

Synthesis of lead-based 1212 and 3212 superconductors by an aqueous sol-gel method

Research Article

Giedre Nenartaviciene, Ramunas Skaudzius, Rimantas Raudonis,
Aivaras Kareiva*

Department of General and Inorganic Chemistry,
Vilnius University,
LT-03225 Vilnius, Lithuania

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Abstract: The aqueous sol-gel synthesis technique for the preparation of $(\text{Pb,Sr})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_{7\pm x}$ (Pb-1212) and $(\text{Pb}_2,\text{Cu})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_{8\pm x}$ (Pb-3212) superconductors using two different complexing agents, namely 1,2-ethanediol and tartaric acid was studied. The phase transformations, composition and micro-structural features in the polycrystalline samples were studied by powder X-ray diffraction analysis (XRD), infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). XRD analysis of the ceramic samples obtained by calcination of Pb-Sr-Y-Ca-Cu-O acetate-glycolate precursor gels in air, for 10 hours at 800°C and at 825°C, showed the presence of homogeneous Pb-1212 and Pb-3212 crystallites as major phases. The XRD patterns of the ceramics obtained from Pb-Sr-Y-Ca-Cu-O acetate-tartrate precursor gels, however, showed multiphase character. The critical temperature of superconductivity (T_c (onset)) observed by resistivity measurements were found to be 91 K and 75 K for Pb-1212 and Pb-3212 samples, respectively.

Keywords: Ceramics • Superconducting materials • Chemical synthesis • Sol-gel growth

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1. Introduction

Until the discovery of high-temperature superconductors (HTS) in 1986 [1] applications of bulk superconductors had been difficult due to poor thermal stability. High-temperature superconducting power equipment has the potential to become a key 21st century technology for improving the capacity, efficiency, and reliability of the electric delivery system. As an example, higher-capacity HTS power lines could provide a new approach to building transmission and distribution systems that will reduce the footprint and allow additional capacity to be placed in service within existing rights-of-way. During the past 20 years, researchers have achieved significant improvements in the material properties of bulk superconductors, and have investigated the feasibility of their use in various fields. A combination of bulk HTS and permanent magnets allows the construction of low-loss magnetic bearings that are currently being used in high-efficiency flywheels for energy storage. Bulk HTS has demonstrated an ability to trap magnetic flux and some samples have even exhibited surface magnetic

field magnitudes of an order higher than those of Fe-Nd-B magnets. These properties of bulk HTS led to the realization of some attractive engineering applications. Superconducting components made using an YBCO conductor can enable megawatt-class power airborne systems due to the reduction in size and weight over the conventional counterparts. Improvements in these areas as well as better stability will lead to unprecedented power densities for military applications [2-6].

Compounds with formula $(\text{Pb}_2,\text{Cu})\text{Sr}_2(\text{Ln,Ca})\text{Cu}_2\text{O}_{8\pm x}$ (Pb-3212), where Ln is Y or another lanthanide, were shown in 1988 by Cava *et al.* [7] to be high temperature superconductors with critical temperature of superconductivity (T_c) reaching values up to 70 K. The crystal structure of the Pb-3212 compounds contains the structural elements which are well known from other HTS superconducting oxides. The yttrium or lanthanide ions are sandwiched between two CuO_2 layers, and the stacking sequence is $(\text{Ln/Ca})\text{-CuO}_2\text{-SrO-PbO-Cu-PbO-SrO-CuO}_2$ [8]. Soon after the discovery of the Pb-3212, a $(\text{Pb,Sr})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_{7\pm x}$ (Pb-1212) series

* E-mail: aivaras.kareiva@chf.vu.lt

of lead-based compounds with T_c reaching ≈ 90 K was discovered by Subramanian *et al.* [9] and Lee *et al.* [10]. The structure of Pb-1212 compounds resembles that of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with the rock-salt type (Pb,Sr)O layers replacing the CuO chain wherein, Sr atoms replace Ba atoms, and some of the Y atoms are replaced by Ca atoms [11]. The authors [7-22] prepared polycrystalline Pb-1212 and Pb-3212 samples by solid state reactions of the respective oxides and carbonates while using different atmospheres and sintering temperatures for the preparation of superconducting phases. The solid-state synthesis from oxide and carbonate powders usually requires extensive mechanical mixing and lengthy heat treatments at high temperatures. These processing conditions, however, do not allow control over the micro-structure, grain size and grain size distribution in the resulting powders.

