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Sodium Sulfate Doped with Sodium Vanadate and Rare Earth Sulfate as a Solid Electrolyte for a Sulfur Dioxide Gas Detector

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Sodium sulfate doped with $NaVO_3$ and $Ln_2(SO_4)_3$ (Ln=Eu, Pr, and Y) show higher electrical conductivity for Na^+ ions and maintains a high temperature phase, Na_2SO_4-I, without showing phase transformation. The electromotive force (EMF) using solid solutions, Na_2SO_4–$NaVO_3$–$Ln_2(SO_4)_3$ (Ln=Pr and Y), as solid electrolytes exhibits good agreement with the calculated value, the temperature as low as 673 K which is approximately 300 K lower than pure sodium sulfate can be.

Influence of sulfur dioxide exhausted from coal power plants and automobiles to the environment has been taking place and becoming a serious problem. Especially, acid rain resulting from the absorption of sulfur dioxide and nitrogen dioxide by water is considerably affecting the surroundings in North America and some other countries.

Recently, some attempts have been made to utilize sodium sulfate as a solid electrolyte for a SO_2 gas sensor.[1–4] However, in practical use, a phase transformation from Na_2SO_4–III (a low temperature phase) to Na_2SO_4–I (a high temperature phase)[5–21] is a serious obstacle. In addition, other disadvantages in using sodium sulfate alone as an electrolyte are its lower electrical conductivity and the difficulty in obtaining a SO_2–SO_3 equilibrium on the surface of the electrolyte. Mono-, di-, and trivalent cations have been doped in order to improve their electrical and thermodynamic properties.[22–26] In our previous study,[27] sodium sulfate doped with $NaVO_3$ and $Ln_2(SO_4)_3$ (Ln=Eu and Pr) has been found to show no phase transformation, to maintain a Na_2SO_4–I-similar phase, and to increase the electrical conductivity.

In the present study, effects of doping with rare earth sulfates and sodium vanadate into sodium sulfate on the electrical conductivity and on the phase transformation of the solid solutions are examined, and also EMF measurements by applying Na_2SO_4–$NaVO_3$–$Ln_2(SO_4)_3$ (Ln=Pr and Y) as an electrolyte for a SO_2 gas concentration cell are to be discussed.

Experimental

Materials. Rare earth sulfate was prepared by adding concentrated H_2SO_4 into rare earth oxide. Sodium vanadate was synthesized by heating the mixture of Na_2CO_3 and NH_4VO_3 (by molar ratio 1:2) at 823 K for 5 h in air. A mixture of appropriate amount of Na_2SO_4 and $Ln_2(SO_4)_3$ (Ln=Eu, Pr, and Y) were pelletatized and heated at 1073 K for 3 h in air. In Na_2SO_4–$NaVO_3$–$Ln_2(SO_4)_3$ (Ln=Eu, Pr, and Y) systems, the heated pellets were ground, remade into pellets and sintered 3 h at 1073 K in air.

Measurements. Phases and thermal properties were measured with X-ray diffraction method and thermal analysis. Electrical conductivity measurements were carried out by a complex impedance method[28] using a Hewlett Packard vector impedance meter 4800 A. The apparatus for the electrical conductivity measurements is shown in Fig. 1. EMF measurements were performed by constructing a SO_2 gas concentration cell which is depicted in Fig. 2. The inner quartz tube compartment was separated by spring loading the electrolyte with a quartz rod. A gold O-ring was used in order to separate the test and the reference SO_2 gas completely. The SO_2 gas concentration was regulated by changing SO_2 and O_2 gas flow rate. A Pt net was applied as an electrode so that the electrolyte could maintain good contact with the SO_2 gas. EMF measurements were performed with a Takeda Riken Digital Multimeter TR-6855. The response time, which is here defined as the time required from the test gas arrival at the electrolyte to the attainment of about 96% of the calculated EMF, was also measured.

