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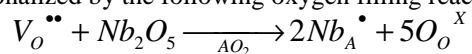
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Bi₂O₃ is recognized as the best oxygen ionic conductor. Its high conductivity is highly dependent on its crystal structure. In δ -Bi₂O₃ which exhibits defective fluorite structure, the concentration of oxygen vacancies is as much as 25 mol%. Unfortunately this structure is only stable at high temperature (723~823°C). At temperatures lower than 723°C monoclinic α -Bi₂O₃ was obtained. In alkaline earth doped bismuth oxide systems, δ -phase also transformed rapidly to rhombohedral phase, as described by J. C. Bovin^[1,2]. It is believed that the amount of oxygen vacancies and the size of doping ions play an important role in the phase transformation of doped Bi₂O₃ system. First of all, Bi_{0.824}Ca_{0.176}O_{1.412} was chosen as the matrix composition which gives rhombohedral phase after calcined at 700°C (figure 1(a)).

The crystal structure and microstructure of samples were examined in aid with XRD, SEM and TEM. The conductivity measurement was conducted using 2-probe DC technique. This rhombohedral tends to react with moisture and has low mechanical strength. It has been shown that the cubic structure of Y₂O₃ doped Bi₂O₃ exhibits better mechanical strength and structural stability against moisture^[3]. Thus, it is necessary to enhance the stability of cubic phase in CaO-Bi₂O₃ system and ionic conduction of Bi_{0.824}Ca_{0.176}O_{1.412} with various amount of Nb₂O₅ dopant.

Figure 1 shows the XRD trace for Bi_{0.824}Ca_{0.176}O_{1.412} doped with up to 10 m/o Nb₂O₅. With the addition of 4 m/o Nb₂O₅, the reflections of rhombohedral phase significantly reduced. On the contrary, two cubic phases were observed. These two phases are similar to cubic fluorite structure. Thus the addition of Nb₂O₅ enhanced the stability of cubic Bi_{0.824}Ca_{0.176}O_{1.412}. The structure stability can be rationalized by the following oxygen filling reaction.



In Bi_{0.824}Ca_{0.176}O_{1.412}, the formation of rhombohedral phase is due to excess oxygen vacancies. According to reaction (1), the addition of one Nb₂O₅ will fill up one oxygen vacancy and then make the structure more stable. In addition to phase changes, the conductivity of Bi_{0.824}Ca_{0.176}O_{1.412} was also affected by the doping of Nb₂O₅. For undoped Bi_{0.824}Ca_{0.176}O_{1.412}, the conductivity was 0.085 S/cm at 800°C. For 6 mol% Nb₂O₅-doped Bi_{0.824}Ca_{0.176}O_{1.412}, the conductivity was enhanced to 0.722 S/cm at 800°C as shown in figure 2. It is known that the cubic fluorite phase has a higher conductivity than rhombohedral phase. Therefore, the addition of Nb₂O₅ in rhombohedral Bi_{0.824}Ca_{0.176}O_{1.412} does not only stabilize the high temperature cubic phase, but also enhances the ionic conductivity.

Acknowledgement

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1. J. C. Bovin and D. J. Thomas, *Solid State Ionics*, 3/4, 457-462 (1981)
2. J. C. Bovin and D. J. Thomas, *Solid State Ionics*, 5, 523-526 (1981)

3. C. -C. Huang and K.-Z. Fung, "Degradation of Rhombohedral (Y_{0.25}Bi_{0.75})₂O₃ Solid Electrolyte" in the Proceedings of the Seventh International Symposium on **Solid Oxide Fuel Cells (SOFC-VII)**, the Electrochemical Society, Inc., 2001.

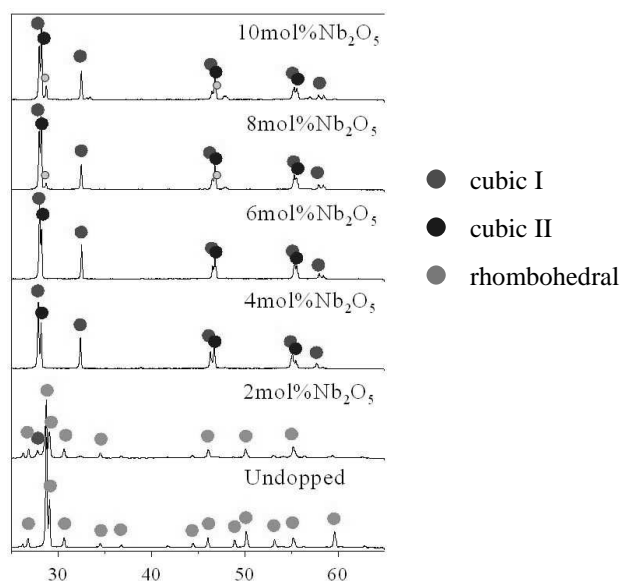


Figure 1. XRD patterns of Nb₂O₅-doped Bi_{0.824}Ca_{0.176}O_{1.412} sintered at 850 °C (undoped sample was sintered at 700°C) for 20h.

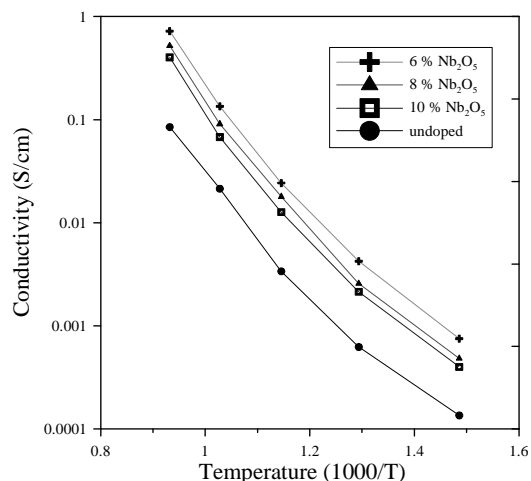


Figure 2. Conductivity of Nb₂O₅-doped Bi_{0.824}Ca_{0.176}O_{1.412} plotted as a function of temperature.