

Fabrication and properties of single crystals and LPE films in some HTSC systems

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Abstract

High quality single crystals and thin films of some HTSC systems with low-level dopants are grown by employing methods of electrochemical and controlled crystallization on seeds and LPE technique. Data of neutron and X-ray analyses and physical properties investigations confirm the perfect quality of the crystals.

1. Introduction

What does a man need perfect single crystals of HTSC for? The answer to this question can be found if one takes into consideration the absence of a preferable theory, despite the appearance of a lot of theoretical and experimental papers following the discovery (1) of high T_c superconductivity 6 years ago.

Progress toward understanding of these materials is closely connected with the validity of the experimental data, which in turn depends on the sample quality. Batlogg (2) presented generic phase diagram for layered cuprates. As electrons concentration in the CuO_2 layers changes by doping of the parent compound, the transition from the dielectric antiferromagnetic with long-range magnetic order to:

- 1) an insulator with spin glass type magnetic ordering,
- 2) a metal with superconducting ground state, and lastly to
- 3) a normal metal occurs. This diagram is, so far, of tentative character for some cuprate families, since it is not always possible to vary chemical composition over a sufficiently broad range. However, it is known that for all high- T_c superconducting compounds, the transition dielectric-metal is observed at very high concentrations of doping impurities $n = 10^{21} - 10^{22} \text{ cm}^{-3}$. In this case, the impurities distribution is unstable as regards new phase formation and appearance of mixed state. Though it is possible that the high threshold concentration value can be caused by a large number of defects present in the lattice. Thus, the defects reduction can elucidate a real phase diagram for these compounds.

This paper will present the results on growth and study of properties of perfect single crystals and LPE films obtained by our team for the past two years.

The paper is organized as follows: the next part of it reviews the data on controlled growth of cuprate single crystals. In the third part, the results on the electrochemical process of single crystals preparation and phase formation in the $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (BCBO) system will be discussed. The fourth part examines the

experimental evidence obtained on single crystalline $\text{YBaCuO} / \text{PrBaCuO}$ heterostructures prepared by LPE technique. The concluding part of the paper includes the results of investigation of physical properties of the R_2CuO_4 perfect single crystals.

2. Controlled growth of cuprate single crystals

2.1 $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system (LSCO)

$(\text{La}_{2-x}\text{Sr}_x)_2\text{CuO}_4$ quasiternary compounds possess a number of unique physical properties. Its solution is complicated by the incongruent melting and by the fact that all the materials of the technological equipment are heavily corroded by the fluxes. The use of superstoichiometric CuO , as a solvent, excludes the incorporation of the impurities into the single crystals. Some groups have made significant progress in the growth of large single crystals LSCO with significant Meissner fractions, but crystals perfection was not very good (2-5).

We employed the technique of growth of a limited number of seeds on a platinum crystal holder in the dynamic regime (6). From a comprehensive study of the phase diagram for $\text{La}_2\text{O}_3\text{-CuO}$ system, we determined primary crystallization ranges of La_2CuO_4 and two recently discovered phases $\text{La}_8\text{Cu}_7\text{O}_{19}$ and $\text{La}_2\text{Cu}_2\text{O}_5$ (Fig.1). In this system of flux melt, the LSCO crystallizes only at high concentration of the crystal forming oxides. With a view to limit the number of seeds, a special crystal holder was designed.

High-quality bulk $\text{La}_2\text{CuO}_{4+\delta}$ crystals (Fig.2) were synthesized in the following way. The fluxed melt was homogenized at temperatures, by 15-30°C higher than saturation temperature, and there after rapidly cooled down to the temperatures by 1-2°C higher than that of spontaneous crystallization. Then the temperature was lowered at a rate of 1-2°C/24 hrs, with the fluxed melt mass being 500-1500g.

The growth of high-quality single crystals of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x > 0.1$ is to date impeded by a very

low distribution coefficient of Sr^{2+} and its inhomogeneous distribution over the crystal volume obtained by the well-known method of spontaneous crystallization from a fluxed melt or float-zone technique (4,5).

