Phase transitions in sodium–bismuth titanate

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The high-temperature phase transitions in $Na_{0.5}Bi_{0.5}TiO_3$ have been studied by neutron scattering. The transition at 813 K results from the condensation of a soft mode at the M point, while the diffuse transition at 600 K results from the condensation of the R_{25} mode and, simultaneously, from the disappearance of the superstructure which arose previously.

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The $Na_{0.5}Bi_{0.5}TiO_3$ crystal has the perovskite structure in its high-temperature phase (at $T > 813$ K). As the crystal is cooled to room temperature, it undergoes two

phase transitions: a first transition at 813 K and a second, diffuse transition over the interval 620–470 K. On the basis of optical measurements of the domain structure[1,2] it is believed that the crystal becomes tetragonal after the first of these transitions and rhombohedral after the second.

In this letter we are reporting a study of the phase transitions in this crystal by neutron scattering. All the measurements were carried out with the Neĭtron-3 spectrometer, installed in a VVR-M water-cooled, water-moderated fission reactor; the energy of the incident neutrons was constant at[3] 14 MeV. As a monochromator we used (002) pyrolytic graphite, and as analyzer we used a (111) copper single crystal or, in several cases, plastically deformed germanium. The sodium-bismuth titanate single crystal had a volume of 1.5 cm^3, and its tendency toward a mosaic structure was less than 15′, according to measurements with a γ diffractometer. During the measurements the sample temperature was regulated within ±1°.

We found that a superstructure arises at the $(h+1/2, k+1/2, l)$ points at the phase transition at 813 K. This superstructure results from the condensation of a soft mode at the M point of the cubic Brillouin zone. Comparison of the measured and calculated intensities of the quasielastic neutron scattering at the M point shows that the condensing mode is the mode[4] M_3, which corresponds to rotations of the oxygen octahedra around one of the axes of the cubic lattice. Figure 1a shows curves of the inelastic neutron scattering at the (3/2, 1/2, 0) point of the reciprocal lattice, according to measurements at various temperatures. At 1000 K we see two

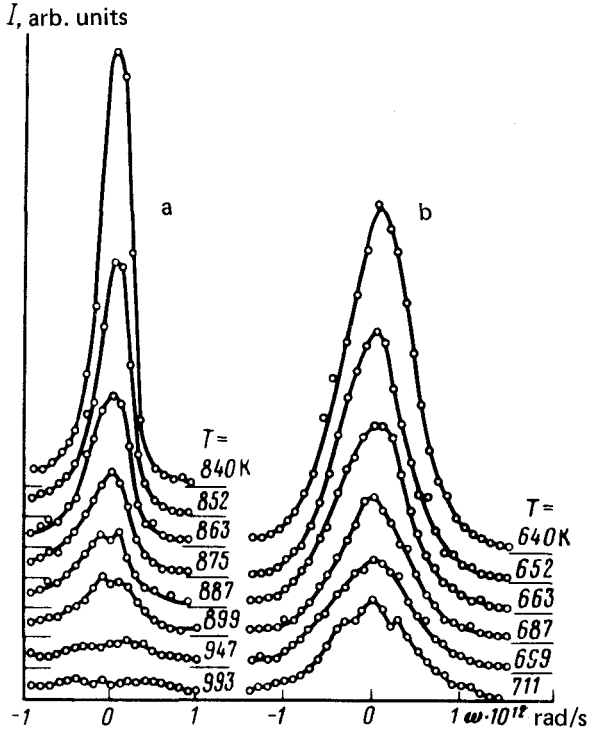

FIG. 1. Temperature dependence of the quasielastic neutron scattering. a—At the M point, (3/2, 1/2, 0); b—at the R point, (3/2, 1/2, 1/2), of the cubic Brillouin zone.