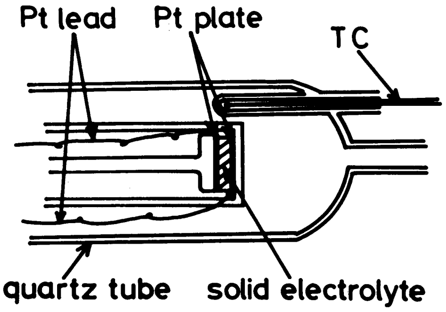

Fig. 1. The apparatus for the electrical conductivity measurements.

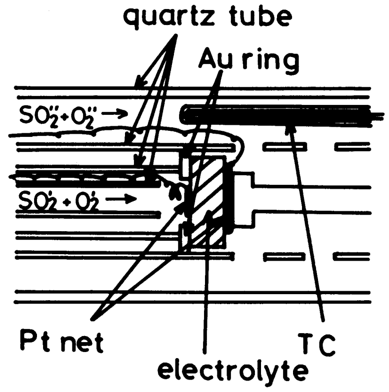

Fig. 2. The apparatus for the electromotive force (EMF) measurements.

Results and Discussion

Electrical Conductivity, Phases, and Thermal Properties. The Na_2SO_4-$Ln_2(SO_4)_3$ (Ln=Eu, Pr, and Y): Sodium sulfate doped with $Ln_2(SO_4)_3$ (Ln=Eu, Pr, and Y) ex-

Table 1. The phases and thermal properties of Na_2SO_4-$Pr_2(SO_4)_3$

Sample No.	Na_2SO_4 (mol%)	$Pr_2(SO_4)_3$ (mol%)	Phases	DTA peaks T/K
1	99.1	0.9	α+Na_2SO_4-V	573
2	98.4	1.6	α+Na_2SO_4-V	573
3	95.2	4.8	γ	573
4	90.7	9.3	γ	853

α phase is similar to phase Na_2SO_4-III.[18,19] γ phase is different from any Na_2SO_4 phase.

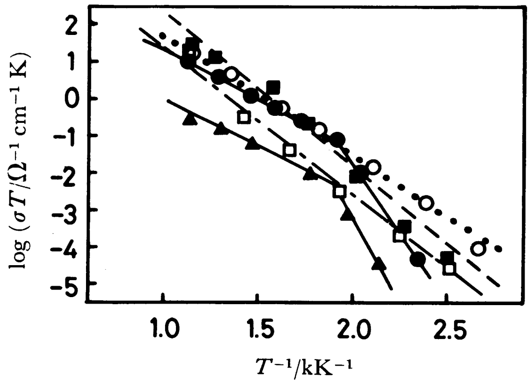

Fig. 3. Temperature dependences of electrical conductivities for the Na_2SO_4-$Pr_2(SO_4)_3$.
—□— $Na_2SO_4 : Pr_2(SO_4)_3=90.7 : 9.3$, —■— $Na_2SO_4 : Pr_2(SO_4)_3=95.2 : 4.8$, ···○··· $Na_2SO_4 : Pr_2(SO_4)_3=98.4 : 1.6$, —●— $Na_2SO_4 : Pr_2(SO_4)_3=99.1 : 0.9$, —▲— Na_2SO_4.

Table 2. The phases and thermal properties of Na_2SO_4-$NaVO_3$-$Y_2(SO_4)_3$

Sample No.	Na_2SO_4 (mol%)	$NaVO_3$ (mol%)	$Y_2(SO_4)_3$ (mol%)	Phases	DTA peaks T/K
1	98.3	0.7	1.0	α	485
2	96.9	1.1	2.0	α	408, 463
3	95.7	1.3	3.0	β	—
4	93.6	2.4	4.0	β	—
5	91.4	3.6	5.0	β	573 (very small)

α phase is similar to phase Na_2SO_4-III.[18,19] β phase is similar to phase Na_2SO_4-I.[18,19]

