# Crystal growth of spin-ladder compound $La_2Cu_2O_5$ and ladder-like compound $CaCu_2O_3$

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## Abstract

We report single crystal growth of the spin-ladder compound $La_2Cu_2O_5$ (4-leg) and spin-ladder-like compound $CaCu_2O_3$ (2-leg). Crystal growth of $La_2Cu_2O_5$ has been carried out by the self-flux method using a modified slow cooling technique. Single crystals of $CaCu_2O_3$ have been grown by the travelling solvent floating zone method under oxygen pressure (∼5 bar). An optimum solvent for growth of $CaCu_2O_3$ was found to be $Ca_{0.8}Sr_{0.2}Cu_2O_3$. The grown crystals were characterized for their purity and structure by using optical polarized microscope, energy dispersive X-ray spectroscopy, and X-ray diffraction methods.
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## 1. Introduction

Since the discovery of high-$T_c$ superconductors, the one-dimensional (1D) $S = 1/2$ nearest-neighbor Heisenberg antiferromagnet (AF) chain and its two-dimensional (2D) analog, the square lattice antiferromagnet, have been extensively investigated both theoretically and experimentally. A particular system that has attracted much recent attention is the spin-ladder systems. Studies on spin-ladder compounds are important in view

of a variety of intriguing properties originating from the low dimensionality and quantum fluctuations and their possible relevance to high-$T_c$ superconductivity. The spin ladders exhibit fundamentally different properties for even and odd number of legs. Even-legged ladders exhibit a spin liquid ground state with a gap in the magnetic spectrum, while the odd-legged ladders exhibit a ground state isomorphous to that of the 1D chain. Based on the theoretical studies, Dagatto and Rice predicted that, under modest hole doping, the even-leg ladders might become superconducting [1]. Physical realizations of the spin ladders, for example $SrCu_2O_3$ (2-leg), $Sr_3Cu_2O_5$ (3-leg) have been found, and the main predictions for the nature of the ground state

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have been confirmed experimentally [2]. Super-conductivity has been discovered in the 2-leg ladder system $Sr_{14-x}Ca_xCu_{24}O_{41}$ ($x = 13.6$) under high pressure of 3 GPa [3]. However, our understanding of these intriguing materials is incomplete and also it is not clear how the physical properties of the spin ladders evolve with increasing the number of legs in the spin-ladder compounds.

The compound $La_2Cu_2O_5$, $n = 2$ member of the new homologous series of lanthanum cuprate $La_{4+4n}Cu_{8+2n}O_{14+8n}$, consists of 4-legs along its short axis ($\parallel b$-axis). Recently, we have succeeded in growing single crystals of $La_2Cu_2O_5$ by using a MSC technique [4]. Here an attempt has been made to grow $La_2Cu_2O_5$ crystals with improved size and quality.

The $S = 1/2$ quasi-1D antiferromagnet $CaCu_2O_3$ exhibits a structure [5] very similar to that of the 2-leg spin-ladder compound $SrCu_2O_3$ [2]. However, while the Cu–O–Cu bond angle in the rungs is 180° in the Sr compound, it equals 123° in $CaCu_2O_3$; colloquially, the ladder is "buckled". It should also be mentioned that the actual composition of $CaCu_2O_3$ is Ca deficient with a balancing excess in Cu, and an oxygen deficiency corresponding to the formula $Ca_{0.86}Cu_{2.14}O_{2.93}$ [6]. Consequently, the magnetic properties of $CaCu_2O_3$ is quite different compared with that of $SrCu_2O_3$. Till date, the $Cu_2O_3$ has not been investigated in detail, partly due to the unavailability of single crystals. Crystallization of $CaCu_2O_3$ was thought to be difficult due to the fact that the liquidus range available for crystallization is very narrow in the temperature–composition phase diagram [8,9]. We report the successful crystal growth of $CaCu_2O_3$ by TSFZ method.

