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THERMAL BEHAVIOUR AND S-O BONDING STATE OF ALKALINE-EARTH METAL SULFITES

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The thermal behaviours of magnesium sulfite, strontium sulfite and barium sulfite were investigated in the atmospheres of argon and air. the thermal behaviours of magnesium sulfite were different from those of the other two sulfites. The oxidation of magnesium sulfite in air does not occur.

The bonding state of the SO_3^{2-} in each sulfite was compared. The SO_3^{2-} in magnesium sulfite was coordinated through the sulfur, while those in the other sulfites were coordinated through the oxygen.

It appears that the difference in thermal behaviour between magnesium sulfite and the other sulfites depend upon the difference in bonding state of the SO_3^{2-}

Keywords: alkaline-earth metal sulfites, S–O bonding state

Introduction

Several experiments were carried out concerning the thermal behaviour of alkaline-earth metal sulfites [1–6] using thermogravimetry (TG), differential thermal analysis (DTA) and infrared absorption spectroscopy (IR). Lutz and Suradi [1] reported that strontium or barium sulfate and their sulfides were formed from their sulfites at high temperature. Saeki, Matsuzaki, Kobayashi and Masumizu [2] studied the reactions of magnesium sulfite at 450° to 800°C by X-ray diffraction measurements of the products formed at high temperature.

Thus far, the effect of atmosphere on their thermal behaviour and chemical bonding of the products obtained by their heating have only been slightly studied. Because the chemical bonding of their products changes with thermal reactions in different atmospheres, the thermal reaction mechanism might be clarified by studying the chemical bonding of each reaction product. In a previous paper, the changes in the S–O bonding state of calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2H_2O$) was studied by its thermal reaction. It was found

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that the S–O bonding state of the thermal products in nitrogen was somewhat different from that in hydrogen, and that its thermal behaviour in nitrogen were different from those in hydrogen [3].

In this study, thermal behaviours of magnesium, strontium and barium sulfites were investigated in the atmospheres of argon and air. Further, we investigated the S–O bonding state of each sulfite and sulfate formed by the thermal reaction in order to study the correlation between each thermal behaviour and S–O bonding state.

Experimental

Preparation of alkaline-earth metal sulfite

Guaranteed reagents of each alkaline-earth metal nitrate and ammonium sulfite monohydrate were used. Water as the solvent was purified using the ion-exchange resin and distillation method. An aqueous solution of the alkaline-earth metal nitrate was mixed at room temperature with an aqueous solution of ammonium sulfite using a magnetic stirrer (600 rpm) in flowing nitrogen (N_2). The concentration of each solution and reaction times are shown in Table 1. The volume ratio of each solution was 1:2 for the strontium sulfite preparation, and 1:1 for the others. The resulting precipitates were filtered off, washed with water, methyl alcohol and diethyl ether, and then dried over silica gel in a desiccator.

Table 1 Concentration of the solution and reaction time for the preparation of each sulfite

Sulfite	Concentration of each solution/ mol·dm^{-3}		Reaction time/ h
	Ammonium sulfite aq.	Nitrate aq.	
Magnesium	0.5	0.5	332
Strontium	1.0	1.0	3
Barium	0.2	0.2	38

The products analyzed by their X-ray diffraction (XRD) showed that the magnesium salt and strontium salt prepared in this experiment were $MgSO_3{\cdot}6H_2O$ and $SrSO_3$, respectively, and that the barium salt was characterized as $Ba_x(SO_3)_z$ with ASTM350869. We could not prepared a pure sample of only $BaSO_3$.

Measurement of TG and DTA curves, XRD, infrared absorption spectra and mass spectra

TG and DTA measurements of each sulfite were carried out under flowing argon gas (Ar)(200 ml/min) and flowing air (50 ml/min) using a MAC Science TG-DTA 2020 and Rigaku TG-DTA, respectively. The weight of the samples was about 10 mg, and the heating rate was 10 deg/min. Mass spectra were taken using the electron impact ionization method with a quadruple mass spectrometer VG Gas Analysis connected to a TG-DTA 2020 to detect gas produced in the argon atmosphere. Ionization potential was 20 eV, and mass number was detected between 10 and 100. The samples were cooled to room temperature after heating them in air to each required temperature, and then the XRD and IR measurements were carried out. XRD patterns were taken using a Rigaku RU-300 X-ray diffractometer. IR spectra were measured by the KBr disk method using a Nicolet 20DXB Fourier transform infrared spectrometer.

