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Sol gel synthesis of calcium manganese oxide nanopowder

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Abstract: In this paper calcium manganese oxide ($Ca_{0.74}Mn_{0.253}O_1$) nanopowder was synthesized via a sol gel method. The synthesized oxide was characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The magnetic and electrical properties of the synthesized nanopowder were demonstrated. XRD and IR results revealed the formation of $Ca_{0.74}Mn_{0.253}O_1$ and the TEM investigation showed the formation of heterogeneous particles with sizes range from 30 to 100 nm. Investigation of the magnetization as a function of magnetic field indicated the paramagnetic behaviour of the synthesized material. The electrical conductivity was found to increase with the increase in temperature.

Keywords : Calcium manganese oxide, Nanoparticles, Sol-gel, Perovskite, thermoelectric materials**.**

1. Introduction

In recent years, oxide based materials have attracted considerable attention for their applications in diverse fields such as, e.g., catalysis, batteries, solar cells, electronic and thermoelectric devices[1,2,3,4,5]. Due to their relatively high thermal and chemical stability oxide materials can be regarded as potential candidates for high-temperature applications. Amongst the important oxide materials are perovskite-type oxides which have been the subject of intense research over the last two decades due to their unique characteristics [6,7,8,9,10,11,12]. The main advantage of the perovskites is the flexibility of the doping which enables a broad selection of material property combinations [8,9,10].

Perovskite $CaMnO_3$ is regarded as one of the important n-type oxide-based thermoelectric materials, due to its high Seebeck coefficient (> 400 μV K^{-1}), relatively low thermal conductivity (~ 4 W m^{-1} K^{-1}) and tunable electrical resistivity [13]. The thermoelectric properties of $CaMnO_3$ are strongly correlated to its electronic structure and the crystal structure [14,15]. The demand of green energy to reduce greenhouse gas emission has stimulated the extensive research in the field of thermoelectrics, Thermoelectric materials are important for power generation devices that convert heat into electrical energy thanking to their thermoelectric effect.

Recently, it was demonstrated that $CaMnO_3$ has superior electrocatalytic activity for the oxygen electrochemistry as it exhibits enhanced performance in oxygen reduction/ evolution reactions in comparison with MnO_2 [16]. Furthermore, Ca–Mn–O oxides have gained much interest in biomimetic and electrochemical applications[16,17,18,19]. The low cost, high abundance and ecological friendliness of Ca-Mn-O oxides make them attractive candidates as non-precious electrocatalysts. Recently, it was reported that interconnected nanoporous $CaMnO_3$ nanoparticles can employed as an efficient electrocatalyst in lithium-oxygen batteries. It showed substantial energy efficiency and enhanced cycling performance[20].

There are different routes for synthesis of Ca-Mn-O oxides such as conventional solid state reactions [21] and wet chemical methods such as, co-precipitation[22], solution combustion synthesis [23] and sol gel [20] techniques. Sol gel methods are commonly used for the synthesis of oxides as size and morphology of the synthesized oxides can be controlled.

In this paper, $Ca_{0.74}Mn_{0.253}O_1$ oxide was prepared via a sol gel technique using $CaCl_2$ and $MnCl_2$ as precursors. The synthesized material was characterized by XRD, TEM, FT-IR and TGA-DSC measurements. The magnetization of the synthesized material with respect to the magnetic field was demonstrated. The electrical conductivity was also investigated.

2. Experimental

$Ca_{0.74}Mn_{0.253}O_1$ was synthesized via a sol gel method in isopropanol (Alfa, 99.5%) using $CaCl_2$ (Alfa, 99 %) and $MnCl_2$ (Alfa, 99 %) as precursors. Distilled water was used for hydrolysis the precursor solution, ammonium hydroxide (Sigma Aldrich 98%) was used to adjust the pH. The synthesized samples were calcined in a muffle oven at the desired temperature for 2 h and were cooled down to the ambient temperature in the oven.