## 2. Experimental

A modified slow cooling (MSC) technique and TSFZ method have been used to grow single crystals of $La_2Cu_2O_5$ and $CaCu_2O_3$ respectively. In MSC, a flux-poor starting composition (between 1:4.75 and 1:3.75 molar ratio of $La_2O_3$ and CuO) is chosen to attain enough supersaturation

and a rapid cooling from high temperature to a proper crystallization temperature is adopted to avoid the unwanted phase formation [4,7]. The starting charges were prepared by mixing pre-sintered $La_2Cu_2O_5$ powder and CuO in appropriate amounts, ground well and loaded into Pt crucible with a volume of 60 cm$^3$. The charge ($\sim$50 g) was heated to 1130 °C in a tubular furnace under flowing oxygen atmosphere, held for 10 h and then rapidly cooled to the crystallization temperature ($T_s$) in 10 min. Slow cooling was effected from $T_s$ (between 1050 and 1070 °C) to 1000 °C at the rate of 1 °C/h. Finally it was furnace cooled to room temperature. In order to improve the crystal size and quality, we have investigated the influence of (i) crucible material (alumina and platinum) and size, (ii) crystallization temperature, and (iii) rapid cooling process.

Initially phase pure polycrystalline samples of $CaCu_2O_3$ were prepared through solid-state reactions of appropriate amounts of $CaCO_3$ (99.9%, Merck) and CuO (99.99%, MaTeck). The powders were thoroughly mixed and sintered in oxygen atmosphere at 1020 °C. After the sintering process the product was quenched to room temperature. The resultant product was ground well and placed into a rubber tube and then hydrostatically pressed under 1500 kg/cm$^2$. The pressed cylindrical rod ($\sim$6 mm in diameter and $\sim$10 cm long) was sintered again at 1020 °C for 75 h under flowing oxygen atmosphere. Since the predicted crystallization field of $CaCu_2O_3$ is very small and uncertain, we used solvents containing "Sr" with the following composition $Ca_{0.8}Sr_{0.2}Cu_2O_3$.

Crystal growth of $CaCu_2O_3$ was carried out using an infrared radiation furnace equipped with four ellipsoidal mirrors (Crystal Systems Inc.). The upper and lower shafts were rotated at a rate of 30/30 rpm in opposite directions. Zone travelling rate was chosen between 0.25 and 1.00 mm/h. We used 300 W halogen lamps to obtain a steep temperature gradient. Experiments were carried out under oxygen pressure of 5 bar. Under these conditions, we were able to grow large single crystals of $CaCu_2O_3$. Grown crystals were characterized by X-ray diffraction and EDX analyses.

## 3. Results and discussion

### 3.1. Crystal growth of $La_2Cu_2O_5$

A typical $La_2Cu_2O_5$ single crystal grown by MSC is shown in Fig. 1. Bar shaped crystals with maximum dimensions of $0.2 \times 3.0 \times 0.15$ mm$^3$ have been separated out from the surface of the melt. X-ray diffraction studies on $La_2Cu_2O_5$ crystals confirmed the crystallinity as well as phase purity [4]. For excess CuO (1:4.75), a number of tiny crystals grew on the surface of the melt. On the other hand, the flux-poor starting compositions (1:3.75) yielded large square shaped crystals. Closer observation under optical microscope revealed that the square shaped crystals are made up of a number of tiny needle-like crystals. Powder X-ray diffraction studies have confirmed that the crystals are of phase pure $La_2Cu_2O_5$. This result indicates that the starting composition of 1:4.25 is the appropriate value for crystallizing larger quantity of the starting compound. Creeping has been commonly observed in all the experiments. However, it was found to be less pronounced in Pt crucible compared to that of alumina crucible. Crystal size could not be improved by choosing the larger crucibles. The temperature gradient inside the crucible was found to be very sensitive to crystal yield and morphology. Crystals grew on the surface of the melt. This is contradictory to the "dr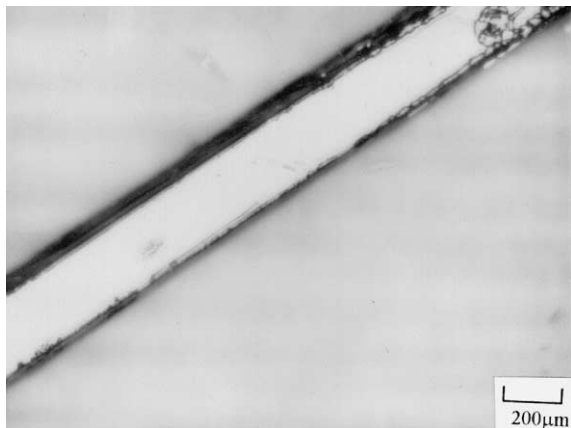use-like" growth pattern observed in standard slow cooling (SSC) growth of $La_2Cu_2O_5$ from CuO-rich starting composition (1:5.25–1:5.0) under flowing oxygen atmosphere [4]. Compared to SSC method, the crystal yield is higher in MSC.

