Cubic relaxors: Structure and lattice dynamics.

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Outline of the talk

- Structure determination in case of disorder
- Polar nanoregions in PMN
- Elastic distortions and the Huang scattering
- PMN-PbTiO3 solid solutions – nanodomains
- Phonon dispersion curves in PMN
Diffraction on split lead ion

In simple perovskites ABO$_3$ ions are sitting in special high-symmetry positions:

- $r_A = (000)$,
- $r_B = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$,
- $r_O = (\frac{1}{2} \frac{1}{2} 0), (0 \frac{1}{2} \frac{1}{2}), (\frac{1}{2} 0 \frac{1}{2})$.

Structure factor $F(\tau) = \sum f_i e^{-Wi} e^{i\tau r_i} = f_A e^{-W_A} + f_B e^{-W_B} \cos(\tau r_B) + f_O e^{-W_O} [\cos(\tau r_{O1}) + \cos(\tau r_{O2}) + \cos(\tau r_{O3})]$.

Split Pb ion

- $A = \text{Pb}$; $(-u-u-u) - p_1$; $(-u-u-u) - p_2$; $(-uuu) - p_3$; $(u-u-u) - p_4$;
- $(u-uu) - p_5$; $(-uu-u) - p_6$; $(uu-u) - p_7$; $(-u-uu) - p_8$;

$S_{\text{Pb}} = \sum_{j=1..8} p_j e^{i\tau u_j} = \sum p_j [\cos(\tau u_j) + i\sin(\tau u_j)]$

$P_j$ are the probabilities of the corresponding shifts.
Diffraction on split lead ion II

In centrosymmetric case $\Sigma p_i \sin(\tau u_j) = 0$
In noncentrosymmetric case $Sp_i \sin(\tau u_j) \neq 0$
Most essential is to determine the $p_i$
Averaging should be performed over the coherent volume. In typical X-ray or neutron experiment it is of about (10-15)nm$^3$

Observability of the PNRs strongly depends on SIZE and MORPHOLOGY of the regions
From Split Atom to Continuous Distribution

- On increase of the RMS displacements separation of positional and thermal parameters becomes meaningless. Probability Density Function should be used instead.
The uniform disorder of the Pb atom over a sphere in the averaged unit cell implies that the crystal consists of $N$ regions with approximately equal volumes. In every region $j$ atom Pb is shifted from its crystallographic position $(0,0,0)$ of vector $\mathbf{b}_j$, where $|\mathbf{b}_j|=R$ for any $j$, while the directions $\mathbf{b}_j$ are uniformly distributed in the space. The scattering factor of this atom is written as

$$f(\mathbf{H}) \ast S(\mathbf{H}, R) \quad (1)$$

where $f(\mathbf{H})$ - the atomic form-factor and $S(\mathbf{H}, R)$ is given by

$$S(\mathbf{H}, R) = \int p(\mathbf{b}) \exp(2\pi i \mathbf{H}\mathbf{b}) d\mathbf{b} = \sin(2\pi HR)/2\pi HR \quad (2)$$

Integration in (2) is executed over a sphere of radius $R$. $p(\mathbf{b})$ is the probability density function, which is constant for any $\mathbf{b}$ vector and $p(\mathbf{b})=p_0=1$ in the case of the uniform atomic disorder.

While the temperature decreases the regions with the special direction $\mathbf{b}_k$ of the ion displacement arise that contribute the asymmetry part in function $p(\mathbf{b})$, i.e.

$p(\mathbf{b}_k) = p_0 + d$ and $p(-\mathbf{b}_k) = p_0 - d$. Therefore (2) will be written as

$$S(\mathbf{H}, R) = p_0 \int \exp(2\pi i \mathbf{H}\mathbf{b}) d\mathbf{b} + i*2d/K \sum \sin(2\pi i \mathbf{H}\mathbf{b}) \quad (3)$$
If $K$ is much more than 1 and the directions $b_k$ are uniformly distributed over space one can replace the second term in (3) by its averaged value. Finally,

$$S(H, R) = A \frac{\sin q}{q} + i B \frac{(1-\cos q)}{q}$$

(4)

where $q = 2\pi HR$. The coefficient $A$ in (4) corresponds to the weight of the statistical positions, where atom $Pb$ is uniformly disordered and the $B$ coefficient describes the degree of asymmetry of this statistical distribution.
Probability density function (PDF) for Pb\(^{2+}\) ion calculated in the Spherical Layer Model.

