

# *Rapid Solid-State Synthesis of Oxides by Means of Irradiation with Light*

**D. Daraselia, D. Japaridze, Z. Jibuti,  
A. Shengelaya & K. A. Müller**

**Journal of Superconductivity and  
Novel Magnetism**

Incorporating Novel Magnetism

ISSN 1557-1939

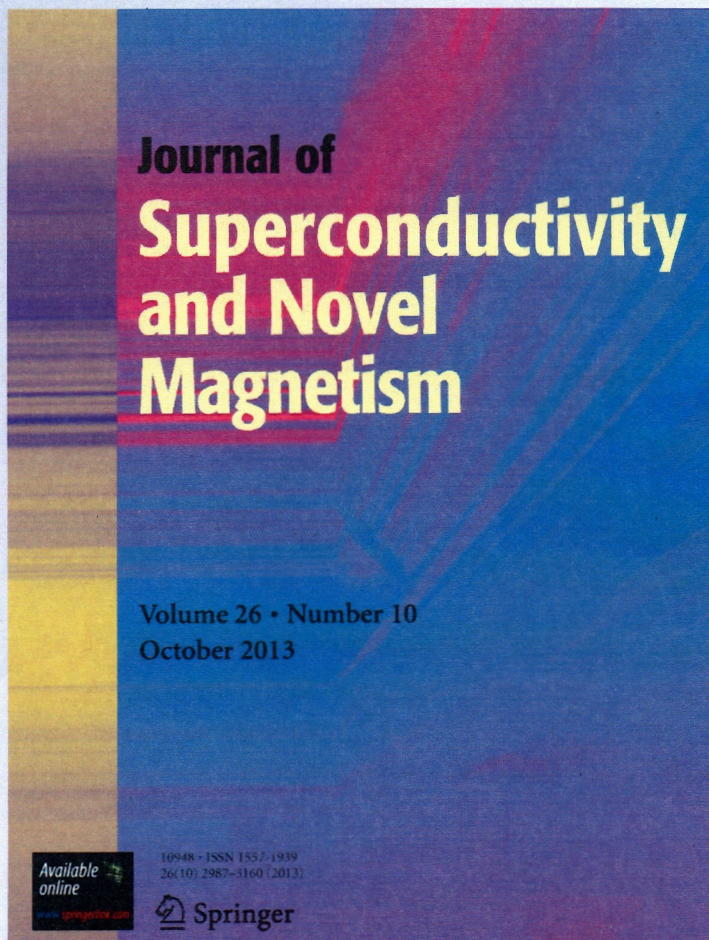
Volume 26

Number 10

J Supercond Nov Magn (2013)

26:2987-2991

DOI 10.1007/s10948-013-2307-0





## Rapid Solid-State Synthesis of Oxides by Means of Irradiation with Light

D. Daraselia · D. Japaridze · Z. Jibuti · A. Shengelaya · K.A. Müller

Received: 1 July 2013 / Accepted: 2 July 2013 / Published online: 3 August 2013  
© Springer Science+Business Media New York 2013

**Abstract** A novel kind of synthesis for oxide materials, especially complex ones, has been developed. The process involves the intense irradiation of the powder mixture of the starting oxides by light at elevated temperature. The spectral range tested extends from infrared to ultraviolet with sufficient intensity for the solid-state reaction between the reagents to take place. The resulting reaction speed exceeds the conventional thermal one by up to two orders of magnitude. This method should be applicable for the synthesis of epitaxial thin films of high- $T_C$  superconductors used in RA-BITS or IBAD technologies, high-Q filters, and magnetic oxide films for magnetoelectronics.

