



Microwave advantages in inorganic synthesis of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ powders for perovskite ceramics

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Abstract

In this work the advantage of the use of the microwave technology was exploited for the preparation of perovskite ceramics. Microwave-assisted hydrothermal method has been applied to the preparation of strontium-doped lanthanum manganites with different stoichiometric ratio of the three oxides, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.3, 0.5, 0.6$). In particular, pure black narrow dispersed crystallites of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ of $0.68 \pm 0.18 \mu\text{m}$ were prepared in only 45 minutes at 240°C and a KOH concentration of 21 M. The complete chemical, mineralogical and microstructural characterization of the powders reveal the same structural properties of the perovskite powders previously synthesised by ceramic and conventional hydrothermal routes.

Keywords: microwave, hydrothermal, perovskite ceramics, manganites

I. Introduction

Solid inorganic materials, used for the preparation of electroceramics such as rechargeable and long-life batteries, magnetic inorganic materials and miniaturised titanate capacitors [1], are often synthesised via chemical route to avoid high temperature elemental losses or other contamination sources. Recently hydro- or solvo-thermal co-precipitation methods replaced high temperature calcinations for complex oxide preparation [2]. Co-precipitation reactions involve the simultaneous occurrence of nucleation, growth, coarsening, and/or agglomeration processes. Due to the difficulties in isolating each process for independent study, the fundamental mechanisms of co-precipitation are still not thoroughly understood. Nevertheless, when dielectric heating is applied via microwave irradiation the homogeneity of the temperature reached within the reaction vessel strongly favours homogenous versus heterogeneous nucleation mechanisms [3]. Literature often reports of microwave synthesis of micro or nanopowders of perovskite ceramics, such as titanates, niobates and manganites, with a monomodal particle or grain size distribution either in the synthesis or in the sintering routes [4–7]. In particular, the microwave-assisted hydrothermal processes when compared to the conventional ones enhance pow-

der crystallinity, while decrease processing time and produce monodispersed particle. These advantages are even more evident if compared to the “ceramic route”, where extended periods dedicated to grinding and firing of solid precursors followed by annealing in controlled gas atmosphere are necessary.

In a previous work monodispersed strontium manganite particles have been obtained by this technique under mild synthesis condition [4], i.e. far from water supercritical point. On the basis of this experience in the present work, the advantages of the microwave-assisted hydrothermal method applied, for the first time, to the one-step preparation of strontium-doped lanthanum manganites $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ have been evaluated. In a previous study [8] on synthesis of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ with microwave-hydrothermal technique a firing step of 900°C was used to produce the crystalline manganite. Here the single phase manganite is obtained by hydrothermal synthesis in less than 1 hour and fully characterized microstructurally and mineralogically.

II. Experimental

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.0%), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (97.0 %) and $\text{Sr}(\text{NO}_3)_2$ (99.0%) were supplied by Fluka; KMnO_4 (99.5%) by Carlo Erba; KOH pellets by Sigma-Aldrich. All the chemicals were used as received. Synthesis of strontium-doped lanthanum manganites with different sto-

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ichiometric ratio, i.e. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.3, 0.5, 0.6$) using microwave-assisted hydrothermal method was performed mixing 1.95 ml of 0.350 M lanthanum nitrate, 1.95 ml of 0.350 M strontium nitrate and 2.73 ml of manganese(II) nitrate solutions prepared in deionised water. To this mixture 1.17, ml of 0.350 M potassium permanganate and a suitable amount of potassium hydroxide (as mineralizer) were added. The reaction mixture was placed in a 100 ml Teflon® autoclave which was sealed and placed in the microwave applicator (Ethos TC, Milestone) using 2.45 GHz frequency with maximum power of 1000 W. The power of microwave oven was automatically adjusted in such a way to reach the temperature of 240°C in 15 minutes, with dwell time of 30 minutes. After the reaction the autoclave was naturally cooled to room temperature. The solid product was washed several times with deionised water and 1 M nitric acid solution and then dried at 50°C. The dried powders were analysed by a computer assisted X-ray powder diffractometer (Model X'Pert PRO Philips, Eindhoven, Netherlands) using $\text{CuK}\alpha$ radiation. The X-ray diffraction patterns were collected in a 2θ range of 5–80° at room temperature, with a step size of 0.02° and a time per step of 6 s. Phase composition identification was carried out by comparing the experimental profiles with database structures (ICSD - Inorganic Crystal Structure Database, The National Institute of Standards and Technology (NIST) and Fachinformationszentrum Karlsruhe (FIZ), version 2006-1). The sample morphology and the size distribution were examined by Philips XL-30 electron scanning microscope (SEM), and images elaborated with ImageJ software.

