Sampling the phase diagram of the cuprate superconductors

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Introduction

In 2004 the DFG (Deutsche Forschungsgemeinschaft) founded the research unit FOR 538: ” Doping Dependence of Phase Transitions and Ordering Phenomena in Cuprate Superconductors ”, which consisted of 7 different projects, one of which is ”Crystal Growth of p and n-doped cuprate superconductors”. Goal of this project is the growth and characterization of high purity single crystals of the high temperature superconductors to provide samples for different spectroscopic experiments within the ”Research Unit High Temperature Superconductivity ”. By the end of the year 2006 the renewed proposal for the Research united was not only reviewed positively again, but was even enlarged and now consists of 9 groups. The project crystal growth within the research unit is of particular importance in that sense, that it provides the common sample basis to the different experimental projects within the research unit. Only such a common sample basis of high quality single crystals of the cuprates makes the comparison of the results obtained by the various experimental techniques reliable.

Sample space

In order to cover the whole phase diagram of the high temperature superconductors, which is one of the central ideas of this research unit, crystals with well defined and homogeneous doping of both, the p and n-doped compounds need to be grown. On the hole doped side of the phase diagram we focused on the systems of $YBa_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2CaCu_2O_8$. There are restrictions in the accessible doping regime for the $YBa_2Cu_3O_{7-\delta}$ even when co-doping with Ca is applied (see Fig. 1).

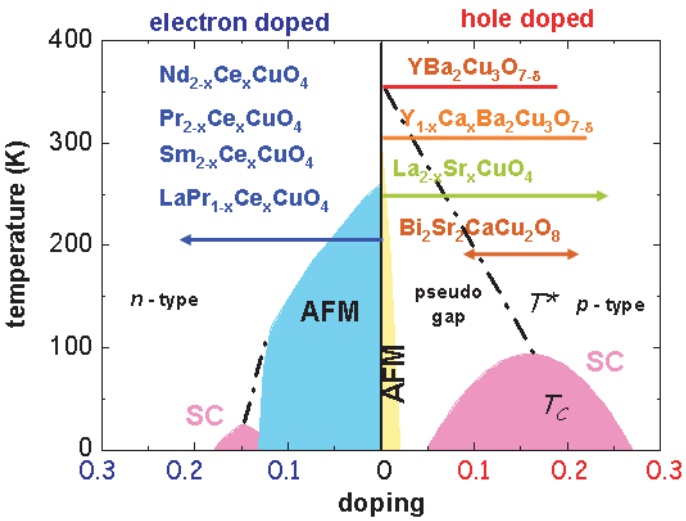

Figure 1: Accessible regions of the phase diagram for the different compounds of the high temperature superconductors

For the $Bi_2Sr_2CaCu_2O_8$ system one is actually limited to a relatively small region around optimal doping. For this reason we have started to grow single crystals of the $La_{2-x}Sr_xCuO_4$ system, since they can be used to access the reminder part of the phase diagram as well as it is possible to access the whole doping range of the hole doped side by using one compound only. Moreover, they allow a more direct

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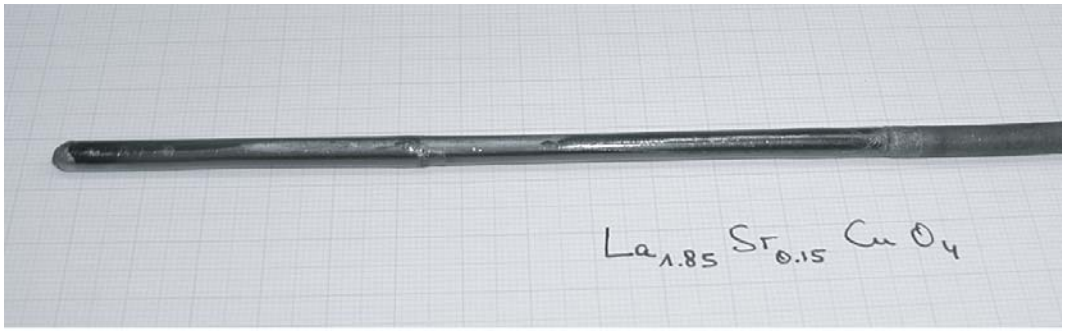

Figure 2: Single crystal of $La_{2-x}Sr_xCuO_4$ grown in the mirror furnace at WMI. The last about 6 cm on the left end of the sample are formed by a single crystallite.

comparison of the n- and p-doped side of the phase diagram, due to the similarity of both the critical temperature and the structure with the electron doped 214-compounds.

