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## Structural Characterization of New Perovskites

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### 1. Introduction

The perovskite is a calcium titanium oxide mineral species composed of calcium titanate, with the chemical formula  $\text{CaTiO}_3$ . The mineral was discovered in the Ural mountains (Russia) by Gustav Rose in 1839 and is named after Russian mineralogist L. A. Perovski (1792-1856).

The perovskite crystal structure was published in 1945 from X-ray diffraction data on barium titanate by the Irish crystallographer H. D. Megaw (1907-2002). It is a true engineering ceramic material with a plethora of applications spanning energy production (SOFC technology), environmental containment and communications.

The general stoichiometry of the perovskite structure is  $\text{ABX}_3$ , where  $A$  and  $B$  are cations and  $X$  is an anion. The  $A$  and  $B$  cations can have a variety of charges and in the original perovskite mineral ( $\text{CaTiO}_3$ ) the  $A$  cation is divalent and the  $B$  cation is tetravalent.  $\text{CaTiO}_3$  exhibits an orthorhombic structure with space group  $\text{Pnma}$ .

The traditional view of the perovskite lattice is that it consists of small  $B$  cations within oxygen octahedra, and larger  $A$  cations which are XII fold coordinated by oxygen.

Figure 1 shows a picture of the mineral perovskite which, as it was mentioned above, is composed by calcium titanate.



Fig. 1. Perovskite mineral species ( $\text{CaTiO}_3$ ).

## 2. Methods of synthesis

There are different methods of synthesis used in the field of Solid State Chemistry. Among them, one of the most used is that known as ceramic method. The ceramic method consists

of the grinding of the stoichiometric quantities of the corresponding starting compounds and subsequent heating by using furnaces at relatively high temperatures. However, it is not the most efficient method many times.

The sol-gel method and, used more and more every day, the freeze-drying method, seem to offer purer materials by reducing the heating time and working at not so high temperatures. Besides, other methods complete the list of synthesis processes of solid materials.

### 2.1 Ceramic method

The well known as ceramic method consists of the mixing and grinding of the starting compounds in stoichiometric quantities, being afterwards heated in furnaces at relatively high temperatures for relatively long dwelling times. Eventually, the desired material will be obtained, with a smaller or higher grade of impurities.

The main disadvantage of this method is the low homogeneity of the obtained product, which demands repeated procedures of intermediate homogenization and thermal treatment at high temperature. Thus, the method requires the grinding (intermittently) of the material during the heating treatment in order to minimize the drawback created by the interface (Figure 2) resulting of the reaction between the starting reagents. Figure 2 shows how that interface would be formed by A and B chemically combined. That interface increases its size as a function of the time of reaction, giving rise to a slower and less efficient transfer of A and B in opposite direction to meet and react. Thus, by grinding the grain formed by A, B, and AB, one will be able to increase the contact surface between A and B and therefore to make more efficient the reaction. We should just take into account that the solid state reactions are extremely slow, and that is why the high temperature and high dwelling times are required, but besides, a high contact surface between the reagents is desired to increase the velocity of the reaction. As a result, high crystalline materials are obtained, which are not acceptable for catalytic applications.

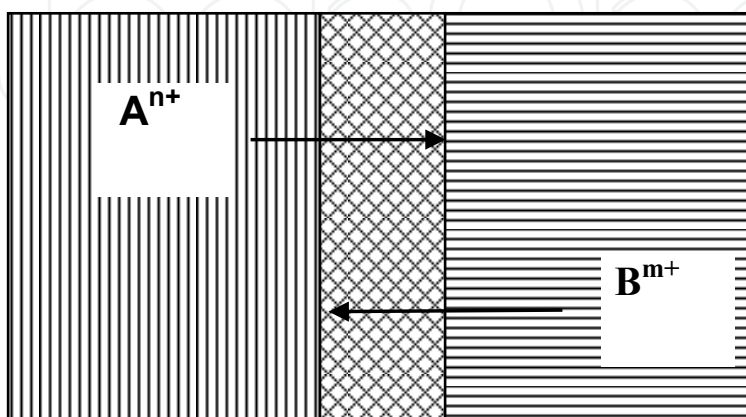


Fig. 2. Reaction between grains corresponding to  $A^{n+}$  and  $B^{m+}$ . The cross-lined area corresponds to the interface created between them.

## 2.2 Sol-gel method

The sol-gel method is a wet-chemical process widely used in the field of materials science. The starting point is the colloidal solution (*sol*) that acts as the precursor for an integrated network (*gel*) of either discrete particles or network polymers.

Perovskites can be synthesized starting from the oxides or salts of the different metals wanted to be part of the final structure by dissolving them in a solution containing a complexing agent (citric acid, e.g.) and heating it up to form gel. Immediately after, a drastic heating leads to the decomposition of the organic part and therefore to the formation of a fine and intimate distribution of the different metals in the resulting precursor, meaning this a high contact surface between them that allows a more efficient reaction at a relatively high temperature and a prudent dwelling time.

## 2.3 Freeze-drying method

The freeze-drying method, also known as lyophilisation, is a process consisting of the freezing of the solution of the starting reagents and the subsequent reducing of the surrounding pressure to allow the frozen solvent to sublime directly from the solid phase to the gas phase.

