing conditions are: A, as synthesized; B, 300°C in O_2; C, 300°C in Ar; D, 400°C in Ar; E, 500°C in Ar; and F, 600°C in Ar.

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