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Molten salt synthesis of lanthanum cuprate, $La_2CuO_{4+\delta}$

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Abstract Lanthanum cuprate (LCO) was synthesized from lanthanum and copper precursors in molten sodium nitrate–potassium nitrate eutectic. The chemical reactions were studied by thermogravimetric analysis and X-ray powder diffraction was used to identify the crystalline phases. The chemical reactions of copper and lanthanum precursors in alkaline nitrate eutectic were studied and the basicity of the reaction mixture was increased in order to precipitate the crystalline mixed oxide. Scanning electron microscopy investigation has shown the obtaining of lanthanum cuprate as large platelet crystals of quadratic shape. The synthesis conditions are favourable for a direct formation of a superoxygenated lanthanum cuprate, $La_2CuO_{4+\delta}$.

Keywords Lanthanum cuprate · Molten salt synthesis · Sodium nitrate-potassium nitrate eutectic · Lux–Flood basicity

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1 Introduction

Molten salts, especially oxosalts, provide a reaction medium with great capabilities for simple or mixed oxides synthesis [1–4]. The ionic liquid medium facilitates the ion mobility and the ion exchange that determine a good homogeneity of the reaction mixture. Therefore, the synthesis of a compound with suitable structure and morphology requires a good understanding of molten salt systems. For a certain system, the acid–base nature of the reagents is the determining feature, but other parameters are also important [1, 2]. In molten nitrates or nitrites, the reactions are performed at relative low temperature (250–550 °C) and due to this, interesting properties could be expected. Previously, we have developed a novel method to synthesise lanthanum-based oxide materials ($LaMO_3$, M=Mn, Fe, Co, Ni) by chemical reactions of metal precursors in molten salts [1].

Lanthanum cuprate is one of the most studied copper oxide-based compounds and recently, it has received special attention due to the intriguing properties of its superoxygenated forms [5–7], however the uniform oxidation of large crystals is difficult and requires long-time processing [8]. We report for the first time the formation of a superoxygenated lanthanum cuprate directly by synthesis in molten alkaline nitrate eutectic as reaction medium.

2 Experimental

All the metal precursors ($La(NO_3)_3{\cdot}6H_2O$, $LaCl_3{\cdot}6H_2O$, La_2O_3, $Cu(NO_3)_2{\cdot}3H_2O$, $CuCl_2{\cdot}2H_2O$, CuO) are commercially available, GR grade >98% and were used as received. Alkaline nitrate eutectic, $NaNO_3$–KNO_3 (molar ratio 1:1) was obtained from dried salts. The metal precursors, copper and lanthanum salts or lanthanum oxide were mixed in stoichiometric amounts with alkaline nitrate eutectic in excess, in order to obtain LCO. The eutectic formed the

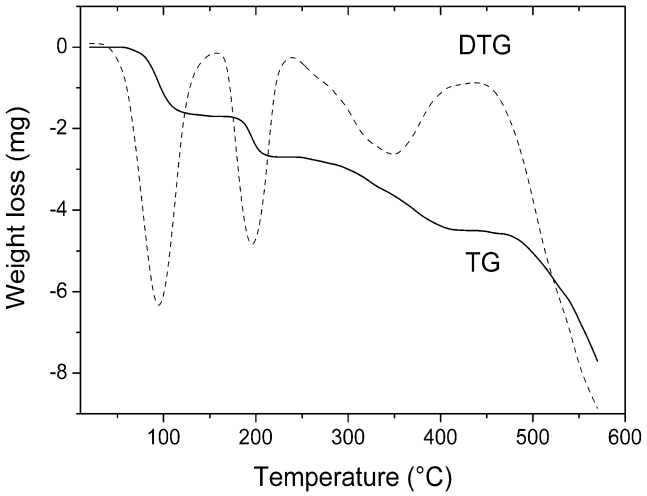

Fig. 1 TG and DTG curves of the reaction system, La_2O_3–Cu $(NO_3)_2{\cdot}3H_2O$–Na_2O_2 in $NaNO_3$–KNO_3 eutectic

reaction molten medium and 32 mol of alkaline nitrates were added for the formation of 1 mol LCO. After chemical reaction at 450 °C, 6 h, the cooled solid was stirred with water in order to dissolve and remove the alkaline nitrate eutectic. The insoluble compound was filtered off, washed and dried at 100 °C.