The solubility curves and temperature region of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ phase existence have been studied to optimize the conditions of seeded growth and chemical compositions of the as-grown single crystals. As a result, homogeneous truncated bipyramid-like single crystals of $10 \times 10 \times 1.5 \text{ mm}^3$ in size with x up to 0.4 have been grown (6).

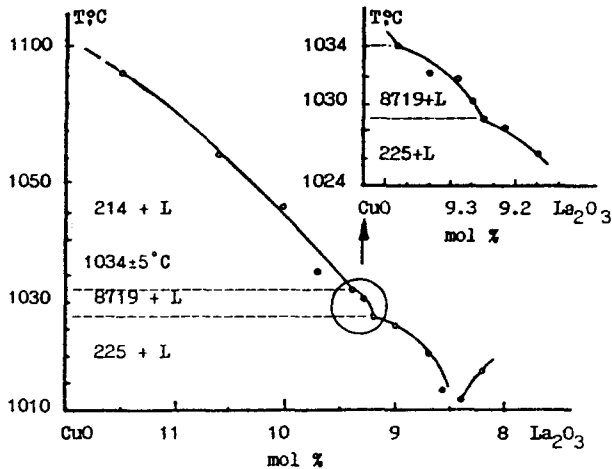


Fig.1. Portion of refined quasi-binary phase diagram of the $\text{La}_2\text{O}_3\text{-CuO}$ system.

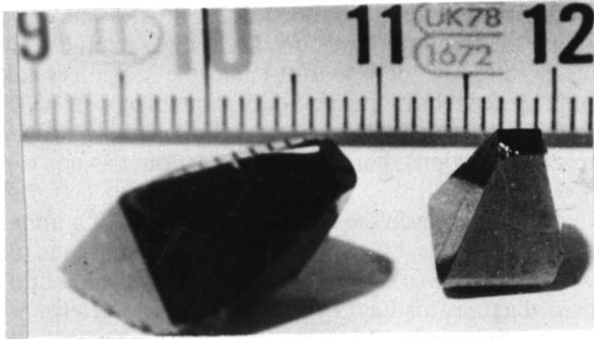


Fig. 2. The as-grown single crystals of $\text{La}_2\text{CuO}_{4+\delta}$.

2.2. Growth of single crystals of $\text{R}_{2-x}\text{Ce}_x\text{CuO}_4$ ($\text{R}=\text{Pr, Nd, Sm, Eu, Ga}$)

Based on the data of phase equilibria in the $\text{R}_{2-x}\text{Ce}_x\text{CuO}_4\text{-CuO}$ systems the fluxed melt compositions of single crystals have been chosen (7). Depending on rheological properties of the fluxed melts and growth morphology, two methods of crystal growth were used. The first one is the controlled seeded growth with continuous stirring of the fluxed melt, the second - the growth of single crystal plate on a platinum wire on the surface of the fluxed melt in a static regime. In the

latter case, we managed to obtain single crystal discs up to 70 mm in diameter and up to 3 mm in thickness. As shown by the EPMA analysis, the Ce^{4+} ions are uniformly distributed in the single crystal volume and their distribution coefficient exceeds unity (8).

2.3. Growth and study of bulk $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) single crystals.

It is widely accepted that YBCO is one of the most important compounds of HTSC. Numerous attempts have been made to obtain YBCO single crystals of large size and high quality. Bulk single crystals faceted by the (001), (101) and (011) planes were first grown (9). Large crystals, named "block crystals" were obtained under peritectic condition by several groups and were used for neutron diffraction experiments (10-12). Recently, Takei (13) has prepared single crystals from the solid-melt mixtures.

We have found that YBCO single crystals could be obtained most efficiently from flux melt involving small amount of Y_2O_3 solved in the BaO-CuO mixture close to the eutectic one (14). The advantages of this system are represented by fairly low viscosity within the whole growth temperature range.