**Keywords** Complex oxides · High-temperature superconductors · Magnetoelectronics · Solid-state synthesis · Light irradiation

The unprecedented growth of microelectronics over the past 50 years has largely been based on compounds of silicon or combinations of III-V elements, such as gallium and arsenic. However, with the rapid progress in the miniaturization of semiconductor electronic devices, intrinsic limitations are beginning to be felt by the technology sector. Therefore, novel approaches involving new materials, such as functional oxides, are being explored, and the field of oxide electronics becomes more and more important. Advantages of

oxide electronics lie in the possibility of size reduction due to characteristic lengths on the nanometer scale and in novel properties of oxides that are completely absent in conventional semiconductors. For example, transition-metal oxide compounds exhibit a broad range of functional properties, such as high dielectric constant, piezoelectricity and ferroelectricity, superconductivity, spin-polarized current, and ferromagnetism.

Stimulated by the discovery of high- $T_C$  superconductivity in cuprates [1], tremendous progress has been achieved in the physics and technology of oxides over the past 20 years. This has led to numerous scientific and technological breakthroughs, such as optically-transparent conductors for solar cells, high-temperature superconductivity, colossal magneto-resistance, multiferroicity, diluted magnetic semiconductors, etc.

Oxides are most commonly prepared by solid-state reaction involving the repeated grinding and heating of the reactant powders of oxides, carbonates, etc. This implies long-term (tens of hours) heating of reactants in powder form at high temperatures (800–1200 °C) in a furnace, which is a highly time- and energy-consuming process and increases product costs. Moreover, the long-term high-temperature synthesis may result in deviations from stoichiometry. Therefore, there is a significant worldwide effort to develop technologies to considerably reduce the temperature and time needed for solid-state reactions.

It is known that the diffusion process of doped atoms in semiconductors can be significantly accelerated by light irradiation. In the past decades, such photostimulated processes have been used effectively in semiconductor electronics for the creation of ohmic contacts and p–n junctions, defect annealing, recrystallization of amorphous layers, etc. [2–6]. Although the mechanism of this phenomenon is still under discussion, experiments indicate that the rate of pho-

D. Daraselia · D. Japaridze · Z. Jibuti · A. Shengelaya (✉)  
Department of Physics, Tbilisi State University, Chavchavadze 3,  
0128 Tbilisi, Georgia  
e-mail: alexander.shengelaya@tsu.ge

K.A. Müller  
Physik-Institut der Universität Zürich, Winterthurerstr. 190, 8057  
Zürich, Switzerland



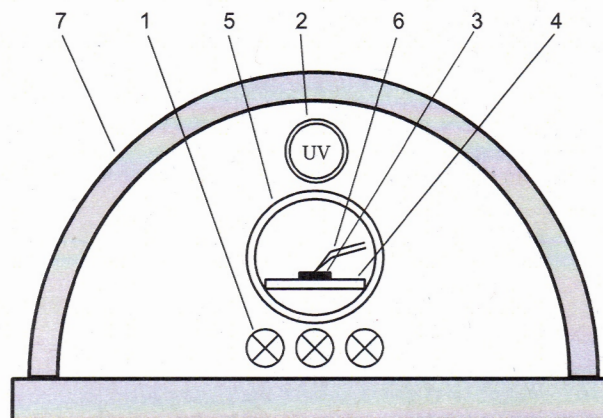
to stimulated diffusion may exceed the conventional thermal-diffusion rate by several orders of magnitude [7–10]. As the solid-state reaction also depends on the diffusion of ions, it is natural to check whether the synthesis of oxide materials can be accelerated by light irradiation. However, at present, the influence of photonic irradiation on the solid-state synthesis of materials is largely unexplored.

In this letter, we report the first results of the photostimulated synthesis of  $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$ ,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  high-temperature superconductors (HTS) and colossal magnetoresistive manganite (CMR)  $\text{La}_{1.8}\text{Ca}_{0.2}\text{MnO}_3$ . It has been shown that light irradiation leads to a dramatic increase of the reaction speed and a lowering of the reaction temperature. The photostimulated solid-state reaction (PSSR) method demonstrated is quite general and opens up the possibility of fast synthesis of a wide range of technologically important bulk and thin-film oxide materials.

