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Temperature Dependent Raman Spectra of $Rb_{1-x}(ND_4)_xD_2AsO_4$ Mixed Crystals

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The Raman spectra (50-1000 cm^{-1}) of B_2-$y(xy)x$ symmetry have been measured as a function of temperature (80-300 K) in the mixed ferroelectric-antiferroelectric system $Rb_{1-x}(ND_4)_xD_2AsO_4$ (D*RADA-x) for ammonium concentrations x = 0.55, 0.69 and 1.0. As temperature decreases, x = 0.55 and 0.69 begin to show similar B_2 spectra with the pure D*ADA. It reveals that x = 0.55 and 0.69 possess an antiferroelectric order in the low-temperature region. The stretching modes ν_1 (near 755 cm^{-1}) of the AsO_4 group and the in-plane bending modes δ(O-D) (near 824 cm^{-1}) of x = 0.55 and 0.69 exhibit a gradual softening and hardening with decreasing temperature, respectively. These phenomena may relate to the formation of phase coexistence of antiferroelectric and paraelectric clusters.

I. INTRODUCTION

In the mixed ferroelectric (FE)-antiferroelectric (AFE) system $A_{1-x}(ND_4)_xD_2BO_4$ [A=Rb (or K, Cs) and B=As (or P)], there is competition between the FE and the AFE orderings, each characterized by specific configurations of the acid deuterons. [1–8] The random distribution of the Rb and ND_4 ions is the main source to produce frustration which can increase local structural competition such that the long-range order of electric dipole disappears. Instead of a typical sharp FE or AFE phase transition, the phase coexistence becomes a characteristic in this type of mixed compounds.

By a group theoretical analysis for the KDP-type structure (which contains two molecular units in a primitive unit cell); at zero wavevector, the vibrational modes in the tetragonal symmetry (space group $I\bar{4}2d - D_{2d}^{12}$) can be decomposed into the following irreducible representations: $\Gamma_{\mathrm{vib}} = 4A_1(R) + 5A_2(\mathrm{Silent}) + 6B_1(R) + 6B_2(R, IR) + 12E(R, IR)$. [9] The symmetry species A_1, B_1, B_2 and E are Raman active. The situation in the mixed system D*RADA-x is more complicated than one in the parent crystals, because some Rb (or ND_4) ions have been substituted by ND_4 (or Rb) ions. In this case, the selection rule of the free AsO_4 group is expected to be broken much easily than in the pure crystal.

In the recent years, many measurements in D*RADA-x system have been achieved on ferroelectric-side crystals x = 0.1, 0.10 and 0.28. [2–5] However, only a few experiments were done on antiferroelectric-side compounds ($x \geq 0.50$). [6,7] A complete understanding for this mixed system is still lacking. This motivated us to carry out the polarized Raman scattering on D*RADA-0.55, 0.69 and 1.0. Here, we pay special attention to the stretching mode ν_1 (near 755 cm^{-1}) and the in-plane bending mode δ(O-D) (near 825 cm^{-1}).

II. EXPERIMENTAL PROCEDURE

Single crystals of $Rb_{1-x}(ND_4)_xD_2AsO_4$ (x = 0.55, 0.69 and 1.0) were grown from aqueous solutions with certain ratios of RbD_2AsO_4 (D*RDA) and $ND_4D_2AsO_4$ (D*ADA) by slow evaporation of D_2O in atmosphere of argon gas. The ND_4 concentrations were determined from the ratio of Rb and N atoms by X-ray photoelectron spectroscopy (XPS). The green light with λ = 514.5 nm from an argon ion laser was used as an excitation source. A double grating monochromator equipped with a water cooled PMT detector was used. Right- angle spectra were taken from scattering geometry $y(xy)x$ which corresponds to the B_2 symmetry. Here x and y relate to the crystal a-, and b-axes, respectively. The damped harmonic oscillator model was used to fit the spectra, from which the Raman shifts were obtained, i.e. [10]

$$S(\omega) = \frac{\chi_0 \Gamma \omega \omega_0^2}{(\omega^2 - \omega_0^2)^2 + \Gamma^2 \omega^2} \cdot \frac{1}{1 - e^{-\hbar\omega/kT}}, \qquad (1)$$

where ω_0 and Γ correspond to the frequency shift and half-width, respectively. χ_0 is the susceptibility constant (in arbitrary units), k is Boltzmann's constant and T is absolute temperature.