In the lab, the process is carried out by placing the solution in a decantation funnel and dropping it slowly in a container with liquid nitrogen in order to freeze it in small rounded “grains”. Right after the dropping ends, the frozen ‘grains’ of solution are placed in an Erlenmeyer flask which is immediately connected to a freeze-dryer (Figure 3). Now the



Fig. 3. Freeze-dryer with several Erlenmeyer flasks connected containing different frozen solutions.

freeze-dryer will carry out its function: to provoke the sublimation of the solvent. For that, the frozen solution undergoes an important vacuum created by a pump, allowing the solvent to sublime and being the latter frozen once again into a big drum at a very low temperature inside the device.

After one/two day(s) the dried solution – called now *precursor* – is disconnected from the freeze-dryer and treated at certain temperature in order to allow the reaction between the different reagents which are mixed in extremely fine and close way. This method allows much lower both dwelling times and heating temperatures, at the time that makes easier the way to get pure phases.

## 2.4 Melt method

One method often employed is to melt the reagents together and then later anneal the solidified melt. If volatile reagents are involved these are usually put in an ampoule that is evacuated (the reagent mixture is kept cold – by keeping the bottom of the ampoule in liquid nitrogen, e.g.) and then sealed. The sealed ampoule is then put in an oven/furnace and given a certain heat treatment.

## 2.5 Pechini method

Pechini method is a widely used method consisting of the mix of metal nitrate solution of the starting materials with a stoichiometric amount of citric acid. The resulting solution is stirred on a hot plate and the temperature stabilized at about 90°C, at which point ethylene glycol is added at a mass ratio of 40:60 with respect to citric acid. The temperature is maintained constant up to the resin formation, which polymerizes at about 300°C. The precursor powders are heated for several hours at various temperatures.

This method, as a soft-chemistry one, leads to homogeneous and low crystalline products at relatively low temperatures, but they usually require expensive initial compounds and/or complicated synthesis procedures.

## 2.6 Other methods

Some relative new methods are worth being mentioned, like the solution combustion method, the sonochemical method, and the microwave assisted synthesis.

### 2.6.1 Solution combustion method

Combustion synthesis is an effective, low-cost method for production of various useful materials. Today, it has become a very popular approach for preparation of nanomaterials.

Solution combustion synthesis (SCS) is a versatile, simple and rapid process, which allows effective synthesis of variety of nanosize materials. This process involves a self-sustained reaction in homogeneous solution of different oxidizers (e.g., metal nitrates) and fuels (e.g., urea, glycine, hydrazides). Depending on the type of the precursors, as well as on conditions used for the process organization, the SCS may occur as either volume or layer-by-layer propagating combustion modes. This process not only yields nanosize oxide materials but

also allows uniform (homogeneous) doping of trace amounts of rare-earth impurity ions in a single step.

### 2.6.2 Microwave assisted method

Microwave heating allows a rapid heating rate, however, the final yield decreases compared with the conventional methods. It leads to the synthesis of materials by consumption of less energy.

### 2.6.3 Sonochemical method

The sonochemical method is that in which the molecules undergo a chemical reaction due to the application of powerful ultrasound radiation (20 kHz–10 MHz).

Ultrasonic irradiation differs from traditional energy sources (such as heat, light, or ionizing radiation) in duration, pressure, and energy per molecule.

## 3. Perovskite-type structures

Many transition metal oxides show the very versatile perovskite structure. The rich variety of physical properties such as high-temperature superconductivity and colossal magnetoresistance observed in these compounds makes them very attractive from both fundamental and applied perspectives.

The general chemical formula for perovskite compounds is  $ABX_3$ , where  $A$  and  $B$  are two cations of very different sizes, and  $X$  is an anion that bonds to both. The  $A$  atoms are larger than the  $B$  atoms, and besides, its ionic radii close to that on the anion  $X$ , thus they can form together a cubic close packing. The smaller  $B$  cation is usually a 3d-transition metal ion which occupies the octahedral interstices of the close packing.  $X$  is oxygen or a halide ion. The ideal cubic-symmetry structure has the  $B$  cation in 6-fold coordination, surrounded by an octahedron of anions, and the  $A$  cation in 12-fold cuboctahedral coordination. In short, it can be also described as a network of edge sharing octahedra  $BX_6$ . The relative ion size requirements for stability of the cubic structure are quite stringent, so slight buckling and distortion can produce several lower-symmetry distorted versions, in which the coordination numbers of  $A$  cations,  $B$  cations or both are reduced. The orthorhombic and tetragonal phases are the most common non-cubic variants.

For the stoichiometric oxide perovskites, the sum of the oxidation states of  $A$  and  $B$  cations should be equal to six. The occupancy of  $A$  and  $B$  positions of different ions with appropriate ionic radii as well as for mixed occupancy of both cation positions led to the preparation of numerous compounds with wide spectrum of physical and chemical properties. Among the most famous representatives of perovskite class are the dielectric  $BaTiO_3$ , high-temperature superconductor  $YBa_2Cu_3O_{7-x}$ , materials exhibiting colossal magnetoresistance  $R_{1-x}A_xMnO_3$ , where  $R = La^{3+}$ ,  $Pr^{3+}$  or other rare earth ion,  $A = Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ , multiferroic materials, etc.