Results and discussion

Thermal behaviour of $MgSO_3{\cdot}6H_2O$

TG and DTA curves of $MgSO_3{\cdot}6H_2O$ in Ar and in air are shown in Fig. 1. These are in good agreement with he results obtained by Lutz *et al.* [7] and Saeki *et al.* [2].

In Ar, a large decrease in sample weight was observed below 200°C, which corresponds to the removal of water, and the DTA showed an endothermic peak. The evolution of H_2O was also identified by mass spectrometry. Thus, as previously mentioned [2, 4, 5], the thermal behaviour is determined as the dehydration of water in $MgSO_3{\cdot}6H_2O$ (Eq. (1)).

$$MgSO_3{\cdot}6H_2O \rightarrow MgSO_3 + 6H_2O \qquad (1)$$

At the same time, the evolution of sulfur dioxide (SO_2) was observed in the mass spectrum (Fig. 2). Accordingly, the decomposition of $MgSO_3$ (Eq. (2)) appeared to occur in the following way.

$$MgSO_3 \rightarrow MgO + SO_2 \qquad (2)$$

In the temperature range of 200° to 550°C, the sample weight decreases in two steps. It is about 27% of the total weight loss. The overlapping peaks (an endothermic peak and an exothermic peak) are observed in the DTA curve. It appears that a few other reactions occur simultaneously. Saeki *et al.* [2] considered

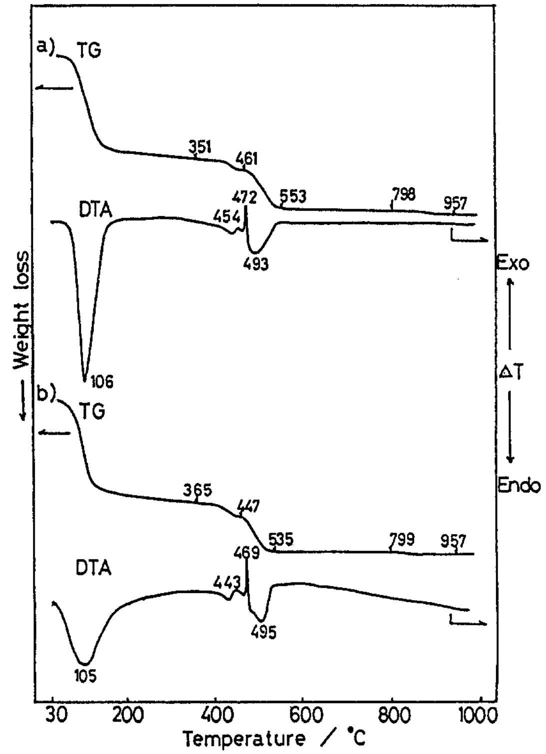

Fig. 1 TG and DTA curves of $MgSO_3 \cdot 6H_2O$ *a*) in Ar, *b*) in air

the thermal decomposition process of $MgSO_3$ in Ar, and reported that reaction (2) occurred below 250°C and reactions (2), (3) and (4) occurred below 300°C.

$$4MgSO_3 \rightarrow 2MgSO_4 + MgS_2O_3 + MgO \qquad (3)$$

$$MgS_2O_3 \rightarrow MgSO_3 + S \qquad (4)$$

On the other hand, Wittich [6] claimed reaction (5) appeared to be the total reaction for reactions (2), (3) and (4), in the temperature range of 210° to 250°C.

$$5MgSO_3 \rightarrow 2MgSO_4 + 3\ MgO + 2SO_2 + S \qquad (5)$$

Expected weight loss due to reaction (5) is about 24%, which agrees with the value shown in Fig. 1. Thus, reaction (5) may proceed in this temperature region. At about 850°C weight loss is approximately 1% and the mass spectrum shows the evolution of SO_2. It seems that the decomposition of unreacted $MgSO_3$ (Eqs (2) or (5)) occurs at such high temperatures. The TG and DTA curves in air are similar to the ones in Ar. These results imply that the thermal behaviour in air and in Ar are similar to each other.