The morphology and particle size of the as prepared samples were investigated by a high resolution transmission electron microscope (HRTEM, JEM/1230 model, Japan). The phase composition of the as prepared and calcined samples was investigated using a Philips- diffractometer Model PW 2013, Netherlands, operating at 35 KV and 20 mA with a source of CuK_α radiation. The main functional surface groups of the prepared samples were determined by Fourier transform infrared spectroscopy FT-IR using KBr pellets JASCO,FT/IR 460 plus. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out by a Universal V4.7 TA-Instruments analyzer at a heating rate of 10 °C /min. starting from room temperature up to 1000 °C in air. A computerized LRC Bridge (Hioki model 3532-50 LCR Hi Tester) was used to measure the conductivity for the synthesized samples in the temperature range from 50 to 400 ^oC, in the frequency range from 42 Hz to 5 MHz. The measurements were performed after sufficient time at each temperature for establishing of equilibrium values for conductivity. A Vibrating Sample Magnetometer, VSM Lakeshore 7410 USA, was used for magnetic property measurements with a maximum applied field of ± 1.9 kOe.

3. Results and discussion

A solution of 1M $CaCl_2$ and 1M $MnCl_2$ in isopropanol was prepared and hydrolyzed by addition of an appropriate amount of water. The solution was kept stirring to form a gel. Afterwards, the pH was adjusted at 8 by ammonium hydroxide and stirring maintained. Then the mixtures were centrifuged to recover the product. The product was then calcined at 500 ^oC for 2 hours. The synthesized material was characterized by means of X-ray diffraction and transmission electron microscopy TEM to explore the structural composition and morphology. Fig1 shows the XRD patterns of the obtained material. The XRD diffractogram of Fig. 1 shows the characteristic peaks of $Ca_{0.74}Mn_{0.253}O_1$ and all recorded peaks are well indexed according to the JCPDS (PDF-98-006-0702) card [24]. This suggests the formation of $Ca_{0.74}Mn_{0.253}O_1$ as the sole product of the employed synthesis process. The TEM micrograph of Fig. 2 shows the formation of heterogeneous particles with sizes range from 30 to 100 nm.

The IR spectrum of the synthesized compound is depicted in Fig. 3. As shown in the observed spectrum, a broad band is recorded at ~ 3200-3600 cm^{-1} attributed to O-H stretching of adsorbed water molecules and surface hydroxyl groups; the bending vibration band of the O-H of the adsorbed water is observed at 1630 cm^{-1}. Two bands observed at 1458 and 1029 cm^{-1} are associated with the C-OH bending vibration of adsorbed isopropanol, the employed solvent, molecules. Strong bands located between 700 and 430 cm^{-1} are measured which can be assigned to M-O stretching vibrations of CaMnO. The XRD and IR results reveal the synthesis $Ca_{0.74}Mn_{0.253}O_1$.