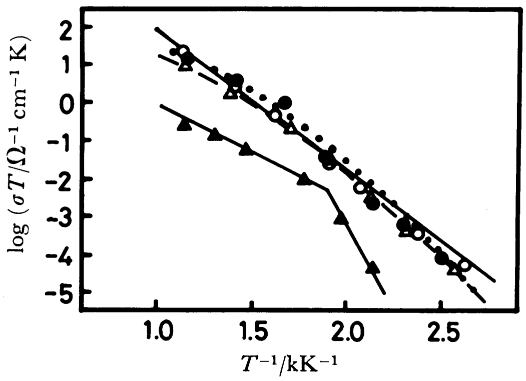

Fig. 4. Temperature dependences of electrical conductivities for the Na_2SO_4-$NaVO_3$-$Y_2(SO_4)_3$ which exhibit β phase.
—○— $Na_2SO_4 : NaVO_3 : Y_2(SO_4)_3=91.4 : 3.6 : 5.0$,
···●··· $Na_2SO_4 : NaVO_3 : Y_2(SO_4)_3=93.6 : 2.4 : 4.0$,
—△— $Na_2SO_4 : NaVO_3 : Y_2(SO_4)_3=95.7 : 1.3 : 3.0$,
—▲— Na_2SO_4.

hibits almost the same electrical conductivity, phases, and thermal properties with one another.

The representative results of Na_2SO_4-$Pr_2(SO_4)_3$ are listed in Table 1. Sodium sulfate doped with 0.9 mol% or 1.6 mol% $Pr_2(SO_4)_3$ exhibits phase α which is similar to the Na_2SO_4-III phase [18,19] including a starting material (Na_2SO_4-V phase). The other two samples show phase γ which is different from any Na_2SO_4 phase. All samples exhibit an endothermal peak in DTA curves, indicating that the phase transformation still exists.

Electrical conductivity measurements in the systems of Na_2SO_4-$Pr_2(SO_4)_3$ are shown in Fig. 3. Doping $Pr_2(SO_4)_3$ into Na_2SO_4 increases the concentration of cation vacancies of the sulfate, and then the electrical conductivity enhances. A break or bend in log(σT) *vs.* $1/T$ curves is due to the phase transformation in the sulfate. The solid solution of sodium sulfate doped with 1.6 mol% $Pr_2(SO_4)_3$ did not exhibit any break. The III-I phase transformation appeared to be fairly suppressed. However, the phase transformation was found to still remain on DTA measurement. The sulfate doped with 4.8 mol% $Pr_2(SO_4)_3$ gives the highest electrical conductivity (from 571 K to 873 K) in the Na_2SO_4-$Pr_2(SO_4)_3$ systems.

This fact means that the number of cation vacancies which is effective for cation conduction becomes a maximum with the doping. By doping $Pr_2(SO_4)_3$ more than 4.8 mol%, cation vacancies appear to make clusters and then the electrical conductivity in Na_2SO_4-$Pr_2(SO_4)_3$ systems rather decreases.

Although the electrical conductivities of the sulfates increase with the $Ln_2(SO_4)_3$ (Ln=Eu, Pr, and Y) doping, the phase transformation still remains. Therefore, the bicomponent solid solutions do not seem to be appropriate as solid electrolytes for a SO_2 gas detector.

The Na_2SO_4-$NaVO_3$-$Ln_2(SO_4)_3$(Ln=Eu, Pr, and Y) Systems: The phases and thermal properties of sodium sulfate doped with $NaVO_3$ and $Ln_2(SO_4)_3$ (Ln=Eu, Pr, and Y) are all similar.

A typical behavior (Na_2SO_4-$NaVO_3$-$Y_2(SO_4)_3$) is presented in Table 2. Samples No. 1 and 2 show phase α which is similar to the phase Na_2SO_4-III.[18,19] On the other hand, samples No. 3, 4, and 5 show phase β which resembles the phase Na_2SO_4-I.[18,19] From DTA measurements, the samples which show phase α exhibit endothermal peaks, that is, a phase transformation still remains. The samples which exhibit phase β show no endothermal peak, indicating that no phase transformation occurs.