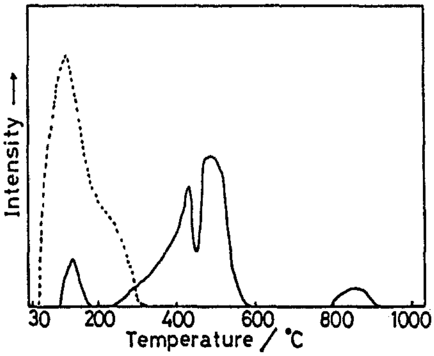

Fig. 2 Mass spectrum of $MgSO_3{\cdot}6H_2O$ in argon ---- : H_2O (mass number = 18), — : SO_2 (mass number = 64)

Figure 3 shows XRD patterns of the thermal products of $MgSO_3{\cdot}6H_2O$ in air. Only a broad amorphous pattern was observed up to 400°C. This suggests that only an amorphous product was obtained up to 400°C. At 440°C, crystalline

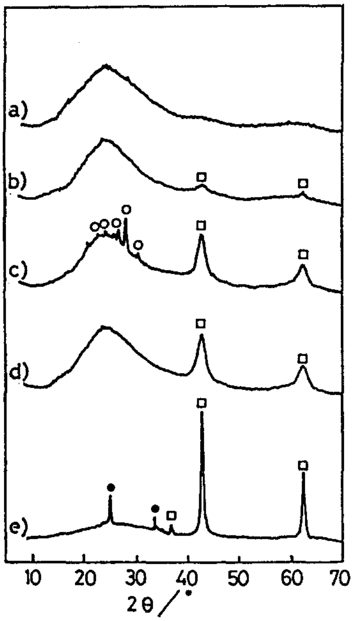

Fig. 3 XRD patterns of the products obtained by heating $MgSO_3{\cdot}6H_2O$ in air to indicated temperature *a)* 400°C, *b)*440°C, *c)* 480°C, *d)* 535°C, *e)* 830°C o: $MgSO_3$, □: MgO, ●: $MgSO_4$

reflections appeared with the broad amorphous pattern. This suggests that not only an amorphous product but also MgO crystals are formed.

At 480°C, several crystalline peaks were observed, corresponding to the formation of $MgSO_3$ and MgO. The peak intensities corresponding to MgO became stronger than those at 440°C. These facts suggest that amorphous $MgSO_3$ is partly crystallized and at the same time, it also decomposes to MgO. The exothermic peak at 469°C and the endothermic peak at 495°C may be attributed to the crystallization of $MgSO_3$ and the decomposition of $MgSO_3$ to MgO, respectively. Saeki *et al.* [2] also reported an exothermic peak at about 460°C on the DTA curve of $MgSO_3 \cdot 6H_2O$ in Ar, and concluded that it is due to the crystallization of $MgSO_3$. From the mass spectrum experiments, the evolution of SO_2 at about 460°C decreased because the decomposition could be inhibited by the crystallization of $MgSO_3$.

At higher temperatures, the amorphous pattern was again observed, in addition to the crystal reflections of MgO. The crystalline reflections corresponding to $MgSO_3$ disappeared, while those corresponding to MgO increased in intensity. The observed weight loss from 300° to 535°C was about 26%. This result supports supports reaction (5). Because the crystalline peaks due to $MgSO_4$ were not detected in the XRD pattern, $MgSO_4$ exists in an amorphous state.

In the XRD at 830°C, there was seen a decrease in intensity of the amorphous peak, an increase in the reflection peaks of MgO and the appearance of the crystalline reflection peaks of $MgSO_4$. There was observed a slight weight loss at about 830°C (Fig. 1).

