



Solid solutions formation in Sr–K–Ca–Na–Cu–O system

Elizabeth Chavira*, Emiliano Hernández, Oracio Navarro, Leticia Baños,
José Guzmán

Instituto de Investigaciones en Materiales, UNAM, A.P. 70-360, 04510, México, D.F., Mexico

Abstract

The synthesis and some experimental results of the new system: $(\text{Sr}, \text{K})_{1-x}(\text{Ca}, \text{Na})_x\text{Cu}_n\text{O}_{2\pm z}$ are shown. The series of polycrystalline samples with x up to 1.0 ($n = 1, 2$), were prepared by solid-state reaction at different temperatures (750–990°C), in air and at ambient pressure below melt temperature. Single-phase solid solutions are observed for $0.0 \leq x \leq 0.5$ at 750°C ($n = 1$) and for $0.0 \leq x \leq 0.1$ at 780°C ($n = 2$). Both single phases are isostructural to the Cu_2SrO_3 compound, with an orthorhombic unit cell. The compositions in the range $0.6 \leq x \leq 1.0$ ($n = 1$) have different crystalline structures and those in the range $0.2 \leq x \leq 0.5$ ($n = 2$) show the presence of non-reacted CuO. Also, characterization studies by scanning electron microscopy and differential thermal analysis are shown. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Differential thermal analysis; Scanning electron microscopy; Synthesis; X-ray powder diffraction

Cuprate systems have received considerable attention over the last 13 years, due to the observation of high-temperature superconductivity in these systems [1]. This research improved our knowledge of the chemistry of cuprates and brought to light some remarkable results. For example, using a high-pressure technique, Azuma et al. [2] reported the synthesis of SrCuO_2 with a transition temperature T_c up to 100 K and Uehara et al. [3] succeeded in the preparation of structures with higher numbers of layers such as $(\text{CO}_3)_x\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n}$ system reaching a $T_c = 115$ K for the third layer compound. In this report, we present the synthesis and characterization of the new cuprate system $(\text{Sr}, \text{K})_{1-x}(\text{Ca}, \text{Na})_x\text{Cu}_n\text{O}_{2\pm z}$ ($x \leq 1$; $n = 1, 2$).

Samples were synthesized from mixtures of high-purity SrCO_3 , K_2CO_3 , CaCO_3 , Na_2CO_3 and CuO, which were subjected to two heat treatments at 720°C and 750°C for $n = 1$ and at 720°C and 780°C for $n = 2$, in air, for 20 h, with intermediate regrinding and then cooled slowly inside a furnace. Prior to weighing, carbonates were preheated for a few minutes at 100°C to completely

dehydrate the samples. The proper amount of K_2CO_3 was weighed in a glove bag filled with Ar gas to avoid its contamination and decomposition.

The system was examined by powder X-ray diffraction (XRD), differential thermal analysis (DTA) and scanning electron microscopy (SEM). The XRD analysis was done at room temperature in a SIEMENS D5000 diffractometer, with Cu $\text{K}\alpha_1$ radiation and a graphite monochromator. DTA was performed with a TA Instruments 2910, with $\Delta T = \pm 0.001^\circ\text{C}$ resolution. For the SEM analysis we used a Leica–Cambridge equipment model Stereoscan 440, equipped with an Oxford/Link System electron probe microanalyser (EPMA).

A single-phase solid solution was obtained in the system: $(\text{Sr}, \text{K})_{1-x}(\text{Ca}, \text{Na})_x\text{Cu}_n\text{O}_{2\pm z}$ at 750°C for $n = 1$ ($0.0 \leq x \leq 0.5$) [4] and at 780°C for $n = 2$ ($0.0 \leq x \leq 0.1$), both in air and at ambient pressure. Analyzing the XRD pattern of the $(\text{Sr}, \text{K})_{0.9}(\text{Ca}, \text{Na})_{0.1}\text{Cu}_2\text{O}_{2\pm z}$ composition (Fig. 1), we observed that it is isostructural to the one for Cu_2SrO_3 compound reported by Klockow Eysel in JCPDS-ICDD file No. 39-0250, which has an orthorhombic unit cell. All the lines of the diffractogram have a shift to high angles (2θ), due to the substitution of different cations in the crystalline structure.