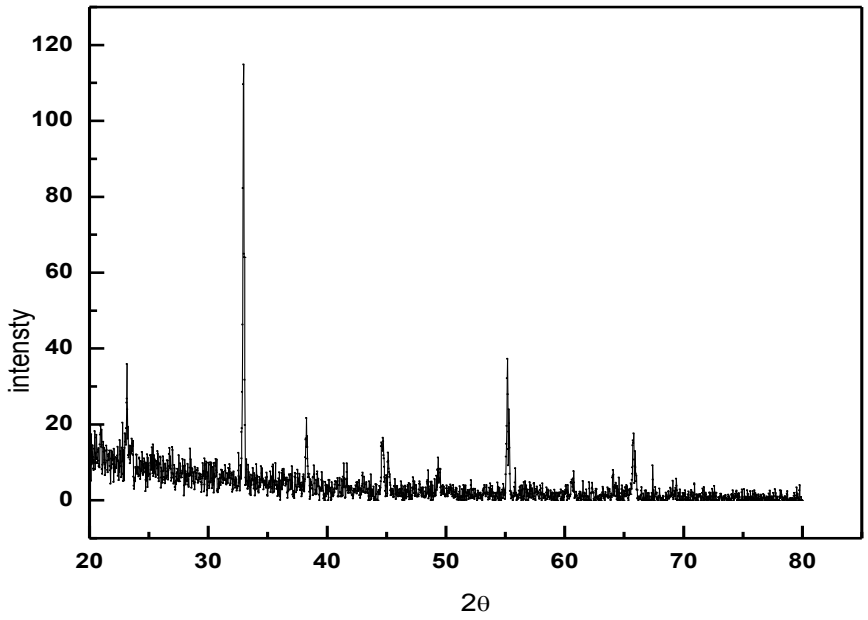

Fig. 1. XRD patterns of the synthesized oxide

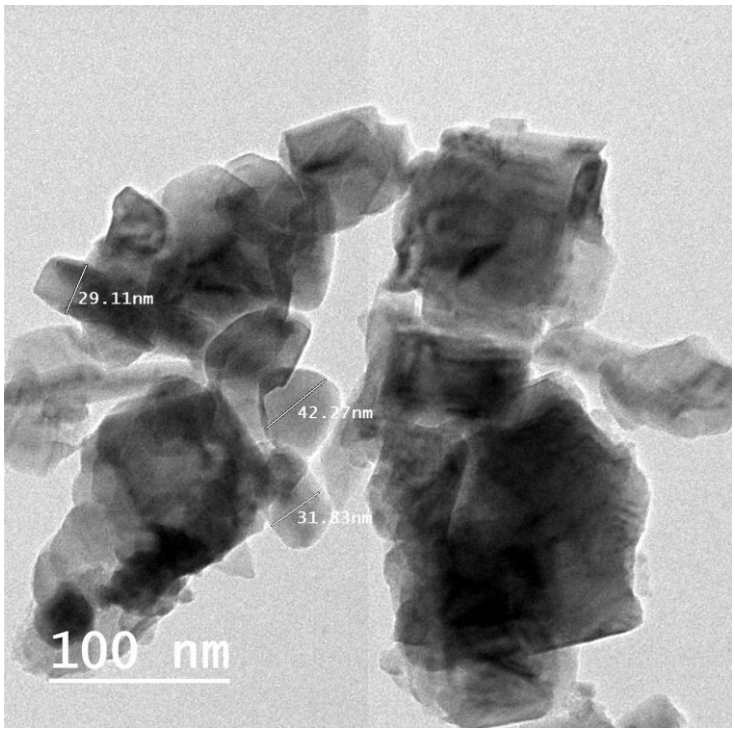

Fig. 2. TEM micrograph of the synthesized $Ca_{0.74}Mn_{0.253}O_1$

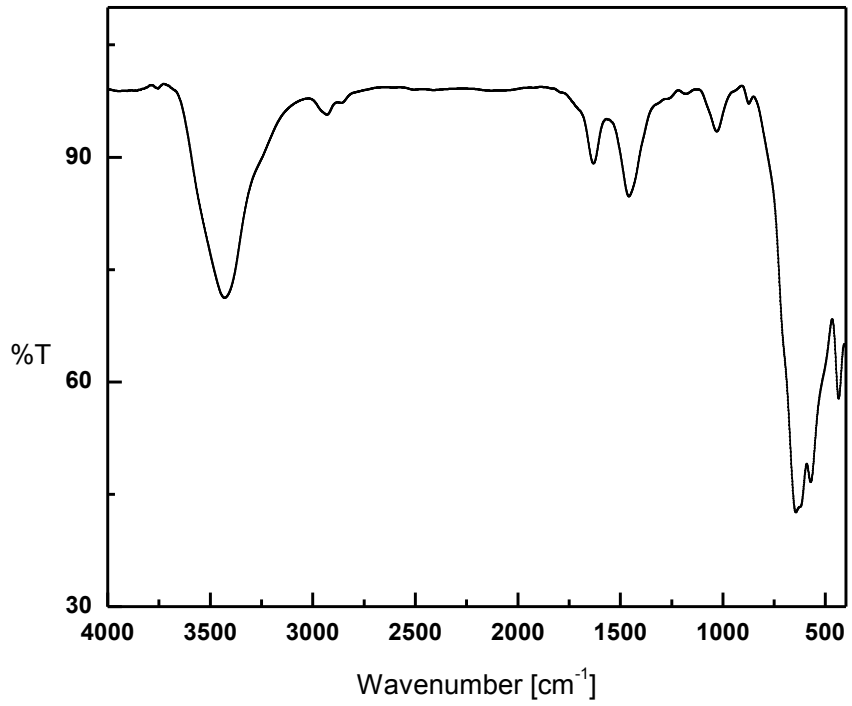

Fig. 3. FT-IR spectrum of the synthesized $Ca_{0.74}Mn_{0.253}O_1$

The thermal behaviour of the synthesized $Ca_{0.74}Mn_{0.253}O_1$ was investigated using differential scanning calorimetry and thermogravimetric analyses, Fig. 4. The TGA curve shows three distinct weight loss zones. In the temperature range from 30- 100 ^oC a slight weight loss of about 0.5 % was observed as a result of the evaporation of physically adsorbed water. From 100 to 600 ^oC, the TGA curve exhibits slow decrease in the weight loss which can be ascribed to the removal of organic impurities. A significant mass loss of about 4 % is observed in the temperature range of 700-900 ^oC which can be assigned to removal of the surface hydroxyls and

or evaporation chemisorbed water. The DSC curve exhibits three significant peaks at 80, 700 and 850 ^{o}C which are associated with evaporation of adsorbed water, removal organic impurities and chemisorbed water respectively.

