Photoluminescence of transparent strontium–barium–niobate-doped silica nanocomposites

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Optically transparent nanocomposites of strontium–barium–niobate (SBN) and silica were fabricated via a novel sol–gel method. The nanocomposites were annealed in temperatures of 600–800 °C to yield the nanometer-sized tetragonal tungsten–bronze phase of SBN crystallites. Photoluminescence studies at temperatures from 10 K to room temperature were performed. The undoped silica matrix showed a strong emission band at 3.2 eV and a weak emission band at 2.65 eV. They were noticeably suppressed in our SBN/SiO2 nanocomposites. Extra sharp peaks on top of the 3.2 eV band were seen. An additional emission band at 2.3 eV due to transitions within the NbO6 complex of SBN crystallites was also observed. This emission band showed a large blueshift with decreasing SBN crystallite size. This demonstrates that the photoluminescence spectra of ferroelectric-doped silica nanocomposites have a strong dependence on crystallite size. © 2001 American Institute of Physics. [DOI: 10.1063/1.1427419]

Ferroelectric strontium–barium–niobates (SBNs) are well known for their unusual nonlinear optical and pyroelectric properties. They have been extensively studied for use in optoelectronics. Most of the research efforts, however, were focused on SBN bulks and thin films.1,2 The syntheses of SBN nanoparticles and the studies of the associated nanometer-sized effect have not been reported. In ferroelectric materials, the ferroelectricity usually disappears with a grain size smaller than a certain limit. The critical sizes, obtained either from empirical formula or numerical estimation, are in the range of 10–100 nm for most ferroelectrics.3,4 Although this critical size effect on ferroelectricity has been discussed in many articles,4,5 it is not well understood so far. Besides this critical size effect, issues pertaining to the energy band structures of different grain sizes have also been raised.6 Therefore, it is of great interest to examine the relationship between the energy structure and the critical size in ferroelectric materials.

In this letter, a modified sol–gel technique was utilized to fabricate SBN-doped silica nanocomposites. The synthesis of Sr0.5Ba0.5Nb2O6 (SBN) sol has been reported in detail elsewhere.2 The silica sol, on the other hand, was prepared with a standard method using tetraethoxysilane. The two sols were blended and refluxed, then poured into a glass utensil. The sol was set for over 10 days to form a pale brown stiff gel. The gel was then allowed to dry in clean atmosphere for 1 week. Finally the dried gel was annealed in a temperature from 600 to 800 °C for 2 h to obtain a transparent SBN-doped silica nanocomposite. To avoid the solution becoming rapidly precipitated and opaque, a peptizing reagent was added. The SBN molar percentage of our nanocomposites was about 8%. For comparison purpose, we also performed measurements on a large SBN single crystal, which was grown from the flux method.

The x-ray diffraction (XRD) profile in Fig. 1 shows that the structure of pure silica is amorphous. By varying the annealing temperature and duration, nanocomposites with different SBN crystallite size were obtained. Compared with SBN powders, the SBN nanocomposites have weaker and broader diffraction peaks. In this study, the embedded crystallite size, as estimated by Scherrer’s equation, was between 8 and 23 nm. Room-temperature Raman spectra were obtained via excitation with 514.5 nm laser light from a cw argon gas laser. The laser power was maintained at 50 mW to avoid laser annealing of the samples. The scattered light was

![XRD profiles of (a) SBN/SiO2 nanocomposites annealed at 600 °C: amorphous and transparent; (b) 700 °C: tetragonal tungsten–bronze (TTB) phase crystallite and transparent; (c) 800 °C: TTB phase crystallite and opaque; and (d) sol–gel derived SBN powder.](image-url)
and crystallite size are shown in Fig. 3. In general, the nanocomposites measured at 10 K for nanocomposites of different SBN gel silica posed by sharp peaks. The broad profile originates from sol–gel silica, intrinsic defect. 7 The position of this peak, as expected, is independent of the embedded SBN crystallite size. The sharp peaks, on the other hand, are originated from SBN crystals. Compared with those from SBN single crystal, these peaks from nanocomposites have much higher intensities. This is probably due to the resonance effect. Sol–gel silica has a strong emission peak located at 3.2 eV, which is close to the absorption edge of the embedded SBN. 8 The size of the embedded SBN nanocrystals, however, has no effect on the position of these peaks. Since Sr2+, Ba2+, and Nb5+ ions have electron configuration of (4s24p6), (5s25p6), and (4s24p6), respectively, i.e., the outermost electrons are p electrons, these transitions are unlikely to be due to the crystal field splitting of the multiplets of Sr2+, Ba2+, and Nb5+. We suggest that these transitions may be related to the transition between the Nb5+ polaron state and the valence band. 8 The 2.65 eV emission band of the pure sol–gel silica [Fig. 3(a)] may be related to the triplet to ground state transition of neutral oxygen vacancy defects. 9