III. Results

The reaction conditions used for the microwave hydrothermal synthesis of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and the corresponding main phases present in the as-made products are given in Table 1. In the case of $x = 0.5$ (sample

PVK05) powders obtained after microwave assisted hydrothermal treatment of 30 minutes at a temperature of 240°C and a KOH molarity of 21 M were constituted of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (ICSD 85641) and $\text{La}(\text{OH})_3$ (ICSD 200090) as revealed by XRD analysis and depicted in Fig. 1. When the syntheses for $x = 0.5$ were carried out at lower temperature as well as KOH concentrations the perovskite $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ was afforded, but was not pure due to the presence of the two mineral phases $\text{La}(\text{OH})_3$ and $\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$ (ICSD 83236). Attempts to prepare single phase manganites with $x = 0.3$ (sample PVK03) or $x = 0.6$ (PVK06) proved unsuccessful, since $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ was always produced along with $\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$ and $\text{La}(\text{OH})_3$ for the sample PVK03 and only $\text{La}(\text{OH})_3$ for the sample PVK06 (Fig. 1).

The SEM images of the as-prepared samples PVK03, PVK05 and PVK06 revealed that the material consists of interpenetrated cube-shaped crystallites of dimension

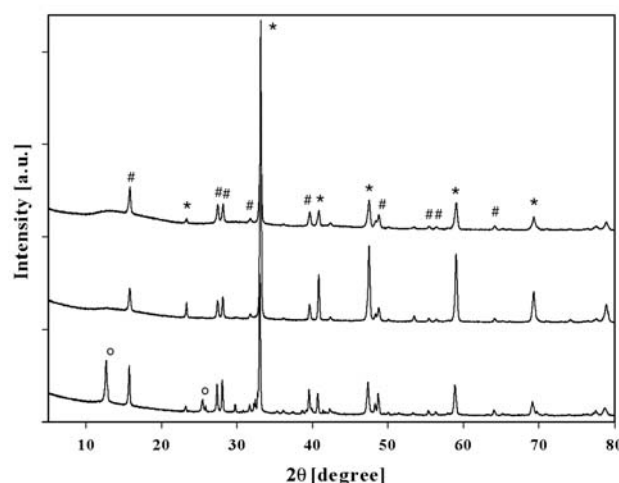


Figure 1. XRD spectra of sample PVK03 (bottom), PVK05 (middle), PVK06 (top) obtained without any purification (* $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, # $\text{La}(\text{OH})_3$, ° $\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$)

Table 1. Reaction conditions used to investigate the microwave-assisted hydrothermal syntheses of strontium-doped lanthanum manganites

Sample	Target compound	Mixture	[KOH] [mol/l]	T [°C]	t [min]	Products*
PVK03	$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ($x = 0.3$)	La(III) : Mn(II) : Mn(VII) : Sr(II) : KOH : H_2O = 7.0 : 7.4 : 2.6 : 3.0 : 1250 : 3250	21	240	30	$\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, $\text{La}(\text{OH})_3$, $\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$
PVK05	$\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ ($x = 0.5$)	La(III) : Mn(II) : Mn(VII) : Sr(II) : KOH : H_2O = 5.0 : 7.0 : 3.0 : 5.0 : 1250 : 3250	21	240	30	$\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, $\text{La}(\text{OH})_3$
PVK06	$\text{La}_{0.4}\text{Sr}_{0.6}\text{MnO}_3$ ($x = 0.6$)	La(III) : Mn(II) : Mn(VII) : Sr(II) : KOH : H_2O = 4.0 : 6.8 : 3.2 : 6.0 : 1250 : 3250	21	240	30	$\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, $\text{La}(\text{OH})_3$
PVK06F**	$\text{La}_{0.4}\text{Sr}_{0.6}\text{MnO}_3$ ($x = 0.6$)	La(III) : Mn(II) : Mn(VII) : Sr(II) : KOH : H_2O = 4.0 : 6.8 : 3.2 : 6.0 : 1250 : 3250	21	240	30	$\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$
PVK05F**	$\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ ($x = 0.5$)	La(III) : Mn(II) : Mn(VII) : Sr(II) : KOH : H_2O = 5.0 : 7.0 : 3.0 : 5.0 : 1250 : 3250	21	240	30	$\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$

Microwave Oven Method: 15 minutes up to the settled temperature T , with dwell time of t minutes. *On the basis of powder X-ray diffraction analysis; **after filtration and washing with nitric acid solution (1 M).