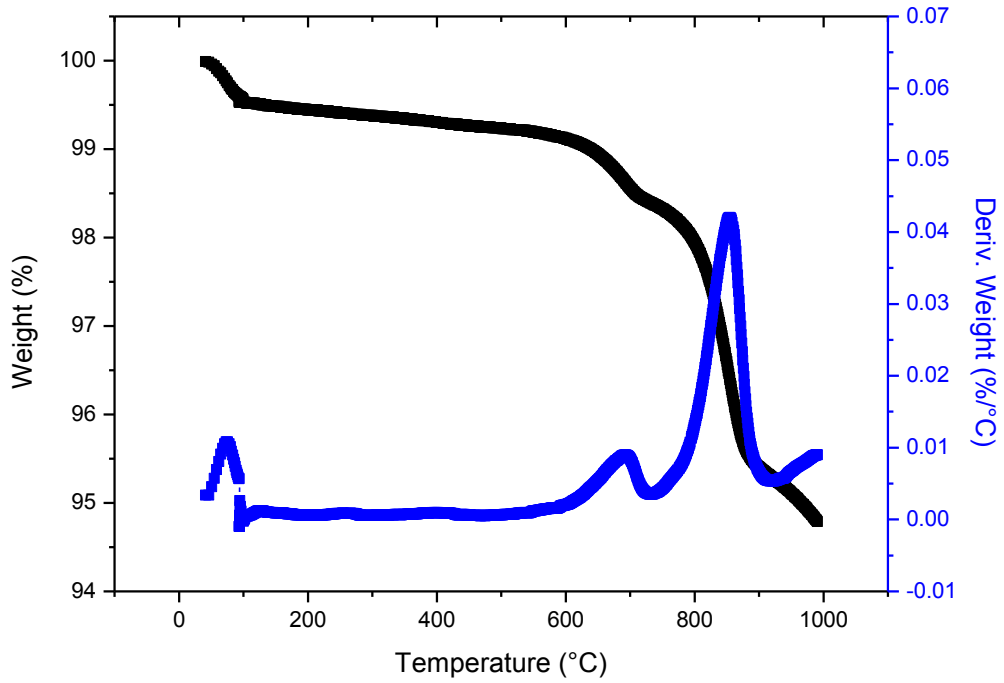

Fig. 4. TGA-DSC curves of the synthesized $Ca_{0.74}Mn_{0.253}O_1$

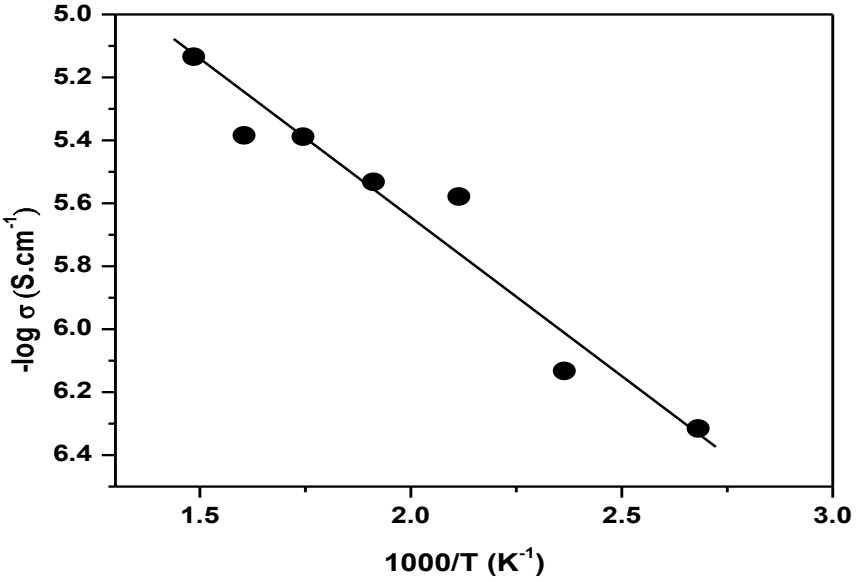

Fig. 5. Temperature dependence of the electrical conductivity for the synthesized $Ca_{0.74}Mn_{0.253}O_1$

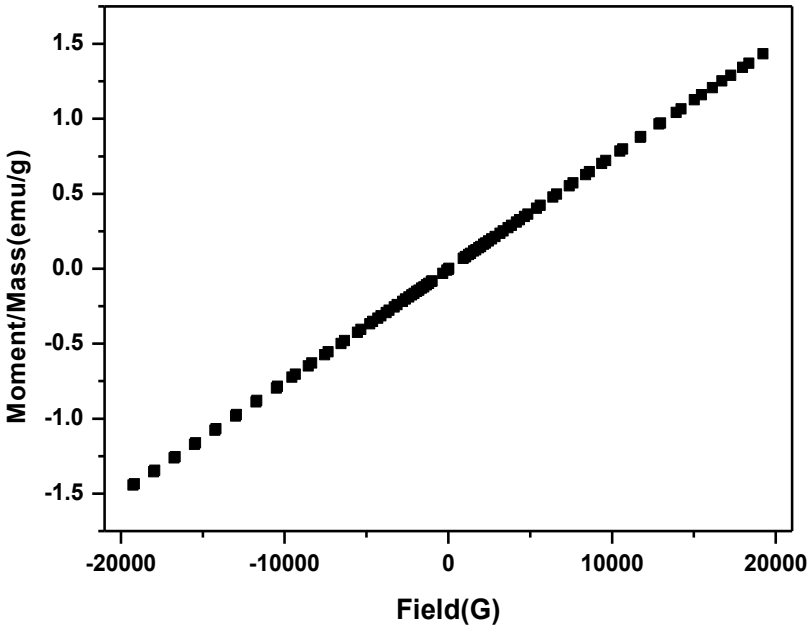

Fig. 6. Magnetic hysteresis loop (M-H) of the synthesized $Ca_{0.74}Mn_{0.253}O_1$

Room temperature magnetization behavior of the synthesized was also investigated. Room temperature magnetic characteristic of the synthesized $Ca_{0.74}Mn_{0.253}O_1$ was investigated using a vibrating sample magnetometer. As known, when a material is placed within a uniform magnetic field, a magnetic moment or magnetization will be stimulated in the sample. In a vibrating sample magnetometer, the sample is positioned within sensing coils, and is kept to be mechanically vibrating. The changes in the magnetic flux generate a voltage in the sensing coils which is proportional to the magnetic moment of the sample. Fig. 5 shows the magnetization, magnetic moment, curve of CaMnO as a function of the magnetic field. As seen, a straight line magnetic hysteresis loop is observed indicating the paramagnetic nature of the synthesized $Ca_{0.74}Mn_{0.253}O_1$.