The structure of an ideal cubic perovskite is shown in Figure 4, where the  $A$  cations are shown at the corners of the cube, and the  $B$  cation in the centre with oxygen ions in the face-centred positions. The space group for cubic perovskites is  $Pm\bar{3}m$  (221); the equivalent positions of the atoms are detailed in Table 1.



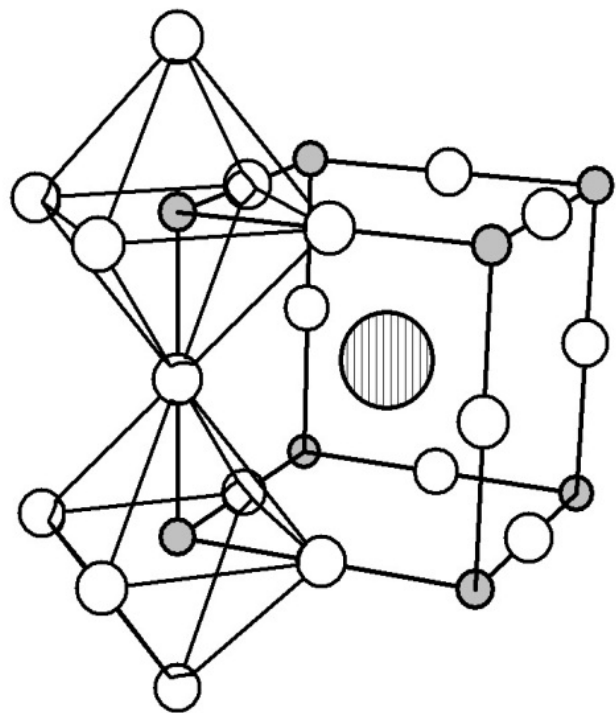


Fig. 4. Structure of the ideal cubic perovskite,  $ABO_3$  ( $A$ : big stripped circle,  $B$ : small grey circles,  $O$ : empty circles).

Perovskite materials exhibit many interesting and intriguing properties from both the theoretical and the application point of view. Colossal magnetoresistance, ferroelectricity, superconductivity, charge ordering, spin dependent transport, high thermopower and the interplay of structural, magnetic and transport properties are commonly observed features in this family. These compounds are used as sensors and catalyst electrodes in certain types of fuel cells and are candidates for memory devices and spintronics applications.

Site	Location	Coordinates
$A$ cation	$2a$	$(0,0,0)$
$B$ cation	$2a$	$(1/2,1/2,1/2)$
$O$ anion	$6b$	$(1/2,1/2,0)(1/2,0,1/2)(0,1/2,1/2)$

Table 1. Atomic positions in cubic perovskites

Many superconducting ceramic materials (the high temperature superconductors) have perovskite-like structures, often with 3 or more metals including copper, and some oxygen positions left vacant. One prime example is yttrium barium copper oxide which can be insulating or superconducting depending on the oxygen content.

Chemical engineers are considering this material as a replacement for platinum in catalytic converters in diesel vehicles.

Figures 4 and 5 show different ways to represent the perovskite structure. Figure 5 represents the undistorted cubic structure; the symmetry is lowered to orthorhombic, tetragonal or trigonal in many perovskites.

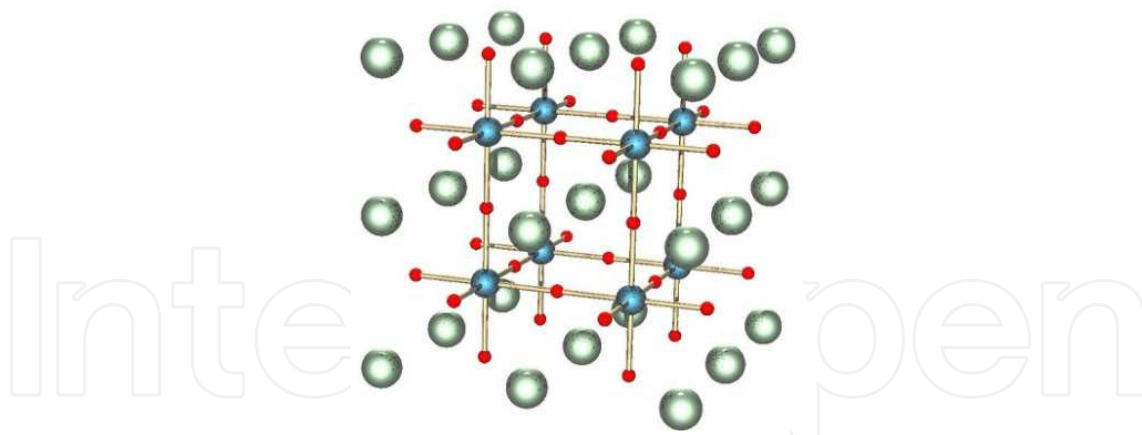


Fig. 5. Perovskite structure ( $ABX_3$ ). The small spheres are X atoms (usually oxygens), the medium spheres are B-atoms (a smaller metal cation, such as Ti(IV)), and the big spheres are the A-atoms (a larger metal cation, such as Ca(II)).