Over the last few decades, sol-gel techniques have been used to prepare a variety of mixed metal oxides. In these sol-gel processes, good quality of the oxide products was expected primarily due to the purity of the precursor materials used and chemical homogeneity obtained from the synthetic route [23-26]. The molecular level mixing and the tendency of partially hydrolysed species to form extended networks facilitate the structure evolution, thereby, lowering the crystallisation temperature of multicomponent metal oxide ceramics. Recently, we described the use of an aqueous sol-gel method for the synthesis of monophasic non-substituted $\text{YBa}_2\text{Cu}_4\text{O}_8$, as well as superconducting Y-124 samples substituted in the yttrium, barium and copper positions by other elements [27-29]. We also showed the importance of the nature of the complexing agent in the sol-gel process in order to obtain monophasic superconducting Y-124 oxide [30,31]. However, to our knowledge, the sol-gel method has been employed only once for the preparation of lead-based superconductors [32]. The main objective of the present study was therefore, to synthesize $(\text{Pb,Sr})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_{7\pm x}$ and $(\text{Pb}_2,\text{Cu})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_{8\pm x}$ superconductors *via* a simple aqueous sol-gel method. It was, also the aim of this study to investigate the influence of the two complexing agents, 1,2-ethanediol and tartaric acid, on the phase purity and superconducting properties of Pb-1212 and Pb-3212 superconductors prepared by an aqueous sol-gel route. In addition, the purpose of this study was to show that adjusting the nature of complexing agent can be used to control the physical properties of the end product during sol-gel preparation of the superconducting cuprate.

2. Experimental Procedures

The $(\text{Pb}_{0.5}\text{Sr}_{0.5})\text{Sr}_2(\text{Y}_{0.2}\text{Ca}_{0.8})\text{Cu}_2\text{O}_7$ (Pb-1212) and $\text{Pb}_2\text{Sr}_2(\text{Y}_{0.2}\text{Ca}_{0.8})\text{Cu}_3\text{O}_8$ (Pb-3212) superconducting samples were prepared by two sol-gel routes, namely acetate-tartrate and acetate-glycolate syntheses. As starting compounds, stoichiometric amounts of analytical grade $\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$, $\text{Sr}(\text{CH}_3\text{CO}_2)_2$, $\text{Y}(\text{CH}_3\text{CO}_2)_2 \cdot 4,16\text{H}_2\text{O}$, $\text{Ca}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$, and $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ were used. In the sol-gel process $\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$ first was dissolved in 50 mL of 0.1 M acetic acid at 55 - 60°C. Next, a solution of $\text{Sr}(\text{CH}_3\text{CO}_2)_2$, $\text{Y}(\text{CH}_3\text{CO}_2)_2 \cdot 4,16\text{H}_2\text{O}$, $\text{Ca}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$, and $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ in 0.1 M acetic acid, were added over several hours with intermediate stirring with the temperature maintained at 55 - 60°C. Finally, a solution of tartaric acid in water or 1,2-ethanediol (2 mL) as complexing agents was added to the reaction solution. The solutions so obtained were concentrated in about 8 hours at 60 - 65°C in an open beaker under continuous stirring resulting in formation of transparent blue gels. After drying further in an oven at 100°C, blue powders with a fine grain texture were obtained. These powders were calcined for 10 hours at 800°C in air, subjected to grinding in an agate mortar, pelletized and heated for 10 hours at the requisite temperature of 825°C / 850°C / 900°C, in an atmosphere of air at ambient pressure.

