

# Physics of Transition Metal Oxides

## Lecture 5

### Dielectric properties of oxides

1

## Dielectric properties of insulating oxides

This is one of the largest fields of applications of oxides in electronics. Dielectrics are widely used in capacitors, microwave devices, and filters.

What we look at is the response of a material to an electric field. Some of the important parameters are:

The *electric field*  $E$

The *polarization*  $P$  (dipole moment per unit volume)

The *electric displacement*  $D$

If we have microscopic dipoles in the material, these will align with an external field and thus

$$P = \epsilon_0 \chi E,$$

where  $\epsilon_0$  is the *dielectric permittivity* of free space (vacuum) and  $\chi$  is the *electric susceptibility*.

2

In *anisotropic* materials  $P$  and  $E$  are not parallel and the relationship is not linear when the field is very strong.

Electric displacement is given by

$$D = \epsilon_0 E + P.$$

We can thus write

$$D = \epsilon_0 \epsilon_r E, \quad \epsilon_r = 1 + \chi,$$

or

$$P = \epsilon_0 (\epsilon_r - 1) E.$$

What we usually look at is  $\epsilon_r$ , the *relative dielectric constant*. This gives us the *index of refraction*

$$n = \sqrt{\epsilon_r},$$

i.e. the speed of light in a medium  $v = c/n$ .

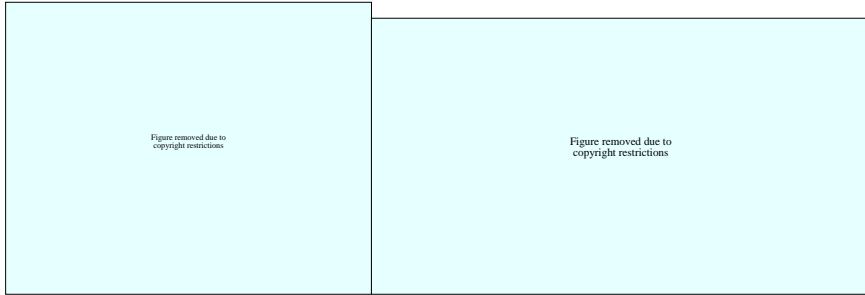
3

In practice,  $\epsilon_r$ , called the *dielectric constant*, is not a constant at all, but depends on temperature, pressure, and measurement frequency.

Compound	Temperature (K)	$\epsilon_{opt}$	$\epsilon_{static}$
TiO <sub>2</sub> (  c)	300	8.4	170
	0	-	257
TiO <sub>2</sub> (  a)	300	6.8	86
	0	-	111
SrTiO <sub>3</sub>	0	6	~30000
CaTiO <sub>3</sub>	300	6	180
	100	-	330
PbTiO <sub>3</sub>	300	7	300
CaZrO <sub>3</sub>	300	-	25
MoO <sub>3</sub>	300	5	20
KTaO <sub>3</sub>	0	-	~4000
WO <sub>3</sub>	300	5	variable

There is a rough inverse correlation between  $\epsilon_{opt}$  and the gap width. Thus TiO<sub>2</sub> has a large  $\epsilon_{opt}$  and a wide gap. It is transparent in the visible region and has a very high refractive index (good for micro-optics). Large  $\epsilon_{opt}$  also implies high reflectivity, which is why TiO<sub>2</sub> powder is used as a pigment in white paint.

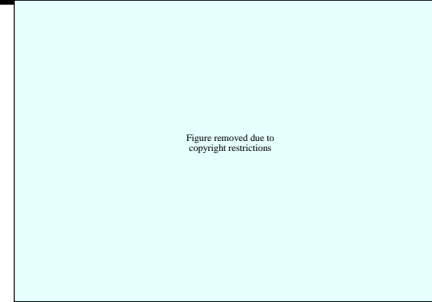
4



Cox92 P.111

Large changes in dielectric constant usually happen close to structural phase transitions, as shown here for  $\text{PbTiO}_3$ .

Especially in various perovskites the structure appears to be on the edge of stability (ionic radius). This results in very large lattice polarizability. That is why the perovskite group includes many *ferroelectric* oxides, like  $\text{NaNbO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ .



