Preparation and Characterization of Apatite-like Neodymium Silicates and its Application to Potentiometric O_2 Gas Sensor

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Introduction

In 1995, we reported that the ionic conductivity of apatite-type lanthanoid silicates, $Ln_{10}(SiO_4)_6O_3$ (Ln=La, Nd, Sm, Gd, Dy, Ho, Er and Yb) and the sole carrier in these materials is the O^{2-} ion [1]. However, it is experimentally very difficult to remove a trace amount of Ln_2SiO_5 impurity when these apatites are prepared by solid-state reaction. A novel enhancement of conductivity in $La_{9.33}(SiO_4)_6O_2$ by Al-doping results in conductivities comparable to those of the oxygen-excess composition $La_{10}(SiO_4)_6O_3$ [2]. It is expected that an adding of Al_2O_3 is effective to form the dense ceramics.

In this work, Nd_2O_3-Al_2O_3-SiO_2 sinters prepared by solid-state reaction were characterized by XRD, SEM and AC impedance analysis and also the sensing behavior of the potentiometric O_2 sensor using the sinters was examined.

Experimentals

Reagent grade of Nd_2O_3, Al_2O_3 and amorphous SiO_2 were used as starting materials. The materials were mixed with ball-mill with nylon pot and YSZ balls without any additives. The mixed powders were calcined at several temperatures in ambient air and the products were examined by XRD (Kα-Cu, Rigaku RINT2200V). The compacted discs in 300 kg/cm were prepared and sintered at 1600 ^oC in ambient air. The surface and body were examined with SEM (JEOL, JSM-5310). The conductivity in ambient air was determined by impedance analyzer with the disc with Au electrodes. The EMF response were measured in the oxygen concentration ranging from 100 % to 0 %.

Results and Discussion

Firstly, we tried to prepare a single phase of $Nd_{10}(SiO_4)_6O_3$ (oxygen excess composition) by the soild state reaction. XRD results for the $Nd_{9.33+x/3}Si_{6-x}Al_xO_{26}$ system are shown in Fig.1. Even for the mixture sintered at 1600^oC for 8 hours, a single phase of $Nd_{10}(SiO_4)_6O_3$ could not be obtained and Nd_2SiO_5 phase was detected as a minor product. By the partial replacing Si with Al, the relative intensity of Nd_2SiO_5 decreased with an increase in x. Single phase was obtained for x=1.5. The calculated lattice constants were increased with an increase in x value because of larger ionic radius of Al^{3+} ion than that of Si^{4+} ion. For the sinterability of this system, the particles were well sintered and grains were defined clearly for all the samples. It seems that the concentration of the closed pores decreased with an increase in the Si content.

The potentiometric O_2 gas sensor using O^{2-} ion electrolyte is expressed as (I)O_2,Pt/oxygen ionic electrolyte/Pt, ref.(II). The output signal in volt was determined by the difference of the oxygen concentrations between sample gas and the reference gas, $E_{obs} = E_o + (RT/nF)ln(P_{O2(I)}/P_{O2(II)})$ and the electron number, n, was 4. The electrical conductivity of the sintered samples was examined by AC impedance analysis in ambient air. In the Cole-Cole plots, arcs and spike were observed in a high and low frequency region from 100 Hz to 10 MHz. The conductances were estimated from the intercept of the spike and/or the arcs in the low frequency end on the Z' axis, and are shown in Fig.2. Fortunately, the highest conductance was observed for x=1.5. Fig. 3 shows the EMF response behaviors for the potentiometric O_2 gas sensor using x=1.5. It was confirmed that the rising and recovery time were shortened with an increase in the operating temperature from 300 ^oC to 700 ^oC. For both case i.e. increase and decrease in the concentration, the results were well fitted to the linear relation with n=4.0. From the observed results, it seems that the fabricated sensor shows a preferable sensing characteristics at 400 ^oC or higher.

References

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2. E.J.Abram, D.C.Sinclair and A.R.West, *J.Mater. Chem.*,11(2001)1978-1979.

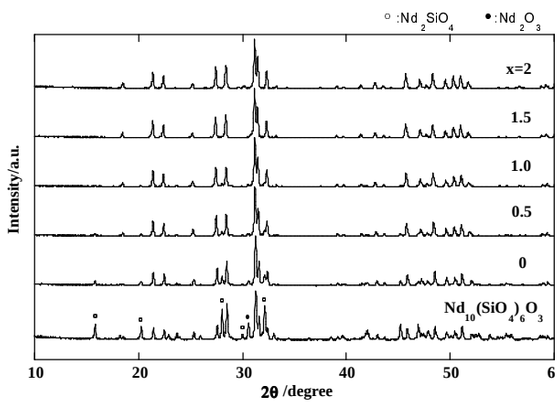

Fig. 1 XRD patterns of $Nd_{10}(SiO_4)_6O_3$ and $Nd_{9.33+x/3}Si_{6-x}Al_xO_{26}$ prepared b the sintering at 1600 °C for 8 hrs.

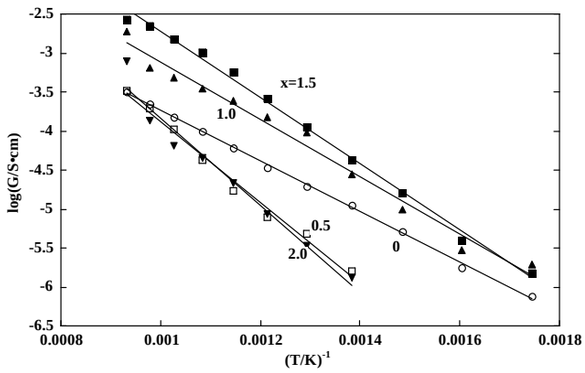

Fig. 2 The temperature dependence of the conductivity of the $Nd_{9.33+x/3}Si_{6-x}Al_xO_{26}$ syste

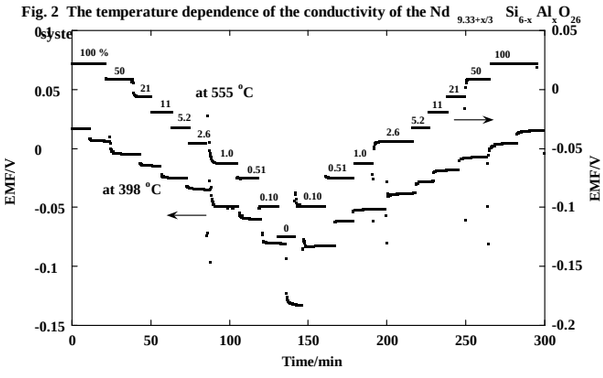

Fig. 3 The EMF response for the $Nd_{9.83}Si_{4.5}Al_{1.5}O_{26}$ (x=1.5) at 398 °C and 555 °C