The electrical properties of the synthesized $Ca_{0.74}Mn_{0.253}O_1$ were also investigated. The conductivity on $Ca_{0.74}Mn_{0.253}O_1$ samples was determined as a function of temperature; Fig. 6. shows the plot of *log* σ versus

1000/T. As seen, the conductivity of $Ca_{0.74}Mn_{0.253}O_1$ increases as the temperature increases within the investigated temperature range (from 50 to 400 ^oC) revealing the semiconducting nature the synthesized material. The increase in electrical conductivity with temperature is normally attributed to the rise in the thermally enhanced mobility of charge carriers according to the hopping conduction mechanism [25]. The variations in electrical conductivity might be described by Verwey's hopping mechanism [26]. In accordance with Verwey, the electrical conductivity in perovskites is generally caused by hopping electron among ions of the same element that has more than one oxidation state, randomly distributed over crystallographically equivalent lattice sites. The charges can transfer under the impact of the applied field contributing to the electrical response of the material.

Conclusions

We showed in this paper that calcium manganese oxide $Ca_{0.74}Mn_{0.253}O_1$ nanoparticles can be prepared via a sol gel route using $CaCl_2$ and $MnCl_2$ as precursors. The XRD results indicated the synthesis of $Ca_{0.74}Mn_{0.253}O_1$ as the recorded XRD patterns were well indexed according to the JCPDS (PDF-98-006-0702) card. The particles sizes were found to be in the range of 30 to 100 nm as obtained from the TEM examination. The synthesized material exhibited paramagnetic characteristics as evidenced from the linear dependence of the magnetization with the applied magnetic field. The electrical conductivity of $Ca_{0.74}Mn_{0.253}O_1$ showed a significant increase with the increase in the temperature within the investigated temperature range (from 50 to 400 ^oC) revealing the semiconducting nature the synthesized $Ca_{0.74}Mn_{0.253}O_1$.

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References

1. F. Bozon-Verduraz, F. Fievet, J-Y. Piquemal, R. Brayner, K. El Kabouss, Y. Soumare, "Nanoparticles of metal and metal oxides: some peculiar synthesis methods, size and shape control, application to catalysts preparation" *Braz J Phys.* 39 (2009) 134.
2. C. Cardoso, R. P. Borges, T. Gasche and M. Godinho, **" *Ab-initio* calculations of** the Ruddlesden–Popper phases $CaMnO_3$, $CaO(CaMnO_3)$ and $CaO(CaMnO_3)_2$", *J. Phys.: Condens. Matter*. 20 (2008) 035202.
3. M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, "Ionic liquids for the convenient synthesis of functional nanoparticles and other inorganic nanostructures", *Angew Chem Int Ed* 43 (2004) 4988.
4. B.Y. Kokuoz, K. Serivalsatit, B. Kokuoz, O. Geiculescu, E. McCormick, J. Ballato, *"* Er-Doped Y_2O_3 Nanoparticles: A Comparison of Different Synthesis Methods", *J Am Ceram Soc* 92 (2009) 2247.
5. R.Y. Hong, J.H. Li, L.L. Chen, D.Q. Liu, H.Z. Li, Y. Zheng, " Synthesis, surface modification and photocatalytic property of ZnO nanoparticles", J. Ding, *Powder Technol* 189 (2009) 426.
6. J. W. Fergus,*"* Oxide materials for high temperature thermoelectric energy conversion*",* *J. Eur. Ceram. Soc*. 32 (2012) 525.
7. K. Koumoto, R. Funahashi, E. Guilmeau, Y. Miyazaki, A. Weidenkaff, Y. Wang and C. Wan, " Thermoelectric Ceramics for Energy Harvesting*", J. Am. Ceram. Soc*. 96 (2013) 1.