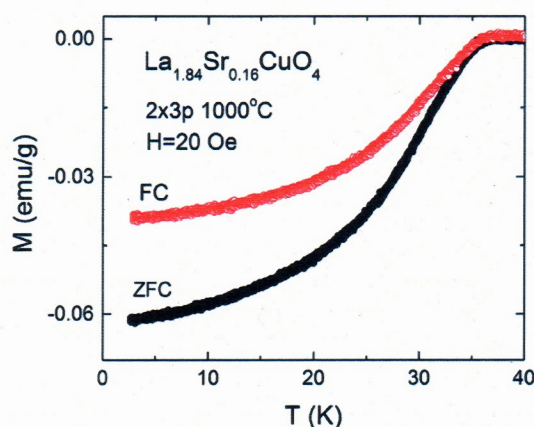
The  $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  HTSs were synthesized from  $\text{La}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{SrCO}_3$ , and  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ ,  $\text{CuO}$  starting reagents in powder form, respectively. The colossal magnetoresistive manganite  $\text{La}_{1.8}\text{Ca}_{0.2}\text{MnO}_3$  was synthesized from  $\text{La}_2\text{O}_3$ ,  $\text{MnO}_2$ , and  $\text{CaCO}_3$  powder precursors. Initial precursors in stoichiometric ratio were mixed thoroughly and pressed to form pellets of 12 mm diameter and about 0.4 mm thickness. These pellets were then sintered in two different home-built photon irradiation setups.

Setup I contains a bank of 19 halogen lamps, each with 1 kW power and a color temperature of 3200 K. With this setup, a maximum temperature of 1200 °C could be reached in 7 sec. Light irradiation was performed in pulsed mode, with the pulse length being 20 sec. The sample was mounted on a quartz plate, and its temperature was measured by a quick-response thermocouple attached to the upper surface of the pellet. In the light-irradiation setup II, a combination of halogen and ultraviolet lamps was used as shown in Fig. 1: three halogen lamps (1) of 1 kW electrical power each and the same color temperature as in setup I and a Wild-fire IronArc® metal halide 400-W UV lamp LMP-400D (2). The sample (3) is placed on the surface of a flat, transparent quartz plate (4) mounted in a section of high-quality optical quartz tube (5). This construction allows the irradiation process to be performed in oxygen or other gas atmosphere. The UV lamp is mounted above the quartz tube collinearly to the halogen lamps. The sample temperature is measured by a fast response K-type thermocouple (6), in direct contact with the sample surface. The setup is covered by a ceramic (kersil) arc (7), and the glazed inner surface of this arc acts as reflector. The system is equipped with a lamp power controlling unit. Using this setup, samples can be irradiated with an intensive light in a broad spectral range because the halogen lamps provide mostly infrared and visible light and the metal halide lamp provides UV light.

The samples were characterized by X-ray diffraction, and their magnetic properties were studied using a vibrational



**Fig. 1** Schematic cross section through the home-built photon irradiation setup II for fast solid-state synthesis of oxide materials



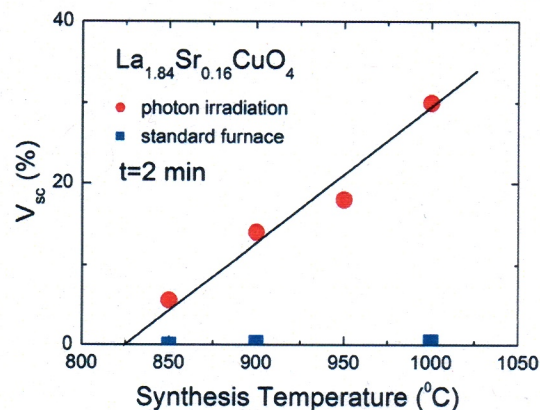
**Fig. 2** Temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetic moment for the  $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$  sample in a magnetic field of 20 Oe. The sample was synthesized by light irradiation at  $T = 1000$  °C (total irradiation time: 2 min)

sample magnetometer (VSM) from CRYOGENIC Ltd operating in a temperature range of 2–300 K and in magnetic fields of up to 5 T. Prior to the magnetization measurements, the samples were crushed into powder to minimize surface effects and to probe the bulk magnetic properties.