In our nanocomposites, a more dominant band at 2.3 eV from SBN crystal was observed. This band has a very large full width at half maximum and becomes narrower at smaller SBN crystallite size. Additionally, the peak position shifts to higher energy with decreasing SBN crystallite size. Accordingly to the effective mass approximation, for a spherical ultrafine particle of radius R, the blueshift of energy gap with respect to the bulk is given by 6, 10

$$\Delta E = \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\varepsilon R},$$

where $m_e$ and $m_h$ are the effective masses of the electron and hole respectively, and $\varepsilon$ is the dielectric constant. The inset shows the dependence of this peak energy as a function of inverse square of the mean radius of SBN. The energy seems to vary as the inverse square of the dimension. However, there is some uncertainty in measuring the crystallite size. Besides, the exciton interaction (1/R term) may also affect this dependence. Further investigation is needed to unravel the dependence of peak energy as a function of dimension. Furthermore, the PL intensity of the nanocomposites is substantially stronger than that observed from the SBN single crystal. This can be partially explained by the impedance matching effect due to a smaller dielectric constant of the sol–gel silica matrix. However, the estimated increase in PL intensity from the nanocomposite due to the impedance matching effect is only a few times. In our actual measurement, the PL intensity of the nanocomposites (including the concentration effect, i.e., the nanocomposites have only 8 mol. %) are much stronger.

This 2.3 eV luminescence band is considered to be intrinsic and caused by de-excitation from the most filled molecular orbitals localized at O2− ions (the 2p orbital from the valence band) to one of the least filled molecular orbitals localized mainly at Nb5+ ions (the 4d orbitals in the conduction band) within the NbO6 complex. 10 Alternatively, this transition can be regarded as the transition of unwanted Cr3+ in SBN crystal due to trace amounts of Cr in the ppm level. 8 In our studies, the second possibility mentioned above is unlikely. In Cr doped SBN, a broad absorption band around 650 nm, related to the transition of Cr3+ ions, should be observed. 8 However, in our absorption measurement, 12 no such absorption peak was identified. Therefore, our results suggest that the excitation of this emission band is originated primarily from transitions between different orbitals within the NbO6 complex in SBN. In lowering the crystallite size,
this PL shifts to higher energy. This means that the energy gap between the $2p$ orbital from the valence band and the $4d$ orbitals in the conduction band widens. The shift in our PL measurement is indeed very similar to the size effect observed in In$_2$O$_3$ doped silica.\textsuperscript{10}

Figure 4 shows the typical temperature dependent PL spectra of our nanocomposites. The temperature dependent PL spectra of pure sol–gel silica are also inserted in Fig. 4 for comparison. As the temperature is increased from 10 to 290 K, the 2.3 eV emission gets weaker and ultimately only the 2.65 eV emission band of the silica remains. The broad profile of the 3.2 eV emission band, on the other hand, persists throughout the temperature range studied. The sharp peaks, however, diminish at room temperature. The inset shows the 3.2 eV luminescence peak of silica. It exhibits a smaller intensity and downshifts to $\sim 3.1$ eV as the temperature is increased from 10 K to room temperature. This confirms that the room temperature PL spectra of our nanocomposites are dominated by the host sol–gel silica matrix.

In conclusion, we have fabricated transparent ferroelectric nanocomposites based on dispersing SBN nanoparticles within pores of sol–gel derived silica. PL studies of the nanocomposites revealed an emission band at 2.3 eV due to transitions within the NbO$_6$ complex of SBN crystallites. A large blueshift with decreasing SBN crystallite size was observed. This demonstrates that the energy structure of the nanoferroelectric materials has a strong dependence on their crystallite size.

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\item S. G. Lu, C. L. Mak, and K. H. Wong (unpublished).
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