

Demonstration of spin-phonon coupling in infrared and THz spectra of $\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3$ and $\text{Sr}_{1-x}\text{Ba}_x\text{Mn}_{1-y}\text{Ti}_y\text{O}_3$ ceramics

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Spin-phonon coupling has been investigated in several materials because it is used to probe and design new multiferroics.¹ Importance of the spin-phonon coupling was emphasized for example in EuTiO_3 where ferroelectricity and ferromagnetism have been induced in epitaxial strained thin films,^{1,2} although the bulk EuTiO_3 is a quantum paraelectric antiferromagnet. Recent first principles calculations predicted a large spin-phonon coupling in various manganites, chromides and ferrites with perovskite structure,³ so these materials can theoretically become new bulk multiferroics with appropriate doping or as thin films under strain.

In this work, we focus on polycrystalline $\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3$ ($x=0, 0.4, 0.43$ and 0.45) and $\text{Sr}_{1-x}\text{Ba}_x\text{Mn}_{1-y}\text{Ti}_y\text{O}_3$ ($x=0.5$ and 0.6 and $y=0.06$ and 0.1) perovskites for which we demonstrate phonon anomalies near ferroelectric and antiferromagnetic phase transitions. Pure SrMnO_3 crystallizes in cubic perovskite $Pm\bar{3}m$ crystal structure and exhibits magnetic phase transition to antiferromagnetic G-type phase near 230 K.⁴ Close to this temperature, the 23% hardening of the lowest-frequency phonon was revealed in the IR spectra due to spin-phonon coupling.⁵ Although SrMnO_3 is paraelectric down to liquid He temperatures, recent first principles calculations predicted that system can become ferroelectric and even ferromagnetic under a biaxial strain.⁶ Neither strain-induced ferroelectricity nor ferromagnetism have been confirmed experimentally in SrMnO_3 thin films but Sakai et al.⁷ expanded the SrMnO_3 lattice with Ba substitution and successfully induced ferroelectricity in $\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3$ ($x \geq 0.45$) crystals at $T_C \approx 400$ K while Néel temperature of $T_N \approx 180$ K is the same. Important fact is that in this case the large spontaneous polarization ($P_S \approx 13 \mu\text{C}/\text{cm}^2$) is driven by displacement of magnetic Mn^{4+} cations, so exceptionally strong magnetoelectric coupling is expected and should be verified.

Initially we performed low frequency (100 Hz – 1 MHz) and microwave (1 MHz – 1.8 GHz) dielectric studies on $\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3$ ceramics ($x=0.4, 0.43$ and 0.45). Unfortunately, leakage current strongly influenced the dielectric measurements and therefore a giant permittivity was observed in these compounds above 100 K. Conductivity was strongly reduced in THz and completely suppressed in IR spectra. THz permittivity exhibits a step up on cooling below T_N confirming the strong spin-phonon coupling in these ceramics. Moreover, IR spectra of $\text{Sr}_{0.55}\text{Ba}_{0.45}\text{MnO}_3$ reveal phonon anomalies near 350 K supporting ferroelectric phase transition observed already in structural studies with X-ray and neutron diffractions.^{7,8}

Hopping conductivity is expected to be strongly reduced by Ti doping. For that reason we investigated $\text{Sr}_{1-x}\text{Ba}_x\text{Mn}_{1-y}\text{Ti}_y\text{O}_3$ (SBMTO) samples. Dielectric spectra in the kHz range still show a giant permittivity in paramagnetic phase, but decrease by several orders of magnitude was observed in conductivity and permittivity of SBMTO at Néel temperature near 170 K. Microwave permittivity and conductivity remains influenced by hopping conductivity, nonetheless permittivity of $\text{Sr}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.94}\text{Ti}_{0.06}\text{O}_3$ exhibits a peak at ferroelectric phase transition near 400 K. Ferroelectric phase transition is seen as well in phonon permittivity (see Figure 1) obtained from fits of the THz and IR reflectivity spectra. Moreover, phonon permittivity exhibits significant increase on cooling below T_N , evidencing the presence of spin-phonon coupling. Spectra of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Mn}_{0.9}\text{Ti}_{0.1}\text{O}_3$ did not reveal a ferroelectric phase transition, however the manifestation of spin-phonon coupling was still present in phonon permittivity near T_N . No change of

THz permittivity of SrMnO_3 and $\text{Sr}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.94}\text{Ti}_{0.06}\text{O}_3$ ceramics was observed in external magnetic field up to 7 T. It indicates that magnetodielectric effect is quite small for the G-type antiferromagnetic phase despite of huge spin-phonon coupling present in investigated ceramics.

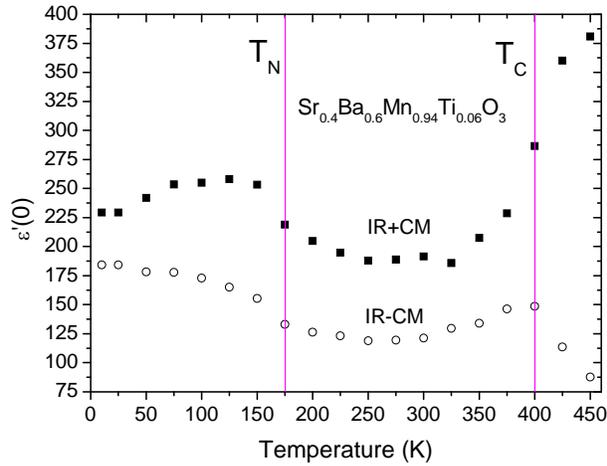


Figure.1 Temperature dependence of static permittivity of $\text{Sr}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.94}\text{Ti}_{0.06}\text{O}_3$ obtained from the fits of phonon spectra measured in THz and IR range. Dielectric relaxation of central mode (CM) presented below phonon frequencies comes from lattice anharmonicity as well as from hopping conductivity mostly at higher temperatures.

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