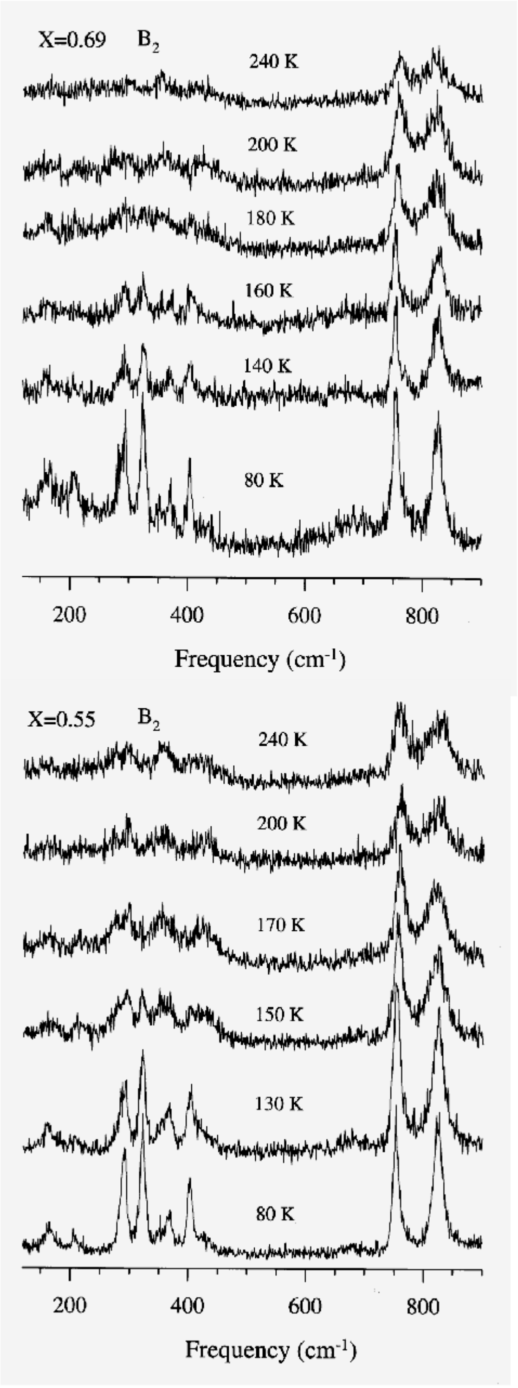

Fig. 1. Temperature-dependent Raman spectra of D*RADA - (a) $x = 0.69$, and (b) $x = 0.55$ measured from the B_2-$y(xy)x$ geometry between 50-1000 cm^{-1}.

III. RESULTS AND DISCUSSION

Actual temperature-dependent B_2-$y(xy)x$ Raman spectra are shown in Figs. 1(a)-1(b) for $x = 0.69$ and 0.55, respectively. Both compounds display similar Raman spectra and high scattering efficiency in the high-frequency region (720-850 cm^{-1}). The main Raman lines observed from the B_2 configuration are at frequencies near 290, 320, 400, 760 and 820 cm^{-1}.

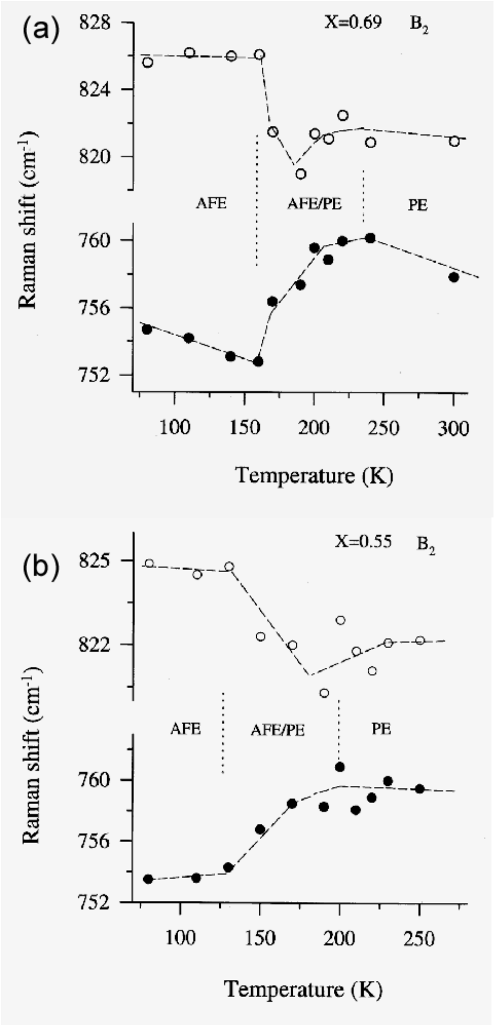

Fig. 2. Frequency vs. temperature variations of two Raman vibrations (measured from the B_2 symmetry) of D*RADA-(a) $x = 0.69$, and (b) $x = 0.55$. These two modes correspond to the in-plane bending mode δ(O-D) (near 822 cm^{-1}) and the stretching mode ν_1 (near 755 cm^{-1}) of the AsO_4 group. The dashed lines are guides for the eye and the dotted lines are the estimates of various phase boundary.