It was found that superconducting samples of  $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$  could be obtained by light irradiation in setup I. The samples were irradiated for periods of 20 sec. After each irradiation step, the sample was allowed to cool and then irradiated again from another side for 20 sec. The superconducting properties were studied as a function of the total photon exposure time and the reaction temperature. Figure 2 shows, as an example, the superconducting transition in a polycrystalline sample of  $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$  irradiated with three pulses on each side separately at  $T = 1000$  °C.

Figure 2 shows that the sample is superconducting with an onset  $T_C$  near 37 K, which is close to the optimum  $T_C = 38$  K observed in bulk  $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$ . The superconduct-





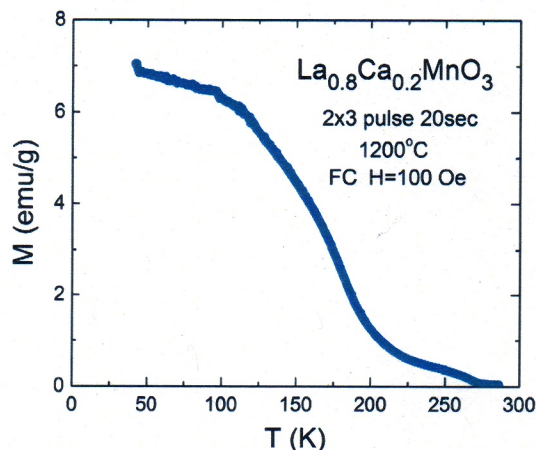
**Fig. 3** Superconducting volume fraction of  $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$  samples obtained by the photon irradiation and the conventional furnace-heating process at different synthesis temperatures. For all samples, the total synthesis time was 2 min

ing volume fraction estimated from zero-field-cooled (ZFC) magnetization is about 30 %, revealing the bulk nature of the superconductivity. Note that the strong diamagnetic moment in the superconducting state is a very useful indicator to characterize the extent of synthesis because the size of the diamagnetic moment is proportional to the superconducting volume fraction.

To determine the role of the thermal factor in our synthesis process, we performed the following control test: An identical pellet for synthesis of  $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$  was inserted for 2 min into a conventional furnace preheated to 1000 °C. The sample obtained in this way showed only traces of superconductivity, with a volume fraction below 0.5 %. A similar comparison of the superconducting volume fractions of light-irradiated and normal furnace-prepared samples was performed at different temperatures. For all samples, the total synthesis time was 2 min. The results are shown in Fig. 3. As can be seen, the superconducting volume fraction is negligible in furnace-prepared  $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$  samples up to 1000 °C. In fact, it is well known that the synthesis of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  samples by standard solid-state reaction in a furnace requires tens of hours and temperatures well above 1000 °C. On the other hand, in the  $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$  samples prepared under light irradiation in setup I, the superconducting phase forms already at about 825 °C and increases linearly with increasing temperature.

We can conclude that, compared with synthesis in a normal furnace, light irradiation during the synthesis of the  $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$  HTS drastically enhances the rate of the solid-state reaction. This process can be called photostimulated solid-state reaction (PSSR).

We also synthesized the colossal magnetoresistive (CMR) manganite  $\text{La}_{1.8}\text{Ca}_{0.2}\text{MnO}_3$  by PSSR using setup I. The pellet of the mixture of precursor materials was irradiated with three pulses of 20-sec duration on each side sep-