A ferromagnetic hysteresis loop is familiar, with three important characteristics,

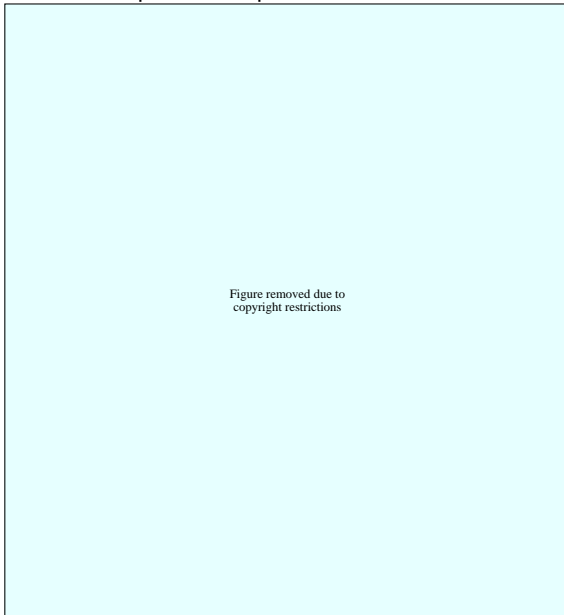
- Coercive field
- Remanent magnetization
- Saturation magnetization



In a ferroelectric material we have a similar hysteresis loop of polarization vs. electric field and the same coercive, remanent, and saturation parameters.

Hippel54 p.270

Another good example is  $\text{BaTiO}_3$ , with several structural transitions and several peaks in the dielectric constant temperature dependence.



Rao98 p.287

Ferroelectric hysteresis loops of  $\text{BaTiO}_3$  are shown here as a function of temperature:



Hippel54 p.271

## Soft-mode theory

*Soft-mode theory* is used to explain these large changes of the dielectric constant close to a phase transition.

First we look at the contribution of lattice polarization to the static dielectric constant. This can be expressed as

$$\epsilon_s - \epsilon_{\text{opt}} = \sum_i \Omega_i^2 / \omega_i^2,$$

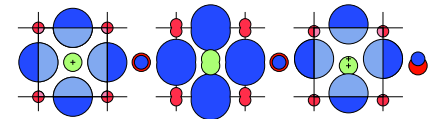
where  $\omega_i$  is the frequency of a vibration mode, and  $\Omega_i$  is related to the *effective charge* carried by the ions in this vibration mode. The important modes are the *transverse-optic modes*, which contribute to a long-range dipole field.

The long-range dipole field results in an attractive force, which counteracts the usual short-range repulsive forces. The vibrating ions interact with the long-range field and usually the frequency of one mode gets reduced, giving a very large contribution to the dielectric constant. Remember,

$$\mathbf{P} = \epsilon_0(\epsilon_r - 1)\mathbf{E}.$$

9

In an extreme case, the frequency would drop to zero, the static dielectric constant would be infinite and instead of an atomic vibration we would have a static displacement, i.e. a ferroelectric material.



The temperature dependence arises from the anharmonic distortion of the short-range forces. These give a temperature dependence of

$$\omega^2 = C(T - T_0)$$

for a mode frequency  $\omega$ . If only a single mode contributes to the dielectric constant, we would have

$$\epsilon_s = C' / (T - T_0).$$

This would be basically similar to a Curie-Weiss law for magnetic systems.

10

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In many materials the critical temperature  $T_0$  is less than zero and a complete mode softening does not happen. In some cases it appears to be very close to zero, as in  $\text{KNbO}_3$  or  $\text{SrTiO}_3$ . In  $\text{SrTiO}_3$  there is a huge increase in  $\epsilon$ , but the value stays constant below 10K without entering a ferroelectric state. The transition can be induced by an external electric field. When  $T_0 > 0\text{K}$ , then it can be called *Curie temperature*, below which we have a ferroelectric phase.

## The simple soft-mode theory predicts:

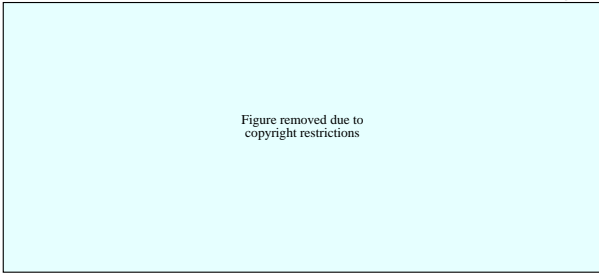
- The vibrational spectrum of a solid should show a transverse optic mode which softens (frequency drops) to zero at the Curie temperature.
- The static dielectric constant should follow the Curie-Weiss form

This theory neglects damping of modes, detailed anharmonic effects, and it is a mean-field theory, i.e. it does not include the effects of fluctuations. These are responsible for the *quantum paraelectric* phase of  $\text{SrTiO}_3$  at low temperatures.