The Pb-1212 and Pb-3212 oxides so synthesized were characterized by means of powder X-ray diffraction analysis performed with a Philips MPD 1880 diffractometer, using $\text{CuK}\alpha_1$ radiation. Infrared spectra of the samples as KBr pellets in the range of 4000–400 cm^{-1} were recorded on an EQUINOX 55/S/NIR FTIR spectrometer. Scanning electron microscope (SEM) JEOL 820 was used to study the morphology and microstructure of the ceramic samples. Energy dispersive X-ray (EDX) analysis was performed, in vacuum, in the specimen chamber of an EDX coupled scanning electron microscope. A standard, four-probe technique was used for measuring the temperature dependence of the resistivity in the range 20 – 300 K. Pellets of Pb-1212 and Pb-3212 oxides with a diameter of 8 mm were prepared with Enerpac press using ~ 0.5 g of material pressed at 1.2 - 1.5 kbar for 30 min.

3. Results and discussion

The $(\text{Pb}_{0.5}\text{Sr}_{0.5})\text{Sr}_2(\text{Y}_{0.2}\text{Ca}_{0.8})\text{Cu}_2\text{O}_7$ and $\text{Pb}_2\text{Sr}_2(\text{Y}_{0.2}\text{Ca}_{0.8})\text{Cu}_3\text{O}_8$ compounds were characterized by FTIR spectroscopy. Fig. 1 shows the FTIR spectra of Pb-1212 ceramics prepared by calcinations of

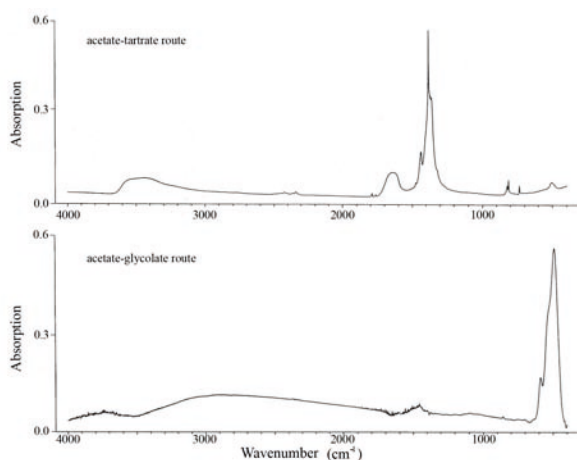


Figure 1. FTIR spectra of Pb-1212 ceramics prepared using different complexing agents in the sol-gel processing: 1,2-ethanediol (at bottom) and tartaric acid (at top).

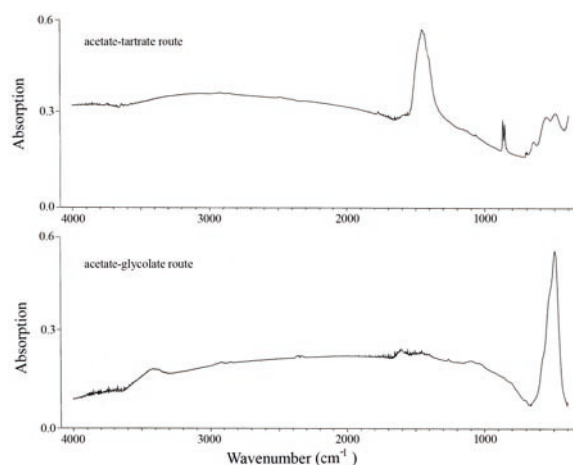


Figure 2. FTIR spectra of Pb-3212 ceramics prepared using different complexing agents in the sol-gel processing: 1,2-ethanediol (at bottom) and tartaric acid (at top).

acetate-tartrate and acetate-glycolate gel precursors for 10 h at 825°C. Interestingly, in the FTIR spectrum of Pb-1212 superconductor synthesized using tartaric acid, the absorption bands attributable to the ionic carbonate (CO_3^{2-}) were detected at 1470 - 1390 cm^{-1} ; $\sim 870 \text{ cm}^{-1}$ and $\sim 1750 \text{ cm}^{-1}$ [33,34]. However, the FTIR spectrum of Pb-1212 superconductor synthesized using 1,2-ethanediol showed no absorption bands attributable to the ionic carbonate (see Fig. 1, vide infra) and only specific peaks in the region of 700 - 400 cm^{-1} attributable to the characteristic M-O vibrations could be observed. Fig. 2 shows the FTIR spectra of Pb-3212 ceramics prepared by calcinations of acetate-tartrate and acetate-glycolate gel precursors for 10 h at 825°C. Again, the FTIR spectra for both ceramic specimens show characteristics similar to that of Pb-1212. The FTIR spectrum of Pb-3212 synthesized by acetate-tartrate sol-gel route contains strong bands which are typical vibrations for the CO_3^{2-} . Moreover, the FTIR spectrum of Pb-3212 obtained by acetate-glycolate route does not show any characteristic features for carbonate bands. The results obtained from IR measurements clearly demonstrate the existence of the impurity phases in the product obtained by acetate-tartrate sol-gel synthetic approach.