The concentration stability range for the YBCO phase is given in Fig.3. As the cooling rate reduces, the crystal habit changes from simple faceted forms to more complicated ones emerging in the tangential growth mechanism. As a result one could observe crystals with well developed (101) and (011) faces (Fig.4). After annealing in oxygen atmosphere single crystals with dimensions up to $4 \times 3 \times 3 \text{ mm}^3$ have $T_c = 93\text{K}$ and $\Delta T_c < 0.3\text{K}$.

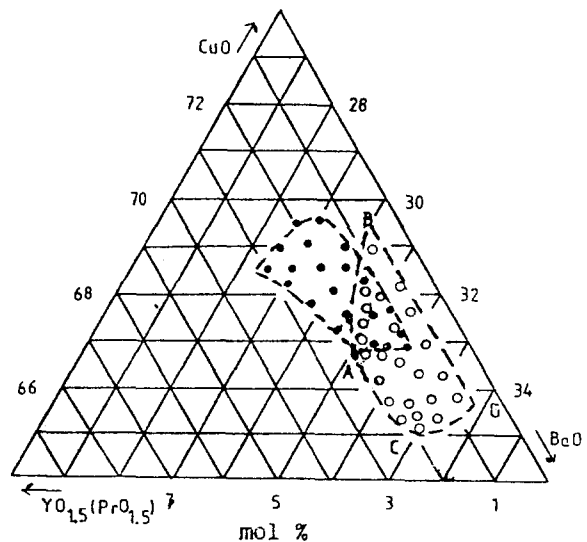


Fig.3. Quasi-ternary phase diagram with primary crystallization fields of YBCO (.) and PrBCO (°).

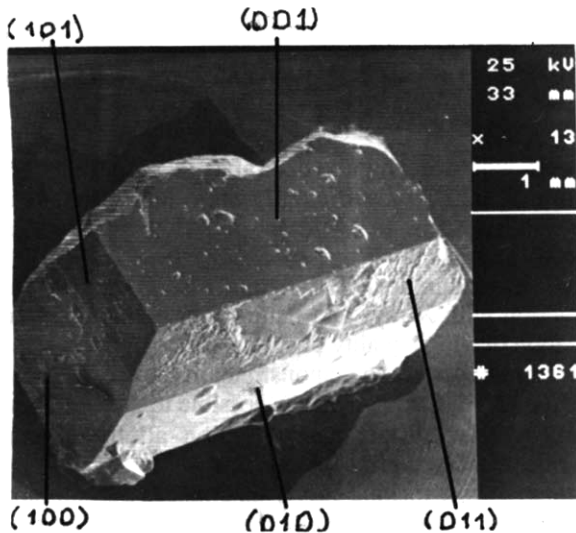


Fig.4. The as-grown single crystals YBCO.

A major problem related to the growth of YBCO single crystals is impurity ion inclusions due to interactions between the melt and the crucible materials. This problem can be solved by using a composite ceramic crucible without foreign ion inclusions. YBCO single crystals with a surface of up to 25 mm² and 0.2 mm thickness were grown from a Y₂O₃ crucible (15).

To obtain YBCO single crystals, we used two growth techniques. First, spontaneous crystallization from the melt, and second, growth of a limited number of seeds on a rotating yttrium holder. The crucible containing Y₂O₃, BaO and CuO mixture of oxides in a molar ratio close to 1:2:3 was fabricated by the explosion technique with subsequent annealing at 950°C for 24 hrs (16). AC susceptibility measurements of the as-grown crystals revealed the T_C at 90K with $T_C^{on} = 94K$.

2.4. Growth of YBCO single crystals on seeds

YBCO compound is known to have the narrow composition and temperature range of primary crystallization as well as extremely low stability in supercooled state. Therefore, one could attain the controlled growth on seeds of large perfect single crystals only at extremely low degree of solution over-saturation under conditions of controlled mass transfer.

To the best of my knowledge, these investigations are well under way in Chernogolovka and Minsk. The Zhokhov's team employs a furnace with a system of two stand-alone horizontal heaters, rotatable crucible and stationary seeds (17). Upon homogenizing the solution and depositing nutrient on the bottom of the crucible, the axial temperature gradient changes from negative to positive and the growth of seeds at constant over-saturation under conditions of intensive mass transfer occurs.

