

Morphology effect dependent of the synthesis method of $K_xIr_{1-x}O_2$ system

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ABSTRACT

Recently ternary oxides containing both alkaline-earth metal and platinum group metal have attracted attention due to their wide range of electrical and magnetic properties. Particularly, mixed metal oxides contained iridium has been the interest of a lot of research activity [1-4]. We focus our attention on the synthesis of the $K_xIr_{1-x}O_2$ with $0.00 < x < 0.25$ solid solution (ss). The ss was obtained by the solid-state reaction and sol-gel method via acrylamide polymerization using IrO_2 and K_2CO_3 as starting materials. The sample prepared by solid-state reaction and annealed at $650\text{ }^\circ\text{C}$ for 170 h showed a DRX pattern with signals comparables to IrO_2 compound. However, 20 displacements have been observed. These displacements seem to be attributable to the potassium ion introduction to the IrO_2 structure. On the other hand, the xerogel produced by sol-gel method via acrylamide polymerization annealed between $500\text{ }^\circ\text{C}$ and $630\text{ }^\circ\text{C}$ generates XRD patterns that show the co-existence of hollandite, $K_{0.25}IrO_2$, (PDF 85-2185) Ir (PDF 87-0715) and IrO_2 (PDF 15-0870) signals. Following thermal treatment at $650\text{ }^\circ\text{C}$ for 170 h we have only signals corresponding to IrO_2 with tetragonal structure. Similar 20 displacements of the samples were observed by solid-state reaction and sol-gel method via acrylamida polymerization. The morphology of the samples was observed through SEM. The sol-gel process generates very thin crystals with form of needles with thickness between 100-150 nm and the ss obtained by solid-state reaction produce aggregates.

Keywords: chemical synthesis, nanoparticles, XRD, SEM.

1 INTRODUCTION

In transition metal oxides, a variety of electronic phases appear. In fact, one of the most important discoveries is high-Tc superconductivity in copper oxides. The oxides of 5d transition element such as, tungsten bronzes or rhenium oxide have been known for their good electric conduction and several iridium oxides exceptionally show interesting electronic states [5]. Those findings are related to the material structure having an impact over their electrical and magnetic properties.

The crystal structure of IrO_2 was reported by K&K Laboratories, Inc., Jamaica, New York, USA using X-ray powder diffraction (XRD) data (PDF 15-0870). The unit cell was given as tetragonal, $a = 4.4983$, $c = 3.1544\text{ \AA}$ with a space group P42/mnm (No. 136).

Bestaoui N. et al. prepared the ternary oxide K_xIrO_2 ($x \approx 0.25$) by solid-state reaction at $1000\text{ }^\circ\text{C}$ for 1 h. The structure corresponds to a slight distortion of the well-known hollandite-type structure with a monoclinic cell. [5].

In this work, we were interested at the method of synthesis of hollandite-type K_xIrO_2 . In our research group, the synthesis of metal oxides ceramics is carried out by two different methods such as sol-gel via acrylamide polymerization and solid-state reaction. The advantage using this sol-gel method is the generation of nano-structured materials and the solid-state reaction let us to compare different parameters such as morphology, particles size, reaction times, annealing temperatures, etc.

2 EXPERIMENTAL

The synthesis of $K_xIr_{1-x}O_2$ system was carried out by two different methods previously mentioned. The reagents used were the K_2CO_3 (99.999%, CERAC Milwaukee, USA) and IrO_2 (99.9%, CERAC Milwaukee, USA). Prior to weighting, K_2CO_3 was preheated during 10-20 min. at $100\text{--}120\text{ }^\circ\text{C}$ for dehydration. IrO_2 was weighted in argon flowing glove bag to avoid the oxidation of this reagent.