These conclusions were supported by XRD measurements. The XRD patterns of Pb-1212 ceramic samples are presented in Fig. 3. Evidently, only minor amount of Pb-1212 phase was formed using tartaric acid in the sol-gel processing. Moreover, the diffraction lines observed at around 24 and 26° could be attributed to the SrCO_3 phase. However, acetate-glycolate synthesis route gave almost monophasic Pb-1212 compound [PDF 42-51] (the lines are indexed in Fig. 3B).

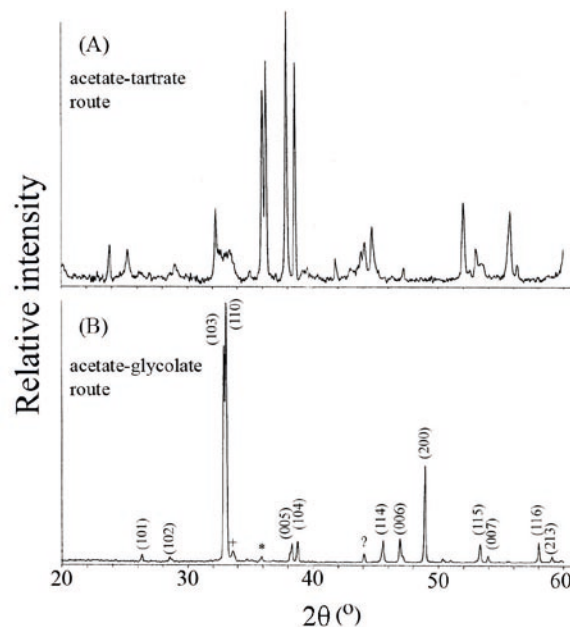


Figure 3. XRD patterns of Pb-1212 compounds synthesized by acetate-tartrate (A) and acetate-glycolate (B) sol-gel synthesis routes. Side phases are marked: (+) - CaPbO_3 , (*) - Sr_2PbO_4 , (?) - unidentified product.

As seen, only minor amount of impurity phases, such as CaPbO_3 , Sr_2PbO_4 and unidentified phases were formed during synthesis. The X-ray diffraction patterns for the Pb-3212 products are shown in Fig. 4. Again only in acetate-glycolate synthesis, the Pb-3212 phase [PDF 44-408] containing small amount of impurity phases was formed. According to the XRD analysis, sintering of acetate-tartrate precursor gel also produced fully crystalline ceramics, however, the formation of

lead-based superconducting phases does not proceed using this synthetic approach.

To support the results obtained, the acetate-tartrate Pb-Sr-Y-Ca-Cu-O gel precursors were also annealed at higher temperatures (850°C and 900°C). The XRD patterns of Pb-1212 and Pb-3212 ceramic samples obtained at 850°C are presented in Fig. 5. Evidently, the higher calcination temperature does not promote the formation of superconducting Pb-1212 and Pb-3212 phases. The similar results were obtained when the specimens were annealed at 900°C.

Temperature dependences of resistivity of Pb-1212 compounds prepared by acetate-tartrate and acetate-glycolate sol-gel synthesis routes (Fig. 6) as was expected show that the compound obtained by acetate-tartrate route is non-superconducting. However, $(\text{Pb}_{0.5}\text{Sr}_{0.5})\text{Sr}_2(\text{Y}_{0.2}\text{Ca}_{0.8})\text{Cu}_2\text{O}_7$ superconductor synthesized by acetate-glycolate route showed $T_c(\text{onset}) \approx 91$ K with rather broad transition width which is typical for lead-based superconductors. Again, the Pb-3212 compound obtained by acetate-tartrate route was non-superconducting and the $(\text{Pb}_2\text{Cu})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_{8+x}$ superconductor synthesized by acetate-glycolate route showed $T_c(\text{onset}) \approx 75$ K (Fig. 7).

