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Structure and optical properties of Sn^{4+} doped $Ba(Mg_{1/3}Nb_{2/3})O_3$ transparent ceramics

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Abstract

Sn^{4+} doped $Ba(Mg_{1/3}Nb_{2/3})O_3$ (BMN) transparent ceramics were synthesized by a solid state reaction. Sn^{4+} doping changes the crystal structure from hexagonal symmetry to cubic symmetry without birefringence and improves the microstructure. The tilting of oxygen octahedra caused by Sn^{4+} doping influences the A–O and B–O bond characters. The optical transmittance of the transparent ceramic sintered at 1550 °C for 48 h in oxygen atmosphere was 53%. A high refractive index of 2.09–2.22 was achieved in the wavelength range of 400 to 1000 nm. Effective ultraviolet absorption was also obtained when the cut-on wavelength shifted to the edge of the visible region. The optical properties meet the miniaturization requirement for optical functional elements.

Keywords: C. Optical properties; D. Perovskites; Ordered–disordered structure; Microstructure-final

1. Introduction

Transparent ceramics, such as Al_2O_3 [1], $MgAl_2O_4$ [2], Nd:YAG [3] and PLZT [4], have been broadly investigated for their broad range of applications, varying from optical windows to laser and optoelectronic switches. However, the miniaturization of optical functional elements, such as lens for optical information storage, waveguides for flat optical components and substrates for fluorescent components, still presents a challenge for optical materials with high refractive index. Compared with glass and plastic, transparent ceramics made from dielectric materials have a relatively high refractive index because of their high permittivity. Al_2O_3, the representative of transparent ceramics, has a refractive index of 1.76. However, Al_2O_3 exhibits a birefringence effect due to its hexagonal structure, which causes scattering of light and low transmissivity [5,6]. High transmissivity for the applications utilizing optical transparency requires materials with isotropous cubic crystal structure that do not exhibit birefringence [7]. Therefore, researchers face the issue of searching for the transparent ceramics with high refractive index and cubic crystal structure.

$Ba(Mg_{1/3}Nb_{2/3})O_3$ (BMN), a complex perovskite, is a type of microwave dielectric material that exhibits a much higher permittivity (32) than that of Al_2O_3 (9.8) [8,9], providing the application potential of a high refractive index material. It is known that BMN exists in both ordered and disordered forms, with hexagonal and cubic symmetry, respectively [10]. It is notoriously difficult to obtain a completely ordered or disordered structure in BMN. According to a previous study, substitution of B-site cations is an effective way to reduce the ordering degree of $A(B'B'')O_3$. In the cases of $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) and $Pb(Zr_{1-x}Ti_x)O_3$ (PZT), disordered ceramics were fabricated with cations that are partially substituted by M^{4+} (M=Ti, Sn, Zr and Hf) and La^{3+}, respectively [11–14]. However, Sn^{4+} doped BMT transparent ceramics are still found to be mixed phase of the ordered–disordered type [15]. In the case of BMN, substitution of B-site cations by ions that

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have charges and radii that are between those of Mg^{2+} and Nb^{5+} ions may cause a disordering of the B-site cations, which in turn results in a transformation to a cubic structure. In addition, the microstructure is another critical factor influencing the optical transmittance of transparent ceramics. Long-time sintering, the conventional method to achieve microstructure homogeneity, would also lead to ordered hexagonal structure with birefringence. We are faced with a challenge to obtain the disordered crystal structure and suitable microstructure simultaneously.

In this paper, Sn^{4+} doped BMN transparent ceramics were fabricated via a solid state reaction. The influences of doping on the structures and the optical properties in BMN were investigated.

2. Experiment

2.1. Production processing

$Ba[Sn_{0.1}(MgNb_2)_{0.3}]O_3$ powders were prepared with the raw materials of $BaCO_3$ ($\geq$99.95%), Nb_2O_5 ($\geq$99.5%), MgO ($\geq$99.99%), and SnO_2 ($\geq$99.0%), which were ball milled with agate balls in ethanol in a nylon jar for 24 h. Next, the mixture was calcined at 1300 °C for 4 h. For comparison, pure BMN powders were prepared by the same procedure. The calcined powders were ball milled again for 12 h; the dried powders were granulated and pressed into plates with a diameter of 22 mm and then cold isostatically pressed with pressure of 200 MPa. Finally, the plates were sintered at 1550 °C for 24 h or 48 h in oxygen atmosphere to restrain the Sn^{4+} turning into Sn^{2+} and to eliminate oxygen vacancies and pores. The Sn^{4+} doped ceramics sintered for 24 h and 48 h were named S24 and S48, respectively. The pure BMN ceramic material sintered at the same temperature with the same oxygen atmosphere for 48 h and was named P48. All of the sintered samples were well polished for testing.