For the electron doped side of the phase diagram only 214-compounds are available to probe the phase diagram. We concentrated our efforts on the crystal growth of $Pr_{2-x}Ce_xCuO_4$, $Nd_{2-x}Ce_xCuO_4$ $Sm_{2-x}Ce_xCuO_4$ or mixtures such as $LaPr_{1-x}Ce_xCuO_4$.

Research Status and Own Previous Work

There are several families of cuprate superconductors. However, by materials or technical reasons there are only a few families that are suitable for achieving the goals of our research unit. There are the following compounds of the high temperature superconductors, from which a set of high quality single crystals with different doping level can be produced:

- $YBa_2Cu_3O_{7-\delta}$:
  Due to the peculiarities of the phase diagram (the small solubility in the solvent) of the 123-compounds, high quality crystals of the 123-compounds without solvent inclusions have to be grown in a crucible. Due to the highly reactive melts of the CuO-BaO flux system all usual refractory crucible materials are heavily corroded by the flux and the crystals grown in such experiments were contaminated by the crucible material. The problem has been solved with the development of the adapted crucible material $BaZrO_3$ [1, 2], in which crystals with a purity of up to 99.995 % can be grown. In general it should be remarked that due to the perfection of the available crystals the stoichiometric compound $YBa_2Cu_3O_{7-\delta}$ would be the ideal sample system for a systematic study of high temperature superconductors. However, unfortunately some regions in the over-doped range can not be accessed by this compound. Furthermore, $YBa_2Cu_3O_{7-\delta}$ does not cleave easily, which makes the use of this compound more complicated for techniques requiring cleaved surfaces such as angle resolved photo emission.

- Bi-2212 ($Bi_2Sr_2CaCu_2O_8$):
  Besides the 123-compounds, the Bi-based family of high temperature superconductors with 3 different compounds are interesting candidates for sample systems for the coordinated work within our research unit. The family consists of the following three members: the single layer compound $Bi_2Sr_2CuO_6$ with a transition temperature of T_c up to 40 K, the double layer compound $Bi_2Sr_2CaCu_2O_8$ with T_c around 96-98 K and the 3-layer compound $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ with a T_c of around 110 K. While the first crystals of these compounds have been grown from the flux with the same problem of crucible corrosion like in $YBa_2Cu_3O_{7-\delta}$, meanwhile the development of crystal growth in mirror furnaces has made the use of crucibles obsolete and has led to a considerable improvement of the crystal quality in these systems. Nevertheless, the crystal quality is

limited by the intergrowth of the three superconducting phases and by a partial solubility of Bi on Sr sites. The optimization of the growth parameters [3–6] has led to a pronounced improvement of the crystal quality in the last years. In particular, for the double layer compound Bi-2212 high quality crystals of several grams and with low defect concentration can be grown using the zone melting technique in a mirror furnace. Due to the fact that this compound cleaves very easily perpendicular to the *c*-direction, samples of this system are ideal for angle resolved photo emission spectroscopy and other surface sensitive spectroscopies used within the research unit. However, as already stated above crystals of large size and good crystalline quality are only obtained in a narrow region around optimal doping.

- 214-Systems ($La_{2-x}Sr_xCuO_4$, $Nd_{2-x}Ce_xCuO_4$ and $Pr_{2-x}Ce_xCuO_4$):
  The so-called 214-systems with the compounds $La_{2-x}Ba_xCuO_4$ and $La_{2-x}Sr_xCuO_4$ have been the first cuprate superconductors discovered. [7] Starting from the antiferromagnetic compounds Re_2CuO_4 doping with Sr^{2+} on the hole doped side or with Ce^{4+} on the electron doped side leads to the formation of solid solutions, which become superconducting at certain doping levels. The formation of simple solid solutions in these compounds makes them in principle very attractive as a basis of a sample set. However, on the other hand, the formation of solid solutions makes it quite difficult or even impossible to grow big homogeneous samples in crucibles. This is caused by the fact that the distribution coefficient of the dopant is unequal to unity, which obviously leads to concentration gradients of the dopant during the growth process. Fortunately, this problem has been greatly overcome by the development of the TSFZ-method (travelling solvent floating zone). With this method large and homogeneous crystals of the 214-compounds can be grown (see Fig. 2), especially in long lasting growth experiments, when the equilibrium state for the dopant concentration has been reached within the solvent.