Therefore, it seems than MgO exists as an amorphous structure at 535°C, while amorphous MgO and $MgSO_4$ are crystallized at 830°C. The TG curve of $MgSO_4 \cdot H_2O$ showed a slight weight loss at about 850°C. Then, reaction (6) may occur.

$$MgSO_4 \rightarrow MgO + SO_3, \qquad SO_3 \rightarrow SO_2 + 1/2O_2 \qquad (6)$$

We used IR spectroscopy to examine the S–O bonding state of the thermal products at each temperature. Figure 4 shows the IR spectra of each product. There are two bands at 938 and 666 cm^{-1} corresponding to the vibrations of SO_3^{2-} in the spectra of the products at 400° and 440°C. These are in good agreement with the result by Lutz *et al.* [7]. These bands are assigned to an asymmetrical stretching vibration (ν_3 SO_3) and symmetrical bending vibration ($\nu_2 SO_3$), respectively [8]. Considering these broad bands, SO_3^{2-} may have several kinds of symmetry.

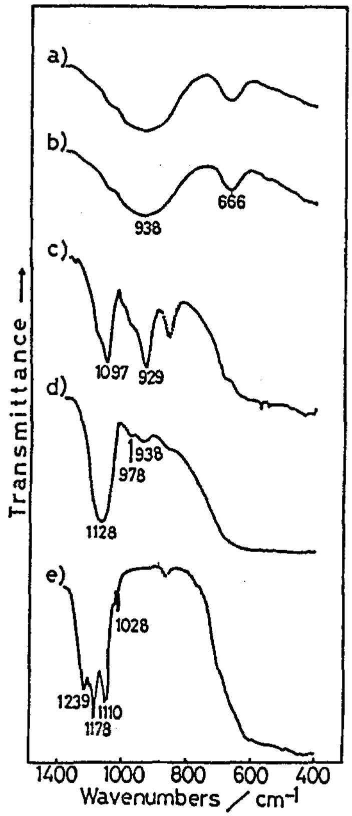

Fig. 4 IR spectra of the products obtained by heating $MgSO_3 \cdot 6H_2O$ in air to indicated temperature *a*) 400°C, *b*) 440°C, *c*) 480°C, *d*) 535°C, *e*) 830°C

The spectrum of the product at 480°C is different from those at 400° and 440°C. That is, ν_3SO_3 became somewhat sharp and shifts to 929 cm^{-1}. The new band observed at 1097 cm^{-1} was assigned to the asymmetrical stretching vibration of SO_4^{2-} (ν_3SO_4). The bands due to MgO appeared strongly below 700 cm^{-1}. It is recognized that SO_4^{2-} exists in the product.The infrared spectra of various sulfites and sulfates have been reported by several researchers [8–11]. These studies show that the free sulfite ion or the sulfur-coordinated sulfite has C_{3v} symmetry to be a pyramidal structure, in which the ν_3SO_3 and the ν_4SO_3 bands are doubly degenerated. When the sulfite ion is coordinated in a complex to possess Cs symmetry, ν_3SO_3 and ν_4SO_3 each split into two modes. The sulfate ion has T_d symmetry to be pyramidal structure, in which the ν_3SO_4 band is triply degenerated. When the symmetry of the sulfate ion is lowered to C_{3v}, this band splits to two bands. In the case of C_{2v}, this band splits into three bands. In this spectrum, the splitting of $\nu_3\mathrm{SO_3}$ and $\nu_3\mathrm{SO_4}$ were not observed. Therefore, it is considered that $\mathrm{SO_3^{2-}}$ approximately has C_{3v} symmetry to coordinate to the magnesium through the sulfur and the symmetry of $\mathrm{SO_4^{2-}}$ is T_d. The crystallization of $\mathrm{MgSO_3}$ can be attended by the sulfur-coordinated $\mathrm{SO_3^{2-}}$ species. The IR band at 859 $\mathrm{cm^{-1}}$ may arise from impurities which was ascribed to $\mathrm{CO_3^{2-}}$.