#### 4. Structural characterization of perovskites

The synthetic methodology and the characterization of the perovskite often go hand in hand in the sense that not one but a series of reaction mixtures are prepared and subjected to heat treatment. The stoichiometry is typically varied in a systematic way to find which ones will lead to new solid compounds or to solid solutions between known ones. A prime method to characterize the reaction products is X-ray powder diffraction (XRD), because many solid state reactions will produce polycrystalline powders. Thus, powder diffraction will facilitate the identification of known phases in the mixture. If a pattern is found that is not known in the diffraction data libraries an attempt can be made to index the pattern, i.e. to identify the symmetry and the size of the unit cell. Obviously, if the product is not crystalline enough the characterization is typically much more difficult.

Once the unit cell of a new phase is known, the next step is to establish the stoichiometry of the phase. This can be done in a number of ways. Sometimes the composition of the original mixture will give a clue, if one finds only one product -a single powder pattern- or if one was trying to make a phase of a certain composition by analogy to known materials but this is rare. Often considerable effort in refining the synthetic methodology is required to obtain a pure sample of the new material. If it is possible to separate the product from the rest of the reaction mixture elemental analysis can be used. Another way involves SEM and the generation of characteristic X-rays in the electron beam.

The easiest way to solve the structure is by using single crystal X-ray diffraction. The latter often requires revisiting and refining the preparative procedures and that is linked to the question which phases are stable at what composition and what stoichiometry. In other words what does the phase diagram look like. An important tool in establishing this is thermal analysis techniques like DSC or DTA and, increasingly also, the synchrotron temperature-dependent powder diffraction. Increased knowledge of the phase relations often leads to further refinement in synthetic procedures in an iterative way. New phases are thus characterized by their melting points and their stoichiometric domains. The latter is important for the many solids that are non-stoichiometric compounds. The cell parameters obtained from XRD are particularly helpful to characterize the homogeneity ranges of the latter.



In order to analyse the different morphological and surface characteristics of particles in the perovskites, SEM (scanning electron microscopy) can be used. Figure 6 shows a micrograph obtained for  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$  (the figure shows the texture and relief created by the elimination of volatile substances produced in the combustion of organic compounds during thermal treatment).

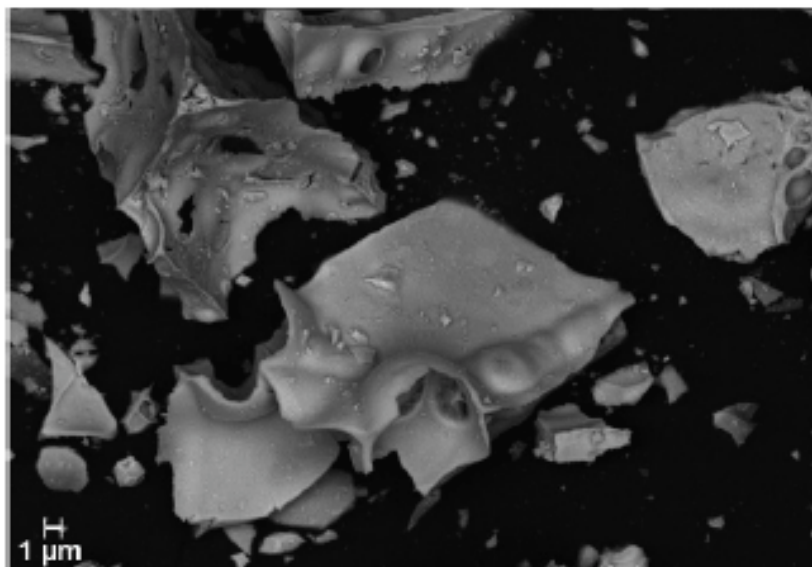


Fig. 6. SEM for  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ .

#### 4.1 Further characterization

In many -but certainly not all- cases new solid compounds are further characterized by a variety of techniques that straddle the fine line that (hardly) separates solid-state chemistry from solid-state physics.

##### 4.1.1 Optical properties

For non-metallic materials it is often possible to obtain UV/VIS spectra. In the case of semiconductors that will give an idea of the band gap. Surfaces of  $\text{ABO}_3$  perovskites and defects therein are extremely relevant for such important fields of technology as photocatalysis, gas-sensors and for applications as materials for ferroelectric memories, and the optical properties of them can be proved to be extremely interesting.

##### 4.1.2 Electrical properties

Four-point (or five-point) probe methods are often applied either to ingots, crystals or pressed pellets to measure resistivity and the size of the Hall effect. This gives information on whether the compound is an insulator, semiconductor, semimetal or metal and upon the type of doping and the mobility in the delocalized bands (if present). Thus, important information is obtained on the chemical bonding in the material.

The impedance spectroscopy is also a very useful method used for electrical properties characterization of perovskite-type materials, especially for bulk ceramic samples.

