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Study of surface acoustic phonon modes in relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$

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Surface acoustic phonon modes in pelletized polycrystalline $Pb(Mg_{1/3}Nb_{2/3})O_3$ are investigated in the frequency range from 5 to 40 cm^{-1} at various temperatures from 25 to 550 °C. These spectra support the hypothesis of the core-shell nanoclusters with 1:1 ordered, negatively charged nanocore surrounded by the charge compensating positively charged disordered nanoshell. These surface acoustic modes exist even up to 550 °C revealing the existence of the charged core-shell nanoclusters which is well beyond the dissolution temperature of the polar clusters in the material. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1776328]

The complex perovskite lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), is one of the most important relaxor types of ferroelectric materials due to its high dielectric constant, large piezoelectric and pyroelectric coefficients. The dielectric dispersion of PMN is characterized by a broad, frequency dependent dielectric maxima where the temperature of maximum dielectric permittivity shifts to the higher temperatures with increase in frequency.[1] X-ray and neutron diffraction studies indicate that the average symmetry of this compound is cubic over a wide temperature range with the existence of nanometer sized polar clusters of local rhombohedral $R3m$ symmetry.[2–4] The dielectric response of relaxor ferroelectric materials is viewed as the relaxation of these polar clusters over a wide temperature and frequency range. These polar clusters dissolve at about 325 °C, which is well above the diffuse phase transition temperature. High resolution electron microscopic studies revealed the existence of the nanometer 1:1 ordered domains created by periodic alteration between Mg and Nb ions on the octahedral site of the perovskite structure whose composition is $Pb(Mg_{1/2}Nb_{1/2})O_3$.[5–7] The size of the 1:1 ordered nanoclusters is estimated to vary between 2 and 6 nm at room temperature.[5,7] The 1:1 ordered nanoclusters carry net negative charge and to maintain overall charge neutrality, it has been proposed that an equal and oppositely charged Nb^{5+}-rich disordered matrix with the composition $PbMg_{1/4}Nb_{3/4}O_3$ should be present.[6] Boulesteix *et al.*[6] proposed a plum-pudding kind of a model where the 1:1 ordered, charged nanoclusters are embedded in Nb^{5+}-rich disordered matrix.

Raman scattering is the appropriate technique to study characteristic properties associated with the nanoscale regions. There have been many reports on the Raman active optical phonon modes of PMN.[8–12] All these studies show the appearance of Raman active optical phonon modes from 1:1 ordered, charged nanoclusters. One of the characteristic properties associated with the nanosized clusters is to exhibit surface acoustic phonon modes. It is well known that metallic and semiconductor nanoparticles dispersed in an insulating matrix like glass exhibit confined acoustic phonon modes.[13,14] In this letter, we report surface acoustic phonon modes arising from the 1:1 ordered, charged nanoclusters and the positively charged nanoshells surrounding these nanoclusters in PMN at various temperatures from 25 to 550 °C.

A polycrystalline sample of PMN with density exceeding 96% of the theoretical density prepared by the Swartz–Shrout method[15] was used in this study. X-ray diffraction analysis of the sintered pellet was carried out to confirm the formation of pure perovskite phase of PMN. For recording Raman spectra, one side of the pellet was finely polished with 0.25 μm diamond paste and subsequently heat-treated at 500 °C for 5 h to remove the residual surface stress left from polishing.

Polarized and depolarized Stokes and anti-Stokes Raman spectra were recorded using 488 and 514.5 nm lines of an Ar-ion laser covering the frequency range 5–40 cm^{-1} in the backscattering geometry using double grating monochromator (SPEX 14018) and PMT (FW ITT 130) with a resolution of 1.4 cm^{-1} at 25, 200, 350, and 550 °C. The spectra were fitted with Lorentzian functions for the Raman modes and an exponential background for the Rayleigh tail.

X-ray diffraction (XRD) pattern of PMN (STOE, Germany) confirmed the formation of pure perovskite PMN phase with cubic structure. A faint superlattice peak at $2\theta = 19°$ corresponding to 1:1 ordered, charged nanoclusters could be observed. The size of the nanoclusters as estimated from the width of the 19° 2θ peak using Debye–Sherrer formula is about 2 nm and is in agreement with that reported using TEM.[5] Low frequency dielectric dispersion studies on our sample confirm the relaxor nature of the compound.

