I. PEROVSKITES

1.1 Background

Perovsites are materials having the same type of crystal structure as the calcium titanium oxide $\mathrm{CaTiO_3}$ (Fig 1), with a general formula of $\mathrm{ABO_3}$. In this structure, an A-site ion, on the corners of the lattice, is usually an alkaline or rare earth element. B site ions, on the center of the lattice, could be 3*d* to 5*d* transition metals.

Due to interplay between electron, lattice, and spin degrees of freedom, the cubic (undistorted) structure of $\mathrm{CaTaO_3}$ is rarely survived: the symmetry is lowered to tetragonal, orthorhombic, or trigonal in majority of perovskites. The crystal structure of $\mathit{Re}\mathrm{TiO_3}$ (*Re* being a trivalent yttrium or rare-earth ion) is pseudocubic perovskite with strong $\mathrm{GdFeO_3}$-type distortion, which is caused by the tilt of the $\mathrm{TiO_6}$ octahedra, Fig 1 (Right). $\mathrm{GdFeO_3}$-type distortion plays an important role in the electronic and magnetic properties of perovskite titanates $\mathit{Re}\mathrm{TiO_3}$. The magnitude of the distortion depends on the ionic radius of the *Re* ion: upon the decrease of ionic radius in the rare-earth series the deviation of the Ti–O–Ti bond angle from 180° occurs, *i.e.*, the lattice distortion increases. Besides the bond geometry changes, tilting of the $\mathrm{TiO_6}$ octahedra affects the one-electron bandwidth of the 3*d* electron in a way that it gets smaller with the decrease of ionic radius. With the increase of $\mathrm{GdFeO_3}$-type distortion the Ti magnetic order changes from *G*-type antiferromagnetic, with the magnetic moment in the *a* direction ($\mathrm{LaTiO_3}$), to ferromagnetic, with the magnetic moment in the *c* direction ($\mathrm{YTiO_3}$).

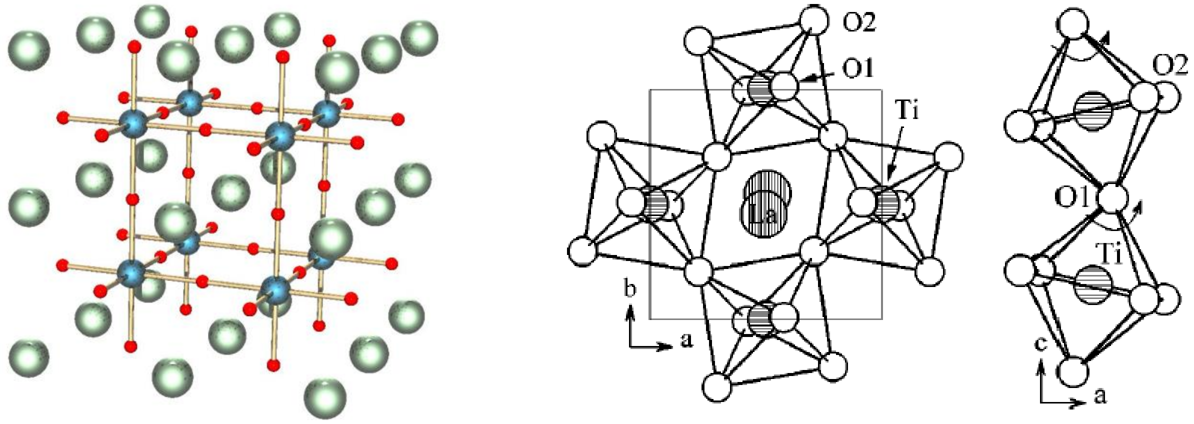

FIG. 1. Left: Crystal structure of cubic $\mathrm{CaTiO_3}$. Color code: Ti-blue, Ca-grey, O-red.
Right:Orthorhombic $\mathrm{LaTiO_3}$.

1.2 Layered Perovskites

Perovskites may be structured in layers, with the $\mathrm{ABO_3}$ structure separated by thin sheets of intrusive materials. Ruddlesden-Popper (RP) phase has general formula $\mathrm{A_{n-1}A'_2B_nX_{3n+1}}$, where A and A*'* represent alkali, alkaline earth, or rare earth metal, while *B* refers to transition metal. Aurivillius phase consist of *n* perovskite-like layers $(\mathrm{A}_{n-1}\mathrm{B}_n\mathrm{O}_{3n+1})^{2-}$ sandwiched between bismuth-oxygen sheets $(\mathrm{Bi_2O_2})^{2+.}$