4.1.3 Magnetic properties

Magnetic susceptibility can be measured as a function of temperature to establish whether the material is a *para-*, *ferro-*, *ferri-* or *antiferro-* magnet, among others. Again the information obtained pertains to the bonding in the material. This is particularly important for transition metal compounds. In the case of magnetic order neutron diffraction can be used to determine the magnetic structure.

Magnetic measurements are usually carried out with a SQUID magnetometer under different applied magnetic field. Figure 7 shows a picture of one of those SQUID magnetometers.



Fig. 7. SQUID magnetometer.

As an example, Figure 8 shows the magnetic susceptibility versus temperature data for the perovskite  $\text{Sr}_2\text{Ru}_{0.5}\text{Co}_{1.5}\text{O}_6$ .

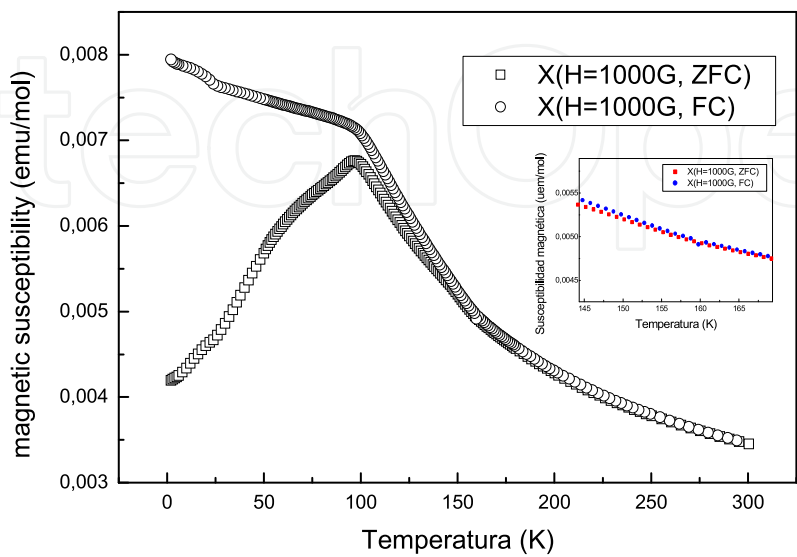


Fig. 8. Magnetic susceptibility versus temperature for  $\text{Sr}_2\text{Ru}_{0.5}\text{Co}_{1.5}\text{O}_6$ .

## 5. X-ray diffraction

About 95% of all solid materials can be described as crystalline. In 1919 A. W. Hull published a paper titled “A New Method of Chemical Analysis”. Here he pointed out that “... every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others. ”

The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases. It is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials.

Today about 50,000 inorganic and 25,000 organic single components, crystalline phases, diffraction patterns have been collected and stored on different databases. The main use of powder XRD is to identify components in a sample by a search/match procedure. Furthermore, the areas under the peak are related to the amount of each phase present in the sample.

Many solid state reactions produce polycrystalline powders, therefore, for a high percentage of perovskites, the powder XRD is one of the main tools to characterize the material. Thus, it is indispensable to have a diffractometer in the laboratory.

Typically, a diffractometer consists of a tube of X-ray (source of radiation), a monochromator to choose the wavelength (for example, in the case of an anode of copper, the  $K\alpha_2$  component could be eliminated by using a primary monochromator), slits to adjust the shape of the beam, a sample and a detector. In a more complicated apparatus also a goniometer can be used for fine adjustment of the sample and the detector positions. When an area detector is used to monitor the diffracted radiation a beamstop is usually needed to stop the intense primary beam that has not been diffracted by the sample. Otherwise the detector might be damaged. Usually the beamstop can be completely impenetrable to the X-ray or it may be semitransparent. The use of semitransparent beamstop allows the possibility to determine how much the sample absorbs the radiation using the intensity observed through the beamstop. Figure 9a) shows an X-ray powder diffractometer commonly seen in laboratories. Figure 9b) shows a detail of its geometry.

Ideally, every possible crystalline orientation is represented very equally in a powdered sample. The resulting orientational averaging causes the three-dimensional reciprocal space that is studied in single crystal diffraction to be projected onto a single dimension.

Bragg's law gives the angles for coherent and incoherent scattering from a crystal lattice. When X-rays are incident on an atom, they make the electronic cloud move as does any electromagnetic wave. The movement of these charges re-radiates waves with the same frequency (blurred slightly due to a variety of effects); this phenomenon is known as Rayleigh scattering (or elastic scattering). The scattered waves can themselves be scattered but this secondary scattering is assumed to be negligible. A similar process occurs upon scattering neutron waves from the nuclei or by a coherent spin interaction with an unpaired electron. These re-emitted wave fields interfere with each other either constructively or

destructively (overlapping waves either add together to produce stronger peaks or subtract from each other to some degree), producing a diffraction pattern on a detector or film. The resulting wave interference pattern is the basis of diffraction analysis. This analysis is called Bragg diffraction.



a)



b)

Fig. 9. X-ray powder diffractometer.