$V-U$ (V for vertically polarized incident beam and U for unpolarized scattered light) polarized Stokes and the anti-Stokes Raman spectra of PMN in the low frequency range 10–25 cm^{-1} are shown in Figs. 1 and 2, respectively. The Stokes spectra show peaks at 14.0 and 18.1 cm^{-1} (a), 13.5 and 17.6 cm^{-1} (b), and 14.5 and 18.8 cm^{-1} (c) when the measurement was carried out at various spots. The anti-Stokes spectra show peaks at −14.2 cm^{-1} (a), −11.4 cm^{-1} (b), and −10.8, −14.2, and −19.5 cm^{-1} (c) when measured at different spots. The depolarized ($V-H$) Raman spectra did not show any peak in this region.

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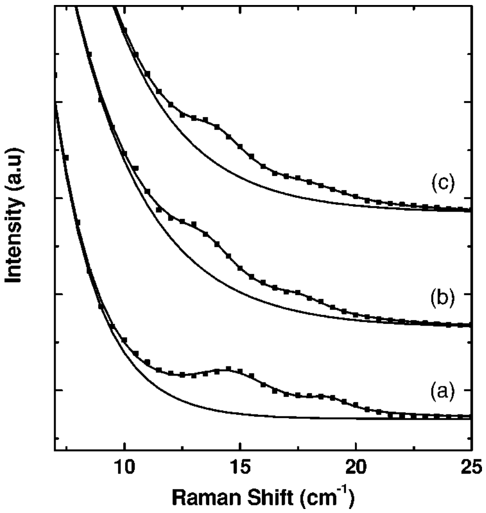

FIG. 1. $V-U$ polarized Stokes Raman spectra of PMN at 25 °C at different spots (a), (b), (c). Dots are experimental data and the solid lines are the fit. The exponential background is given for clarity.

The low frequency Raman scattering from a nanosized cluster is considered to be due to an elastic vibration of the nanocluster itself. This corresponds to torsional and spheroidal modes of vibrations of a spherical or an ellipsoidal cluster. Spheroidal mode of vibration strongly depends on the cluster material through v_t and v_l, the transverse and longitudinal acoustic velocities, respectively. These modes are characterized by two indices l and n, where l is the angular momentum quantum number and n is the branch number. $n=0$ represents surface acoustic modes and $n \geqslant 1$ represents inner modes. It has been shown that the spheroidal modes with $l=0,2$ are Raman active and torsional modes are Raman inactive.[16,17] The mode with $l=2$ appears both in polarized and depolarized geometries whereas the mode with $l=0$ appears only in the polarized geometry. The Raman peak frequencies of the spheroidal surface acoustic modes $(n=0)$ can be expressed as

$$\omega_s^0 = \xi_0 \frac{v_l}{dc}, \quad \omega_s^2 = \xi_2 \frac{v_t}{dc}, \tag{1}$$

where ω_s^0 and ω_s^2 are the peak frequencies of the spheroidal modes with $l=0$ and 2, respectively, d is the diameter of the particle, and c is the velocity of the light in vacuum. ξ_0 and ξ_2 are the characteristic constants. In the present study, the modes are detected only in the polarized $V-U$ geometry indicating that the modes correspond to the surface acoustic phonon vibrations for $l=0$.

In order to explain the observed features of the surface acoustic phonon modes, we propose the following core-shell model. Negatively charged 1:1 nanoclusters are present in the sample as evidenced by our x-ray diffraction pattern. In order to compensate the charge of the nanocluster, a positively charged nanoshell surrounds each nanocluster. The proposed core-shell model presents two interfaces; one between the core and the shell and another between the shell and the outer disordered cubic phase of PMN. The first interface separates the negatively charged core and the positively charged shell. The second interface separates the positively charged shell and the neutral outer medium. We attribute two modes in Fig. 1 to $l=0$ acoustic modes arising from these interfaces, one from each interface.

The surface acoustic phonons near these two interfaces can give rise to Raman modes. Hence, a particular core-shell can result in two Raman modes in the low frequency regime. Since the composition of core phase and shell phase are definite, the size of the shell is fixed for any size of the core. Hence, the ratio of the core diameter to the shell outer diameter is fixed. Let ω_1 be the frequency of the mode at the interface between the positively charged shell and the disordered outer medium (outer interface) and ω_2 be the frequency of the mode at the interface between the negatively charged 1:1 ordered region and charge compensating positively charged shell (inner interface). The mode frequencies 13.5, 14, and 14.5 cm^{-1} in Figs. 1(a)–1(c) might arise from the outer interface while the mode frequencies 17.6, 18.1, and 18.5 cm^{-1} might arise from the inner interface. The ratio between these frequencies is 1.3±0.1 in all three spectra of Fig. 1. Thus,