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This plot shows the square of the frequency of the lowest TO mode and  $1/\epsilon_s$  as a function of temperature in  $\text{PbTiO}_3$ . Approximate straight lines are visible, but they drop to zero below the transition temperature.

The phonon spectrum is usually measured by Raman scattering.



Fox01 p.221

This is a form of inelastic light scattering, i.e. the photon energy changes in the scattering process. There are two names for the same process

- *Raman scattering* inelastic light scattering from optical phonons
- *Brillouin scattering* inelastic light scattering from acoustic phonons



13

A phonon can be either absorbed or emitted. The conservation of energy and momentum tell us that

$$\begin{aligned}\omega_1 &= \omega_2 \pm \Omega \\ \mathbf{k}_1 &= \mathbf{k}_2 \pm \mathbf{q}\end{aligned}$$

The + sign corresponds to phonon emission (Stokes scattering) and the - sign corresponds to phonon absorption (anti-Stokes scattering). Obviously, anti-Stokes processes can only happen if there are lots of phonons, i.e. temperature has to be high enough.

An optical photon has an energy of around 1-2 eV, phonons have an energy of around 10-20 meV. The maximum frequency shift is thus around 1%.

14

The small shift lets us write

$$|\mathbf{k}_2| \approx |\mathbf{k}_1| = \frac{n\omega}{c},$$

where  $n$  is the refractive index and  $\omega$  is the frequency of the incoming light. Conservation of momentum tells us that

$$|\mathbf{q}| = |\mathbf{k}_1 - \mathbf{k}_2|.$$

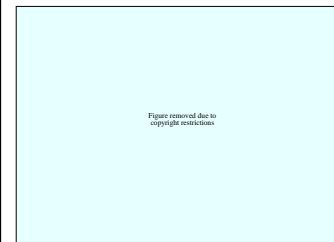
The largest  $|\mathbf{q}|$  thus occurs in back-scattering geometry with

$$q \approx |\mathbf{k} - (-\mathbf{k})| \approx 2\frac{n\omega}{c}.$$

The largest scattering vector that can be measured with visible light is thus about  $10^7 \text{ m}^{-1}$ . This is very small compared to the size of a typical Brillouin zone of  $\sim 10^{10} \text{ m}^{-1}$ .

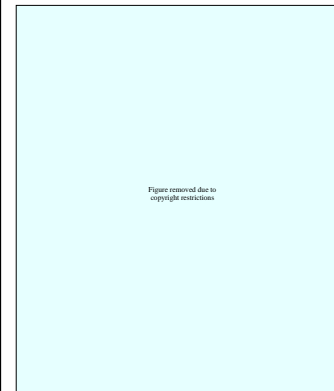
Raman scattering is usually very weak, which is why a very intense light source with a very narrow spectral width is needed, such as a laser.

15



This is what a full Raman spectrum would look like.

Ashcroft76 p.483



The strong laser peak is usually subtracted from the spectrum and only the scattering peaks are shown. In this case the laser is a Nd:YAG at  $1.06\mu\text{m}$ . Measurements done at 300 K. The usual unit for frequency shifts is  $\text{cm}^{-1}$ ,  $1 \text{ cm}^{-1} = 0.124 \text{ meV}$ . The two peaks are the Stokes-shifted TO phonons and LO phonons (higher frequency).

Fox01 p.221

16

Now let's look again at SrTiO<sub>3</sub>. This is a very simple cubic perovskite. At low temperature we have an approximate Curie-like increase of the dielectric constant but there is no drop of  $\epsilon$  at low temperature, i.e., no ferroelectric phase.

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PRB 19 (1979) 3593

PRL 26 (1971) 851

17

In case of oxides, there are usually quite many possible phonon modes. This plot is for SrTiO<sub>3</sub> at 5 K.

We are interested in the *soft modes*, i.e. those with the lowest frequencies, in this case marked with *A* and *E*.

The intensity of the modes are affected by many things, such as defects, impurities, external stress, and external field. This plot shows the effect of an external electric field (dashed line).

The peaks marked by *R* are structural modes.