  - *$La_{2-x}Sr_xCuO_4$:*
    This hole doped compound has some particular advantages compared to the other hole doped systems such as $YBa_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2CaCu_2O_8$, which are the most promising systems for the sample set on the hole doped side of the phase diagram. Firstly, the doping range that is in principle accessible with this compound extends from the undoped antiferromagnet to the overdoped metal. In this way, basically the whole doping regime of the hole doped side of the phase diagram of the cuprates can be accessed by using only a single compound. Secondly, the critical temperature as well as the structure is similar to the electron doped compounds $Nd_{2-x}Ce_xCuO_4$ and $Pr_{2-x}Ce_xCuO_4$, which are considered in this project to serve as the sample basis for the study the electron doped side of the phase diagram of the high T_c superconductors. Certainly, there are also some shortcomings for this compound. In particular, compared to the $Bi_2Sr_2CaCu_2O_8$ system it is much more difficult to cleave them, thereby hampering their use for ARPES experiments. Nevertheless, first experiments have shown that it is possible to cleave them. For the Raman and infrared spectroscopies first experiments have shown that measurements are possible using single crystals with extremely fine polished surfaces. Finally, since large $La_{2-x}Sr_xCuO_4$ crystals with a weight of several grams (see Fig. 2) can be produced in very good quality, they are ideal samples for the inelastic neutron scattering experiments.
  - *$Nd_{2-x}Ce_xCuO_4$ and $Pr_{2-x}Ce_xCuO_4$:*
    Similar arguments as for $La_{2-x}Sr_xCuO_4$ also apply for the electron doped compounds. Upon doping with Ce^{4+} solid solution crystals are formed up to the solubility limit of the different compounds. However, superconductivity exists only in a narrow range of cerium concentrations, e.g. between $x = 0.14$ and $x = 0.17$ in the $Nd_{2-x}Ce_xCuO_4$ compound [8]. The width of this doping regime is known to depend on the rare earth ion. In these materials one of the most striking properties is that Ce-doping alone is insufficient. In addition, removal

of oxygen is a necessary step to achieve superconducting samples. Usually this is done by annealing the samples at elevated temperatures in a low pressure oxygen environment. The way this reduction procedure is performed can lead to different transition temperatures [9] and ultimately can lead to unstable samples that decompose with time. The recipes for both the growth of the crystals as well as for oxygen reduction [9–12] differ between the different groups working in this field. The preparation of big, well-defined and stable crystals of these compounds was and partially remains one of the most challenging parts of our work.

– *$LaPr_{1-x}Ce_xCuO_4$:*
Since the magnetic moment of Nd^{3+} hampers the use of the Nd-214 compound in various experiments and a solubility limit of $x = 0.15$ for Ce^{4+} has been found in the Pr-214 compound, the system of $LaPr_{1-x}Ce_xCuO_4$ might be a solution to access the further overdoped region of the electron doped side of the phase diagram. The superconducting region within this system seems to have a broader doping range and neither the La nor Pr ions have a magnetic moment. Therefore, we will also try to grow single crystals of $LaPr_{1-x}Ce_xCuO_4$.

Own Previous Work

Within the last 3 years the crystal growth laboratory at the Walther-Meißner-Institut has been further extended and the applied crystal growth techniques have been considerably refined to improve the quality of the fabricated single crystals. Moreover, the methods for the characterization of the single crystals have been improved and broadened. For example, the possibility to orient the crystals of the 214-compounds has been brought to high perfection. It is possible to orient to a precision of better then 0.5° and to ultra fine polish the surfaces to a perfection that Raman and infrared spectroscopies can be performed on such samples. This important work has been performed using also the facilities of the crystal laboratory of the Department of Physics (TUM), which is headed by A. Erb.

The production of the crucially important $BaZrO_3$ crucibles has been improved, leading to a higher success rate of the growth of the 123-compounds and thus to a higher output of samples. For the growth process both flux growth in crucibles and crucible free growth using the TSFZ-technique have been applied. The rapid progress in the improvement of growth techniques for known materials systems as well as in the development of novel growth methods was only possible due to the broad expertise and long standing experience available at the WMI. The head of the crystal growth group is well known for his expertise in crystal growth of the high temperature superconductors and has made major innovations in this field such as the development of the flux growth method of $YBa_2Cu_3O_{7-\delta}$ out of $BaZrO_3$-crucibles [1, 2]. Without any doubt this method led to the crystals of highest purity for this compound. This method, which so far has been accomplished only by a few other groups worldwide, meanwhile has been developed to the standard method for the growth of $YBa_2Cu_3O_{7-\delta}$ crystals with highest purity. Moreover, several special methods to homogenize the oxygen distribution and thus the doping homogeneity in the samples have been developed. These developments and the resulting improved sample quality had considerable effects on the physical properties of the samples, like for instance on the flux pinning [13] or the general behavior of the vortex