The single crystal splice with dimensions of 8x6x5 mm³ is obtained after growing for 17 days. We use less

concentrated fluxed melt and very slow supercooling in the temperature range from 980 to 970°C, intensive stirring of the fluxed melt with the crystal holder. The positive axial temperature gradient varied during the process from 0.5 to 2°C/cm. The crystals grown for 5 days are shown in Fig.5.

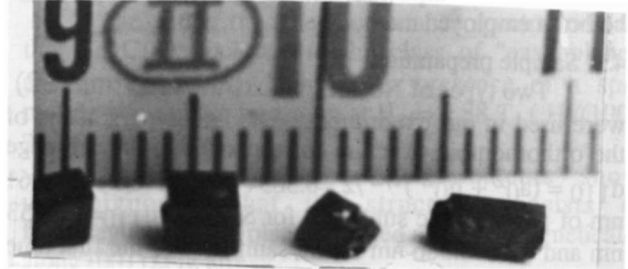


Fig.5. Single crystals of YBCO grown on seeds.

3. Experimental study of superconducting single crystals in the BKBO system

Superconductivity in the BKBO system has been first reported in (18). These compounds have cubic structure over a broad range $0.3 < x < 0.5$ of alkali metal concentration (19). The presence of crystallochemical and phenomenological features common with the layers superconductors indicates a possibility of similar mechanism responsible for high T_C superconductivity. BKBO $0.1 < x < 0.6$ single crystals were grown from the KOH fluxed melt by Norton technique (20) employing the set-up with controlled anode current density. The maximum dimensions of the crystals grown for the 60-100 hrs was 6x6x3 mm³. All crystals had at room temperature cubic structure. The series of the experiments carried out allowed us to make assumptions about the growth mechanism of BKBO single crystals. The oxidation of Bi³⁺ to Bi⁴⁺ proceeds directly on the surface of the growing crystal. On the other hand, high electrical conductivity of the crystals and their low solubility in the KOH melt result in the formation of a large number of nucleation centers. Further, crystal growth occurs on a competitive basis at the expense of the largest crystal growth. Our attempts at localizing the growth of group of crystals via anode current control have not been successful so far.

Determined from the diamagnetic a.c. shielding T_C varies from 4.2K to 34.6K depending on the growth conditions and, possibly, potassium concentration. It is established that optimal concentration ($x=0.4$) of potassium in BKBO single crystals is inadequate requirement of superconductivity to be observed, which is specified mainly by the anode current density.

Recurrent magnetic susceptibility measurements made in BKBO single crystals with $x < 0.30$ revealed the reduction of the Meissner effect against time. During a year the crystals with $x=0.16$ and 0.22 turned to the normal state, with their crystal lattice parameters being constant.

4. Fabrication by LPE and characterization of YBCO thin films.

In terms of growing extended homogeneous single crystal layers of YBCO, the method of liquid phase epitaxy (LPE) is most promising. The LPE technique is an inexpensive process and can produce films with stoichiometric compositions rather easily as compared to the beam employed methods.

4.1 Sample preparation

Two types of NdGaO₃ substrates (S1 and S2) were used in our experiments. The lattice parameters of the orthorhombic structure corresponded to the cell edge $d_{110} = (a_0^2 + b_0^2)^{1/2} / 2 = 0.3854$ nm and $c/2 = 0.3861$ nm of pseudocubic sublattice for S1, and $d_{110} = 0.3853$ nm and $c/2 = 0.386$ nm for S2 samples. For the first time we have grown the single crystalline thin films of YBCO in the growth temperature range from 985- 960°C with the thickness varying from 1 to 100 μm depending on the growth time. The feasibility of preparation of bilayer PBCO/YBCO single crystal structures is demonstrated (21).