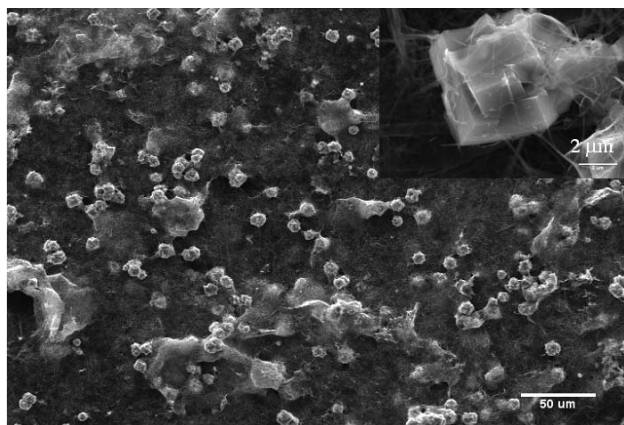


Figure 2. SEM image of the sample PVK03 obtained without any purification. Inset: magnification on the cubic and nanowires structures present in the sample PVK03

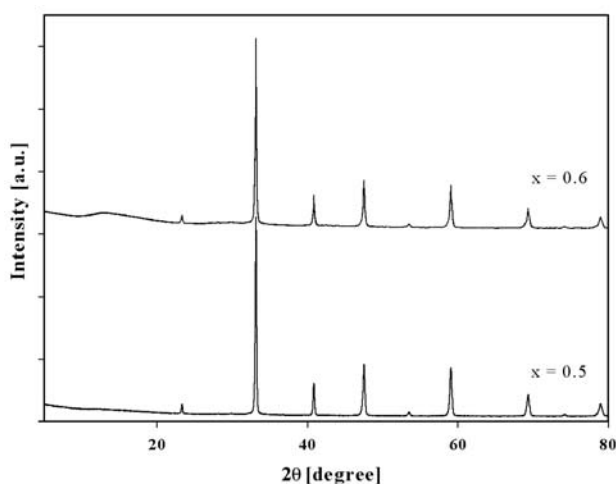


Figure 3. XRD spectra of sample PVK05F (bottom), PVK06F (top) obtained after filtration washing with nitric acid solution (1M)

$\sim 0.7 \mu\text{m}$, $\sim 0.5 \mu\text{m}$ and $\sim 5.2 \mu\text{m}$, respectively. It is important to add that these crystallites are surrounded by lanthanum hydroxide nanowires [9], as shown in the SEM micrograph for the sample PVK03 (Fig. 2 and its inset).

Pure $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (the samples PVK05F and PVK06F) were produced by purification of the samples PVK05 and PVK06 by means of a filtration and

washing (with 1 M nitric acid solution), in order to remove the unreacted lanthanum hydroxide, as shown from XRD spectra in Fig. 3. If the $\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$ phase is present in synthesised powder, as in the sample PVK03, $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ powders were not purifiable. As revealed by XRD analysis the samples PVK05F and PVK06F were constituted of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ phase, which presented a distorted perovskite structure (tetragonal, $I4/mcm$) [10]. The SEM micrographs of PVK05F and PVK06F are reported in Fig. 4a and 4b, respectively. The interpenetrated cubic structure of the $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ crystallites, as prepared without purification, was maintained. By the size distribution analysis (Fig. 5) it is shown that the black $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ crystallites PVK05F and PVK06F have narrow dispersion with grain size of $0.68 \pm 0.18 \mu\text{m}$ and $0.50 \pm 0.12 \mu\text{m}$, respectively. The size of the not purifiable PVK03 powders was one order of magnitude larger ($5.2 \pm 1.5 \mu\text{m}$). Defining the particle dispersion index as the ratio of the crystallite size to the standard deviation, for all of these three samples the particle size dispersion has a constant value of ~ 0.25 .