The chemical reactions have been investigated by thermogravimetry (TG) on a Setaram B 70 digitalised balance, using large Pyrex crucibles. The obtained powders were analysed by scanning electron microscopy (SEM) performed on Hitachi S800 microscope, X-ray powder diffraction (XRD) on Siemens D500 diffractometer with CuK_α radiation, λ=1.5418 Å and the chemical composition was obtained by inductive coupled plasma (ICP). Oxygen content was estimated by TG analysis performed in 95% Ar/5% H_2 purge gas (Netzsch STA 449 F1 Jupiter). For XRD patterns deconvolution, Topas2P® software was used and CaRIne Crystallography® for XRD patterns simulation.

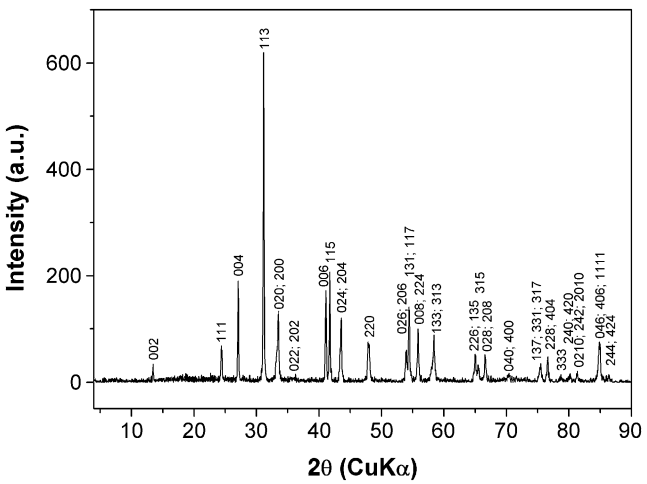

Fig. 2 XRD patterns of LCO obtained at molar ratio, Na_2O_2/Cu^{2+}=2

Table 1 Chemical analysis of LCO obtained at molar ratio, Na_2O_2/Cu^{2+}=2.

Element	Composition		
	Experimental (wt.%)	Theoretical (wt.%)	Experimental (at.%)
Cu	15.1	15.7	13.055
La	67.2	68.5	26.579
Na	0.4	0	0.956

The lattice parameters were refined by the least-square method.

3 Results and discussions

Copper nitrate, $Cu(NO_3)_2{\cdot}3H_2O$, as well as copper chloride, $CuCl_2{\cdot}2H_2O$, reacts in molten alkaline nitrates and forms CuO in 400–450 °C temperature range [2]. In the same conditions, lanthanum salts have different behaviour, forming a very stable cation, LaO^+, up to the temperature of alkaline nitrate eutectic decomposition. These preliminary observations suggest that the synthesis of lanthanum cuprate in molten nitrates from lanthanum and copper salts is very difficult and could take place only at high temperatures when significant decomposition of molten nitrate medium occurs. By using copper and lanthanum oxides instead of their salts, the formation of lanthanum cuprate is time consuming due to the low copper oxide solubility in molten alkaline nitrates. On the other hand, considering the base nature of La_2O_3 according to the Lux–Flood theory (Eq. 1) and the stability of LaO^+ cation, the use of lanthanum oxide and copper salts determines the precipitation in situ of CuO (Eq. 2). Even in this case, the

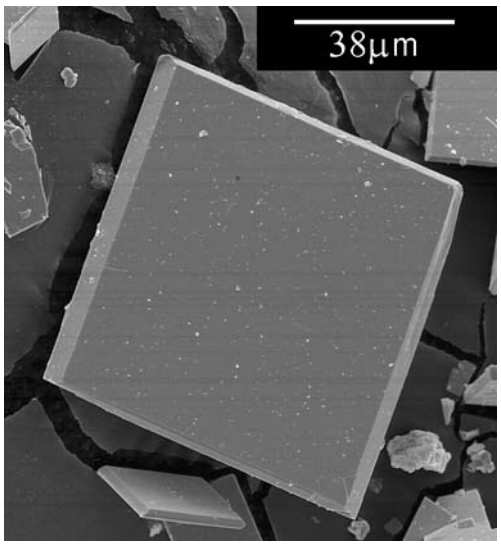

Fig. 3 SEM micrograph of LCO obtained at molar ratio, Na_2O_2/Cu^{2+}=2

basicity of the reaction medium is too low for LCO precipitation without an increase of oxide ions concentration (Eq. 3).