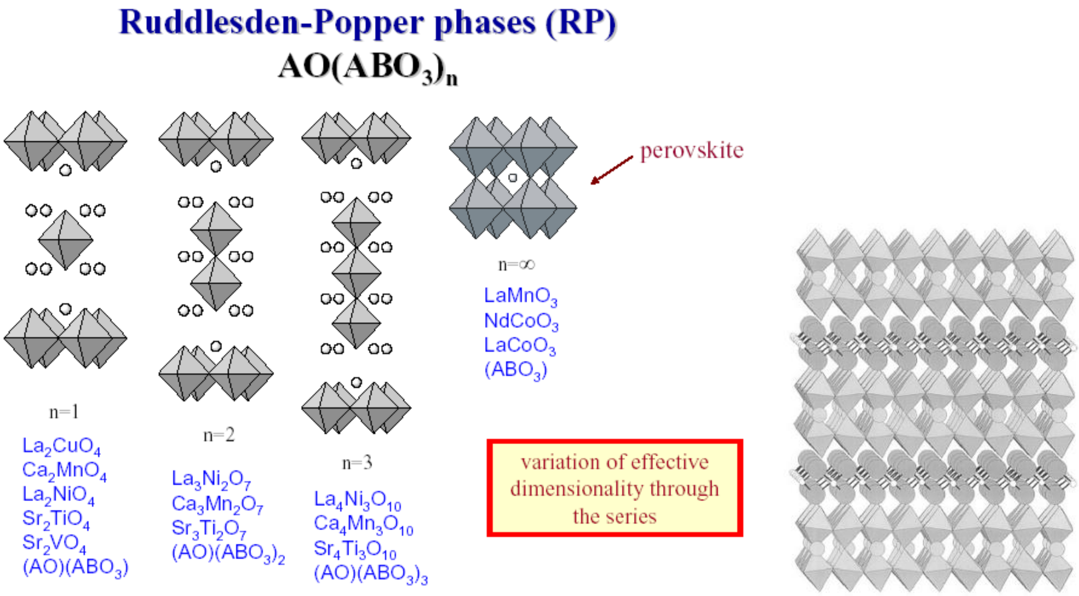

FIG. 2. Left: Pictorial view of Ruddlesden-Popper phases, with n=1,2,3 and ∞.
Right: Aurivillius phase, $Bi_2SrTa_2O_9$, two octahedral perovskite layers separated by puckered bismuth oxide sheets (Right).

1.3 Tentative Classification

Perovskite materials exhibit many interesting and intriguing properties from both the theoretical and the application point of view. Based on their properties one can tentatively assembly perovskites into the following four groups:

- Superconducting perovskites (Section 2);
- Colossal magnetoresistance perovskites (Section 3);
- Piezoelectric & ferroelectric perovskytes (Section 4);
- Other perovskytes (Section 5).

1.4 Common Applications

In a broad sense, the perovslkites are often called, "Functional Materials", due to the interplay of structural, magnetic, and transport properties. Superconductivity, colossal magnetoresistance, and ferroelectricity are discussed in Sects II, III, and IV, respectively.

Here we shall list most common applications for other perovskites:

(a) *Thermopower generation*;

(b) *Ion conductors* in fuel cells/sensors;

(c) *Catalytic materials*. Co-based perovskite material is as a replacement for Pt in catalytic converters in diesel vehicles;

(d) *Photovoltanics*. Synthetic perovskites have been identified as possible inexpensive base materials for high-efficiency commercial photovoltaics. The conversion efficiency of perovskite solar cells leaped from just a few percent in 2010 to more than 16% in current versions. The fast-paced improvement, which hasn’t shown signs of slowing, coupled with inexpensive materials and preparation methods indicates that perovskite solar cells are poised “to break the prevailing paradigm” by combining low cost and excellent performance.

II. SUPERCONDUCTING PEROVSKITES

2.1 Background.

Superconductivity is characterized by zero electrical resistance and expulsion of magnetic fields occurring in certain materials when cooled below a characteristic critical temperature, T_c. Ordinary metallic superconductors (Pb, Nb, Nb_3Sn) usually have the Tc well below 30 K (−243.2 °C). In 1986 a high temperature superconductivity (HTSC) was discovered in Cu-based ceramic material $La1-xBa_xCuO_4$ at 35 K and shortly thereafter in $YBa_2Cu_3O_{7-\delta}$ at 90 K. Current highest achieved Tc is ~133 K (−140° C) in $HgBa_2Ca_2Cu_3O_x$. at ambient pressure. A goal of applied research is room-temperature superconductivity with T_c ~ 300 K.