Fig. 8 shows the SEM micrographs of the superconducting Pb-1212 and Pb-3212 oxides synthesized. The SEM image of the single-phase samples confirms that the distribution of its chemical elements is highly uniform. However, the crystal size

distribution is rather broad. Some individual particles seem to be nanosized plate shaped crystals, however, most grains are agglomerated in different sizes within a range of ~ 2 μm to 20 μm . The composition of Pb-1212 and Pb-3212 oxides were also studied by means of energy dispersive X-ray analysis (EDX) analysis. Data from the elemental analysis of the crystallites are presented in Table 1. The average metal ratios determined by energy dispersive X-ray analysis, in the powders synthesized by acetate-glycolate route correspond to the metal stoichiometry consistent with the Pb-1212 and Pb-3212 phases with no component segregation or non-ideal stoichiometries at the micrometer level being observed in any region of the samples. The average metal ratios in the superconducting acetate-glycolate derived samples with the starting compositions Pb:Sr:Y:Ca:Cu = 8.3:41.7:3.3:13.3:33.3 and Pb:Sr:Y:Ca:Cu = 25:25:2.5:10:37.5 were found to be Pb:Sr:Y:Ca:Cu = 8(1):42(4):3(1):13(2):34(3) for the Pb-1212 and Pb:Sr:Y:Ca:Cu = 25(2):24(3):3(1):10(2):38(4) for the Pb-3212, respectively, which is in a good agreement, within the standard deviations of the distributions. Using these data, the approximate chemical formulae that could be suggested for the superconductors synthesized are $(\text{Pb}_{0.5(1)}\text{Sr}_{0.5(2)})\text{Sr}_{2.0(3)}(\text{Y}_{0.2(1)}\text{Ca}_{0.8(1)})\text{Cu}_{2.0(2)}\text{O}_7$ and $\text{Pb}_{2.0(2)}\text{Sr}_{1.9(2)}(\text{Y}_{0.2(1)}\text{Ca}_{0.8(1)})\text{Cu}_{3.1(3)}\text{O}_8$. On the other hand, the EDX measurements on the acetate-tartrate derived crystallites showed highly uneven distribution of the elements.

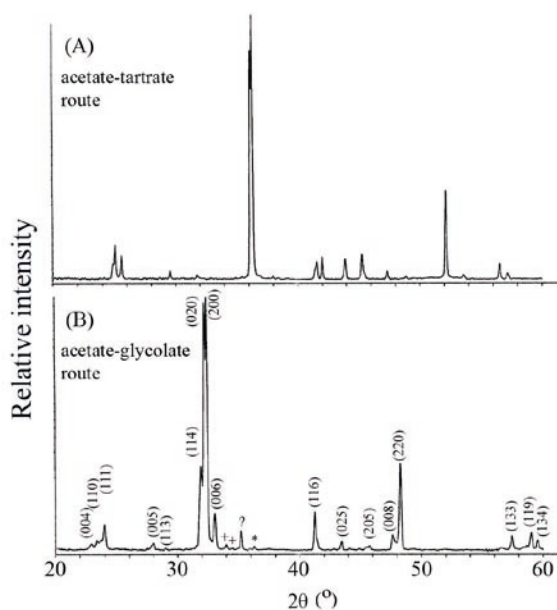


Figure 4. XRD patterns of Pb-3212 compounds synthesized by acetate-tartrate (A) and acetate-glycolate (B) sol-gel synthesis routes. Side phases are marked: (+) – CaPbO_3 , (*) – Sr_2PbO_4 , (?) – unidentified.