The IR spectrum of the product at 535°C showed that $\nu_3\mathrm{SO_4}$ shifted from 1097 $\mathrm{cm^{-1}}$ to 1128 $\mathrm{cm^{-1}}$ and became stronger, while $\nu_3\mathrm{SO_3}$ became weaker. This shows that $\mathrm{SO_3^{2-}}$ reacts to form $\mathrm{SO_4^{2-}}$ in which the S-O bonding is strengthened following decomposition of $\mathrm{MgSO_3}$ to $\mathrm{MgSO_4}$ and MgO, and the T_d symmetry of $\mathrm{SO_4^{2-}}$ is unchanged. In the spectrum of the product at 830°C, the peaks at 1239, 1178, 1110 and 1028 $\mathrm{cm^{-1}}$ are due to sulfate, and they are attributed to $\nu_3\mathrm{SO_4}$ (1239, 1178 and 1110 $\mathrm{cm^{-1}}$ bands) and a symmetrical stretching vibration of $\mathrm{SO_4^{2-}}$ ($\nu_1\mathrm{SO_4}$, 1028 $\mathrm{cm^{-1}}$). This spectrum indicates that the symmetry of $\mathrm{SO_4^{2-}}$ is lowered to C_{2v} from T_d by the formation of an oxygen-coordinated species. The crystal growth of $\mathrm{MgSO_4}$ may be accompanied by the formation of this $\mathrm{SO_4^{2-}}$ species.

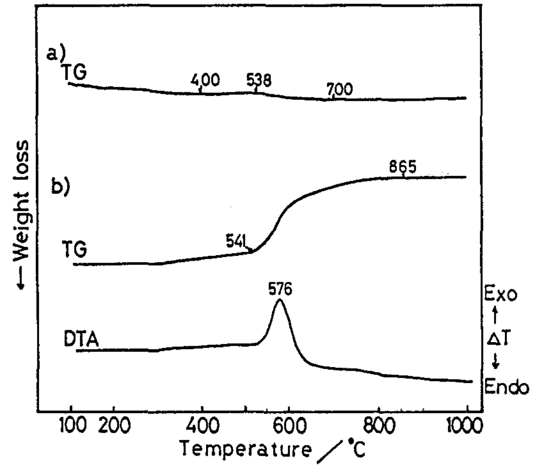

Fig. 5 TG and DTA curves of $\mathrm{SrSO_3}$ *a)* in Ar, *b)* in air

Thermal behaviour of $\mathrm{SrSO_3}$

TG and DTA curves of $\mathrm{SrSO_3}$ in Ar and in air are shown in Fig. 5. In Ar, the small decrease in sample weight on the TG curve and the evolution of $\mathrm{SO_2}$ in the mass spectrum were observed below 400°C. This indicates that reaction (7) occurred.

$$SrSO_3 \rightarrow SrO + SO_2 \qquad (7)$$

In the temperature range of 400° to 700°C in an Ar atmosphere, the TG curve and mass spectrum, in which the decrease in sample weight and the evolution of SO_2 were observed, indicated that reaction (7) also occurs. Lutz *et al.* [1] reported that the observation of an endothermic DTA peak at 560°C is attributed to the disproportionation reaction of the formation of $SrSO_4$ and SrS from $SrSO_3$. But we did not observe this peak.

On the other hand, the TG and DTA curves in air are entirely different from those in the Ar atmosphere. A large increase in sample weight at about 600°C and the exothermic DTA peak were observed at about 580°C.

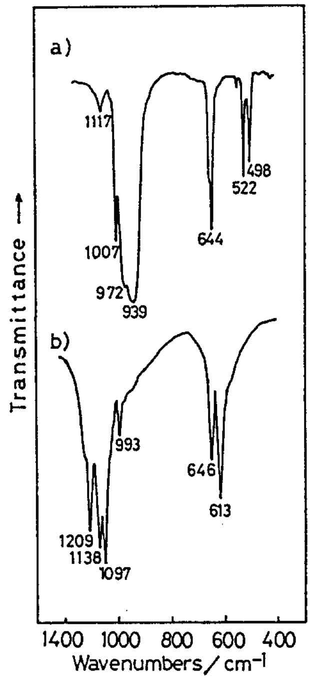

Fig. 6 IR spectra of (*a*) $SrSO_3$, and (*b*) the product obtained by heating $SrSO_3$ in air to 865°C