8. A. Maignan, S. Hebert, L. Pi, D. Pelloquin, C. Martin, C. Michel, M. Hervieu and B. Raveau, " Perovskite manganites and layered cobaltites: potential materials for thermoelectric applications", *Cryst. Eng.* 5 (2002) 365.
9. L. Bocher, M. H. Aguirre, R. Robert, D. Logvinovich, S. Bakardjieva, J. Hejtmanek and A. Weidenkaff, " High-temperature stability, structure and thermoelectric properties of $CaMn_{1-x}Nb_xO_3$ phases", *Acta Mater.* 57 (2009) 5667.
10. F. Kawashima, X. Y. Huang, K. Hayashi, Y. Miyazaki and T. Kajitani, " Structure and High-Temperature Thermoelectric Properties of the *n*-Type Layered Oxide $Ca_{2-x}Bi_{x-\delta}MnO_{4-\gamma}$", *J. Electron.* Mater. 38 (2009) 1159.
11. K. S. Takahashi, M. Kawasaki and Y. Tokura, " Interface ferromagnetism in oxide superlattices of $CaMnO_3/CaRuO_3$", Appl. Phys. *Lett.* 79 (2001) 1324.
12. M. Ohtaki, H. Koga, T. Tokunaga, K. Eguchi, H. Arai, "Electrical Transport Properties and High-Temperature Thermoelectric Performance of $(Ca_{0.9}M_{0.1})MnO_3$ (*M* = Y, La, Ce, Sm, In, Sn, Sb, Pb, Bi)", *J Solid State Chem* 120 (1995) 105.
13. F.P. Zhang, Q.M. Lu, X. Zhang, J.X. Zhang, "First principle investigation of electronic structure of $CaMnO_3$thermoelectric compound oxide", *J. Alloys Compd.* 509 (2011) 542.
14. F.P. Zhang, X. Zhang, Q.M. Lu, J.X. Zhang, Y.Q. Liu, " Electronic structure and thermal properties of doped $CaMnO_3$systems", *J. Alloys Compd.* 509 (2011) 4171.
15. X. P. Han, T. R. Zhang, J. Du, F. Y. Cheng and J. Chen, "Porous calcium–manganese oxide microspheres for electrocatalytic oxygenreduction with high activity", *Chem. Sci.* 4 (2013) 368.
16. M. M. Najafpour, T. Ehrenberg, M. Wiechen and P. Kurz, "Calcium Manganese(III) Oxides (CaMn2O4.xH2O) as Biomimetic Oxygen-Evolving Catalysts", *Angew.Che Int Ed.* 49(2010)2233.
17. M. Wiechen, I. Zaharieva, H. Dau and P. Kurz, "Layered manganese oxides for water-oxidation: alkaline earth cations influence catalytic activity in a photosystem II-like fashion", *Chem. Sci.* 3 (2012) 2330.
18. J. Du, Y. D. Pan, T. R. Zhang, X. P. Han, F. Y. Cheng and J. Chen, " Facile solvothermal synthesis of $CaMn_2O_4$nanorods for electrochemical oxygen reduction", J. Mater. Chem. 22 (2012) 15812.
19. X. P. Han, Y. Hu, J. Yang, F. Y. Cheng and J. Chen, "Porous perovskite $CaMnO_3$ as an electrocatalyst for rechargeable Li–O_2 batteries", *Chem. Commun*, 50 (2014) 1497.
20. W. Hong-Chao, W. Chun-Lei, S. Wen-Bin, L. Jian, S. Yi, P. Hua, Z. Jia-Liang, Z. Ming-Lei, L. Ji-Chao, Y. Na, M. Liang-Mo, "Synthesis and electrical properties of dual doped CaMnO3 based ceramics", Acta Phys. Sin. 60 (2011) 087203
21. M. Santiago-Teodoro, L. Hernández-Cruz, H. Montiel-Sánchez, G. Álvarez- Lucio, M. A. Flores-González, and F. Legorreta-García,"Synthesis, Microstructure and EPR of $CaMnO_3$ and $Eu_xCa_{1-x}MnO_3$ Manganite, Obtained by Coprecipitation", *J. Mex. Chem. Soc.* 55 (2011) 204.
22. M. Tadić , D. Marković, M. Panjan and V. Spasojević, "Solution combustion synthesis method and magnetic properties of synthesized polycrystalline calcium manganite $CaMnO_{3-\delta}$ powder", *Ceramics Int.* 42 (2016) 19365.
23. Z. Lazarevic´, C. Jovalekic´, A. Milutinovic´, D. Sekulic´, V. N. Ivanovski, A. Recnik, B. Cekic´, and N.Z. Romcevic´,"Nanodimensional spinel $NiFe_2O_4$ and $ZnFe_2O_4$ ferrites prepared by soft mechanochemical synthesis", *J. Appl. Phys*. 113 (2013) 187221
24. E. J. W. Verwey and J. H. de Boer, "Cation arrangement in a few oxides with crystal structures of the spinel type", Rec. Trav. Chim. Pays-Bas 55 (1936) 531.

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