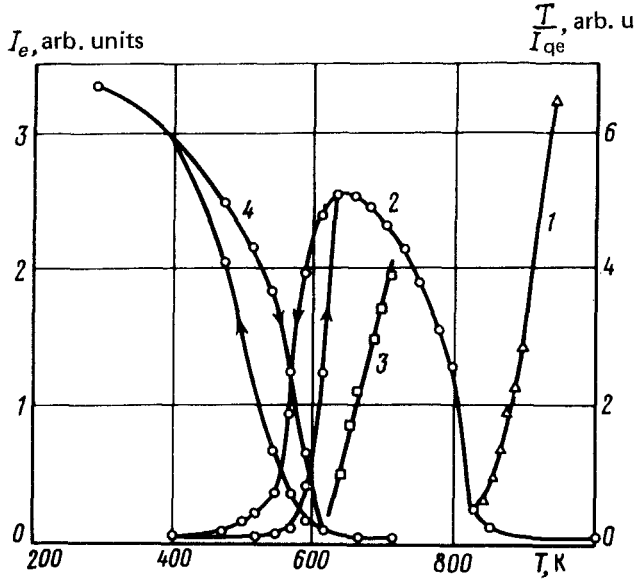

FIG. 2. Temperature dependence of the intensity of the superstructural reflections observed at the boundary of the Brillouin zone at the M point (curve 2) and at the R point (curve 4) and temperature dependence of T/I at the M point (curve 1) and at the R point (curve 3).

resolved peaks, which correspond to the creation and annihilation of a phonon. As the phase transition is approached, the phonon energy decreases, and eventually a temperature is reached at which we observe a single quasielastic-scattering peak. At the phase transition, the quasielastic scattering converts into a superstructural reflection. Curve 2 in Fig. 2 is the temperature dependence of the intensity of this superstructural reflection. As the temperature is lowered from 813 K, at which the superstructure arises, the superstructure disappears; at the same time, a superstructure of the $(h+1/2, k+1/2, l+1/2)$ type arises. This new superstructure was found to result from the condensation of the R_{25} mode. Figure 1b shows curves of inelastic neutron scattering at the (3/2, 1/2, 1/2) point of the reciprocal lattice to illustrate the softening of this phonon mode; Fig. 2 (curve 4) shows the temperature dependence of the intensity of the corresponding superstructural reflection. Also shown in this figure is the temperature dependence of the quantity $T/I \sim \omega^2$, where ω is the phonon frequency, T is the absolute temperature, and I is the integrated intensity of the quasielastic scattering at the R and M points. According to the Curie-Weiss law, the function $T/I = f(T)$ should conform to a straight line which intersects the abscissa at the point $T = T_c$, where T_c is the internal dynamic temperature of the phase transition. From Fig. 2 we see that at small values of the difference $T - T_c$ there is a deviation from this linear behavior for the point R.

The sequence of phase transitions which were observed in the present experiments and which are related to the softening of the M_3 mode and then of the R_{25} mode has also been observed for other perovskites.[4-6] Usually, however, the transition accompanied by the softening at the R point does not lead to the disappearance of the superstructure which arose as a result of the preceding transition at the M point.

Another distinctive feature of this second phase transition is that in its vicinity we observe no anomalies at the X points of the cubic zone; after the M_3-mode transition, these points should become equivalent to the R point. After the transition to the tetragonal phase, the R_{25} mode splits into a doubly degenerate Z_5 mode and a nondegenerate Z_1 mode. The Z_1 mode is related to a rotation of the oxygen octahedra around the same axis of the cubic phase as was involved in the M_3-mode transition, while Z_5 is related to rotations around other principal axes. Since the transition from the tetragonal phase in the perovskites which have been studied previously results from the softening of this Z_5 mode, it may be suggested that this phase transition in sodium-bismuth titanate is caused by condensation of the Z_1 mode. Further support for this suggestion comes from measurements with a conoscope, which show that the sodium-bismuth titanate crystal becomes uniaxial at room temperature.

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