$$\omega_2/\omega_1 = \{(\xi_{02}V_{12})/(\xi_{01}V_{11})\}(d_1/d_2) = 1.3, \tag{2}$$

where 1 and 2 represent outer and inner interfaces, respectively. Duval *et al.*[16] determined the nanocluster size from the measured surface acoustic Raman mode frequency. It is difficult to determine V_{11}, V_{12}, V_{t1}, and V_{t2} in our core-shell nanocluster. Since ξ_{01}, ξ_{02} and V_{11} and V_{12} are unknown quantities at present, it is not possible to find out the diameters of the core-shell structure. d_1 might be about 2 nm as estimated from 19° 2θ XRD width. ω_1 and ω_2 differ a little from spot to spot on the sample due to the possible variation in the cluster size. Anti-Stokes Raman spectra in Fig. 2 show ω_1 in (a) and (c), ω_2 in (c), and a new mode at around -11 cm^{-1} in (b) and (c). ω_2 mode might be very weak in (a) and (b). The new mode might be from either of the interfaces in another cluster size present in that region of the sample.

$V-U$ polarized Raman spectra at 350 and 550 °C are shown in Fig. 3. Three peaks at 13.7, 16.2, 19.2 cm^{-1} and 14.5, 17.9, 21.4 cm^{-1} can be detected at these temperatures, respectively. Among these peaks, the lowest frequency peak might be ω_1, the next ω_2, and the highest frequency peak would be a new mode. ω_2/ω_1 comes out to 1.18 and 1.23 at

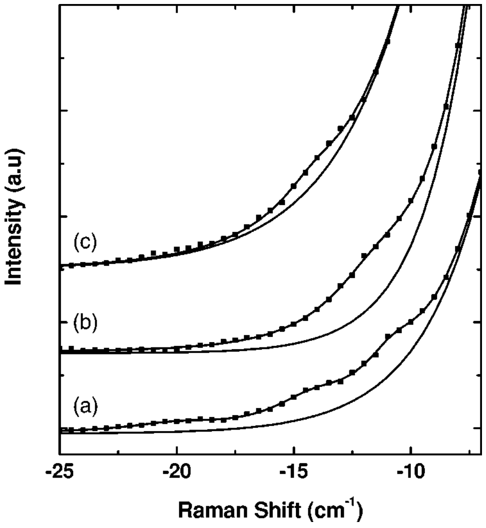

FIG. 2. $V-U$ polarized anti-Stokes Raman spectra of PMN at 25 °C at different spots (a), (b), (c). Dots are experimental data and the solid lines are the fit. The exponential background is given for clarity.

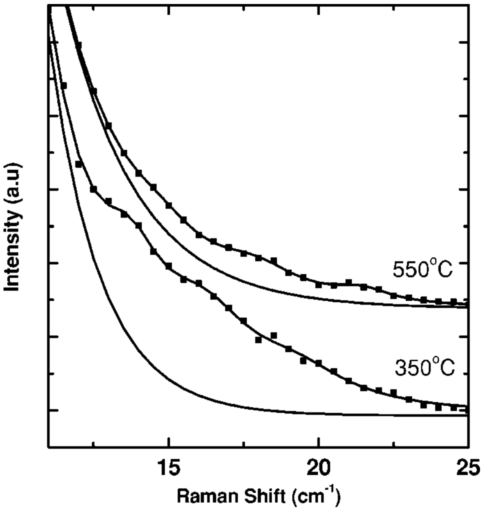

FIG. 3. $V-U$ polarized Stokes Raman spectra of PMN at 350 and 550 °C. Dots are experimental data and the solid lines are the fit. The exponential background is given for clarity.

350 and 550 °C, respectively, due to the possible changes in ξ, V, and d parameters at high temperatures. The new mode might be due to another cluster size that would have been present in the observed region of the sample. This indicates that the 1:1 ordered nanoclusters have not dissolved even at 550 °C. This is also supported by the existence of optical Raman modes at this temperature.[11]

Raman studies of the surface acoustic phonon modes arising from 1:1 ordered, charged nanoclusters and the charge compensating disordered shells were carried out in relaxor ferroelectic $Pb(Mg_{1/3}Nb_{2/3})O_3$. The size of the 1:1 ordered, charged nanocluster from the x-ray diffraction is estimated to be about 2 nm. Surface acoustic Raman modes have been detected in the frequency range 5–25 cm^{-1}. These low frequency modes arise from two different interfaces; one between the 1:1 ordered charged nanoclusters and the surrounding positively charged nanoshell and another between the nanoshell and the outer disordered cubic phase of PMN. These core-shell nanoclusters exist even up to 550 °C.

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