Optical and dielectric properties of quantum-confined SrBi$_2$Ta$_2$O$_9$ mesocrystals

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We report an increase in optical absorption peak energy from 3.9 to 5.3 eV, and a lowering of dielectric constant maximum temperature from 320 to 180 °C for SrBi$_2$Ta$_2$O$_9$ mesocrystals. © *1999 American Institute of Physics.* [S0003-6951(99)04746-4]

Size effects have been of great interest in the science and technology of ferroelectrics.[1] Yamada and Kohiki[2] have demonstrated the size effects, such as increasing the optical absorption energy and decreasing the dielectric constant maximum temperature, for pseudoisotropic BaTiO$_3$ perovskite ($a = 3.9920$, $b/a = 1.000$, and $c = 4.0361$ Å),[3] by using the mesopores of a molecular sieve. The molecular sieve has uniform columnar periodic hexagonal pores ranging 15–100 Å and separated by 8–9 Å walls.[4–6]

SrBi$_2$Ta$_2$O$_9$ is a promising material for fabrication of ferroelectric random access memory devices.[7] The crystal structure of SrBi$_2$Ta$_2$O$_9$ is anisotropic ($a = 5.512$, $b/a = 1.000$, and $c = 25.00$ Å),[8] and consists of both Sr–Ta–O perovskite blocks and Bi$_2$O$_2$ layers. By filling the mesopores of the molecular sieve with SrBi$_2$Ta$_2$O$_9$, we can realize an ordered array of uniform quantum wires of ferroelectrics with a larger dielectric constant separated by an amorphous SiO$_2$ wall with a lower dielectric constant. It is necessary to construct a high-density and multiple-value memory device by using isolated mesoclusters of dipole moments due to the variation of point symmetry of the unit cell and a scanning microprobe. We report on the optical and dielectric properties of SrBi$_2$Ta$_2$O$_9$ mesocrystals fabricated by using the molecular sieve with separated and uniform mesopores.

The molecular sieve used in this experiment was synthesized from a mixture of SiO$_2$ 1.00:n-dodecyltrimetylammonium bromide (C$_{12}$ TMAB) 0.70:NaOH 0.24:H$_2$O 53.7 in molar ratio. The mixture was stirred at room temperature and then heated at 140 °C for 48 h. After washing at 80 °C for 24 h and thermal dehydration at 80 °C for 24 h, the dried mixture was calcinated at 700 °C for 6 h in flowing oxygen to remove the organic molecules incorporated during the templating process from the mesopores. The x-ray diffraction pattern of the 700 °C calcinated molecular sieve can be indexed on a hexagonal unit cell with a ~39 Å ($a = 2d_{100}/\sqrt{3}$ and $d_{100} = 34$ Å) as shown in Fig. 1(a).

As described later, an inclusion of a SrBi$_2$Ta$_2$O$_9$ precursor in the pores of the molecular sieve is accomplished by soaking the molecular sieve in an ethanol solution of Sr, Bi, and Ta ions, and the soaked molecular sieve was calcinated at 800 °C. The 800 °C calcinated molecular sieve (*the molecular sieve sample*) depicted in Fig. 1(b), subjected to the same temperature program, is a reference for the soaked mo-

lecular sieve. As shown in Fig. 1(b), the molecular sieve sample retained its regular array structure, though the pores calculated from the (100) reflection angle shrank by approximately 8% (a~36 Å). It is well known that calcination at elevated temperature diminishes the pore size due to a certain restructuring of the walls. The pore size of the molecular sieve sample described below is estimated to be ~28 Å, since the reported wall thickness was 8–9 Å.[4–6]

The 700 °C calcinated molecular sieve was soaked in the SrBi$_2$Ta$_2$O$_9$ precursor solution, prepared by solving strontium oxalate monohydrate, bismuth chloride, and tantalum chloride into absolute ethanol, with a concentration of 0.005 mol/l, for 24 h with stirring. The soaked molecular sieve was dried and then heated in flowing oxygen at 800 °C for 3 h. As depicted in Fig. 1(c), *the soaked sample* corresponding to the SrBi$_2$Ta$_2$O$_9$ mesocrystals with the molecular sieve shows no x-ray diffraction peaks.