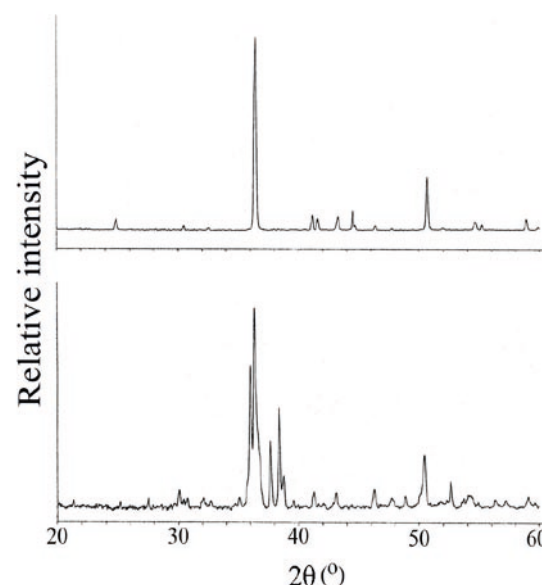


Figure 5. XRD patterns of Pb-1212 (at bottom) and Pb-3212 (at top) compounds synthesized by acetate-tartrate sol-gel synthesis routes at 850°C

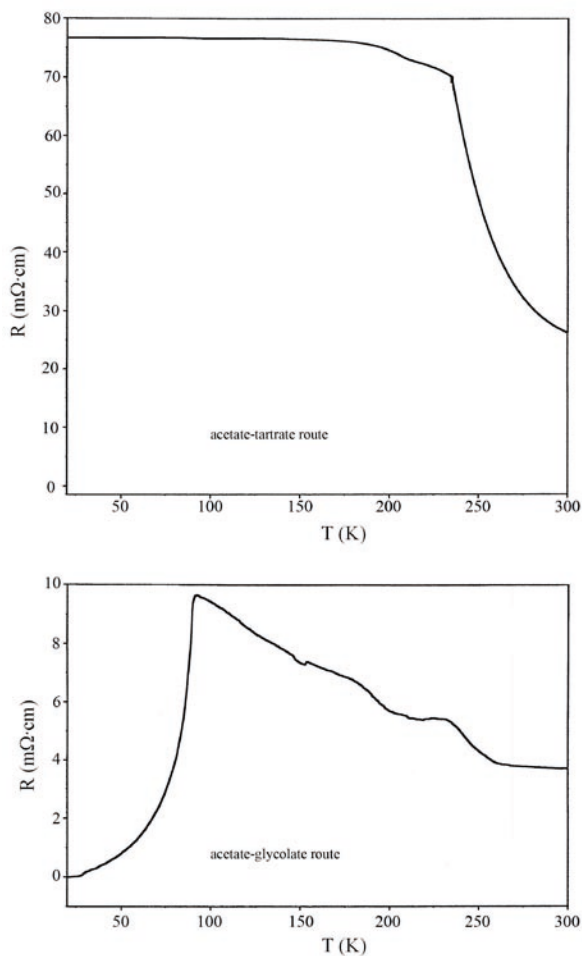


Figure 6. Resistivity vs. temperature for the Pb-1212 compounds synthesized by acetate-glycolate (at bottom) and acetate-tartrate (at top) routes.

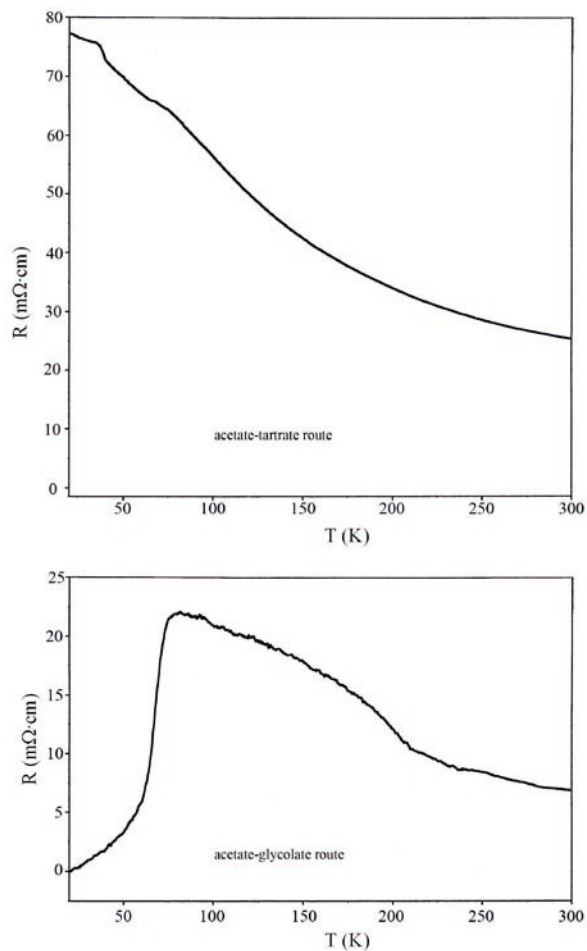


Figure 7. Resistivity vs. temperature for the Pb-3212 compounds synthesized by acetate-glycolate (at bottom) and acetate-tartrate (at top) routes.