The IR spectrum of $SrSO_3$ and the product obtained by heating $SrSO_3$ up to 865°C are shown in Fig. 6. The IR data of $SrSO_3$ are in good agreement with that previously reported [1], in which the peaks at 522 and 498 cm^{-1} are assigned to $\nu_4 SO_3$. This indicates that the symmetry of SO_3^{2-} is approximately C_s

caused by the oxygen-coordinated species. According to Nyberg *et al.* [12], the sulfite ion is coordinated through the oxygen in strontium sulfite and barium sulfite. The results in this study support their explanation.

The crystalline peaks of $SrSO_3$ in the XRD pattern in the product at 865°C and the exothermic peak in the DTA curve suggest that the oxidation reaction (8) occurs at these temperatures.

$$SrSO_3 + 1/2O_2 \rightarrow SrSO_4 \qquad (8)$$

Only the IR peaks based on SO_4^{2-} were observed in the product at 865°C. Three peaks at 1209, 1138 and 1097 cm^{-1} are attributed to ν_3SO_4, showing that SO_4^{2-} is coordinated through the oxygen to the metal in the product.

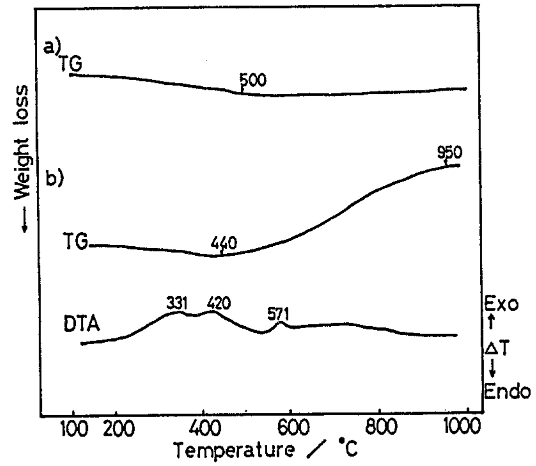

Fig. 7 TG and DTA curves of $Ba_x(SO_3)_z$ *a)* in Ar, *b)* in air

Thermal behaviour of $Ba_x(SO_3)_z$

The TG and DTA curves of $Ba_x(SO_3)_z$ in Ar and in air are shown in Fig. 7. In the Ar atmosphere, a weight loss was observed below 500°C, suggesting that a small amount of water was contained in $Ba_x(SO_3)_z$ as an impurity. The evolution of SO_2 was not observed in the mass spectrum. This suggests that the decomposition to BaO does not occur below 1000°C. Lutz *et al.* [1] observed the endothermic DTA peak at 545°C, and indicated the disproportionation reaction of the formation of $BaSO_4$ and BaS from $BaSO_3$. However, this peak was not detected in this study.

The TG and DTA curves in air are different from those in Ar in which the increase in sample weight at 440° to 950°C and the corresponding exothermic

DTA peaks were observed at 331°, 420°, 571°C, respectively. The thermal behaviour of $Ba_x(SO_3)_z$ in air are entirely different from that in Ar. The observed weight loss below 440°C and the corresponding exothermic DTA peaks in air may be caused by the decomposition of impurities contained in $Ba_x(SO_3)_z$.

To investigate the chemical bonding of SO_3^{2-} and SO_4^{2-} during the reaction of $Ba_x(SO_3)_z$, the S–O bonding of the product formed at temperatures up to 830°C was examined. In the XRD pattern, the crystalline reflection peaks corresponding to $BaSO_4$ were observed, indicating that oxidation occurs.