4.2. Structural investigations

The X-ray diffraction measurements were performed by a conventional Bragg method (θ - 2θ scan) which gives information from planes parallel to the film surface; the ω -rocking curves characterize the degree of preferred orientation in the direction perpendicular to the substrate surface, and a ψ -scan with the axis parallel to the sample surface normal (asymmetrical reflections) probes the plane misorientation. In order to demonstrate that the films were epitaxial and single crystalline X-ray back-reflection Laue photography was taken. θ - 2θ scans give the typical diffraction spectra scanned along the normal direction to the crystal surface as well as the rocking curve of the 005 peak in the YBCO film and the bilayer PBCO/YBCO heterostructure. The FWHM value of the films on the S1 and S2 type substrates are about 0.06-0.12 degree and 0.12 - 0.4 degree, respectively.

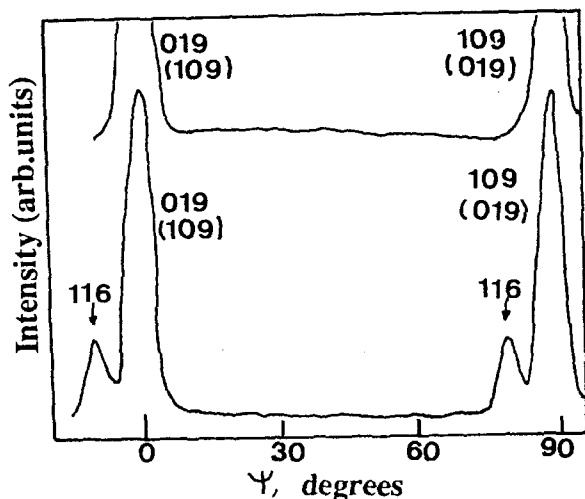


Fig.6. The ψ scan of the (109) peak of the YBCO film and (116) peak of the NdGaO₃.

5. Physical properties of the single crystals of R₂CuO₄

5.1. Dynamic effects in neutron and X-ray scattering by perfect Nd₂CuO₄ crystals

It would be highly desirable to prepare single crystals of HTSC of sufficiently large dimensions and high quality, so as to avoid the masking influence of defects.

The occurrence of dynamic effects due to the interaction with X-rays and neutrons is a characteristic indication of a high quality of crystals. One of the aims of the present paper was to demonstrate, in the specific case of undoped Nd₂CuO₄, that it is possible to prepare high-quality single crystals which exhibit all the typical dynamic effects on the interaction with X-rays and neutrons: narrow rocking curves, anomalous transmission (Borrmann effect), and dynamic oscillations (Pendellosung effect) (22).

We investigated the X-ray rocking curves of Nd₂CuO₄ in the Bragg and Laue geometries using (006) and (200) reflections, respectively. Dynamic oscillations in neutron scattering were studied by the tilt method. When a crystal was tilted, it was found that there were clear oscillations of the neutron scattering intensity around the normal to the reflection plane, as demonstrated in Fig.7.

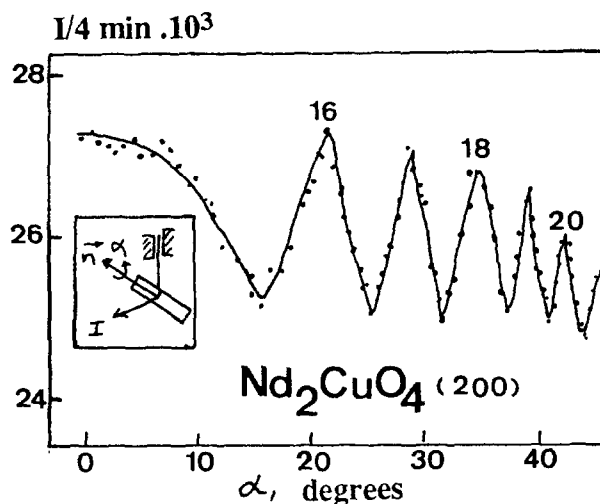


Fig.7. Dynamic oscillations depending on intensity of neutron scattering and crystal geometry for Nd₂CuO₄.