Synthesis:

A. Solid-state reaction. Stoichiometric amounts of K_2CO_3 and IrO_2 were ground in an agate mortar in air atmosphere at ambient pressure. This mixture was analyzed by XRD after annealing in order to follow the crystallization process. The reactions were carried out in an electric furnace ($\pm 4\text{ }^\circ\text{C}$) in high- Al_2O_3 crucibles. The mixture was firstly annealed at $530\text{ }^\circ\text{C}$ for 98 h, $630\text{ }^\circ\text{C}$ for 186 h and $650\text{ }^\circ\text{C}$ for 170 h in air atmosphere.

B. Sol-gel method via acrylamida polymerization. A three-step procedure was employed to prepare the $K_xIr_{1-x}O_2$, $0.00 < x < 0.25$ ss. The first step is the sol formation. A stoichiometric amount of K_2CO_3 was dissolved in acetic acid ($H_4C_2O_2$) (99.8%, J. Baker) aqueous dissolution of 125 ml distilled water amount at around $90\text{ }^\circ\text{C}$ using an electric grill with a magnetic agitation in order to increase the velocity of the dissolution.

The second step is the potassium gel formation. To the dissolution obtained previously we add, if necessary ammonium hydroxide (NH₄OH) (28-30%, J. T. Baker) to adjust the pH between 3.6 and 6.3. To this dissolution, stoichiometric quantities of acrylamide, H₂C = CHCONH₂ (~ 99%, Fluka), N-N' metilenbisacrylamida C₇H₁₀N₂O₂ (≥ 99.5%, Fluka) and α-α' azoisobutinitril, C₈H₁₈N₆-2HCl (≥ 98%, Fluka) were added. The polymerization is performed by heating at 70 °C from 1 to 3 min.

The last step is the xerogel formation. In order to obtain the xerogel, the gel was dehydrated in a microwave furnace until 185 °C for 45 min. in argon flux. Then, the xerogel was grounded using an agate electric mortar. At this time a stoichiometric amount of IrO₂ was added to the potassium xerogel to obtain a homogeneous mixture of these reactants. The xerogel was then placed in high-Al₂O₃ crucibles and annealed at different temperatures starting with 200 °C.

After starting to anneal at 500 °C we carried out XRD analysis to the samples prepared by the two methods to follow the crystallization process.

3 CHARACTERIZATION TECHNIQUES

Powder diffraction diagrams were recorded on a Bruker-axs D8-advance diffractometer using CuK_α radiation. Diffraction patterns were collected at room temperature over the 2θ range 2.5° - 70° for all the samples synthesized with a step size of 0.02° and time per step of 0.6 s.

The morphology of the samples and the Electron Dispersive X-Ray (EDX) was analyzed by SEM on a Cambridge-Leica Stereoscan 400, equipped with an Oxford/Link System electron probe microanalyser (EPMA). The micrographs were taken with a voltage of 20 KV, current intensity of 1000 pA and WD = 25 mm.

4 RESULTS AND DISCUSSION

By solid-state reaction technique we observed that the XRD diffractogram from the reagents mixture show the IrO₂ (PDF 15-0870) and signals having very low intensities attributed to K₂CO₃, Figure 1(a). Others diffractograms were obtained during the annealed process from samples synthesized by the same method at different temperatures. The pattern from Figure 1(b) obtained after annealing at 530 °C for 98 h shows the signals corresponding to IrO₂ with 2θ displacement a little different compared with the IrO₂ (PDF 15-0870). Subsequent annealing at 630 °C and 650 °C are depicted in Figure 1 (c) and (d) showing signals corresponding to IrO₂ with a very short displacement in 2θ values compared with IrO₂ (PDF 15-0870). This displacement is observed with changes in structure parameters (Table 1).

At the present time, we attributed this displacement to the introduction of potassium ion to the IrO₂ structure. Further experiments will probe this preliminary explanation.