IV. Discussion

The microwave-hydrothermal route for preparation of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ provides an advantageous and rapid low-temperature one-step synthesis, whilst the ceramic route required extended periods involving grinding and firing of solids precursors followed by annealing in controlled gas atmosphere. $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ powders have been rapidly produced by the microwave-assisted hydrothermal method in only 45 minutes, while the conventional hydrothermal synthesis requires 24 hours [11]. $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ powders prepared with microwaves were morphologically and structurally similar to the materials previously synthesised by conventional hydrothermal [11,12] or ceramic [13,14] methods. As confirmed by literature [12], even if the doping level was varied only materials of composition $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with $x = 0.5$ were prepared. Due to the uniform and fast heating, the advantage of the microwave technology combined with hydrothermal processing is the efficient synthesis of narrow-

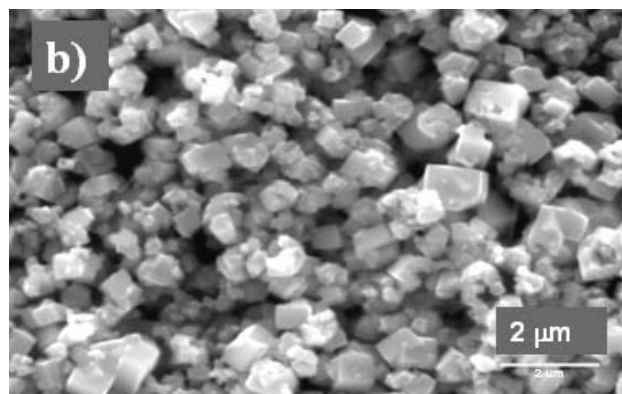
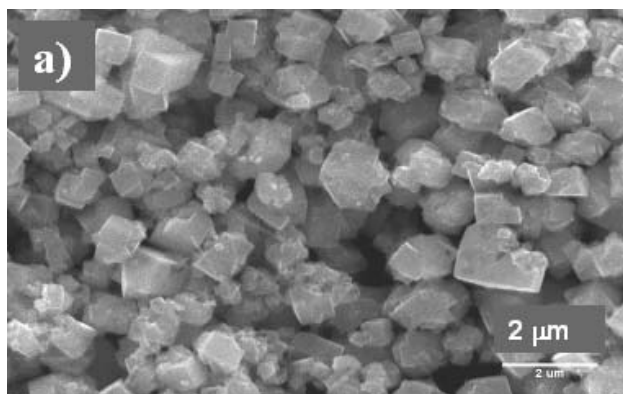


Figure 4. SEM image of the sample: a) PVK05F and b) PVK06F obtained after filtration and washing with nitric acid solution (1M)

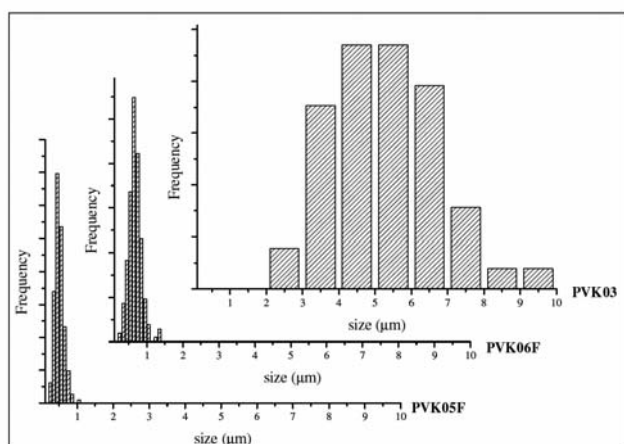


Figure 5. Particle size distribution of sample PVK05F (bottom) and PVK06F (middle) obtained after filtration washing with nitric acid solution (1 M) and sample PVK03 (top) obtained without any purification

ly dispersed perovskite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ particles. In fact, the PVK03, PVK05F and PVK06F samples have different crystal size, but a low and constant particle dispersion index. Investigation on the crystallization process by changing the KOH concentration, reaction times and temperature on the magnetic properties of the obtained perovskite powders is in progress.

V. Conclusions

The efficiency of the low time-consuming microwave process was clearly demonstrated. It is shown that pure black $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ crystallites, with the average size of $\sim 0.6 \mu\text{m}$ and narrow size distribution, were prepared after the purification of the powders obtained after microwave treatment for only 45 minutes at 240°C using a KOH concentration of 21 M. The as-produced fine powders are attractive as a fine-grained ceramics for magnetic applications. The homogenous nucleation and uniform crystal growth peculiar of microwave heating assured a dispersion index of about 0.25, measured as crystallite size to the standard deviation ratio.