5.2. Magnetic structures and the orientation phase transitions in R₂CuO₄ (R= La, Nd, Sm, Eu, Gd)

The neutron experiments were carried out at ILL-Grenoble and PSI-Wurenlingen. Polarized neutron investigations were carried out in Gatchina. Investigation of the Sm₂CuO₄ magnetic structure was performed on the crystal enriched with isotope ¹⁵⁴Sm. These measurements had shown (Fig.8a) that the magnetic

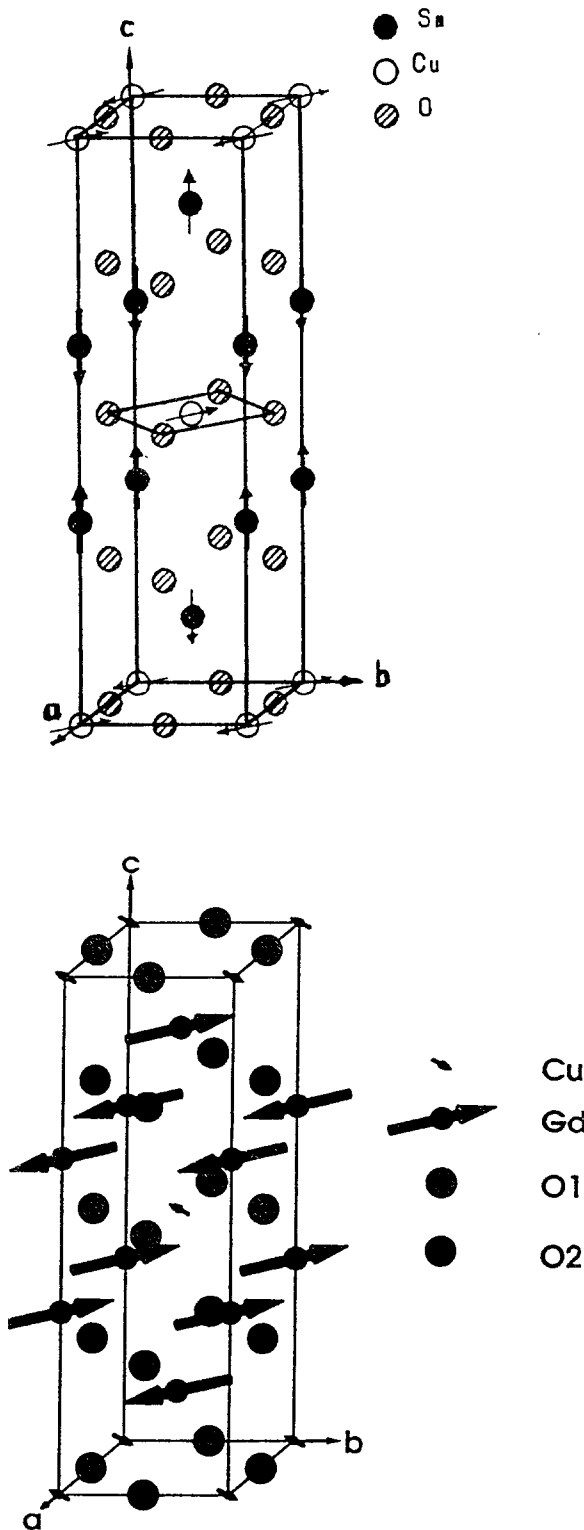


Fig.8. Magnetic structures of Sm_2CuO_4 (a) and Gd_2CuO_4 (b).

structures of Cu^{2+} and Sm^{3+} moments differ each from other as well as their spin directions. This is rather unusual situation when alignment of two spin subsystems is described by two different wave vectors of initial space group $I4/m$. We have carried out neutron diffraction and antiferromagnetic resonance investigations of Gd_2CuO_4 single crystals.

The antiferromagnetic resonance spectra indicate that Gd_2CuO_4 belongs to the class of "easy plane" antiferromagnets and show the presence of a spin reorientation phase transition at $H_c = 0.88 \text{ T}$ ($H//(100)$, $T=1.8\text{K}$).