ALL LEAD IONS ARE SHIFTED!
The discrepancy factors of the structure refinements.

<table>
<thead>
<tr>
<th></th>
<th>110 K</th>
<th>224 K</th>
<th>293 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>0.148</td>
<td>0.141</td>
<td>0.127</td>
</tr>
<tr>
<td></td>
<td>0.106</td>
<td>0.088</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td>0.033</td>
<td>0.028</td>
<td>0.026</td>
</tr>
<tr>
<td>$R_w$</td>
<td>0.231</td>
<td>0.212</td>
<td>0.213</td>
</tr>
<tr>
<td></td>
<td>0.167</td>
<td>0.130</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td>0.056</td>
<td>0.040</td>
<td>0.034</td>
</tr>
<tr>
<td>GOF</td>
<td>4.89</td>
<td>4.04</td>
<td>3.53</td>
</tr>
<tr>
<td>F</td>
<td>3.30</td>
<td>2.40</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>1.45</td>
<td>0.93</td>
<td>0.72</td>
</tr>
</tbody>
</table>

1st line - atom Pb in position (0,0,0) with thermal isotropic parameters (model A);
2nd line - atom Pb is uniformly distributed over the sphere of radius $R$ (model B);
3rd line - atom Pb is asymmetrically distributed over the sphere of radius $R$ (model C).

$$R = \sum \frac{|F_{\text{obs}} - F_{\text{calc}}|}{\sum |F_{\text{obs}}|};$$

$$R_w = \left( \sum w|F_{\text{obs}} - F_{\text{calc}}|^2 / \sum wF_{\text{obs}}^2 \right)^{1/2};$$

$$GOF = \left( \sum w|F_{\text{obs}} - F_{\text{calc}}|^2 / \sum (n-p) \right)^{1/2},$$

$n$ - number of unique reflections, $p$ - number of variables.
The refined parameters of the model C at 110, 224 and 293 K

<table>
<thead>
<tr>
<th>Atom</th>
<th>110 K</th>
<th>224 K</th>
<th>293 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>0.011(1)</td>
<td>0.014(1)</td>
<td>0.015(1)</td>
</tr>
<tr>
<td>$U_{iso}$, A$^2$</td>
<td>0.94(3)</td>
<td>0.94(2)</td>
<td>0.97(1)</td>
</tr>
<tr>
<td>parameter A</td>
<td>0.34(2)</td>
<td>0.25(1)</td>
<td>0.16(1)</td>
</tr>
<tr>
<td>parameter B</td>
<td>0.315(2)</td>
<td>0.313(2)</td>
<td>0.309(2)</td>
</tr>
<tr>
<td>R, A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mg,Nb)</td>
<td>0.004(1)</td>
<td>0.006(1)</td>
<td>0.007(1)</td>
</tr>
<tr>
<td>$U_{iso}$, A$^2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>0.024(3)</td>
<td>0.024(1)</td>
<td>0.023(1)</td>
</tr>
<tr>
<td>$U_{iso}$, A$^2$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
PMN maps of the X-ray diffuse scattering (hk0) plane

PMN 300K Q=(hk0)

PMN 10K Q=(hk0)
PMN
X-ray diffuse scattering polar plot
PMN maps of the X-ray diffuse scattering (hk0.08) plane
Cubic relaxors: Structure and lattice dynamics

\[ \tau = (h00) \]

\[ (-1,1,0) \]

\[ (10,1) \]

\[ (0,11) \]

\[ (10,1) \]

\[ (1,10) \]

\[ (-1,10) \]

\[ (11,0) \]

\[ (-1,11) \]
Huang Scattering

\[ I_H(Q) \approx N_d \left| F(\tau) \right|^2 \frac{Q^2}{q^2} \sum_{\alpha=1}^{v} (m_i C_{qij}^{-1} P_{ajl} n_l)^2 \]