The structure of high-T_c cuprate superconductors has been described as a distorted, oxygen deficient multi-layered perovskite structure. One of the properties of the crystal structure of oxide superconductors is an alternating multi-layer of CuO_2 planes with superconductivity taking place between these layers. The more layers of CuO_2 the higher T_c

The mechanism of high-T_c superconductivity is still highly controversial. Most researchers believe that conventional BCS mechanism is not applicable. The HTSC emerges from antiferromagnetic spin fluctuations in the doped systems.

2.2 Applications

(a) *Electric power transmission and transformers*.

http://www.newscientist.com/article/dn11907-superconducting-power-line-to-shore-up-new-york-grid.html

(b) *Superconducting electromagnets*. SC magnets are widely used in MRI/NMR machines, mass spectrometers, and the beam-steering magnets in particle accelerators.

(c) *Superconducting digital circuits*. Cryotron switches, RF and microwave filters, Josephon junctions are building blocks of many devises and sensors

2.2 LTS offers the following superconducting ceramics:

- Yttrium barium copper oxide ($YBa_2Cu_3O_{7-y}$ $0.4<y<0.9$)

The oxygen stoichiometry is crucial for obtaining Tc~90 K. Good quality thin films can be obtained by sputtering, laser oblation, or e-beam deposition from ceramic target.
Typical(maximal) critical current density, J_c, is ~$2x10^4$ ($2x10^6$) A/cm^2

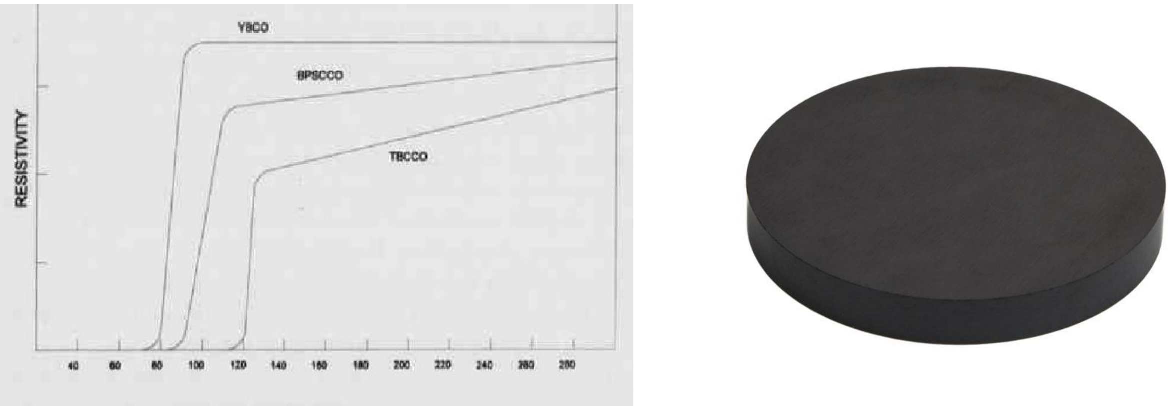

FIG. 3. Left: Typical electrical resistivity vs temperature for pressed ceramic targets
Right: 2"Dia $YBa_2Cu_3O_{6.9}$ target offered by LTS.

- Bismuth strontium calcium copper oxide ($Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+x}$ $n = 1$, 2 and 3)

The Bi–Sr–Ca–Cu–O system has three superconducting phases forming a homologous series as $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+x}$ ($n = 1$, 2 and 3). These three phases are Bi-2201, Bi-2212 and Bi-2223, having transition temperatures of 20, 85 and 110 K, respectively. The Bi-2223 is hard to make as a single phase ceramic. However, high quality films may be produced.

Typical(maximal) J_c is ~$4x10^4$ ($4x10^6$) A/cm^2

- Thallium barium calcium copper oxide ($Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ $n = 1$, 2 and 3)

The Tl-Sr-Ca-Cu-O system has a few phases. Unlike the bismuth SC, the highest Tc~ 124 K is relatively easy to produce. Expellant quality thin films have been produced.

Typical(maximal) J_c is ~10^6 ($3x10^7$) A/cm^2

- Lanthanum barium copper oxide ($Re_{1-x}A_xCuO_{4-\delta}$, Re=La,Nd Pr, A=Ba,Sr)
- Barium potassium bismuth oxide ($Ba_{1-x}K_xBiO_{3+\delta}$)
- Barium lead bismuth oxide ($BaPb_{1-x}Bi_xO_{3+\delta}$)
- Magnesium carbon nickel ($MgCNi_3$)

Please refer to Section VI for routinely and custom made specimens.