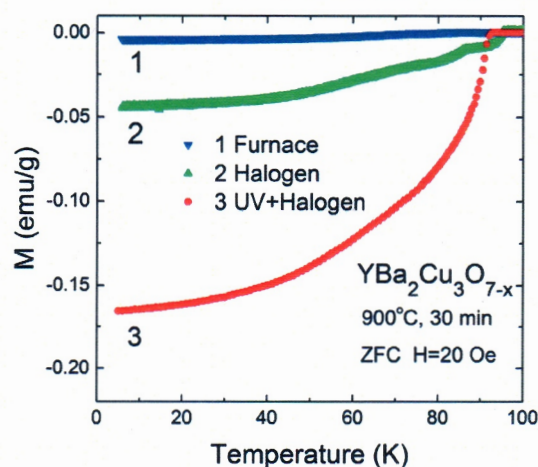


**Fig. 4** Temperature dependence of the field-cooled (FC) magnetic moment for the  $\text{La}_{1.8}\text{Ca}_{0.2}\text{MnO}_3$  sample in a magnetic field of 100 Oe. The sample was synthesized by light irradiation at  $T = 1200$  °C (total irradiation time: 2 min)

arately (total irradiation time: 2 min) at  $T = 1200$  °C. Figure 4 shows the temperature dependence of the field-cooled (FC) magnetic moment for the  $\text{La}_{1.8}\text{Ca}_{0.2}\text{MnO}_3$  sample in a magnetic field of 100 Oe. As can be seen, the sample is ferromagnetic, with the Curie temperature and the low-temperature magnetic moment in agreement with the values reported in the literature for a  $\text{La}_{1.8}\text{Ca}_{0.2}\text{MnO}_3$  CMR manganite [11]. We note that the conventional synthesis of CMR manganites in a furnace requires several hours at 1200 °C.

We also attempted the synthesis of the technologically important  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO) HTS using the PSSR method in setup I, but the samples showed only traces of superconductivity. As the formation of the YBCO phase is related to complex reactions between the starting oxides [12], apparently longer times are needed to synthesize this high-temperature superconductor than for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ . Moreover, reducing the reaction time significantly by increasing the synthesis temperature would not be an option because YBCO melts around 1000 °C. Therefore, it is necessary to perform the PSSR process below this temperature and during a relatively long period of time. We performed such a synthesis in setup II (see Fig. 1), which allows continuous irradiation of samples for time periods of up to 1 h. The superconducting properties of the YBCO samples obtained were studied as a function of the photon exposure time and the reaction temperature. Experiments showed that 900 °C is the optimum temperature for YBCO synthesis by PSSR. Figure 5 shows the superconducting transitions of the YBCO samples obtained at 900 °C irradiated for 30 min using different methods. One sample was irradiated by both UV and halogen lamps. The second sample was irradiated only by halogen lamps. The control sample was inserted into a conventional furnace preheated to 900 °C and quickly removed after 30 min. All reactions were performed in air. To en-





**Fig. 5** Temperature dependence of the zero-field-cooled (ZFC) magnetic moment of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  samples in a magnetic field of 20 Oe. The samples were synthesized at  $T = 900^\circ\text{C}$  during 30 min

sure maximum oxygen content, all samples were annealed in flowing oxygen at  $550^\circ\text{C}$  for 3.5 h after the reaction.

One can see from Fig. 5 that a good-quality superconducting sample with  $T_C = 93\text{ K}$  is obtained after the PSSR process using a combination of UV and halogen lamps. The volume fraction of the superconducting phase estimated from the ZFC magnetization is about 80 %. The sample irradiated only by halogen lamps has 20 % of the superconducting phase and exhibits a broad superconducting transition. This demonstrates the crucial role of UV photons in the synthesis process of YBCO. Figure 5 also shows that the conventional solid-state reaction in a furnace at the same temperature and time is ineffective because the sample obtained under these conditions has only about 2 % of the superconducting phase. In fact, it is known that it takes about 30 h to obtain YBCO at  $900^\circ\text{C}$  [13]. With PSSR using a combination of UV and halogen lamps, it takes only 30 min as evidenced by Fig. 5.

