Electrochemical growth and properties of single crystals in La_2O_3 – MnO – CoO system

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Recently renewed interest grew up to the ternary oxides system of lanthanum, cobalt and manganese due to discovery of so-called colossal magneto resistivity (CMR) in doped orthomanganites $La_{1-x}A^{2+}_xMnO_3$ (A = Sr, Ba, Ca) with perovskite structure. High quality single crystals are essential to get reproducible data and choose only one from numerous theoretical explanations of this phenomenon. Recently McCarrol and co-workers have succeeded in growth of pure and doped lanthanum manganite single crystals by anodic electrodeposition technique using Cs_2MoO_4 – MoO_3 high temperature flux as solvent [1]. We developed and expanded this approach on crystal growth of rare earth cobaltites and mixed compounds in La_2O_3 – MnO – CoO system.

Single crystals were grown in a vertical resistive furnace supplied by silicon carbide heaters. A mixture of MoO_3 (99.99%) and Cs_2CO_3 (99.99 %) in molar ratio 1:2.2 was placed into a platinum crucible to prepare solvent. Previously dried powders of MnO, CoO and La_2O_3 oxides of the same purification served as solute components. The solvent was successively prepared by the following way: a batch of MoO_3 was melted first at 950°C and then cesium carbonate was added by several small batches for gradual decarbonizing. Then solute oxides were added to the solvent and homogenized for 3 hours at 1190-1200°C. An average level of the flux-melt didn't exceed a platinum crucible half height. The platinum crucible served as cathode while a platinum plate fixed on a corundum rod was used as anode under the electrochemical growth process. The anode was deepened by 5 – 8 mm into the flux-melt to rotate slowly in the crucible center. Single crystals were grown in 80 – 100 hrs at the anode current density 5 – 10 mA/cm^2. As shown in Fig. 1, $LaMn_{1-x}Co_xO_{3+\delta}$ single crystals accepted mostly a cubic like shape and weekly developed (111) type faces could be recognized. A primary crystallization temperature range for these compounds was found to be 830 - 1170°C. But, quasi equilibrium growth and smooth crystal faces development were seen only in the temperature interval 1000 – 1050°C.

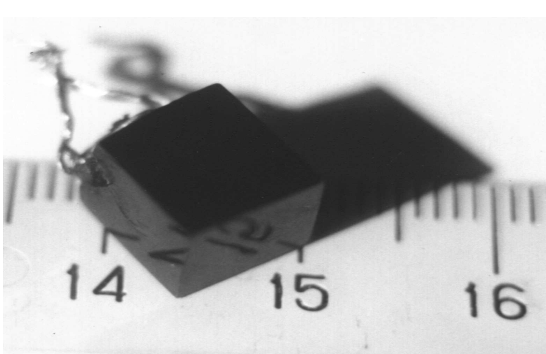

Fig. 1. As–grown $LaMn_{1-x}Co_xO_{3+\delta}$ single crystals.

The temperature – concentration range for $LaMnO_{3+\delta}$ single crystals stable growth is shown in Fig. 2. The as-grown crystals possess variation from orthorhombic to rhombohedral crystal structure following by an average Mn valence increase as growth temperature decrease down to 1000°C and lower. Particularly, as shown by chemical titration approach Mn ions reveal an average valence ~3.0 at 1170°C to increase up to ~ 3.2 at the growth temperature 870°C.

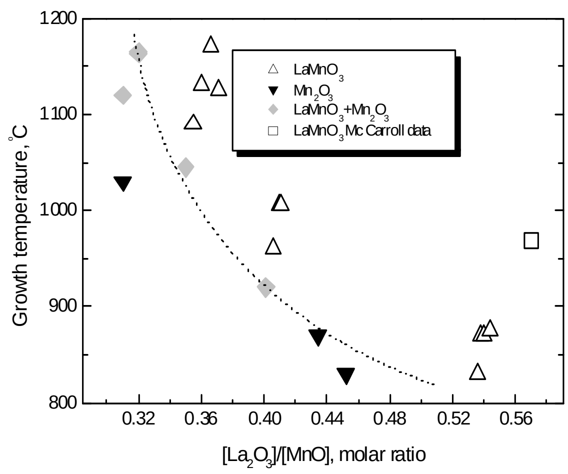

Fig. 2. Range of stable growth of $LaMnO_{3+\delta}$ single crystals

It is known crucible materials corrosion and incorporation of solvent components into grown crystals are the main disadvantages of crystal growth from a high temperature solution. The X-ray fluorescence analysis was used to characterize composition of grown crystals. It was measured that in the case of pure $LaMnO_{3+\delta}$ impurity content of Mo, Cs and Pt does not exceed 0.01, 0.005 and 0.1 molar percent, respectively. Concentration of Mo and Pt tends to increase in cobalt doped crystals reaching to maximal values of 3 and 1 mol. %, respectively for $LaCoO_3$. Cobalt segregation coefficient in the flux and in crystals was found to be smaller than 1 reflecting a smaller Co/Mn ratio for the crystals in comparison to the one in the flux. Cobalt content in the grown crystals increases with growth temperature to become very close to desired value at high temperatures.

$LaMn_{1-x}Co_xO_{3+\delta}$ ($0 \le x \le 0.5$) single crystals grown by electrochemical flux technique reveal a ferromagnetic behavior at low temperatures. Spin glass transition takes place for the crystals at higher cobalt contents, while $LaCoO_{3+\delta}$ samples are paramagnetic. Pure $LaMnO_{3+\delta}$ crystals with a small δ exhibit remarkable anisotropy of magnetization.

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1. W. H. McCarrol, K. V. Ramanujachary, M. Greenblatt. Synthesis of doped rare earth manganate perovskite crystals using fused salt electrolysis. J. Sol. St. Chem. Vol. 130, 1997, P. 327.