III COLOSSAL MAGNETORESISTANCE PEROVSKITES

3.1 Background

The term ***colossal magnetoresistance*** (CMR) was introduced recently to describe the large temperature and magnetic field dependences of the resistivity in manganese based perovskites $Re_{1-x}A_xMnO_3$ with Re being a trivalent yttrium or rare-earth ion and A= Ca, Sr, or Ba. More than 40 years after their discovery the CMR perovskites have attracted renewed interest, especially due to their interesting electronic, magnetic, and structural properties as well as for their potential technological applications.

$LaMnO_3$ is an antiferromagnetic (AFM) insulator with ferromagnetic (FM) coupling in the MnO_2 planes and AFM coupling between the planes. With Ca doping ($0.2<x<0.5$) the system exhibits a paramagnetic to ferromagnetic transition on cooling that is accompanied by a metal to insulator (MI) transition. For higher Ca concentrations the ground state is AFM and nonmetallic.Samples with $0.5<x<0.7$ exhibit charge ordering (CO). Metallic material ($0.2<x<0.5$) at low temperatures are understood in terms of the double-exchange (DE) mechanism proposed by Zener. It has been realized recently that the DE is not the only physics controlling the CMR properties. Millis *et al*. argued that conventional DE is not enough to explain the resistivity data and suggested that a lattice effect must be present to reduce the kinetic energy of the carriers at the MI transition. The atomic displacements are implicitly included in the model, giving rise to a strong coupling of the carriers to Jahn-Teller lattice distortions. There is also convincing experimental evidence that the strong coupling impacts both the carriers and the lattice.

3.2 Applications:

(1) Magnetic data storage (read/write heards);
(2) Sensors;
(3) Hybrid cells (CMR - piezoelectric, CMR - HTSCs junctions)

3.2 LTS offers the following CMR ceramics:

- Lanthanum calcium manganese oxide or, in general, $Re_{1-x}A_xMnO_{3+\delta}$ with Re= Y, La, Ce, Pr, Sm... A= Ca,Sr,Ba, $0 \leq x \leq 1$, and $-0.1 \leq \delta \leq 0.1$

Please refer to Section V for routinely and custom made specimens.

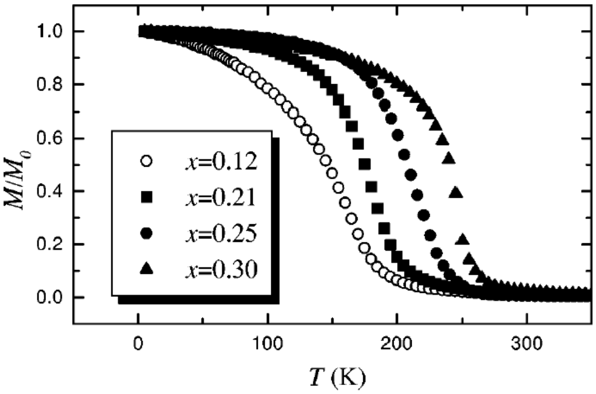

FIG 4. Normalized magnetization as a function of temperature in $La_{1-x}Ca_xMnO_3$ measured at H= 5kOe

IV PIEZOELECTRIC & FERROELECTRIC PEROVSKITES

4.1 Background.

Of the thirty-two crystal classes twenty exhibit ***piezoelectricity*** (*single crystal* don't have a centre of symmetry). Ten of these represent the polar crystal classes, which show a spontaneous polarization without mechanical stress due to a non-vanishing electric dipole moment associated with their unit cell. They are ***pyroelectric***. If the dipole moment can be reversed by the application of an electric field, the material is said to be ***ferroelectric*** **(FE).** *Ceramic powders* with randomly oriented grains must be ferroelectric to exhibit piezoelectricty.

4.2 Applications:

(a) High voltage and power sources (piezo-based ignition systems, piezoelectric transformer)
(b) Sensors (microphones, sonars, strain/tilt sensing, microbalances);
(c) Actuators (piezoelectric motors, acousto-optic modulators, inkjet printers, focused ultrasound delivery);
(d) Vibration dampers;
(e) Frequency standards (quartz clocks, frequency multipliers);
(f) Hybrid cells (photovoltaic - piezoelectric, CMRs and HTSCs junctions with FE barrier)

4.3 LTS offers the following piezoceramics:

- Barium titanate ($BaTiO_3$)
- Lead zirconate titanate ($PbZr_xTi_{1-x}O_3$ $0 \leq x \leq 1$)

