Synthesis of Monoclinic Form of $Gd_{2-x}Na_xCuO_4$ by Direct Precipitation from Molten Salt

Lin ZHANG, Liang Zhong ZHAO*, Jin Biao ZHANG, Cui Ying XU, Shi Hong LIU

Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080

Abstract A new phase of $Gd_{2-x}Na_xCuO_4$ was synthesized by direct precipitation from the mixture of Gd_2O_3 and CuO in the molten KOH/NaOH/KNO_3 solution at temperature as low as 280°C. The resulting precipitate was characterized by using SEM, XRD, EDX, XPS and magnetic method. The XRD data indicate that the precipitated $Gd_{2-x}Na_xCuO_4$ is monoclinic with lattice parameters a=8.6816Å, b=3.7233Å. c=6.0796Å, $\alpha=\gamma=90°$, $\beta=108.75°$ and V=186.1Å^3.

Keywords: Chemical synthesis, gadolinium cuprate; monoclinic phase.

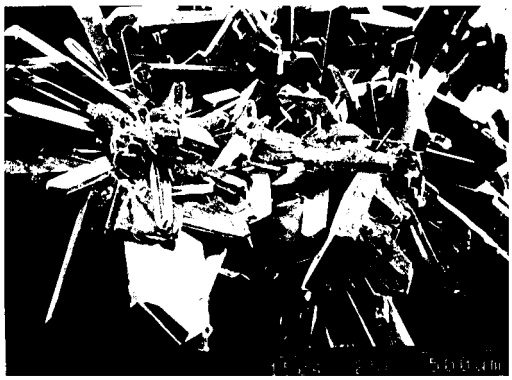
$Gd_{2-x}Na_xCuO_4$, an interesting compound with complex magnetic behavior, has been synthesized by a PbO-based flux method (1) and a solid state reaction (2) at temperatures about 1000°C. Its X-ray diffraction pattern has been indexed with tetragonal lattice parameters (1,3). Here we report a low temperature synthetic route in which the new monoclinic form of $Gd_{2-x}Na_xCuO_4$ is obtained directly by precipitation from a molten KOH/NaOH/KNO_3 solution. The SEM, EDX, XRD, XPS and magnetic characterization of monoclinic $Gd_{2-x}Na_xCuO_4$ are also reported.

In a typical experiment, 3.6g of Gd_2O_3, 0.80g of CuO, 27g of KOH, 27g of NaOH and 6g of KNO_3 were placed in a Teflon crucible and heated to 280°C. The reagents and hydroxides were not dried before use. After one hour, the molten solution was stirred for several seconds, then the crucible was covered with a Ni sheet. The mixture was heated at 280°C for 28 h, during which the precipitate gradually formed. Finally, the solution was poured out of the crucible carefully in order to isolate the heavier $Gd_{2-x}Na_xCuO_4$ precipitate at the bottom of the crucible. After cooling to room temperature, the precipitate was ultrasonically washed with distilled water and dried under an infrared lamp. The obtained $Gd_{2-x}Na_xCuO_4$ crystals were thin plates which were brownish grey in color.

Scanning electron microscopy (SEM), used to show the crystal morphology, used a HITACHI S-530 scanning electron microscope. Energy dispersive X-ray (EDX) analysis was performed on a JEOL JSM-35C scanning microscope equipped with an EDAX-9100 system. Several sites were probed for each sample. Powder X-ray diffraction (XRD)

patterns were recorded using M18XAHF diffractometer with CuKα radiation. X-ray photoelectron spectra (XPS) were recorded using a VG ESCALab 220i-XL electron spectrometer. Magnetic susceptibility measurements were performed using a MPMS (Quantum Design) magnetometer. The samples were cooled in zero fields to 4.5K and then a 10G field was applied.