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18

These are the two soft modes that we look at. The one in (a) corresponds to a cubic-to-tetragonal structural transition at about 105 K. (Marked *R* on the previous slide). The one in (b) would give a ferroelectric polarization. The frequency of this mode is sensitive to an external electric field.

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19

The hardening of a soft mode (increase of the phonon frequency) as a result of an external field will prevent a ferroelectric transition from occurring and we therefore see a sharp drop in the dielectric constant.

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20

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Why the field-dependent  $\epsilon$  is useful? We can plot the dielectric properties as function of field strength at a fixed temperature for SrTiO<sub>3</sub>.

Especially in thin films we can see a rather large  $\epsilon$  change even at temperatures that are much higher than the ferroelectric transition, as shown here 5 K, and 190 K.

This can be used to build tunable filters. A bandpass filter might look like this

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By applying a DC voltage on the capacitors, we can quickly retune the filter to a different frequency.

21

### Some terminology:

*Ferroelectrics* are an analogue of ferromagnets and show a spontaneous polarization in the absence of an electric field. Ferroelectrics have a permanent dipole moment. In some cases neighboring planes orient in an antiparallel configuration. This would give an *antiferroelectric* material. This type of lattice does not show a hysteresis curve, but does show a dielectric constant anomaly close to the transition temperature.

In a *ferromagnet* the orientation of magnetization  $M$  can be switched with an external magnetic field  $H$ .

In a *ferroelectric* the orientation of the electric polarization  $P$  can be switched with an external electric field  $E$ .

In a *ferroelastic* material the direction of spontaneous strain  $\epsilon$  (change of length) can be switched by applying mechanical stress  $\sigma$  (pressure).

These are all known as *ferroic* transitions. In oxides, for example, BaTiO<sub>3</sub> is a ferroelectric, CrO<sub>2</sub> is a ferromagnet, and CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> is a ferroelastic. These are all *primary ferroics*.

22

There are also *secondary ferroics*, where ordering can be induced by an external field. These could be

- Induced electric polarization, characterized by susceptibility  $k_{ij}$ .
- Induced magnetic polarization, characterized by magnetic susceptibility  $\chi_{ij}$ .
- Strain induced by elastic compliance,  $C_{ijkl}$ .

There are also cross-coupled effects, such as stress-induced polarization, *piezoelectrics*, and stress-induced magnetization, *piezomagnetics*.

The mechanisms are often interconnected, spontaneous polarization is caused by or causes a field. The field couples to the lattice, creating lattice strain, thus causing an electrostrictive or piezoelectric response.

23

### Piezoelectricity

A crystal generates a static charge on the surface when pressed or changes its size when placed in an electric field.

All crystals that do not have a center of symmetry (no inversion symmetry) are piezoelectric. Those piezoelectrics that can be *poled* are also ferroelectric. For example, quartz (SiO<sub>2</sub>) is piezoelectric, but not ferroelectric. All ferroelectrics, however, are also piezoelectric.

The piezoelectric response can be maximized by creating solid solutions like Pb(Zr<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3</sub>, also known as PZT, one of the most widely-used piezo materials.

An interesting feature of oxides is that many of the spontaneous ordering mechanisms are combined in a single material:

Ferroelectric-ferroelastic Gd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>, KNbO<sub>3</sub>

Ferroelectric-antiferromagnetic YMnO<sub>3</sub>, HoMnO<sub>3</sub>

Ferroelectric-ferromagnetic Bi<sub>9</sub>Ti<sub>3</sub>Fe<sub>5</sub>O<sub>27</sub>

Antiferroelectric-antiferromagnetic BiFeO<sub>3</sub> Cu(HCOO)<sub>2</sub> · 4H<sub>2</sub>O

Ferroelectric-semiconducting, reduced SrTiO<sub>3</sub>, YMnO<sub>3</sub>

Ferroelectric-superconducting SrTiO<sub>3</sub>

24

Nonlinear optical response is also a common feature of  $d^0$  oxides. In general, dielectric polarization is nonlinear,

$$\mathbf{P} = \epsilon_0(\chi^{(1)}\mathbf{E} + \chi^{(2)}\mathbf{E}^2 + \chi^{(3)}\mathbf{E}^3 + \dots)$$

or for the relative dielectric constant

$$\epsilon_r = 1 + \chi^{(1)} + \chi^{(2)} + \chi^{(3)} + \dots,$$

where  $\chi^{(1)}$  is the usual linear susceptibility. The dielectric constant thus depends on the field strength. The most important terms are  $\chi^{(2)}$  and  $\chi^{(3)}$ , the *second-order* and *third-order* nonlinear susceptibilities. Higher terms vanish quickly.