The plots of log(σT) *vs.* $1/T$ for sodium sulfate doped with $NaVO_3$ and $Y_2(SO_4)_3$(phase β) are given in Fig. 4. The slope of the Na_2SO_4-$NaVO_3$-$Y_2(SO_4)_3$ curves closely approaches that of Na_2SO_4-I (a high temperature phase). The electrical conductivity of Na_2SO_4-$NaVO_3$-$Y_2(SO_4)_3$ systems is increased with doping $Y_2(SO_4)_3$ because of the increase in cation vacancies. In addition, the Na_2SO_4-$NaVO_3$-$Y_2(SO_4)_3$ systems maintain a Na_2SO_4-I-like phase (phase β) which is excellent in Na^+ ion conduction.

As mentioned above, the conductivity of Na_2SO_4-I is considerably high and the three component systems also support the similar structure with the Na_2SO_4-I phase. Therefore, the conductivity of the solid solution is also high. The Na_2SO_4-$NaVO_3$-$Y_2(SO_4)_3$ systems are considered to be very good ionic conductors. In this system, sodium sulfate doped with 3.6 mol% $NaVO_3$ and 5.0 mol% $Y_2(SO_4)_3$ shows the best linearity in the three $\log(\sigma T)-1/T$ curves. The three component systems, including rare earth sulfates other than $Y_2(SO_4)_3$ also give the similar optimum composition of 91:4:5.

EMF Measurements. The EMF measurements were performed with Na_2SO_4-$NaVO_3$-$Ln_2(SO_4)_3$ (Ln=Eu, Pr, and Y) (91:4:5) as solid electrolytes. Temperature dependences of measured EMF/calculated EMF ratio with a fixed SO_2 gas concentration are shown in Fig. 5.

The measured EMF for pure Na_2SO_4 and Na_2SO_4-$Ln_2(SO_4)_3$ (Ln=Eu, Pr, and Y) solid solutions were less than half of calculated EMF. The measured value for sodium sulfate doped with 4.0 mol% $NaVO_3$ and 5.0 mol% $Eu_2(SO_4)_3$ is consistent with that calculated at 623 K and appears to be an appropriate electrolyte. However, the measured value of the EMF has exceeded that calculated at 673 K. This appears to have resulted because Eu^{3+} ions in the systems are easily reduced to a divalent state with SO_2 gas and change in free energies for the reduction might have been added to the calculated EMF value. Thus, the solid solution of Na_2SO_4-$NaVO_3$-$Eu_2(SO_4)_3$ is not appropriate for the electrolyte.

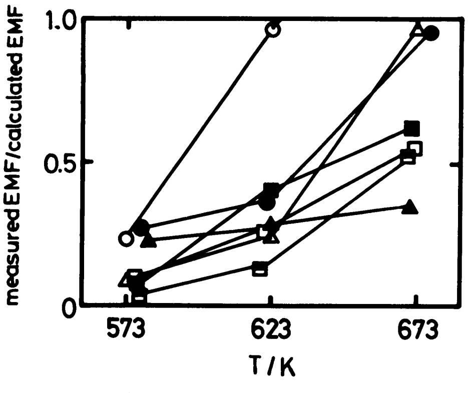

Fig. 5. The ratio of measured EMF/calculated EMF for Na_2SO_4, Na_2SO_4-$Ln_2(SO_4)_3$, Na_2SO_4-$NaVO_3$-$Ln_2(SO_4)_3$ (Ln=Eu, Pr, and Y) with initial SO_2 gas composition, approximately 24 and 8 vol%.
—○— Na_2SO_4 : $NaVO_3$: $Eu_2(SO_4)_3$=91.0 : 4.0 : 5.0,
—●— Na_2SO_4 : $NaVO_3$: $Pr_2(SO_4)_3$=91.1 : 3.9 : 5.0,
—△— Na_2SO_4 : $NaVO_3$: $Y_2(SO_4)_3$=91.4 : 3.6 : 5.0,
—□— Na_2SO_4 : $Eu_2(SO_4)_3$=95.9 : 4.1, —■— Na_2SO_4 : $Pr_2(SO_4)_3$=95.2 : 4.8, —⊟— Na_2SO_4 : $Y_2(SO_4)_3$ =95.0 : 5.0, —▲— Na_2SO_4.