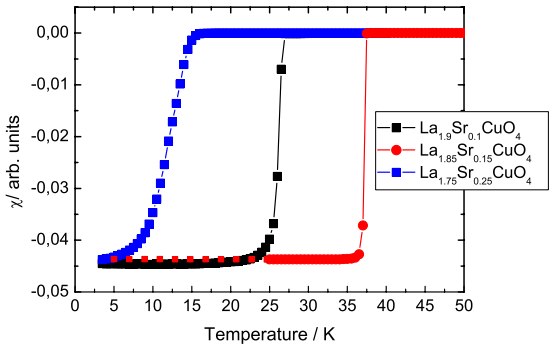

Figure 3: Transition curves of various $La_{2-x}Sr_xCuO_4$ single crystals.The optimally doped one consists of a 588 mg (about 6 mm long disc) heavy piece of the single crystal of $La_{2-x}Sr_xCuO_4$, shown in Fig.2

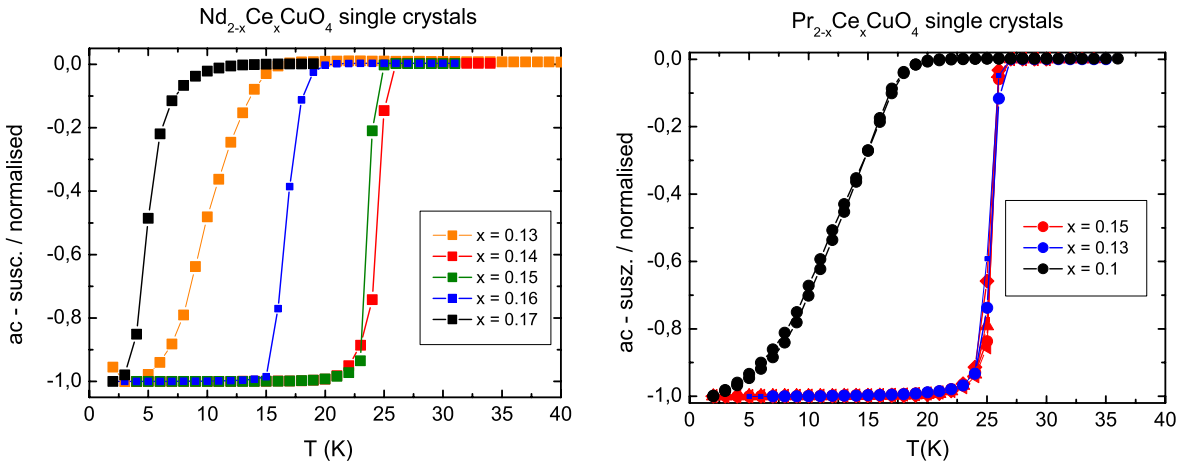

Figure 4: Normalized ac susceptibility plotted versus temperature for several $Nd_{2-x}Ce_xCuO_{4-\delta}$ (**left**) and $Pr_{2-x}Ce_xCuO_{4-\delta}$ (**right**) single crystals with different doping level.

state [14–16] of the high temperature superconductors. The basis of these developments was an intensive study of oxygen diffusion [17, 18] and oxygen ordering.

For the other compounds the TSFZ technique has been used for the growth of single crystals and brought to high perfection. In particular, the use of different values of the oxygen partial pressure for the growth atmosphere during the growth of crystals with different doping concentrations has led to much more stable growth conditions and thus to a higher perfection (typical values of the mosaic spread are below 0.07° for the electron doped 214-compounds and 0.03° for $La_{2-x}Sr_xCuO_4$) and bigger size (up to 6 grams in the case of $La_{2-x}Sr_xCuO_4$) of the crystals.

Results

In the following we summarize the status achieved within the first period of the project for the growth of the various high-T_c compounds .

- $YBa_2Cu_3O_{7-\delta}$
  We have grown Ca-doped $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ crystals with various doping concentration from the undoped ($x = 0$) compound up to a Ca-concentration of $x = 0.14$ in intervals of 0.02. These crystals have been used in various experiments within and outside [19] of the research unit. These studies (Raman and infrared spectroscopy) were mainly focussed on the underdoped region $\delta = 1$ and have brought new insight in the phenomena of the formation of stripes in this compound.