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References

1. R.I. Walton, “Subcritical solvothermal synthesis of condensed inorganic materials”, *Chem. Soc. Rev.*, **31** (2002) 230–238.
2. B.L. Cushing, V.L. Kolesnichenko, C.J. O’Connor, “Recent advances in the liquid-phase syntheses of inorganic nanoparticles”, *Chem. Rev.*, **104** (2004) 3893–3946.

3. A. Rizzuti, A. Corradi, C. Leonelli, T. Chudoba, T. Strachowski, A. Opalinska, W. Lojkowski, “Homogeneous crystal growth in microwave-assisted hydrothermal synthesis of inorganic compounds”, pp. 41–44 in *Proceedings of Global Congress on Microwave Energy Applications Proceedings - GCMEA 2008*. Japan Society of Electromagnetic Wave Energy Applications, Japan, 2008.
4. A. Rizzuti, M. Viviani, A. Corradi, P. Nanni, C. Leonelli, “Microwave-assisted hydrothermal synthesis as a rapid route towards manganite preparation”, *Solid State Phenom.*, **128** (2007) 21–24.
5. A. Manavbasi, J.C. LaCombe, “Dielectric characteristics of donor doped nonlead $\text{Ba}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3$ perovskite material synthesized by microwave-assisted citrate-nitrate sol-gel route”, pp. 261–266 in *Materials and Processes for Nonvolatile Memories II*. Ed. T. Li, Y. Fujisaki, J.M. Slaughter, D. Warrendale, PA, 2007.
6. C.-S. Chen, C.-C. Chou, “Microstructure and dielectric properties of nano-grained X7R type BaTiO_3 ceramic capacitors sintered by 2.45 GHz microwave”, *Phys. Scr.*, **T129** (2007) 170–174.
7. P.K. Patro, A.R. Kulkarni, S.M. Gupta, C.S. Harendranath, “Improved microstructure, dielectric and ferroelectric properties of microwave-sintered $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ ”, *Phys. B: Cond. Matter*, **400** [1-2] (2007) 237–242.
8. S.A. Mirji, Y.B. Kholam, S.B. Deshpande, H.S. Potdar, R.N. Bathe, S.R. Sainkar, S.K. Date, “Microwave-hydrothermal accelerated solid state reaction route for the synthesis of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ ”, *Mater. Lett.*, **58** (2004) 837–841.
9. J.J. Urban, L. Ouyang, M.-H. Jo, D.S. Wang, H. Park, “Synthesis of single-crystalline $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ nanocubes with adjustable doping levels”, *Nano Lett.*, **4** [8] (2004) 1547–1550.
10. A. Rizzuti, “Microwave assisted syntheses of high tech nano and micro-structured materials”, *Internal report*, 2008.
11. J. Spooen, R.I. Walton, “Hydrothermal synthesis of the perovskite manganites $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and alkali-earth manganese oxides CaMn_2O_4 , 4H-SrMnO_3 and 2H-BaMnO_3 ”, *J. Solid State Chem.*, **178** [5] (2005) 1683–1691.
12. J. Spooen, R.I. Walton, F. Millange, “A study of the manganites $\text{La}_{0.5}\text{M}_{0.5}\text{MnO}_3$ (M = Ca, Sr, Ba) prepared by hydrothermal synthesis”, *J. Mater. Chem.*, **15** [15] (2005) 1542–1551.
13. A. Sundaresan, P.L. Paulose, R. Mallik, E.V. Sampathkumaran, “Bandwidth-controlled magnetic and electronic transitions in $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Sr}_x\text{MnO}_3$ ($0 < x < 0.5$) distorted perovskite”, *Phys. Rev. B*, **57** (1998) 2690–2693.
14. P.M. Woodward, T. Vogt, D.E. Cox, A. Arulraj, C.N.R. Rao, P. Karen, A.K. Cheetam, “Influence of cation size on the structural features of $\text{Ln}_{1/2}\text{A}_{1/2}\text{MnO}_3$ perovskites at room temperature”, *Chem. Mater.*, **10** (1998) 3652–3665.