Bragg diffraction (also referred to as the Bragg formulation of X-ray diffraction) was first proposed by William Lawrence Bragg and William Henry Bragg in 1913 in response to their discovery that crystalline solids produced surprising patterns of reflected X-rays (in contrast to that of, say, a liquid). They found that these crystals, at certain specific wavelengths and incident angles, produced intense peaks of reflected radiation (known as Bragg peaks). The concept of Bragg diffraction applies equally to neutron diffraction and electron diffraction processes. Both neutron and X-ray wavelengths are comparable with inter-atomic distances ( $\sim 150$  pm) and thus are an excellent probe for this length scale.

W. L. Bragg explained this result by modeling the crystal as a set of discrete parallel planes separated by a constant parameter  $d$ . It was proposed that the incident X-ray radiation would produce a Bragg peak if their reflections off the various planes interfered constructively.

The interference is constructive when the phase shift is a multiple of  $2\pi$ ; this condition can be expressed by Bragg's law (Equation 1),

$$n\lambda = 2d \sin\theta \quad (1)$$

where  $n$  is an integer,  $\lambda$  is the wavelength of the incident wave,  $d$  is the spacing between the planes in the atomic lattice, and  $\theta$  is the angle between the incident ray and the scattering planes (Figure 10).

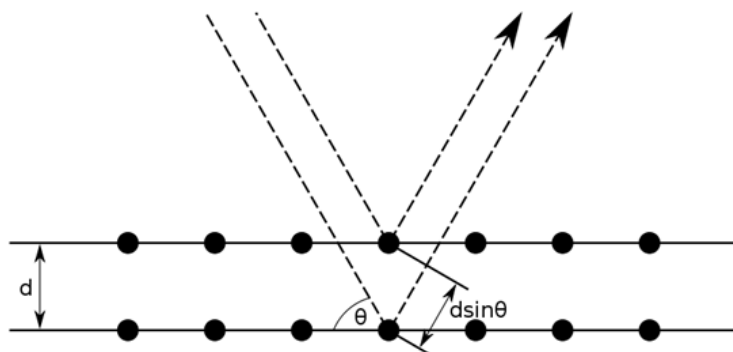


Fig. 10. Bragg diffraction.

The Rietveld method allows us to characterize the polycrystalline materials by a least squares approach to refine a theoretical line profile until it matches the measured profile shown in the pattern. The introduction of this technique was a significant step forward in the diffraction analysis of powder samples as, unlike other techniques at that time, it was able to deal reliably with strongly overlapping reflections.

The Rietveld refinement considers the fitting of a series of parameters linked, most of them, to the structure of the perovskite (or material in general). Some of them are the unit cell parameters, and the profile ones. It is important to reach a certain grade of reliability during the fitting process, and this can be followed by checking the so-called agreement factors (or reliability factors). Table 2 shows an example of lattice parameters and agreement factors obtained after the Rietveld refinement of the cubic perovskite-type solid solution  $\text{Ba}_2\text{In}_{2-x}\text{Co}_x\text{O}_5$  ( $0.50 \leq x \leq 1.70$ ). In Figure 11 an example of a Rietveld refined pattern, exactly for  $\text{Ba}_2\text{In}_{0.3}\text{Co}_{1.7}\text{O}_5$ , can be observed.

Compound	$a$ (Å)	$\chi^2$	$R_p$	$R_{wp}$	$R_{exp}$
$Ba_2In_{1.50}Co_{0.50}O_5$	4.2277(2)	5.02	13.2	18.1	8.07
$Ba_2In_{1.30}Co_{0.70}O_5$	4.1751(1)	3.58	16.5	21.0	11.1
$Ba_2InCoO_5$	4.1623(2)	3.67	12.4	15.3	8.01
$Ba_2In_{0.30}Co_{1.70}O_5$	4.1191(2)	2.28	9.93	13.1	8.65

Table 2. Cell parameters and reliability factors obtained from the Rietveld refinement.

In order to carry out a Rietveld refinement to fit the corresponding theoretical profile – model – a statistically acceptable pattern is necessary. The goodness of the pattern depends on the sample and the measurement parameters. There are several programs suitable to do Rietveld fittings, e.g. Fulprof and GSAS, among others.