Figure 1. SEM image of $Gd_{2-x}Na_xCuO_4$ precipitated from molten KOH/NaOH/KNO_3

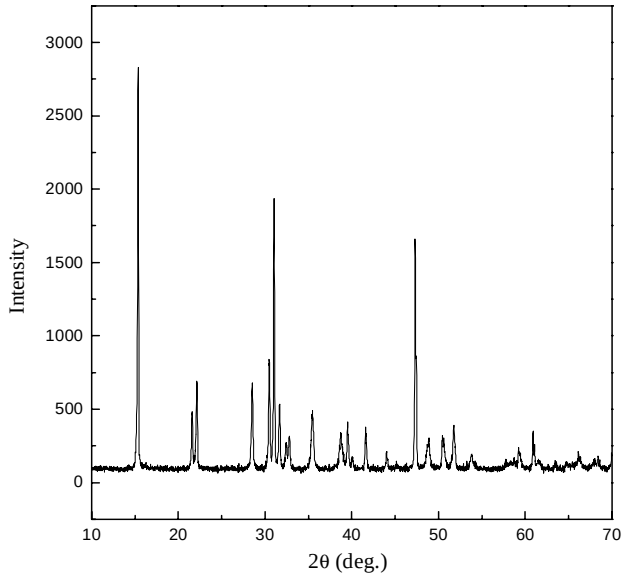


Fused hydroxides are ideal for the preparation of rare earth cuprates because these solvents melt at low temperatures, and dissolve metal oxides. Melts can be made more acidic (H_2O-rich) or basic (O^{2-}rich) by controlling the water content of the melt. Our synthesis starts with a very acidic melt in which Gd_2O_3 and CuO both dissolve. Heating at 280°C results in slow loss of water thereby making the melt more basic and the product insoluble. **Figure 1** shows the SEM image of the precipitated $Gd_{2-x}Na_xCuO_4$. The morphology was markedly thin, plate-like. EDX was used to analyze Gd and Cu contents in the samples. Because of the low concentration, EDX may not be suitable for determining Na, so the Na content was estimated by XPS analysis. EDX results showed a Gd to Cu atomic ratio between 1.8**:**1.0 to 2.0**:**1.0, depending on the content of CuO impurity. Small amount of Na (x~0.1) was detected by XPS.

Figure 2 shows the XRD pattern of the precipitated $Gd_{2-x}Na_xCuO_4$. The precipitate was confirmed to be monoclinic form of $Gd_{2-x}Na_xCuO_4$ by qualitative phase analysis. The diffraction pattern was indexed using TREOR (4). The figure of merits were M(20)=36 and F(20)=31. After least square refinement and unit cell reduction, the cell was indexed as monoclinic with a=8.6816Å, b=3.7233Å. c=6.0796Å, α=γ=90°, β=108.75° and V=186.1Å^3. It is notable that this is the first direct synthesis of the monoclinic form of $Gd_{2-x}Na_xCuO_4$, only the tetragonal form of Gd_2CuO_4 can be obtained directly by the previously reported synthetic method due to the high temperatures that are required. However, by using the present precipitation method the precipitate also contained small amount of CuO impurity as detected by X-ray diffraction.

XPS data indicate that the $Cu2p_{3/2}$ binding energy of the $Gd_{2-x}Na_xCuO_4$ precipitate (933.1eV) is about 0.9eV lower than that of $Gd_{1-y}Na_yCu_2O_4$ prepared by the anodic electrocrystallization method (5). This has been attributed to the fact that the Cu atoms in $Gd_{2-x}Na_xCuO_4$ are less oxidized than that in $Gd_{1-y}Na_yCu_2O_4$.

Figure 2. XRD pattern of $Gd_{2-x}Na_xCuO_4$ precipitated from molten $KOH/NaOH/KNO_3$



The magnetic susceptibility of $Gd_{2-x}Na_xCuO_4$ was measured as a function of temperature. The results show that the monoclinic $Gd_{2-x}Na_xCuO_4$ is not superconducting.

Acknowledgments

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