### 3.2. Crystal growth of $CaCu_2O_3$ by TSFZ method

Fig. 2 shows the phase diagram for the CaO–CuO pseudo-binary system at 1 atm oxygen [8,9]. It can be noticed that the liquidus is drawn by dotted lines which means that this part of the phase diagram still contains an open question. In addition, there is a more stable $Ca_2CuO_3$ phase just above the desired phase $CaCu_2O_3$ region. Thus the crystallization field is very small both in terms of temperature and composition. In order to obtain single crystal from such a small crystallization field, one of the most plausible techniques is the TSFZ method. We have carried out a systematic study on the stability of the molten zone and the corresponding phase(s) crystallized. Solvents containing a small quantity of "Sr" corresponding to the composition $Ca_{0.8}Sr_{0.2}Cu_2O_3$ is found to be useful in stabilizing the molten zone. Crystal growth at the rate of 1 mm/h under 5 bar oxygen pressure resulted in a good quality crystal. Fig. 3a shows an optically polarized micrograph of a cross-section normal to the growth direction of the last 1-cm part of the 8-cm long crystalline boule. EDX analysis confirmed that the whole region is a phase pure $CaCu_2O_3$. Ruck et al. [6] have reported Cu substitution at the Ca-site for



Fig. 1. A typical $La_2Cu_2O_5$ single crystal grown by MSC.


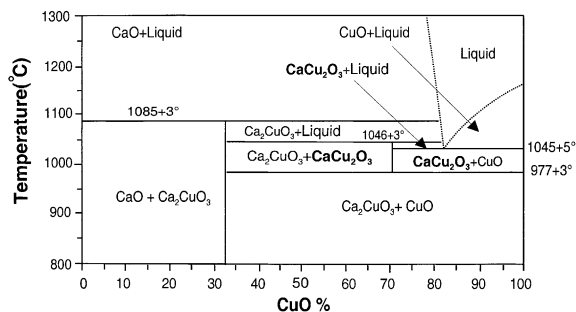
Fig. 2. Phase diagram for the CaO–CuO pseudo-binary system at 1 atm oxygen referred from Refs. [8,9]. Note that the compound $CaCu_2O_3$ corresponds to $Ca_3Cu_7O_{10}$ of the original phase diagram in Refs. [8,9] and that of $Ca_{0.86}Cu_{2.14}O_{2.93}$ in Ref. [6].

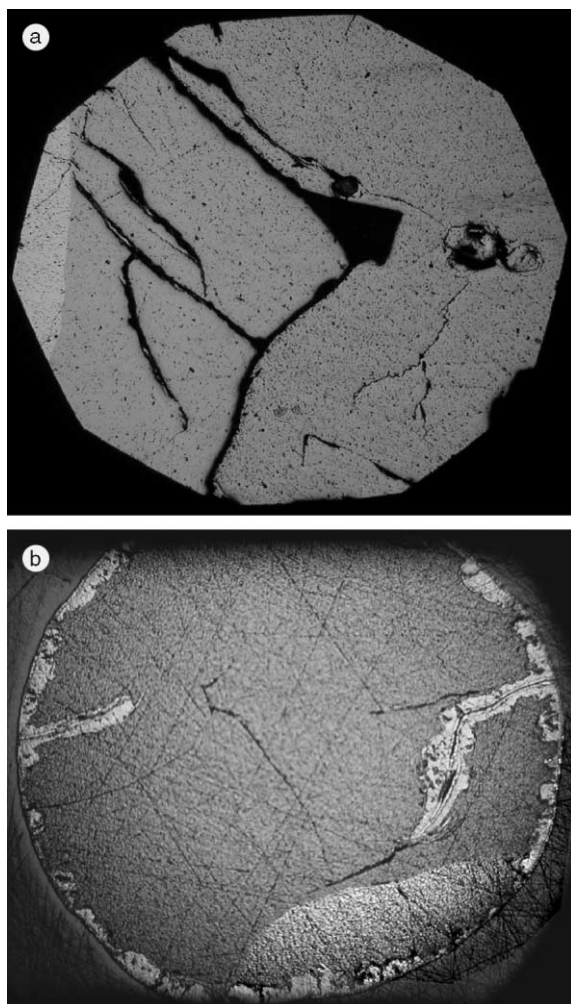Fig. 3. Polarized optical micrograph of a transverse section of (a) the last 1-cm part of the $CaCu_2O_3$ boule (b) the last 2-cm part of the same crystalline boule.

cooling after termination of the growth run. However, the next 1-cm part (from the growth end) of the boule is free from any internal crack (Fig. 3b). The peripheral region of this piece contained impurity phase (mainly $Ca_2CuO_3$). The remaining portion of the boule contained the impurity phases such as $Ca_2CuO_3$ and $CuO$ even in the core part. It should be mentioned that the slow growth rates (0.25 and 0.50 mm/h) yielded the crystalline boules containing large volume of $Ca_2CuO_3$. These observations could be attributed to the fact that the $CaCu_2O_3$ decomposes into $Ca_2CuO_3$ and $CuO$ at temperatures lower than about 1000 °C in oxygen.