The systems of Na_2SO_4-$NaVO_3$-$Ln_2(SO_4)_3$ (Ln=Pr and Y) give almost the same EMF as calculated one at 673 K. In the temperature range higher than 673 K, the electrolytes became soft because of $NaVO_3$. The EMF measurements in variation of the test SO_2 gas concentration were conducted with the Na_2SO_4-$NaVO_3$-$Ln_2(SO_4)_3$ (Ln=Pr and Y) systems as solid electrolytes at 673 K.

Results of the EMF measurements with the Na_2SO_4-$NaVO_3$-$Pr_2(SO_4)_3$ electrolyte are presented in Fig. 6. The calculated EMF is cited from theoretical one of Jacob and Rao.[2] The measured EMF shows good

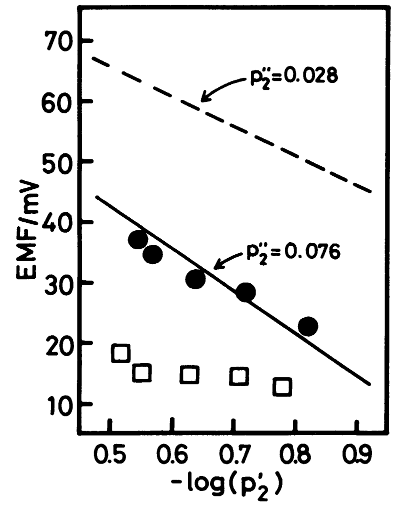

Fig. 6. Variation of the EMF for the concentration cell; $Pt|O_2(p_1'), SO_2(p_2')|Na_2SO_4$ (3.9 mol% $NaVO_3$, 5.0 mol% $Pr_2(SO_4)_3$)$|O_2(p_1''), SO_2(p_2'')|Pt$, with $p_1''=0.924$, $p_2''=0.076$ (●) and $p_1''=0.972$, $p_2''=0.028$ (□) at 673 K.
—— and – – are calculated EMF,[2] respectively.

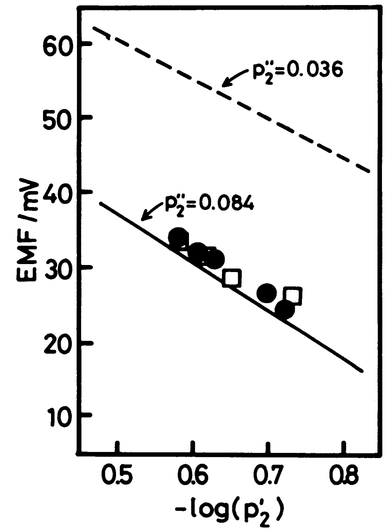

Fig. 7. Variation of the EMF for the concentration cell; $Pt|O_2(p_1'), SO_2(p_2')|Na_2SO_4$ (3.6 mol% $NaVO_3$, 5.0 mol% $Y_2(SO_4)_3$)$|O_2(p_1''), SO_2(p_2'')|Pt$, with $p_1''=0.916$, $p_2''=0.084$ (●) and $p_1''=0.964$, $p_2''=0.036$ (□) at 673 K.
—— and – – are calculated EMF,[2] respectively.

accordance with the calculation in which the initial reference SO_2 gas concentration is 7.6 vol%. Sodium sulfate doped with $NaVO_3$ and $Pr_2(SO_4)_3$ is able to use for a solid electrolyte, a temperature as low as 673 K which is approximately 300 K lower than pure sodium sulfate can be operative. In the case that the initial reference SO_2 gas concentration is 2.8 vol%, the measured EMF is appreciably smaller than the calculated EMF. The EMF results for the Na_2SO_4-$NaVO_3$-$Y_2(SO_4)_3$ electrolyte are also presented in Fig. 7. The measured EMF also shows good agreement with the calculated EMF if the initial reference SO_2 gas concentration is 8.4 vol%. The difference between the measured and the calculated EMF also becomes larger when the initial reference SO_2 gas concentration is 3.6 vol%.