2.2. Characterization

The phase composition and crystal structure were investigated using X-ray diffraction (XRD, Philips X'pert pro, Netherlands). Raman scattering measurements were also performed at room temperature, using a Renishaw Raman Microscope (Renishaw, INVIA, England) to further clarify the detail of the crystal structure. The 17 mW output of the 632.8 nm line of a He–Ne laser was used as the excitation source. The microstructures of the samples were observed using a scanning electron microscope (SEM, JSM-5610LV, Japan). The optical transmittances of the samples were measured in the wavelength range of 300 to 900 nm using a spectrophotometer (UV-2550, Japan). Mirror-polished samples on both surfaces were used to measure the refractive index via Spectroscopic Ellipsometry (M-2000V, USA).

3. Results and discussion

The XRD patterns of P48 and S48 are shown in Fig. 1. Both of the samples were found to have a single BMN phase (JCPDS No 17-0173) without any impurities. In the pattern of P48, all of the peaks are well indexed to the $P\bar{3}m1$ space group of hexagonal structure. The peaks located at the 2θ values of 17.747°, 25.061°, 33.556°, 35.866°, 40.325° and 42.388° correspond to the superlattice reflections that are generated by planes whose indices are $(2h+k+l) \neq 3n$ [10]. The ordering degree can be calculated quantitatively by the B-site ordering parameter (S), which can be deduced from the ratio of the X-ray intensities of the diffraction peaks associated with cation ordering [16,17]. In BMN-type structure, the value S is determined by the ratio of the intensity of the strongest supperlattice reflection, (1 0 0), to the strongest peak of the BMN-type structure, (1 1 0). Because the (0 1 2) and (1 0 2) peaks are very close to (1 1 0) they should also be taken into account in the calculations [18]. Thus, the ordering parameter of the B-site was defined as [19]

$$S = \sqrt{\frac{\left(I_{1\,0\,0}/\left(I_{1\,02,0\,1\,2,1\,1\,0}\right)\right)_{obs}}{\left(I_{1\,0\,0}/\left(I_{1\,0\,2,0\,1\,2,1\,1\,0}\right)\right)_{calc}}}$$

where $(I_{1\,0\,0}/(I_{1\,0\,2,\ 0\,1\,2,\ 1\,1\,0}))_{obs}$ and $(I_{1\,0\,0}/(I_{1\,0\,2,\ 0\,1\,2,\ 1\,1\,0}))_{calc}$ are the intensity ratio of the (1 0 0) superlattice reflection to that of (1 0 2, 0 1 2, 1 1 0) main reflections from the observed and the calculated values of complete ordering, respectively. In the BMN ceramic, the value of $(I_{1\,0\,0}/(I_{1\,0\,2,\ 0\,1\,2,\ 1\,1\,0}))_{calc}$ is 3.04% [16]. When S equals 0, the structure is completely disordered, whereas the structure is totally ordered when S equals 1 [20]. The ordering parameter of P48 is approximately 0.81. The value of S and the presence of superlattice reflections indicate that P48 possesses an ordered structure after long-time sintering.

In contrast, there is no superlattice reflection in the pattern of S48. All of the peaks are identified as the $Pm\bar{3}m$ space group of the cubic structure. This result indicates that Sn^{4+} doping results in the completely disordered structure and cubic symmetry. The reason for the disorder is that the ion radius and valence of Sn^{4+} (0.69 Å) are between those of the Mg^{2+} ion (0.72 Å) and the Nb^{5+} ion (0.64 Å), which drives B-site cations in $A(B'B'')O_3$ (Mg and Nb in this case) to arrange randomly [21].

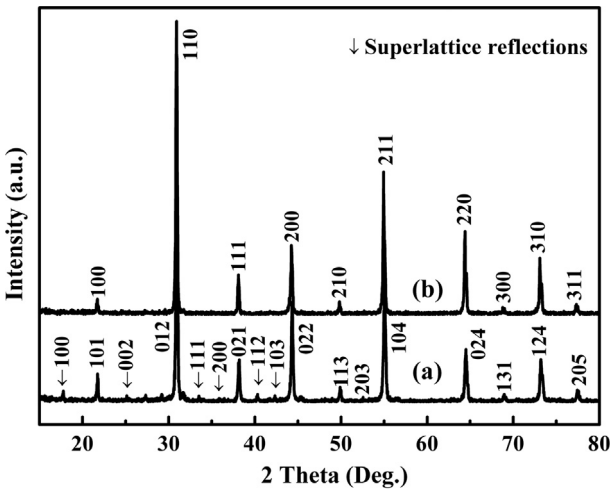

Fig. 1. XRD patterns of the ceramic samples: (a) P48; (b) S48.