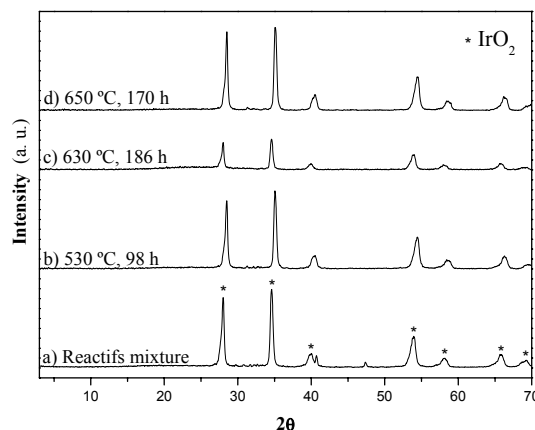


Figure 1: XRD patterns obtained during the annealed process at different temperatures of the reagents mixture synthesized by the solid-state reaction: (a) reactive mixture grounded in an agate mortar, (b) mixture annealed at 530 °C for 98 h, (c) sample annealed at 630 °C for 186 h and (d) sample sintering at 650 °C for 170 h all of them annealed in air atmosphere.

All the patterns obtained in Figure 1 were compared and indexed on the basis of the reported tetragonal unit cell PDF 15-0870 corresponding to IrO₂ compound. The cell parameters are $a = 4.4983 \pm 0.001$ Å and $c = 3.1544 \pm 0.01$ Å with space group P4₂/mm (No. 136).

Sample conditions	a Å	c Å
IrO ₂ (PDF 15-0870)	4.4983 ± 0.001	3.1544 ± 0.01
T=530 °C t=98 h	4.5022 ± 0.001	3.1745 ± 0.01
T=630 °C t=186 h	4.5091 ± 0.001	3.1809 ± 0.01
T=650 °C t=170 h	4.5059 ± 0.001	3.1629 ± 0.01

Table 1: Cell parameters of the XRD patterns obtained from the samples synthesized by solid-state reaction.

The cell parameters a and c were calculated considering the reflections (200) and (211) respectively.

The pattern of Figure 1 (d) corresponding to the sample annealed at 650 °C for 170 h shows the cell parameters $a = 4.5059 \pm 0.001$ Å and $c = 3.1629 \pm 0.01$ Å. Slight changes in the cell parameters values of the precedents samples, Figure 1 (b) and (c), are observed depending on the temperature and reaction time. In addition, these changes seem to be attributed to the introduction of potassium ion into the structure. Futures studies will confirm the quantity of potassium ion introduced to the structure.

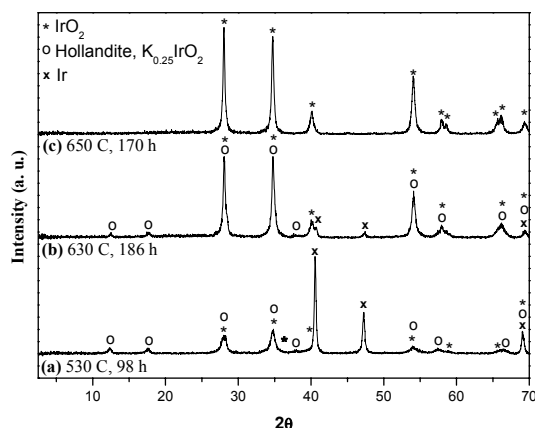


Figure 2: XRD patterns obtained from samples synthesized by sol-gel method and annealed at: (a) 530 °C for 98 h, (b) 630 °C for 186 h and (c) 650 °C for 170 h.

On the other hand, the XRD patterns from the samples prepared by sol-gel via acrylamide polymerization are depicted in Figure 2. The Figure 2(a) shows the XRD pattern of the potassium xerogel mixed with the IrO_2 reagent after annealed this mixture at 530 °C for 98 h. The pattern shows signals corresponding to the IrO_2 reagent, Ir and $\text{K}_{0.25}\text{IrO}_2$ (hollandite). At this temperature the reaction is not complete. The next pattern, Figure 2(b) corresponding to the sample annealed at 630 °C depicts the same three signals. However, the signal corresponding to Ir shows lower intensity compared to the precedent pattern. Finally, the sample annealed at 650 °C for 170 h shows the signals corresponding only to IrO_2 . The comparison of the DRX pattern obtained from this sample and the IrO_2 (PDF 15-0870) shows only difference in the c parameter. This difference seems to be related to a re-ordering to the potassium ion into the IrO_2 structure. This result indicates that at 650 °C the introduction of the potassium ion to IrO_2 tetragonal structure is favourable.