Neutron diffraction measurements show unambiguously that the structure consists of ferromagnetic (001) planes stacked antiferromagnetically along (001) (Fig.8b).

5. 3. Transport and magnetic properties of $\text{La}_2\text{CuO}_{4+\delta}$

The energy spectrum of the charge carriers in $\text{La}_2\text{CuO}_{4+\delta}$ and its evolution with increasing oxygen concentration are of major importance in the insulator-metal transition study in this system. The difficulty here, in our view, is the inability to grow sufficiently homogeneous single crystals, a problem which has not yet been solved. The crystals which we investigated were better than those of the previous experiments (19), making it possible to advance substantially into the region of under controlled growth conditions. Beyond the temperature $210 < T_n < 260\text{K}$ the crystal were subjected to heat treatment in vacuum or in oxygen. It is established that even for crystals with $T_n = 165\text{K}$ the (T) plot has a clearly identifiable peak at $T=T_n$. This result is contrary to the phase diagram (19). At low temperatures the samples with $T_n < 230\text{K}$ have a constant activation energy ϵ . The decrease of ϵ with oxygen concentration suggests that the crystals are close to the insulator-metal transition.

Conclusions

It is quite obvious that at present level of technology of fabricating HTSC crystals the initial or the so-called stoichiometric samples contain a large number of uncontrollable impurities, which hinders the physical pictures in the case of low-level doping. It is therefore important to study adequately doped insulating antiferromagnetic crystals.

Further progress will require continuing interdisciplinary efforts, involving a wide community of solid state researchers to achieve the highest quality of these complex crystals and to apply skillfully the most advanced measurement techniques.

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References

1. J.G.Bednorz and K.A.Muller, *Z.Phys.B*, 64 (1986) 189.
2. B.Batlogg, *Physics Today*, 6 (1991) 44.
3. P.Picone, H. Jenssen and K.Gabbe, *J.Cryst. Growth*, 91 (1988) 463.
4. R.J.Birgeneau, Y.Endoh et al., *Phys. Rev. B*, 39 (1989) 2868.
5. I. Tanaka, K Yamane, H.Kojima, *J.Cryst. Growth*, 96 (1989) 711.
6. S.N.Barilo, A.P.Ges et al., *Adv. Cryog. Ing.*, 36 (1989) 563.
7. S.Barilo, V.Gatalskaya et al., *Proc. ICMC'90 Garmish Parten-Kirchen, Germany* (1990) 307.
8. S. Barilo, A.Ges et al., *Physica C*, 185-189 (1991) 375.
9. T.Wolf, W.Goldacker et al., *J.Cryst.Growth*, 96 (1989) 1010.
10. H.Takei, H.Takeya, *Jpn. J.Appl. Phys.*, 26 (1987) L1425.
11. S.Shomoto, Thesis, Faculty of Sc., Univ. Tokyo, Hongo, Tokyo, 1990.
12. J.Rossat-Mignod, L.P.Regnault et al., *Phys.Rev.B.*, 169 (1991) 58.
13. H.Takei, H.Asaaka et al., *Jpn.J. Appl.Phys.*, 30(1991) L1102.
14. S. Barilo, A.Ges et al., *Physica C*, 185-189 (1991) 459.
15. K. Dembinsky, M.Gervais et al., *Mater. Sci.Eng.*, B5 (1990) 345.
16. S. Barilo, A.Ges et al., *J.Cryst. Growth*, 119 (1992) 403.
17. A. Zhochov, G.A.Emelchenko, *J.Cryst.Growth* (to be published)
18. L.F.Mattheiss and D.R.Hamann, *Phys.Rev.Lett.*, 60 (1988) 2681.
19. Shiyou R., T.D. Jorgensen et al., *Phys.Rev.B.*, 41 (1990) 4126.
20. N.L.Norton, *Mat. Res. Bull.*, 24 (1989) 1391.
21. S.N.Barilo, D.I.Zhigunov et al., *Superconduct.*, 5 (1992) 1082.
22. V.Kvardakov, V.Somenkov et al., *Superconduct.*, 4 (1991) 1263.