We have investigated the phase identification of the grown crystal by powder X-ray diffraction method. The lattice parameters were calculated from the XRD data by using a orthorhombic (P) structure and the lattice constants were estimated as; $a = 9.944(2)$ Å, $b = 4.078(6)$ Å, $c = 3.461(7)$ Å, and $V = 140.37$ Å$^3$. The results are in good agreement with the literature values [5]. The crystallographic axes parallel and perpendicular to the growth direction were determined by means of X-ray Laue diffraction. Fig. 4 shows the back
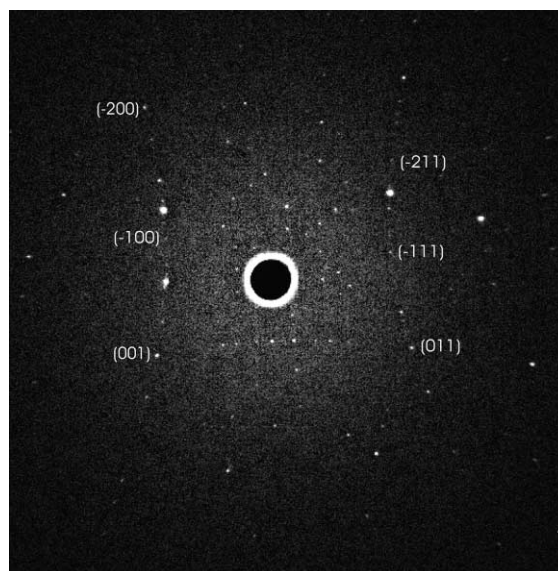
similar samples. They have estimated the non-stoichiometric composition as $Ca_{0.86}Cu_{2.14}O_{2.93}$ ($Ca/Cu = 0.4018$) based on the structural analysis. EDX analysis of our crystal indicated that the Ca-content is lower, and the Cu-content is richer than the stoichiometric value ($Ca/Cu = 0.39 \pm 0.02$). The observed result is in good agreement with the data from X-ray diffraction analysis by Ruck et al. [6]. It can be noticed that there exists large cracks on the transverse cross-section of the last 1-cm part of the boule. This might be due to the thermal stress which the crystal undergoes due to fast



Fig. 4. The Laue back scattering pattern of the longitudinal section of the $CaCu_2O_3$ crystal parallel to the growth axis. The spots with very strong intensity are formed by characteristic $W_L$-radiation.

reflection Laue pattern of the longitudinal section of the $CaCu_2O_3$ crystal parallel to the growth axis. The growth direction was found to be nearly $[\bar{1}00]$; $\psi \approx 10°$ and $\rho \approx 2°$, where $\psi$ and $\rho$ are polar coordinates according to Fig. 4. The homogeneously distributed intensity of the diffraction spots indicates that the crystal is of good quality. Also it corresponds well with the Laue pattern of the same $[\bar{1}\,0\,0]$ direction obtained by a computer simulation. Similar Laue patterns were observed when they were taken from other points of the same specimen.

## 4. Conclusions

Crystal growth conditions for the preparation of large, good quality $La_2Cu_2O_5$ single crystals have been investigated. Optimum starting composition is estimated as 1:4.25 ($La_2O_3$:CuO molar ratio) for crystal growth by the MSC technique. Thus we have succeeded to grow $La_2Cu_2O_5$ single crystals with maximum dimensions of $0.2 \times 3.0 \times 0.15$ mm$^3$. Our initial attempts to grow $La_2Cu_2O_5$ crystals by TSFZ method was not successful, mainly due to the poor stability of the molten zone. However, we have successfully grown single crystals of $CaCu_2O_3$ by TSFZ method in a four-mirror furnace under oxygen pressure (5 bar). The last 2-cm part of the 8-cm long crystalline boule is found to be phase pure $CaCu_2O_3$ as confirmed by EDX and XRD analyses.

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