Similar than the patterns obtained from the samples synthesized by solid-state reaction, the pattern obtained in Figure 2 (d) was compared and indexed on the basis of the reported tetragonal unit cell PDF 15-0870 corresponding to IrO_2 compound.

The cell parameters a and c were calculated considering the reflections (200) and (211) respectively. The pattern of Figure 2 (d) related to the sample annealed at 650 °C for 170 h shows the follow cell parameters $a = 4.4937 \pm 0.001 \text{ \AA}$ and $c = 3.1754 \pm 0.01 \text{ \AA}$.

The morphology of the sample synthesized by solid-state reaction and annealed at 630 °C during 186 h was analyzed by MEB, Figure 3(a). The micrograph reveals a single phase in agree with X-rays analysis. This phase corresponds to the $\text{K}_x\text{Ir}_{1-x}\text{O}_2$, $0.00 < x < 0.25$ ss.

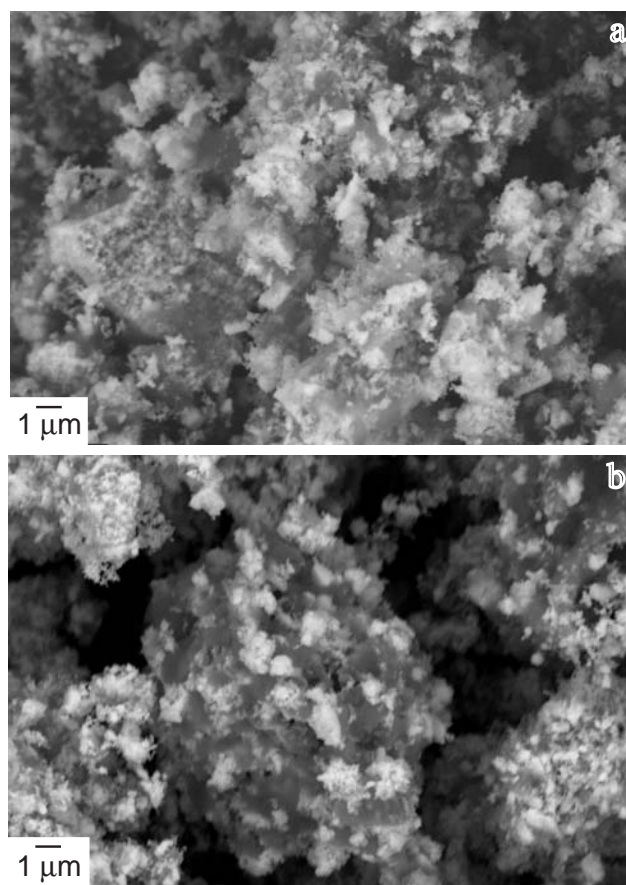


Figure 3: SEM micrographs from samples synthesized by solid-state reaction annealed at: (a) 630 °C for 186 h and (b) at 650 °C for 170 h.

Similar results are observed for the sample annealed at 650 °C for 170 h, where XRD analysis reveals a single phase and MEB analysis shows it, Figure 3(b). Both samples show big aggregates with average size between 2 and 6 μm .

In contrast, the morphology observed for the samples obtained by sol-gel method via acrylamide polymerization is a particular structure like kinds of needles organized similar to the sea urchins, Figure 4. The results presented are the corresponding to the xerogel annealed at 530 °C for 98 h and at 630 °C for 186 h, Figure 4 (a) and (b) respectively.