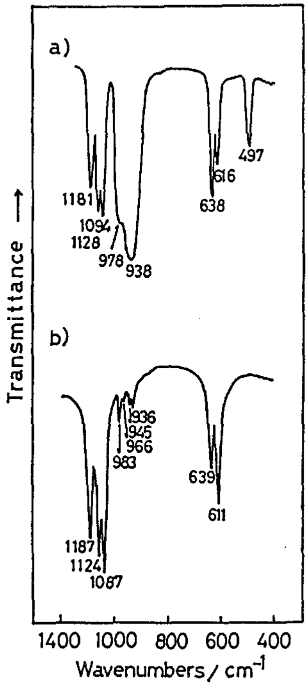

Fig. 8 IR spectra of (*a*) $Ba_x(SO_3)_z$ and (*b*) the product obtained by heating $Ba_x(SO_3)_z$ in air to 830°C

IR measurements were carried out to investigate the S–O bonding in the $Ba_x(SO_3)_z$ and the product at 830°C, and these spectra are shown in Fig. 8. In the IR spectrum of the prepared $Ba_x(SO_3)_z$, peaks of SO_3^{2-} and SO_4^{2-} were observed, suggesting that the SO_3^{2-} and SO_4^{2-} exist in $Ba_x(SO_3)_z$. The three split ν_3SO_4 modes (1181, 1128 and 1094 cm^{-1}) indicate the formation of the oxygen-coordinated sulfate species. The peaks at 978 and 938 cm^{-1} are assigned to the symmetrical stretching vibration of sulfite ion (ν_1SO_3) and ν_3SO_3, respectively. These are attributed to the C_{3v} pyramidal sulfite species.

In the spectrum of the product at 830°C, the peaks based on SO_4^{2-} increased their relative intensity, while those due to SO_3^{2-} decreased. The results correspond to the XRD results due to the oxidation from SO_3^{2-} to SO_4^{2-}. The ν_1SO_3 band (966 cm^{-1}) and the split ν_3SO_3 band (945 and 936 cm^{-1}) were observed. These indicate that the symmetry of SO_3^{2-} becomes C_s and the SO_3^{2-} is still remains coordinated through the oxygen to the metal. Although the SO_3^{2-} mainly has a sulfur-coordinated species of C_{3v} symmetry in $Ba_x(SO_3)_z$, the SO_3^{2-} becomes coordinated through the oxygen accompanying the oxidation reaction. The IR peaks attributed to ν_3SO_4 (1181, 1128 and 1094 cm^{-1}) are slightly shifted from those in the spectrum for $Ba_x(SO_3)_z$ (1187, 1124 and 1087 cm^{-1}). The ν_3SO_4 band is observed to be split into three modes, like as that in $Ba_x(SO_3)_z$. Therefore, the product at 830°C possesses the oxygen-coordinated sulfate species, and the S–O bonding energy is different from that in $Ba_x(SO_3)_z$.

Comparison of the thermal behaviour for each sulfite

Below 1000°C, $SrSO_3$ decomposes in Ar and is oxidized in air. $Ba_x(SO_3)_z$ does not decompose in Ar but is oxidized in air similar to $SrSO_3$. That is, for $SrSO_3$ and $Ba_x(SO_3)_z$ the thermal behaviour in Ar are different from that in air. Concerning the thermal behaviour of $CaSO_3 \cdot 1/2H_2O$, one of the alkaline-earth metal sulfites, we reported that the decomposition to CaO and the disproportionation reaction that forms $CaSO_4$ and CaS from $CaSO_3$ below 1000°C, are observed in nitrogen (N_2) gas and the oxidation of $CaSO_3$ mainly occurs in air or in the mixture of N_2 and O_2 [13, 14]. The thermal behaviour of $CaSO_3 \cdot 1/2H_2O$ in N_2 is also different from that in air. Therefore, $SrSO_3$ and $Ba_x(SO_3)_z$ show a similar thermal behaviour to that for $CaSO_3 \cdot 1/2H_2O$. For $MgSO_3 \cdot 6H_2O$, the thermal behaviour in Ar is similar to that in air, in which the oxidation of $MgSO_3$ is not observed below 1000°C. This indicates that $MgSO_3 \cdot 6H_2O$ usually exhibits a different thermal behaviour from the others and the sample is not oxidized.

Comparison of the chemical bonding state of the sulfite ion in the thermal products in air

The bonding structures of SO_3^{2-} in sulfites of magnesium, strontium and barium are summarized in Fig. 9.