- $Bi_2Sr_2CaCu_2O_8$
  For the $Bi_2Sr_2CaCu_2O_8$ system the main activity was dedicated to the growth of Ni- and Zn-doped samples, which have been used again in various activities within the research group [20]. These crystals reach several cm in length and about 8 mm in diameter and can therefor also be used in neutron experiments. Upon doping with Yttrium on the Ca-site the crystals tend to become smaller in size and the superconducting transitions, which are sharp for the undoped system as well as for Ni-doped samples, tend to become broader with increasing Y-doping. This indicates a spatially inhomogeneous distribution of the Y dopant atoms. To improve the situation, probably the use of different oxygen partial pressure during growth might lead to more homogeneous samples with narrower superconducting transition. To achieve this improvement is especially important for the ARPES experiments on the underdoped side of the phase diagram.

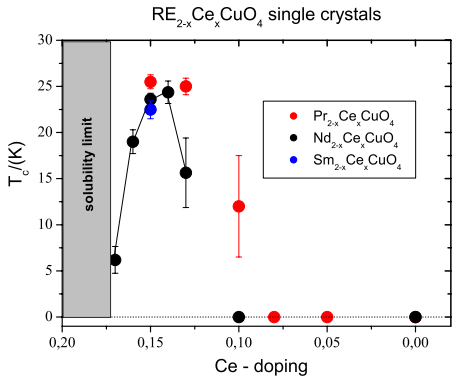

Figure 5: Transition temperatures for various $RE_{2-x}Ce_xCuO_4$ single crystals.

- 214-systems: $La_{2-x}Sr_xCuO_4$, $Nd_{2-x}Ce_xCuO_4$ and $Pr_{2-x}Ce_xCuO_4$
  Within the first period of the project extensive work on the crystal growth of the 214-compounds has been performed. Especially the growth of high quality 214-single crystals on the electron doped side of the phase diagram is very challenging as has already been outlined above. In our systematic study of the growth process we learned that depending on the desired doping level an adapted oxygen partial pressure has to be used for the growth atmosphere. This led to a much better stability of the growth conditions and, in turn, to a higher perfection and larger size of the crystals.

- $La_{2-x}Sr_xCuO_4$
  Our work on the $La_{2-x}Sr_xCuO_4$ compound was started only in the 3rd year of the first project period. Nevertheless, a rapid progress in the crystal growth of this compound was possible due to the broad experience with the electron doped 214-systems. Already the first experiments have led to very big (several grams) and homogeneous single crystals of this compound (see Fig. 2). The crystals with optimal doping have a transition temperature of $T_c = 37.5\,\mathrm{K}$ with a transition width of less than 1 K [21](see Fig. 3). Up to now we have produced crystals in the doping range of x = 0, 0.15, 0.2, 0.25. Crystals of the optimally doping have been distributed to various members of the research unit and abroad. They are currently under investigation.

- $Nd_{2-x}Ce_xCuO_4$, $Pr_{2-x}Ce_xCuO_4$
  Single crystals of the compounds $Nd_{2-x}Ce_xCuO_4$ and $Pr_{2-x}Ce_xCuO_4$ have been successfully grown within the first period of the project. The stability of the growth conditions have been found to strongly depend on oxygen partial pressure and doping for these compounds. After optimization of the growth conditions we reproducibly obtain large single crystals of these compounds. For optimally doped samples of $Nd_{2-x}Ce_xCuO_4$ and $Pr_{2-x}Ce_xCuO_4$ the maximum transition temperatures are $T_c = 23.5\,\mathrm{K}$ and $T_c = 25.5\,\mathrm{K}$, respectively, which are the highest T_c values reported so far [22]. In both cases the transition width was only about 1 K (see Fig. 4). Crystals of the whole series of $Nd_{2-x}Ce_xCuO_4$ and $Pr_{2-x}Ce_xCuO_4$ compounds from the antiferromagnet up to the solubility limit of Cerium, which has been found to be $x = 0.18$ and $x = 0.15$, respectively, have been grown. The crystals have also been proven to be absolutely stable over more than one year without any sign of decomposition. Both the chemical stability and the good superconducting properties were achieved by an optimization of the conditions for the critical annealing process, which is necessary to remove the interstitial oxygen from the crystals after the growth process. On well oriented samples with extremely fine polished surfaces successful Raman- and infrared spectroscopy experiments have been performed. For the ARPES experiments it was possible to cleave

the samples. Fig. 5 shows the dependance of T_c versus doping for different rare earth atoms in the electron doped 214-compounds. It is interesting that the maximum of T_c increases for the lighter rare earth atoms. This is one of the reasons why we want to grow crystals of the $LaPr_{1-x}Ce_xCuO_4$.

Summary

In summary we are able to probe the whole sample space of both the hole and electron doped superconductors with high quality single crystals.

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