The differential thermal analysis for the $(\text{Sr}, \text{K})_{0.9}(\text{Ca}, \text{Na})_{0.1}\text{Cu}_2\text{O}_{2\pm z}$ composition gives several

* Corresponding author. Tel.: +00-52-5-622-4629; fax: +00-52-5-616-1251.

E-mail address: chavira@servidor.unam.mx (E. Chavira)

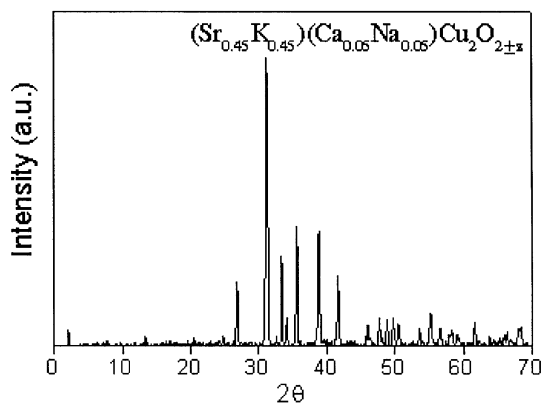


Fig. 1. XRD of the single phase for $x = 0.1$ ($n = 2$).

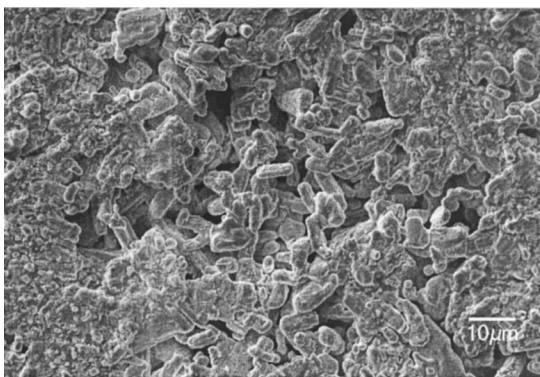


Fig. 2. SEM of single phase for $x = 0.1$ ($n = 2$).

endothermic changes in the curve between 89°C and 202°C, associated with the loss of water molecules. A step at 651°C is also observed corresponding to the carbonate decomposition.

In Fig. 2, we show a SEM micrograph for a concentration of $x = 0.1$ and $n = 2$ taken from a sintering pellet. The sample shows most of the grains sizes within the range of 2–10 μm. With a reaction time of 20 h, the energy dispersive X-ray (EDX) analysis indicates that all cations are present at 780°C. It was also observed that a relatively small increase in temperature of synthesis temperature, from 780°C to 790°C – results in the partial loss of K and Na cations.

In summary, we have determined and characterized the formation of two solid solutions in the $(\text{Sr}, \text{K})_{1-x}(\text{Ca}, \text{Na})_x\text{Cu}_n\text{O}_{2\pm z}$ system; for $n = 1$ ($0.0 \leq x \leq 0.5$) and for $n = 2$ ($0.0 \leq x \leq 0.1$). The structure of these solid solutions is orthorhombic.

Acknowledgements

This work was partially supported by grants from DGAPA-UNAM IN109998, TWAS 96-148 RG/CHE/LA and by CONACYT 25582-E. We also thank C. Vázquez for her technical support.

References

- [1] J.G. Bednorz, K.A. Müller, *Z. Phys. B* 64 (1986) 189.
- [2] M. Azuma, Z. Hiroi, M. Takano, Y. Bando, Y. Takeda, *Nature* 356 (1992) 775.
- [3] M. Uehara, M. Uoshima, S. Ishiyama, H. Nakata, J. Akimitsu, Y. Matsui, T. Arima, Y. Tokura, N. Mory, *Physica C* 229 (1994) 310.
- [4] E. Chavira, E. Hernandez, O. Navarro, L. Baños, J. Guzmán, *Solid State Commun.* 112 (1999) 471.