Rare-earth substitution in $Bi_4Ti_3O_{12}$ system for potential application

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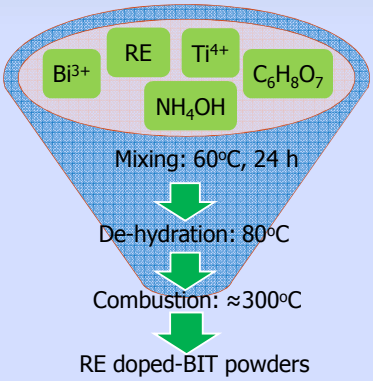
Material & Methods



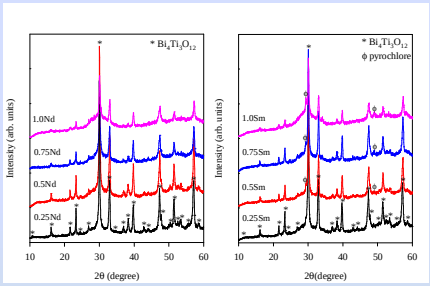
*RE: rare-earth

Motivation

Ion substitution is a feasible method to improve the stability structure of bismuth titanate, $Bi_4Ti_3O_{12}$ (BIT) which also resulted in better ferroelectric properties. In principle, the substitution in BIT can be performed on Bi ions (or A-site), Ti ions (or B-site) or both sites. Based on previous report, the substitution on any sites in BIT showed the different effect on the ferroelectric properties [1]. Nevertheless, the substitution of Bi ions at A-site is more effective than Ti ions at B-site in enhancing the ferroelectric properties. This is because that the B-site cations are similar in ionic radius size to exhibit lesser impact on polarization in BIT. Such various findings making a study on improvement of ferroelectric by ion substitution is very interesting. The ion substitution on A-site is more suitable by any elements that posses a similar ion valences. On this basis, the REs such as La, Nd, Sm, Pr, Eu and Dy ions are more preferred dopant for Bi ions in BIT. In principle, the role of substitution is to displace the volatile Bi ions with RE element which in turn to suppress the Bi vacancies accompanied by oxygen vacancies. In other words, the space charge effect can be minimized and subsequently, resulted in better ferroelectric properties as well as dielectric properties.

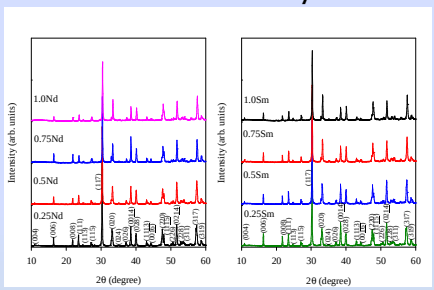
Results & Discussion

Phase detection



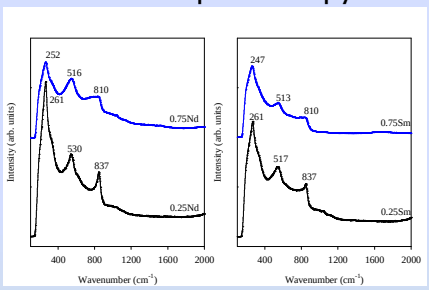
Single phase BIT was formed in BNdT regardless of Nd content. However, the pyrochlore phase ($Bi_{2-x}Sm_xTi_2O_7$) was detected in higher amount with increasing Sm content.

Phase stability



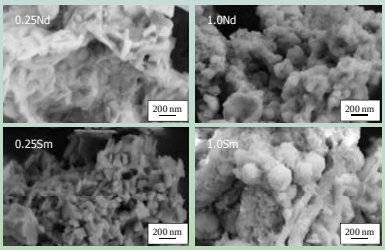
High degree of crystallinity with (117)- axis oriented was achieved after sintering. The BNdT and BSmT ceramics are more stable at temperature as high as 1000°C.

Raman spectroscopy



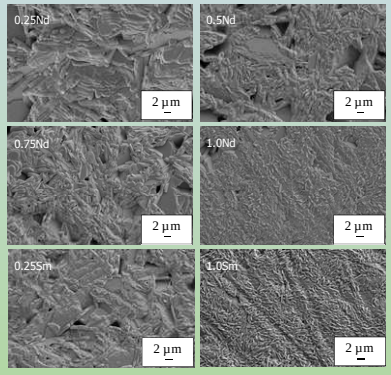
Three important peaks showed the presence of perovskite structure that corresponded to the internal vibration mode of the TiO_6 octahedron. The reduced intensities together with the decrease in peak width suggests that BIT substituted with Nd and Sm have low degree of crystallinity particularly at high rare-earth content.

Powder morphology



The boundary of the substitution powders is not clear particularly at high molarities content. This indicates that the obtained powders are relatively fine due to the substitution effect. This finding also suggests that RE elements i.e. Nd and Sm play the role as grain growth inhibitor.

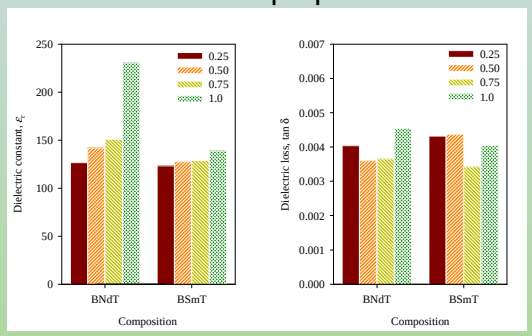
Microstructures



It is clearly seen that all samples contain plate-like morphology. Upon increasing RE content to 1.0, a remarkable decrease in the grain size was observed. In addition to that, the grain size became more uniform. This indicates that Nd and Sm play a significant role on the uniformity of grain size particularly at high molarities content. In addition, the relative densities of the samples with 1.0 for Nd and Sm were approximately 90 and 88%, respectively.

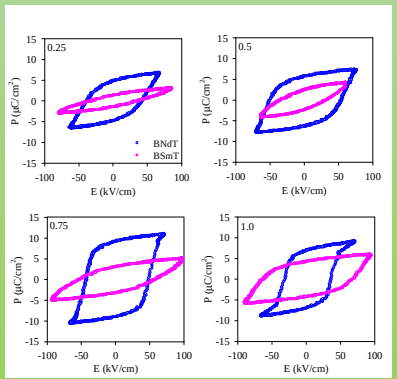
The hysteresis loops of Nd-substituted ceramics were fully saturated from 0.25 to 1.0. In contrast to Sm-substituted ceramics, the saturated hysteresis loops were identified when 1.0. This indicates that the hysteresis loops of BSmT system were improved with increasing Sm content. The result implies that the polarization process could be easier accomplished in BNdT than BSmT.

Dielectric properties



The dielectric constant of Nd substitution abruptly increased of about 82% when the content of RE was increased from 0.25 to 1.0. In contrast, the increase of ε_r in Sm substitution system was fairly small, which is about 12% from 0.25 to 1.0. The obvious difference in ε_r particularly at 1.0 for Nd and Sm can be explained by the relaxation of orthorhombic distortion and octahedral tilting in a layered structure.

Ferroelectric properties



Conclusions

Nd and Sm substituted-BIT was successfully synthesized using single step combustion technique, and subsequently sintered at 1000°C. The improved microstructure with better relative density was obtained at high RE content. The result also corresponded to the increase in dielectric constant and ferroelectric properties.

Reference

[1] Lv, L., Zhang, S., Wang, J., Chen, Y., Liu, Z., Zhao, X., & Cheng, G. (2005). Effects of Zr substitution on structures and ferroelectric properties of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films. Journal of Physics D: Applied Physics, 38, p 1355.

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