In the Figure 4(a) the length of the needles is between 1 and 1.5 μm and their diameters seems to change along their length. The average length of the needles observed in Figure 4(b) is shorter than 1 μm . It seems that when the temperature increases the length of the needles decrease.

The different morphology due to the method of synthesis could be explained by the speed of evaporation or lost of the sample weight during the thermal treatment. By the sol-gel method the speed of weight loss seems to be faster than the loss of weight noted by solid-state reaction.

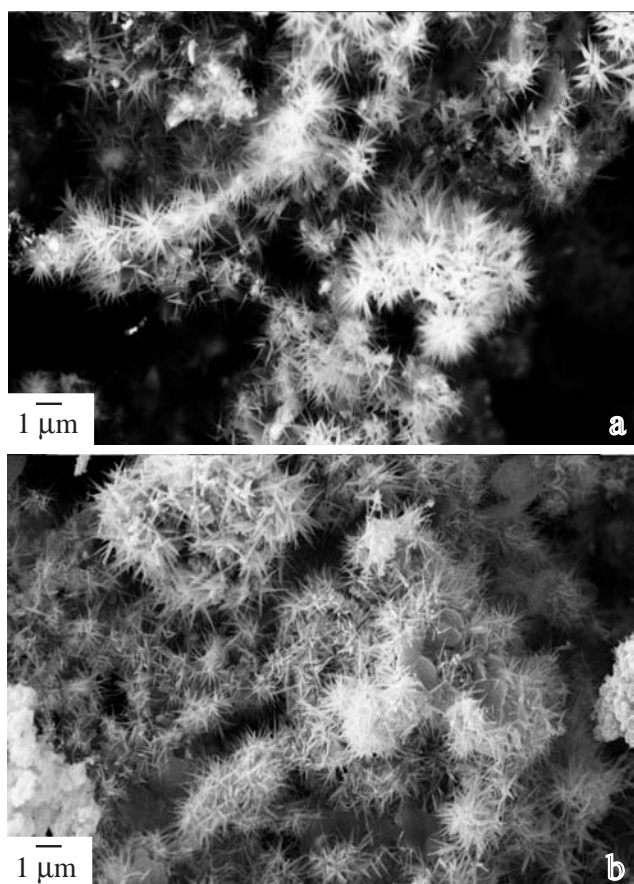


Figure 4: SEM micrographs from samples synthesized by sol-gel method via acrylamide polymerization annealed at: (a) 530 °C for 98 h and (b) at 630 °C for 186 h.

The morphology of the samples synthesized by sol-gel method is not completely reproducible. Actually, different experiments are doing to explain these changes in morphology during the synthesis process. Variables such as ambient humidity, occurrence of the IrO_2 reagent impurity, thermal stability of the phases present during process could be the reason of the reproducibility problem.

5 CONCLUSIONS

This work shows that the method of synthesis to obtain the $\text{K}_x\text{Ir}_{1-x}\text{O}_2$, $0.00 < x < 0.25$ ss has an influence over the morphology of the crystals obtained. One of the variables that could be having an effect over the morphology is the speed of weight loss of the sample during the thermal treatment. On the other hand, the temperature reaction had show to be an important parameter to conserve the ss obtained.

The sol-gel method via acrylamide polymerization has the advantages to produce crystals of $\text{K}_x\text{Ir}_{1-x}\text{O}_2$, $0.00 < x < 0.25$ ss with form similar to needles with a lower temperature that the reported previously (1000 °C) for the hollandite-type structure synthesized by solid-state reaction [4].

In contrast, with the form of crystals obtained by the sol-gel method via acrylamide polymerization, the crystals obtained by solid state reaction are aggregates of particles without a definite form. However, similar that the sol-gel method via acrylamide polymerization we obtained the $\text{K}_x\text{Ir}_{1-x}\text{O}_2$, $0.00 < x < 0.25$ ss at lower temperature that the reported previously.

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