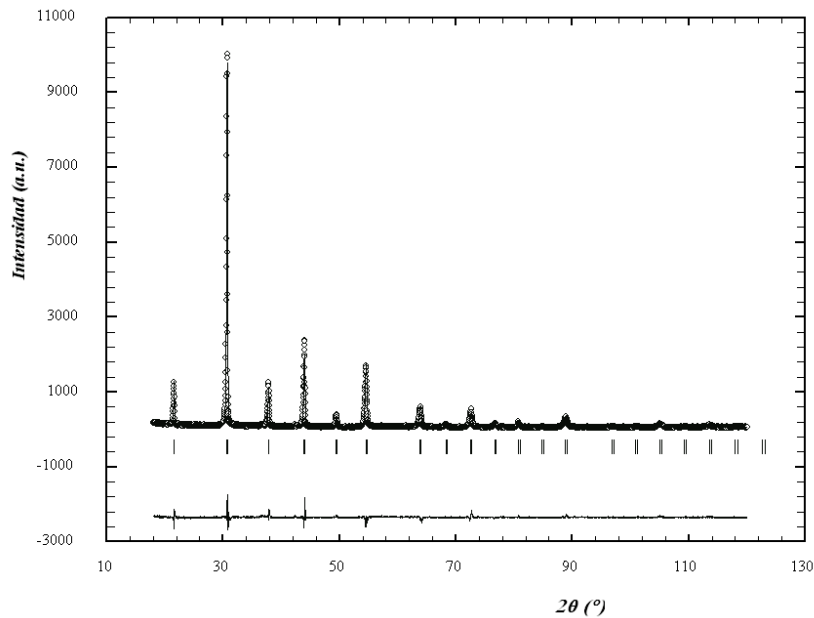


Fig. 11. X-ray diffraction pattern refined by Rietveld method for  $Ba_2In_{0.3}Co_{1.7}O_5$ , showing the observed intensities (circles), the calculated ones (continuous line), the Bragg positions allowed by the space group (vertical lines) and the difference pattern between the observed and calculated ones (bottom of the figure).

5.1 Synchrotron

A synchrotron is a particular type of cyclic particle accelerator in which the magnetic field (to turn the particles so they circulate) and the electric field (to accelerate the particles) are carefully synchronized with the travelling particle beam. In essence, it is a X-ray source with variable wavelength. Thus, it allows going deeper in the X-ray diffraction analysis of the perovskites or any other material. There is a good number of synchrotron facilities all over the world. ESRF in France and Diamond Light Source in the UK constitute two examples (Figure 12).





Fig. 12. Diamond Light Source (UK).

## 6. Neutron diffraction

Neutron diffraction or elastic neutron scattering is the application of neutron scattering to the determination of the atomic and/or magnetic structure of a material. The sample is placed in a beam of thermal or cold neutrons to obtain a diffraction pattern that provides information of the structure of the material. The technique is similar to XRD but due to the different scattering properties of neutrons versus X-rays complementary information can be obtained.

A neutron diffraction measurement requires a neutron source (e.g. a nuclear reactor or spallation source), a sample (the perovskite to be studied or in general any material), and a detector. Sample sizes are large compared to those used in XRD. The technique is therefore mostly performed as powder diffraction. At a research reactor other components such as crystal monochromators or filters may be needed to select the desired neutron wavelength. Some parts of the setup may also be movable. At a spallation source the time of flight technique is used to sort the energies of the incident neutrons (higher energy neutrons are faster), so no monochromator is needed, but rather a series of aperture elements synchronized to filter neutron pulses with the desired wavelength.

Neutron diffraction is closely related to XRD. In fact the single crystal version of the technique is less commonly used because currently available neutron sources require relatively large samples and large single crystals are hard or impossible to come by for most materials. Future developments, however, may well change this picture. Because the data is typically a 1D powder pattern they are usually processed using Rietveld refinement. In fact the latter found its origin in neutron diffraction (at Petten in the Netherlands) and was later extended for use in XRD.

One practical application of elastic neutron scattering/diffraction is that the lattice constant of perovskites and other crystalline materials can be very accurately measured. Together with an accurately aligned micropositioner a map of the lattice parameters through the

material can be derived. This can easily be converted to the stress field experienced by the compound. This has been used to analyze stresses in aerospace and automotive components to give just two examples. There is a good number of facilities all over the world offering a neutron source. Among them, we could mention, for instance, ISIS in the UK, and ILL in France.

Figure 13 shows a picture of the reactor hall at ILL in Grenoble, France. ILL (Institut Laue-Langevin) is one the most important centres in the world to carry out neutron experiments.



Fig. 13. Inside the reactor hall at ILL in Grenoble (France).

## 7. High-resolution transmission electron diffraction

The original form of electron microscope, the transmission electron microscope (TEM) uses a high voltage electron beam to create an image. The electron beam is accelerated by an anode with respect to the cathode, focused by electrostatic and electromagnetic lenses, and transmitted through the sample that is in part transparent to the electrons and in part scatters them out of the beam. When it emerges from the sample, the electron beam carries information about the structure of the sample that is magnified by the objective lens system of the microscope. Hardware correction of spherical aberration for the high-resolution transmission electron microscopy (HRTEM) has allowed the production of images with resolution below  $0.5 \text{ \AA}$  at magnifications above 50 million times. This possibility of having direct images of the atomic arrangement in the structure has made the HRTEM an important tool for nano-technologies research and development.

## 8. Conclusion

The perovskite is a mineral series composed of calcium titanate. Many transition metal oxides show that very versatile perovskite structure. The rich variety of physical properties

such as high-temperature superconductivity and colossal magnetoresistance observed in these compounds makes them very attractive from both fundamental and applied perspectives.

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The X-ray diffraction pattern of a pure substance is like a fingerprint of the substance. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases, and therefore of perovskites.

The Rietveld method allows us to characterize the polycrystalline materials by a least squares approach to refine a theoretical line profile until it matches the measured profile shown in the pattern.

It is possible to go further in the study of the structure of the perovskites by means of neutron diffraction, although it is true to say that large facilities are needed to carry out such study.