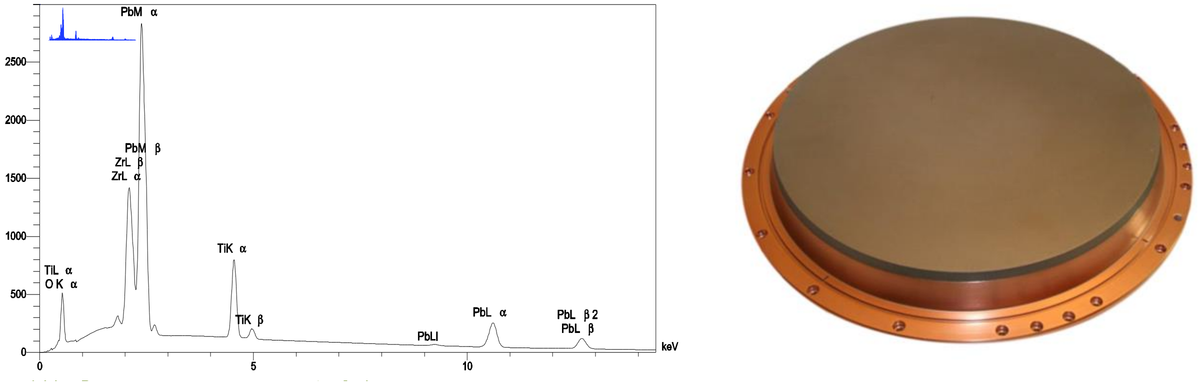

FIG. 5. Left: EDX of the pressed ceramic $PbZr_{0.52}Ti_{0.48}O_3$
Right: Custom formulation lead oxide saturated $(1-x)PbZr_{0.52}Ti_{0.48}O_3 + xPbNdO_3$ target,
D=300 mm, bonded to a Cu backing plate.

- Potassium niobate ($KNbO_3$)
- Lithium niobate ($LiNbO_3$)
- Lithium tantalate ($LiTaO_3$)
- Bismuth titanate ($Bi_4Ti_3O_{12}$), and $Bi_{4-x}La_xTi_3O_{12}$ $0<x<0.9$
- Bismuth ferrite ($BiFeO_3$)

Please refer to Section VI for routinely and custom made specimens.

V. OTHER PEROVSKITES OFFERED BY LTS

- Thermoelectric perovskites: $Ca_3Co_4O_9$, $Sr_{1-x}Ca_xTi_{1-y}Nb_yO_3$ ($x<0.4$, $y<0.03$), $(La_{1-x}Sr_x)CoO_3$, and $Na_yCo_2O_4$
- Strontium ruthenade ($SrRuO_3$)
- Classical Perovskites $ReTiO_3$ with Re= Y, La, Nd, etc.
- Vanadate Perovskites: $SrVO_3$, Sr_2VO_4, $Pb_2V_2O_6$, etc.
- Ferrites ($ReFeO_3$), Re= Nd, Sm, Gd, etc.
- $ACoO_3$ with A=Ca, Sr and $ReCoO_3$ with Re=La, Nd, Sm, etc.
- $ANiO_3$ with A=Ca, Sr, Ba and $ReNiO_3$ with Re=La, Nd, Sm, etc.

VI. ROUTINELY & CUSTOM MADE SPECIMENTS

6. 1 Routinely Produced Specimens (1):

- Pre-sintered targets for DC/RF magnetron sputtering, from 1 to 18” in diameter;
- Pre-sintered targets for pulsed laser deposition (PLD), up to 2” in diameter;
- Ceramic powders;

6.2 Custom orders (2):

Custom formulations for R&D applications:
- Custom dopants, impurity profile, particle size distribution;
- Tailoring specific physical/mechanical properties;
- Extra layers of synthesizing and powder homogenization;
- Synthesizing in reducing / oxidizing flow(s) to deliver requested oxygen stoichiometry;

Comprehensive characterization:
In addition to powder XRD, XRF/ICP-OES, and PSA available for typical specimens, redox back titration, transport, SQUID magnetization, optical microscopy, SEM, Raman, IR-reflectivity, and synchrotron based x-ray diffraction and EXAFS/XANES are available.

Target bonding:
LTS provide target bonding to standard, customer supplied, and custom ordered backing plates. Proprietary *elastomer* bonding agent is used for perovskites exhibiting structural phase transitions in the target operational temperature range.

(1) Many items are in stock. Typical lead time for out of stock items is 2-4 weeks;
(2) Please contact LTS to discuss your specific needs and to obtain a lead time estimate.