The second-order polarization would be (if we look at all the vector components)

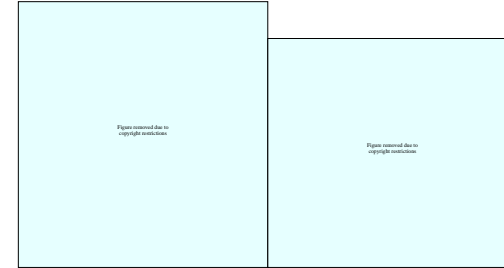
$$P_i^{(2)} = \epsilon_0 \sum_{j,k=x,y,z} \chi_{ijk}^{(2)} E_j E_k,$$

where  $\chi_{ijk}^{(2)}$  is the second-order nonlinear susceptibility tensor, a rank 3 tensor. The two fields,  $E_j$  and  $E_k$ , may come from the same light source or from different sources.

25

For centrosymmetric crystals this value is zero. For materials without a center of symmetry (piezoelectrics), the largest effects are seen in those with a large linear polarizability (those with a large dielectric constant).

Important examples are  $\text{LiNbO}_3$  and  $\text{KTiO}(\text{PO}_4)$  - potassium titanyl phosphate, or KTP. All such materials have a very distorted cluster around the metal ion.



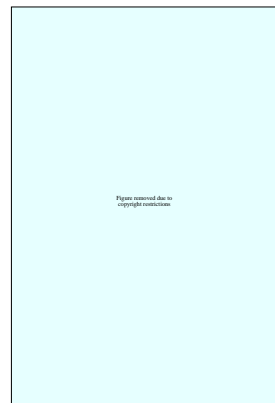
26

One of the most important applications of nonlinear optics is frequency mixing.

$$P_i^{(2)} = \epsilon_0 \sum_{j,k=x,y,z} \chi_{ijk}^{(2)} E_j E_k,$$

If we have two fields with  $E_1 = \mathcal{E}_1 \cos \omega_1 t$  and  $E_2 = \mathcal{E}_2 \cos \omega_2 t$ ,

$$\begin{aligned} P^{(2)}(t) &= \epsilon_0 \chi^{(2)} \times \mathcal{E}_1 \cos \omega_1 t \times \mathcal{E}_2 \cos \omega_2 t \\ &= \epsilon_0 \chi^{(2)} \mathcal{E}_1 \mathcal{E}_2 \frac{1}{2} [\cos(\omega_1 + \omega_2)t + \cos(\omega_1 - \omega_2)t]. \end{aligned}$$



This shows that we get two outgoing beams with frequencies

$$\omega_{\text{sum}} = \omega_1 + \omega_2$$

$$\omega_{\text{diff}} = \omega_1 - \omega_2$$

The most important one is the sum frequency. The process is known as *frequency doubling* or *second harmonic generation*.

27

### Other closed-shell oxides

In addition to the  $d^0$  compounds, there are also other closed shell compounds with a diamagnetic ground state.

Compound	Electron configuration	Metal coordination	Band gap (eV)
$\text{Cu}_2\text{O}$	$3d^{10}$	2 (linear)	2.16
$\text{Ag}_2\text{O}_2$	$4d^{10}$	2 (linear)	
	$4d^8$	4 (square planar)	
$\text{PdO}$	$4d^8$	4 (square planar)	1
$\text{LaCoO}_3$	$3d^6$	6 (octahedral)	0.1
$\text{LaRhO}_3$	$4d^6$	6 (octahedral)	1.6

The  $d^{10}$  configuration exists in  $\text{Cu}_2\text{O}$ . The gap is formed between the filled Cu  $3d$  levels and an empty band of mostly Cu  $4s$  character. For later elements in the same row, such as  $\text{Zn}^{2+}$  in  $\text{ZnO}$  or  $\text{Sn}^{4+}$  in  $\text{SnO}_2$  also have a  $d^{10}$  configuration, but in these the  $d$  electrons have little effect on the electronic properties and behave more like core electrons. In  $\text{ZnO}$  and  $\text{SnO}_2$  the valence band consists of oxygen  $2p$  orbitals, just like to  $d^0$  oxides.

28