RAMAN SCATTERING FROM Ce: BaTiO₃ SINGLE CRYSTAL

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Abstract: Raman scattering from single crystal Ce:BaTiO₃ was investigated from room temperature to 180°C. By comparing with BaTiO₃ and Mn ion-implanted Ce:BaTiO₃, it is determined that the Raman spectra of Ce:BaTiO₃ are identical to BaTiO₃ for peak frequency, line shape and relative intensity. On the other hand, the implantation of Mn ions into Ce:BaTiO₃ broadens two A₁(LO) broad peaks. Based on the disappearance of the E(TO) modes in phase transition, their Curie temperatures T_C are determined. They decrease successively from BaTiO₃ to Ce:BaTiO₃ to Mn,Ce:BaTiO₃. This is consistent with the results of dielectric-constant measurements. We further discuss the persistence of the two asymmetric broad A₁(TO) peaks to the Cubic phase that are identified as first-order Raman scattering.

 $BaTiO_3$ crystal is a prototype ferroelectric material with non-hydrogen-bond and a simple perovskite structure. It exhibits ferroelectricity at room temperature with fairly stable chemical and mechanical properties[1]. It is one of the most extensively studied and widely applied ferroelectrics. Doping with impurities such as Fe, Co and Ce affects the efficiency, sensitivity, speed and spectral response of its photorefractive effect. Trace Ce doping improves the properties of $BaTiO_3[2]$. It is interesting to study the doping effects. In this letter, we study the Raman scattering and its temperature dependence of Ce doped $BaTiO_3$.

Single crystals were grown using the top-seeded-solution method witl1 a TiO₂-BaTiO₃ solution. For impurity doping 25 ppm Ce was added to melts. With x-ray diffraction orienting, we cut the crystals to cubes along < 100 > and polished all faces. They were polarized to single domain. The doping level was low but enough to affect considerably its properties. The implantation of Mn-ion was completed with an ion beam of energies 30-40 keV. The Mn ions were located at a depth $\le 1 \mu m$ from the surface and the maximum concentration was about 20 ppm. No annealing was made so as to preserve the lattice damage and structural defects. The sample is dark red.

The light scattering spectra were obtained using the 5l4.5 nm lines of an Ar ion laser, with 100 mW power. The Raman scattering was measured by a SPEX-l4O3 system. The scanning range was $100 - 900 \text{ cm}^{-1}$ with increment of 1 cm⁻¹ and temperature range was from room temperature to 180 °C using a home-made heater with accuracy better than 0.01 °C.

At room temperature, BaTiO₃ are in the tetragonal phase (C_{4V}). BaTiO₃ has a phase transition at $T_C = 131^{\circ}C$, where it changes from a cubic high-temperature phase belonging to the Pm3m space group to a ferroelectric tetragonal phase belonging to P4mm[3]. Low-level impurity does not change the symmetry of the crystal (x-ray diffraction). Thus there are 8 Raman active modes which can be classified as $3A_I + B_I + 4E$ in Ce:BaTiO₃. Right-angle polarized scattering geometry

shows vibrational modes $A_1(TO)$, $A_1(TO) + B_1$, $A_1(LO)$, E(TO), and E(LO) respectively.

The Ce:BaTiO₃ spectra for modes $A_1(TO)$ and E(TO) as functions of temperature from room temperature to 180 °C are shown in Figs. 1 and 2. All are normalized according to the room-temperature intensity to convenience comparison. The $A_1(TO)$ modes (Fig.1) and E(TO)modes (Fig.2) broaden with temperature and the positions either red shift slightly or change little. This is related to the anharmonicity of the lattice vibration. The E(TO) modes change drastically between 127 °C and 129 °C and disappear suddenly, showing that a tetragonal-to-cubic phase transition occurs. The Curie temperature T_C is thus determined 128 °C, 3 °C lower than pure BaTiO₃ (T_C =131 °C). However, the two strong broad $A_1(TO_1)$ and $A_1(TO_3)$ persist above T_C and their intensities increase with temperature, similar to BaTiO₃. The assertion that $A_1(TO)$ peaks disappear to two broad background features at T_C in forward scattering is hence premature.

Similarly, the spectra of Mn, Ce:BaTiO3 from room temperature to 180°C for the A₁(LO) and E(TO) modes show that all peaks weaken and broaden with temperature. Spectral lines drastically reduce from 124°C to 126°C and vanish, obeying the selection rules. It is thus determined that $T_C \sim 125$ °C, again 3°C lower than that of Ce:BaTiO₃.

In summary, the absorption-corrected Raman spectra of Ce:BaTiO₃ are identical to those of BaTiO₃ but Ce-doping lowers the Curie temperature by about 3°C. It shows that low-concentration doping of Ce does not noticeably change the structure and vibration of BaTiO₃ but lowers its structural stability. The two asymmetric broad A₁(TO) modes at 275 cm⁻¹ and 516 cm⁻¹ peaks are identified as disorder-induced first order scattering and they are sensitive to impurities or defects. We leave two crucial problems for further study, i.e. the doping dependence of the position and damping of the lowest E(TO₁) modes and the central relaxation peak.



Fig.1 Raman spectra of $Ce:BaTiO_3$ Fig.2 Raman spectra of $Ce:BaTiO_3$ measured in x(zz)y geometry at different measured in z(yz)x geometry at different temperature.

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