Dependence of the initial reference SO_2 gas concentration on the measured EMF/calculated EMF ratios at 673 K for the Na_2SO_4-$NaVO_3$-$Ln_2(SO_4)_3$ (Ln= Pr and Y) electrolytes are shown in Fig. 8. The measured EMF/calculated EMF ratio abruptly decreases when the initial reference SO_2 gas concentration becomes less than 5 vol%. The electrolyte can not detect SO_2 gas accurately because the SO_2 gas concentration on the surface for the reference electrode is smaller than 5 vol% and the electrical conductivity of the electrolyte is appreciably low because the operating temperature is as low as 673 K.

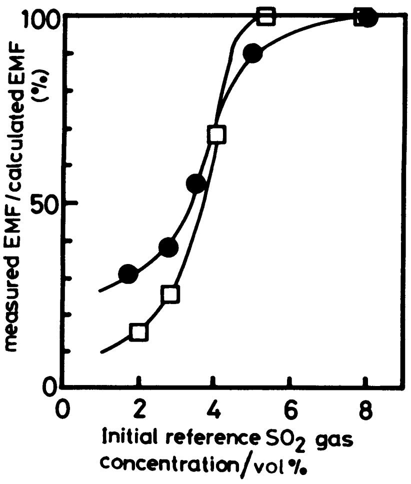

Fig. 8. Dependences of initial SO_2 gas concentration for reference on measured EMF/calculated EMF at 673 K.
☐ Na_2SO_4 : $NaVO_3$: $Pr_2(SO_4)_3$=91.1 : 3.9 : 5.0,
● Na_2SO_4 : $NaVO_3$: $Y_2(SO_4)_3$=91.4 : 3.6 : 5.0.

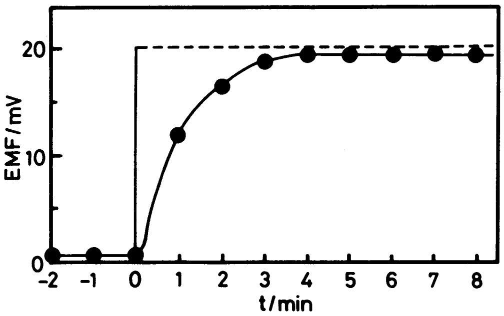

Fig. 9. A typical EMF response for the Na_2SO_4-$NaVO_3$-$Y_2(SO_4)_3$(91.4 : 3.6 : 5.0) electrolyte at 673 K.
The test and the reference SO_2 gas concentration are 20.5 and 9.7 vol%, respectively.
—— is calculated EMF.[2)]

A typical EMF response for the Na_2SO_4-$NaVO_3$-$Y_2(SO_4)_3$ electrolyte at 673 K is presented in Fig. 9. The EMF increases immediately when the test SO_2 gas reaches the surface of the electrolyte. However, about 4 min are necessary for the EMF to attain 96% of the calculated EMF. Jacob and Rao[2)] have described that approximately 4 min are required to attain 98% of the calculated EMF when pure sodium sulfate is used as a solid electrolyte at 973 K. The response time in our measurement coincides with their results. However, operating temperature of ours is approximately 300 K lower than theirs.

In conclusion, sodium sulfate doped with $NaVO_3$ and $Ln_2(SO_4)_3$ (Ln=Pr and Y) has suitable properties for the solid electrolyte because the solid solution shows considerably high electrical conductivity. The sulfate can be utilized as the solid electrolyte for a SO_2 gas sensor even at 673 K which is approximately 300 K lower than pure sodium sulfate can be used. The doping of sodium vanadate as well as rare earth sulfates makes considerable progress in the improvement of the electrolyte.

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