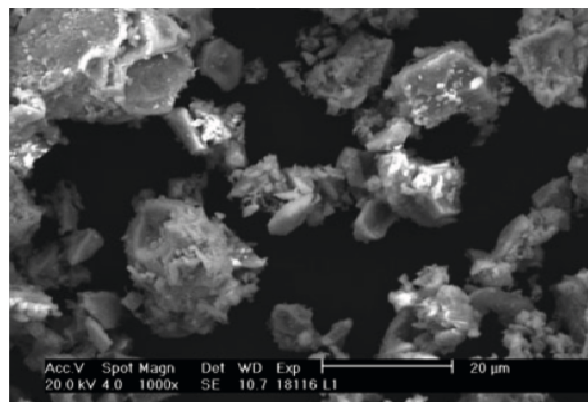
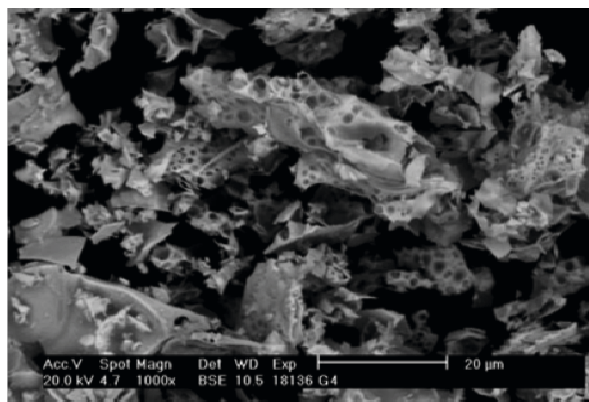


Figure 8. Scanning electron micrographs of Pb-1212 (left) and Pb-3212 (right) superconductors. Magnification 1000X.

Table 1. EDX* analysis of the of Pb-1212 and Pb-3212 compounds synthesized by acetate-tartrate and acetate-glycolate sol-gel synthesis routes at 825°C, with standard deviations within parentheses.

Sample	Synthesis route	Molar percentage of metals (%)				
		Pb	Sr	Y	Ca	Cu
Pb-1212	acetate-tartrate	6(2)	38(3)	3(2)	16(2)	37(4)
	acetate-glycolate	8(1)	42(4)	3(1)	13(2)	34(3)
Pb-3212	acetate-tartrate	30(4)	28(4)	2(1)	7(3)	33(4)
	acetate-glycolate	25(2)	24(3)	3(1)	10(2)	38(3)

*Approximately 10 crystallites of each sample were analyzed.

4. Conclusions

The (Pb,Sr)Sr₂(Y,Ca)Cu₂O_{7±x} (Pb–1212) and (Pb₂,Cu)Sr₂(Y,Ca)Cu₂O_{8±x} (Pb–3212) superconductors were synthesized by sol-gel method using tartaric acid and 1,2-ethanediol as complexing agents in the processing protocol. The products obtained were characterized by X-ray powder diffraction analysis, FTIR spectroscopy, scanning electron microscopy and resistivity measurements. The results lead us to conclude that only minor amount of Pb–1212 or Pb–3212 phases were formed using tartaric acid. However, acetate-glycolate synthesis route gave almost monophasic Pb–1212 and Pb–3212 compounds. The ceramic materials obtained by

acetate-tartrate route were non-superconducting while the Pb-1212 and Pb–3212 superconductors synthesized by acetate-glycolate route showed T_c(onset) ≈ 91 K and ≈ 75 K, respectively. Moreover, the aqueous sol-gel method proposed is very simple, less toxic, inexpensive and thus appropriate for the large-scale production of such materials.

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