\( N_d \) – number of defects; \( m = Q/Q; n = q/q \)
\( \alpha \) - defect orientation number;
\( v \) - number of possible defect orientations
\( Q \) – scattering vector; \( \tau \) – reciprocal lattice vector;
\( q = Q - \tau \)
\( F(\tau) \) – elastic structure factor
\( P_{\alpha j l} \) – elastic dipole force tensor

\[ C_{qij} = c_{ijlm} n_l n_m \]
PMN

tetragonal distortion of the ordered regions

- Nearly tetragonal distortions for (d) c/a 1.075
- For (e) 1.07
  S.A. Prosandeev et al. to be published
PMN (300) calculations

PMN \( p_{xx} = p_{yy} = -1; p_{zz} = 2 \quad Q = (hk0) \)
PMN (300.08) calculations

\[ \text{PMN} \quad p_{xx} = p_{yy} = -1; \quad p_{zz} = 2 \quad Q = (h k 0 \cdot 08) \]
PMNPT10 maps of the X-ray diffuse scattering (hk0) plane
PFM image of PMNPT10

Digital Instruments NanoScope
Scan size 1.000 μm
Scan rate 0.6013 Hz
Number of samples 256
Image Data Aux C
Data scale 2.000 V
<PP> correlation function
PMNPT10
PFM and X-Ray scattering

Piezoresponse Force Microscopy
High-resolution X-ray Scattering

$S(Q)$ vs. $Q$, nm$^{-1}$

$I$, arb. units vs. $q$, nm$^{-1}$
PMNPT10
Formation of the lattice modulation

\[ I = I_{\text{Bragg}} \exp \left[ -\left( \frac{q - q_0}{\Delta q} \right)^2 \right] + \]
\[ I_{S_1} \left( \frac{1}{(q - q_{S_1})^2 + \kappa^2} \right)^\gamma + I_{S_2} \left( \frac{1}{(q - q_{S_2})^2 + \kappa^2} \right)^\gamma \]

Scattering 210K
\( q_s = 0.036 \text{nm}^{-1}; \ 2\gamma = 3.2 \)

PFM 300K
\( q = 0.007 \text{nm}^{-1}; \ 2\gamma = 3.55 \)
PMNPT10
Decay of the diffuse scattering intensity at large $q$

$\log(I) \sim -\gamma \log(q)$; $\gamma = 3.2(1)$

$\log(I) \sim -\gamma \log(|q|)$; $\gamma = 2.7$

Williamsburg 2004
Butterfly-shaped diffuse X-ray and neutron scattering is described in terms of the Huang scattering resulting from the elastic microstrains produced by the elongated defects with the tetragonal symmetry. This conclusion is confirmed by the measurements near several reciprocal lattice points and in several scattering planes. Intensity of this Huang scattering increases on cooling below $T_d$ due to the coupling with local lead displacements. This interpretation is in a good agreement with the results of the first-principle calculation demonstrating small tetragonal distortions of the chemically ordered regions.

Tetragonal distortions prevent the formation of the long-range rhombohedral phase and the developing of the uniform rhombohedral deformation (polarization–deformation decoupling).

(111) electric field can overcome the influence of the deformations and induce the ferroelectric transition.

Doping with PT results in the suppression of the chemical order and so of the tetragonal distortions. The value of the threshold field goes down and, finally, at some concentration, spontaneous transition to the rhombohedral (or nearly rhombohedral) phase takes place.

At intermediate PT concentrations regular nanodomain are formed.
PMN TA phonons (22q)&(11q)

- Temperature evolution of TA phonon signal in PMN near (220) and (110) points
PMN Dispersion curves

\[ E, \text{THz} \]
\[ q, a^* \]
PMN

Q-const scans at large energies

● Lineshapes of high-energy phonons in PMN at T=12K

09.02 – 11.02. 2004

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Williamsburg 2004
PMN $Q=(4 \zeta \zeta)$
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