IR spectra indicate that $SrSO_3$ and $Ba_x(SO_3)_z$ begins to have an oxygen-coordinated sulfite species due to the oxidation. It is known that the SO_3^{2-} is also

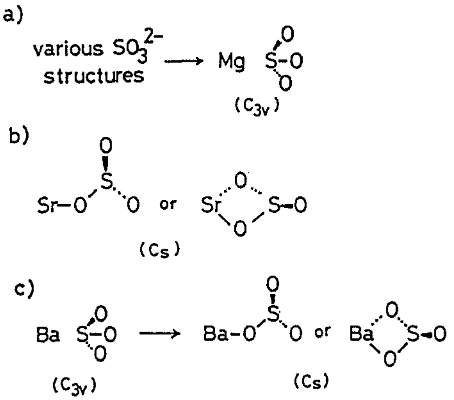

Fig. 9 Bonding state of SO_3^{2-} in each sulfite *a*) magnesium sulfite, *b*) strontium sulfite, c) barium sulfite

coordinated through the oxygen in $CaSO_3 \cdot 1/2H_2O$ [3]. That is, the SO_3^{2-} of calcium, strontium and barium sulfites becomes coordinated through the oxygen to the metal. In magnesium sulfite, however, the SO_3^{2-} is coordinated through the sulfur to the metal at temperatures up to 830°C, at which time SO_3^{2-} disappeared in the IR spectrum. The bonding state of SO_3^{2-} in the thermal products from $MgSO_3 \cdot 6H_2O$ is different from those from the others. It is thought that the SO_3^{2-} coordinated through the oxygen is usually oxidized easier than that coordinated through the sulfur.

It is well known that the differences in the chemical properties between the beryllium and magnesium compounds and the other alkaline-earth metal compounds are caused by their small ionic radius and the high value of their second ionization potential [15]. The reason why the bonding state of the SO_3^{2-} for magnesium sulfite differs from that for the others in this study may be based on these considerations.

Conclusions

The thermal behaviour of the sulfite of magnesium, strontium and barium were investigated at temperatures up to 1000°C in Ar and in air.

For magnesium sulfite, the thermal behaviour in Ar is similar to that in air, and the thermal decomposition to $MgSO_4$ and MgO from $MgSO_3$ takes place below 500°C. For strontium sulfite, the thermal decomposition to SrO occurs somewhat in Ar, while the oxidation to $SrSO_4$ naturally occurs in air. For barium sulfite ($Ba_x(SO_3)_z$), the thermal decomposition does not occur in Ar, while in air the oxidation occurs. The different kinds of atmosphere produces a different thermal behaviour for strontium sulfite and barium sulfite, and these sulfites show a similar thermal behaviour tendency. On the other hand, the oxidation of magnesium sulfite does not occur in air, which is different from the thermal behaviour for calcium, strontium and barium sulfites.

The bonding structure of the SO_3^{2-} in the thermal products obtained in air have been examined. The SO_3^{2-} is coordinated through the sulfur to the metal in magnesium sulfite. The SO_3^{2-} in strontium sulfite is the oxygen-coordinated species. In $Ba_x(SO_3)_z$, the SO_3^{2-} , first, is mainly coordinated through the sulfur, but with further oxidation it becomes an oxygen-coordinated sulfite species. It turns out that magnesium sulfite has a different bonding structure for the SO_3^{2-} as compared to the others.

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Zusammenfassung In Luft und in Argon wurde das thermische Verhalten von Magnesiumsulfit, Strontiumsulfit und Bariumsulfit untersucht. Dabei zeigte Magnesiumsulfit ein anderes Verhalten als die beiden anderen Sulfite. Bei Magnesiumsulfit findet an Luft keine Oxidation statt.

Weiterhin wurde der Bindungszustand von SO_3^{2-} in den einzelnen Sulfiten miteinander verglichen. SO_3^{2-} im Magnesiumsulfit ist über den Schwefel und in den anderen Sulfiten über den Sauerstoff koordiniert.

Die Unterschiede im thermischen Verhalten von Magnesiumsulfit und den übrigen Sulfiten scheinen vom unterschiedlichen Bindungszustand von SO_3^{2-} abzuhängen.