The temperature dependences of the in-plane bending mode δ(O-D) (near 825 cm^{-1}) and the stretching mode ν_1 (near 760 cm^{-1}) of the AsO_4 group from the B_2 symmetry for $x = 0.69$ and 0.55, are plotted in Figs. 2(a)-2(b), respectively. As temperature decreases, the δ(O-D) modes of both $x = 0.55$ and 0.69 show a slight softening followed by a notable hardening. Instead of a hardening, the stretching modes ν_1 (near 760 cm^{-1}) of both samples display a softening and reach a turning point at $T \sim 130$ K (for $x = 0.55$) and $T \sim 160$ K (for $x = 0.69$).

Figure 3 is a comparison of the B_2 spectrum including the pure D*ADA in the low-temperature region. The

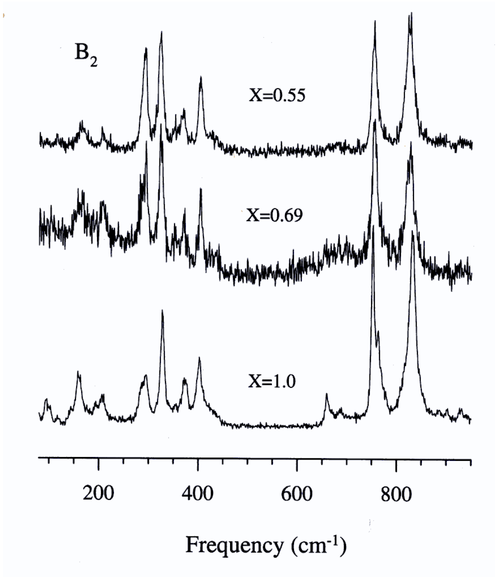

Fig. 3. Raman spectra of the B_2-$y(xy)x$ symmetries measured at 80 K (for $x = 0.69$ and 0.55) and 100 K (for D*ADA).

symmetric stretching mode ν_1 (near 750 cm^{-1}) of the AsO_4 group is non-degenerate with only A_1 symmetry. [11] However, as shown in Figs. 3, the leakage of the ν_1 mode into the B_2 symmetry is practically as strong as the allowed vibrations. The ν_1 leakage which occurs in B_2 configuration is possible as the result of the lowering of local symmetry of the AsO_4 groups from S_4 to C_2 or even to C_1.

What are the origins of these temperature-dependent phenomena shown in Figs. 2(a)-2(b)? With decreasing temperature, the stretching mode ν_1 (near 755 cm^{-1}) of $x = 0.69$ begins a gradual softening at $T \sim 240$ K and then reaches a minimum at $T \sim 160$ K. The ν_1 mode is sensitive to the deuteron ordering near the AsO_4 group. If the deuteron arrangement modulates with the temperature, the mass and force constants of the D_2AsO_4 group will be changed and thus influence the ν_1 frequency. As shown in Fig. 3, $x = 0.69$ has a similar Raman pattern with the pure D*ADA in the low-temperature region. This similarity proves that $x = 0.69$ possesses an AFE phase below certain temperature. The ν_2 mode (near 325 cm^{-1}) which is the strongest component in the low-frequency region (<500 cm^{-1}) for D*ADA, shows up apparently at $T \sim 160$ K. Thus, one can conclude that an AFE phase transition takes place at $T \sim 160$ K in $x = 0.69$. The progressive softening (which begins at $T \sim 240$ K) in the ν_1 mode may imply a gradual growth of the AFE ordering (or a formation of AFE/PE phase coexistence). The freezing-in of the Rb ion reorientations which can increase local structural competition (between FE and AFE orderings) should be responsible for this anomaly.

As shown in Fig. 2(b), a smoother softening in the ν_1 mode was observed in $x = 0.55$. This gradual declining behavior occurs from $T \sim 200$ K and reaches a turning point at $T \sim 130$ K. In addition, the δ(O-D) mode exhibits a hardening that turns into a flat curve near 130 K. As seen in Fig. 3, $x = 0.55$ has almost the same B_2 Raman spectra with the pure D*ADA in the low-temperature region. This similarity reveals that the low-temperature phase ($T < -130$ K) of $x = 0.55$ must be associated with the AFE order. The ν_2 mode (near 325 cm^{-1}) also grows dramatically at $T \sim 130$ K and becomes the dominant peak in the low-frequency region. Thus, we conclude that $x = 0.55$ possesses an AFE phase at $T \leq\sim 130$ K. The softening (in the ν_1 mode) that begins at $T \sim 200$ K may connect to the evolution of AFE/PE phase coexistence as $x = 0.69$.

IV. CONCLUSIONS

From the temperature-dependent Raman spectra of D*RADA-1.0, 0.69, and 0.55, it has been revealed that both $x = 0.69$ and 0.55 possess an AFE order at $T <\sim 160$ K and $T <\sim 130$ K, respectively. A formation of AFE/PE phase coexistence may explain the gradual softening (which begins at $T \sim 240$ K in $x = 0.69$ and $T \sim 200$ K in $x = 0.55$) in the ν_1 mode.

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