The results obtained provide evidence that the solid-state reaction rate in oxides is strongly enhanced under photon irradiation as compared with the usual heat treatment in a furnace under equivalent thermal conditions. This suggests that some nonthermal processes take place during PSSR. One apparent difference between a conventional furnace and lamp heating is the distinct spectral intensity distribution of the irradiation. According to the formula of black-body radiation, at temperatures around  $900^\circ\text{C}$ , the photons emitted from a normal furnace have wavelengths larger than  $1\ \mu\text{m}$  and an energy below 1 eV. These infrared photons mainly contribute to sample heating. Tungsten halogen lamps have a color temperature about 3000 K and emit photons mostly in the near infrared and visible range with energies of 0.5–2 eV. The metal halide lamps used in our experiments provide UV light, with the main intensity in the 250–400 nm wavelength range, which corresponds to photons with an energy of 3–5 eV. While the mechanism is not yet understood,

it is possible that the high-energy photons from the halogen and especially from the UV lamps may lead to an acceleration of various chemical and physical processes and as a result to the observed PSSR. It is clear that such processes should start at the surface of the pellets, as light in the visible/UV range cannot penetrate deep into the samples being studied. However, the photostimulated process, which starts at the surface, must also proceed deep into the material to macroscopic distances because we were able to synthesize bulk samples by PSSR. Further experimental and theoretical studies are needed to establish the microscopic mechanism of this process.

In conclusion, a novel method of photostimulated solid-state synthesis of oxide materials was developed that enables a dramatic increase of the reaction speed and also a lowering of the synthesis temperature. This method involves the irradiation of the mixture of starting oxides by light in a broad spectral range, from infrared to ultraviolet, with sufficient intensity at high temperature for starting the solid-state reaction between the reagents contained in the powder mixture. Using this method, fast synthesis of polycrystalline HTS and CMR oxides was demonstrated. The proposed method may find broad application because most advanced ceramic materials, such as magnets, solid fuel cells, solar cells and catalysts, are produced by solid-state reaction in high-temperature furnaces. Therefore, the preparation of these materials using the PSSR method can significantly reduce both the synthesis time and the temperature. As the penetration of light is usually limited by the sample thickness, we expect that the PSSR method will be even more effective in the preparation of oxide thin films, which have a high technological importance.

**Acknowledgements** This work was supported by the Georgian National Science Foundation grant RNSF/AR/10-16, and the Swiss National Science Foundation, the SCOPES grant No. IZ74Z0-137322.

## References

1. Bednorz, J.G., Müller, K.A.: *Z. Phys. B, Condens. Matter* **64**, 189 (1986)
2. Wirth, H., Panknin, D., Skorupa, W., Niemann, E.: *J. Appl. Phys.* **74**, 979 (1999)
3. Sisiyanu, S.T., Sisiyanu, T.S., Railean, S.K.: *Semiconductors* **36**, 581 (2002)
4. Avsarkisov, S.A., Jibuti, Z.V., Dolidze, N.D., Tsekvava, B.E.: *Tech. Phys. Lett.* **32**, 259 (2006)
5. Jibuti, Z.V., Dolidze, N.D., Eristavi, G.L.: *Tech. Phys.* **53**, 808 (2008)
6. Tsuchiya, M., Sankaranarayanan, S.K.R.S., Ramanathan, S.: *Prog. Mater. Sci.* **54**, 981 (2009)
7. Dzhafarov, T.D.: *Phys. Status Solidi A* **79**, 11 (1983)
8. Mavoori, J., Singh, R., Narayanan, S., Chaudhuri, J.: *J. Appl. Phys. Lett.* **65**, 657 (1994)
9. Singh, R., Cherukuri, K.C., Vedula, L., Rohatgi, A., Narayan, S.: *J. Appl. Phys. Lett.* **70**, 1700 (1997)



10. Ditchfield, R., Llera-Rodriguez, D., Seebauer, E.G.: Phys. Rev. Lett. **81**, 1259 (1998)
11. Markovich, V., Jung, G., Wisniewski, A., Puzniak, R., Fita, I., Yuzhelevski, Y., Mogilyansky, D., Titelman, L., Gorodetsky, G.: J. Supercond. Nov. Magn. **24**, 861 (2011)
12. Pathak, L.C., Mishra, S.K.: Supercond. Sci. Technol. **18**, R67 (2005)
13. Andreouli, C., Tsetsekou, A.: Physica C **291**, 274 (1997)