$$La_2O_3 \rightleftharpoons 2LaO^+ + O^{2-}; \left(\text{Base} \rightleftharpoons \text{Acid} + O^2\right) \quad (1)$$

$$La_2O_3 + Cu^{2+} \rightarrow CuO + 2LaO^+ \quad (2)$$

$$2LaO^+ + CuO + O^{2-} \rightarrow La_2CuO_4 \quad (3)$$

$$Na_2O_2 \rightarrow 2Na^+ + 1/2O_2 + O^{2-} \quad (4)$$

For this purpose, sodium peroxide or sodium nitrite have been added to the molten reaction mixture. In the same time, according to the previous results [3], precursors containing chloride ions were avoided and so, copper nitrate was chosen. Sodium peroxide has given the best results and the synthesis system, La_2O_3–$Cu(NO_3)_2{\cdot}3H_2O$–Na_2O_2 in $NaNO_3$–KNO_3 molten eutectic, has been established. The thermal analysis of this system shows a complete reaction around 400 °C (Fig. 1) and the decomposition of molten eutectic at temperature above 480 °C.

Considering the dismutation reaction (Eq. 4), Na_2O_2 acts as a strong base and to determine the optimum peroxide content in the reaction mixture, Na_2O_2 has been added in different concentrations (Na_2O_2/Cu^{2+}=1, 2, 3 and 4). The XRD data of the sample obtained at the molar ratio Na_2O_2/Cu^{2+}=2, show the obtaining of single-phase lanthanum cuprate (Fig. 2), with an orthorhombic symmetry. Higher molar ratio promotes the precipitation of La_2O_3 and formation of alkali metal cuprates, whereas at molar ratio Na_2O_2/Cu^{2+}=1, copper oxide, as secondary phase has been noticed in the XRD patterns.

Chemical analysis of the obtained sample shows that the atomic ratio, La/Cu is 2, but also a very small amount of sodium (Table 1). It could correspond to a sodium doped lanthanum cuprate as reported by Torardi et al. [9].

At least two main space groups were tested for the tetragonal and orthorhombic symmetry to calculate the lattice parameters of LCO sample. It was found that the orthorhombic *Fmmm* (69) space group fits the experimental data and the calculated lattice parameters are: a=5.3526 Å, b=5.3903 Å, c=13.179 Å. The XRD patterns simulation by CaRIne software confirms the orthorhombic symmetry of LCO sample. It is known that the lattice c parameter values bigger than 13.15 Å are common for doped or superoxygenated lanthanum cuprates. The tetragonal symmetry is characteristic for alkaline or alkaline earth doped lanthanum cuprates, whereas the orthorhombic symmetry is associated with pure or superoxygenated lanthanum cuprates. Corroborating these aspects with the high oxidising character of the reaction medium, we have supposed that a superoxygenated compound was formed. This assumption was confirmed by TG analysis performed in hydrogen reduction atmosphere and the calculated oxygen content corresponds to $La_2CuO_{4.11}$.

LCO samples are black with crystalline aspect. The SEM micrographs show large crystals (Fig. 3) that exhibit platelet morphology with quadratic shape; typical dimensions are $50\times50\times10$ μm^3.

4 Conclusions

The main difficulty of mixed oxides synthesis in molten salts is the management of the reaction medium basicity. In molten alkaline nitrates, the stable lanthanum species are LaO^+ ions and La_2O_3, which is itself a Lux–Flood base. Cu^{2+} ions precipitate as CuO that is a very weak acid. The chemical reaction between La_2O_3 and CuO is never completed in molten alkaline nitrate medium. Only an appropriate basicity allows the formation of cuprate ions in the reaction mixture that react with LaO^+ cations and precipitate LCO. Using controlled amounts of sodium peroxide, LCO was synthesised at 450 °C as large platelet crystals. The oxidising nature of the molten reaction mixture is favourable to the formation of superoxygenated lanthanum cuprate, $La_2CuO_{4+\delta}$. The experimental conditions should be optimised to control the size and the size distribution of LCO particles, from nanocrystals for catalytic purposes, to large and very large crystals for other applications.

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