## 9. Acknowledgment

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## 10. References

- Bragg, W.L. (1913). The diffraction of short electromagnetic waves by a crystal, *Proceedings of the Cambridge Philosophical Society*, Vol.17, pp. 43-57
- Coey, J.M.D., Viret, M., von Molnar, S. (1999). Mixed-valence manganites, *Advances in Physics*, Vol.48 (2), pp. 167-293. doi:10.1080/000187399243455
- Cullity, B.D. (1977). Elements of X-ray diffraction, Addison-Wesley, 2nd ed., ISBN 0-201-01174-3

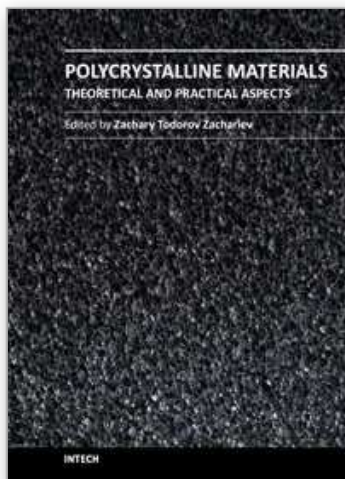
- Didenko, Y.T., Suslick, K.S. (2002). The energy efficiency of formation of photons, radicals and ions during single-bubble cavitation. *Nature*, Vol.418, pp. 394-397
- Ekambaram, S., Patil, K.C., Maaza, M. (2005). Synthesis of lamp phosphors: facile combustion approach. *J. Alloys Comp.*, Vol.393, pp. 81-92
- Gedanken, A. (2004). Using sonochemistry for the fabrication of nanomaterials. *Ultrasonics Sonochemistry*, Vol.11, pp. 47-55
- Gómez-Cuaspué, J.A., Valencia-Ríos, J.S., Carda-Castellón, J.B. (2010). Preparation and characterization of perovskite oxides by polymerization-combustion, *J. Chil. Chem. Soc.*, Vol.4, pp. 55
- Goodenough, J.B. (2004). *Rep. Prog. Phys.*, Vol.67, pp. 1915
- Ibberson, R.M., David, W.I.F. (2002). Structure determination from neutron powder diffraction data, *IUCr monographs on crystallography*, Oxford scientific publications, ISBN 0-19-850091-2
- Larson, A.C., Von Dreele, R.B. (2000). General Structure Analysis System (GSAS). *Los Alamos National Laboratory Report LAUR 86-748*
- Lozano-Gorrín, A.D., Greedan, J.E., Núñez, P., González-Silgo, C., Botton, G.A., Radtke, G. (2007). Structural characterization, magnetic behavior and high-resolution EELS study of new perovskites  $\text{Sr}_2\text{Ru}_{2-x}\text{Co}_x\text{O}_6$  ( $0.5 \leq x \leq 1.5$ ), *Journal of Solid State Chemistry*, Vol.180, pp. 1209-1217
- Lozano-Gorrín, A.D., Núñez, P., López de la Torre, M.A., Romero de Paz, J., Sáez-Puche, R. (2002). Spin glass behavior of new perovskites  $\text{Ba}_2\text{In}_{2-x}\text{Co}_x\text{O}_5$  ( $0.5 \leq x \leq 1.70$ ), *Journal of Solid State Chemistry*, Vol.165, pp. 254-260, doi:10.1006/jssc.2002.9515, available online at <http://www/idealibrary.com>
- Megaw, H.D. (1945). Crystal structure of barium titanate, *Nature*, Vol.155, pp. 484-485, ISSN 00280836
- Navrotsky, A. (1998). Energetics and crystal chemical systematics among ilmenite, lithium niobate, and perovskite structures, *Chem. Mater.*, Vol.10, pp. 2787. doi:10.1021/cm9801901
- Patil, K.C., Aruna, S.T., Mimani, T. (2002). Combustion synthesis: an update. *Solid State Mater. Sci.*, Vol.6, pp. 507-512
- Pechini, M.P. (1967). US Patent No.3.330.697 July 1
- Rao, C.N.R., Gopalakrishnan, J. (1997). New directions in Solid State Chemistry. Cambridge U. Press, ISBN 0-521-49559-8
- Reisfeld, R., Jorgensen, C.K. (1992). Optical properties of colorants or luminescent species in sol-gel glasses, structure and bonding. Springer-Verlag, Heidelberg
- Rodríguez-Carvajal, J. (1993). Recent advances in magnetic structure determination by neutron powder diffraction, *Physica B*, Vol.192, pp. 55
- Roisnel, T., Rodríguez-Carvajal, J. (2000). WinPLOTR: a Windows tool for powder diffraction patterns analysis. *Proceedings of the Seventh European Powder Diffraction Conference (EPDIC 7)*, pp. 118-123, Ed. R. Delhez and E.J. Mittenmeijer
- Rose, H.H. (2008). Optics of high-performance electron microscopes. *Sci. Technol. Adv. Mater.*, Vol.9, pp. 014107
- Toby, B.H. (2001). EXPGUI, a graphical user interface for GSAS, *J. Appl. Cryst.*, Vol.34, pp. 210-213



Witze, A. (2010). Building a cheaper catalyst. *Science News* Web Edition.  
[http://www.sciencenews.org/view/generic/id/57618/title/Building\\_a\\_cheaper\\_catalyst](http://www.sciencenews.org/view/generic/id/57618/title/Building_a_cheaper_catalyst)

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