Powders of SrBi$_2$Ta$_2$O$_9$ obtained from the 0.005 mol/l precursor solution by drying and calcination at 800 °C showed the x-ray diffraction pattern [Fig. 1(d)] being in good
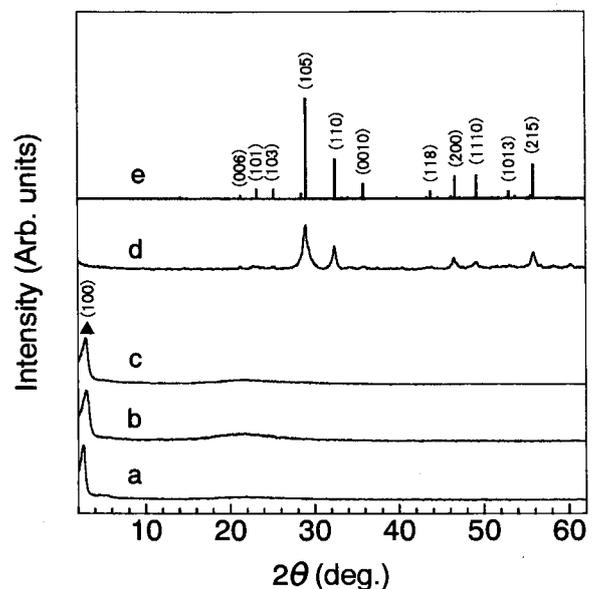

FIG. 1. X-ray diffraction patterns with Cu $K\alpha$ radiation of the molecular sieve calcinated at 700 °C (a), *the molecular sieve sample* calcinated at 800 °C (b), *the soaked sample* with 0.005 mol/l solution (c), *the* SrBi$_2$Ta$_2$O$_9$ *powders* from the solution (d), and the simulated pattern for the SrBi$_2$Ta$_2$O$_9$ crystal (e).
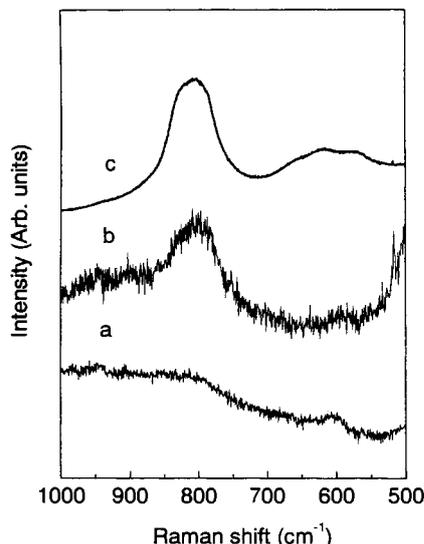
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FIG. 2. Micro-Raman spectra, excited with Ar$^+$ (514.5 nm and 300 mW) and observed in the backscattering geometry with a JASCO NR-1800 spectrometer, of the molecular sieve sample (a), the soaked sample with 0.005 mol/l solution (b), and the SrBi$_2$Ta$_2$O$_9$ powders from the solution (c).

agreement with a simulated one for reported crystal [Fig. 1(e)].[9] The crystalline size of the SrBi$_2$Ta$_2$O$_9$ *powders* was 150 Å, which was estimated from the full width at half maximum (FWHM) of the (105) reflection of Fig. 1(d) by using Scherrer's equation,[10]

$$D = K\lambda/(B \cos \theta),$$

where D is the crystalline size, K the Scherrer's constant of the order of unity for usual crystals,[10] λ the x-ray wavelength, B the FWHM of a diffraction peak, and θ is the diffraction angle. No x-ray diffraction peaks from the SrBi$_2$Ta$_2$O$_9$ crystals for the soaked sample suggests that SrBi$_2$Ta$_2$O$_9$ mesocrystals cannot preserve translational symmetry in both intra- and interpores of the molecular sieve, and also there is no SrBi$_2$Ta$_2$O$_9$ particles at the outside surface of the soaked sample.

Raman spectra of the samples (the molecular sieve sample, the soaked sample, and the SrBi$_2$Ta$_2$O$_9$ powders) shown in Fig. 2 revealed that the crystal structure of the SrBi$_2$Ta$_2$O$_9$ unit cell was formed even for the mesocrystals. The peak at around 800 cm^{-1} of the soaked sample [Fig. 2(b)] is obviously due to the SrBi$_2$Ta$_2$O$_9$ crystal structure[11] since at around 800 cm^{-1} the SrBi$_2$Ta$_2$O$_9$ powders showed a clear peak [Fig. 2(c)] but the molecular sieve sample gave no apparent structure [Fig. 2(a)]. The structures below 600 cm^{-1} and above 900 cm^{-1} of the soaked sample are complicated and reflect those from both the SrBi$_2$Ta$_2$O$_9$ powders and the molecular sieve sample. At present, there has been no experimental or theoretical reports on vibration-mode assignments of the Raman peaks for SrBi$_2$Ta$_2$O$_9$.

The molecular sieve sample showed no apparent absorption peak in the region from 3.0 to 5.5 eV, as seen in Fig. 3(a). The absorption peaks of the soaked sample and the SrBi$_2$Ta$_2$O$_9$ powders were observed at around 5.3 and 3.9 eV, respectively, as depicted in Figs. 3(b) and 3(c). The increase by 1.4 eV in the optical absorption peak energy for the mesocrystals from the particles is an evidence of the quantum-confinement effects.
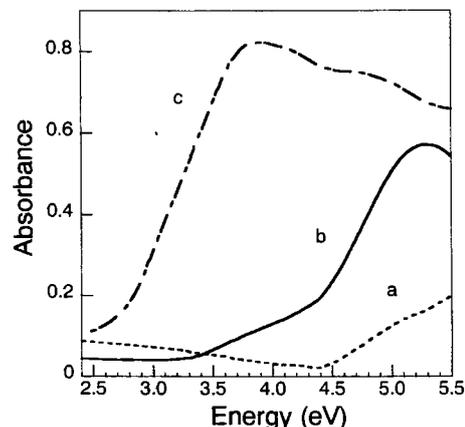

FIG. 3. Optical absorption spectra of the molecular sieve sample (a), the soaked sample with 0.005 mol/l solution (b), and the SrBi$_2$Ta$_2$O$_9$ powders from the solution (c).

The tight-binding calculation of the SrBi$_2$Ta$_2$O$_9$ crystal revealed that the valence-band maximum (VBM) at Γ arose from O p and some Bi s states, while the conduction-band minimum (CBM) at M consisted of Bi p states followed by Ta d states.[12] Both the VBM and CBM are states localized in the Bi$_2$O$_2$ layer. The observed blueshift of the optical absorption peak reflects a quantum-confined effect on the energy dispersion of the band electrons, especially localized in the Bi$_2$O$_2$ layer. A displacement of Ta in the perovskite block should be affected by the confinement as well as that of Bi in the Bi$_2$O$_2$ layer. In SrBi$_2$Ta$_2$O$_9$ the Ta–O bond is primarily responsible for the ferroelectricity, and the Bi–O bond is amplifying the ferroelectric dipole. Therefore, displacement restrictions for the Ta–O and Bi–O bonds in the *ab* plane should result in deterioration of the ferroelectric properties.

The dielectric constant of the pelletized samples (the molecular sieve sample, the soaked sample, and the SrBi$_2$Ta$_2$O$_9$ powders) were measured in the range from 20 to 450 °C at 100 kHz. The temperature dependences of dielectric constant of the molecular sieve sample, the soaked sample, and the SrBi$_2$Ta$_2$O$_9$ powders were different from each other, as shown in Fig. 4. From 100 to 450 °C the mo-
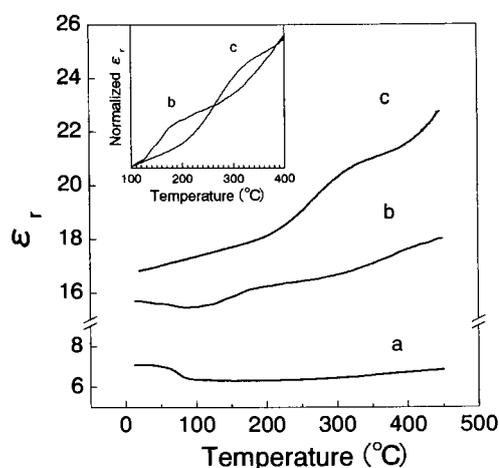

FIG. 4. Temperature dependence of relative dielectric constant of the molecular sieve sample (a), the soaked sample with 0.005 mol/l solution (b), and the SrBi$_2$Ta$_2$O$_9$ powders from the solution (c). Inset: normalized relative dielectric constant at from 100 to 400 °C.

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lecular sieve sample showed no apparent peaks in the dielectric constant lying at low level ($\epsilon_r \sim 7$). For the soaked sample [Fig. 4(b)] enlargements in the dielectric constant below 100 °C and above 300 °C are predominantly due to the matrix (the molecular sieve). As shown by the inset of Fig. 4, the soaked sample showed a dielectric constant maximum at around 180 °C, largely different from that of the $SrBi_2Ta_2O_9$ powders showing its maximum at around 320 °C. The decrease in the dielectric constant maximum temperature by 140 °C was observed for $SrBi_2Ta_2O_9$ mesocrystals. Lowering of the phase transition temperature with decreasing the crystalline size are generally recognized size effects.

For $SrBi_2Ta_2O_9$ mesocrystals formed by using uniform mesopores smaller than 28 Å of the molecular sieve, we showed the enlargement in the optical absorption peak energy by 1.4 eV and the decrease in the dielectric constant maximum temperature by 140 °C, due to quantum confinement.

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