

Homogeneous precipitation of $\text{Cr}^{3+}\text{--M}^{2+}$ ($\text{M} = \text{Ni}, \text{Zn}, \text{Co}, \text{Cu}$) oxalate by oxidation of the polyethylene glycol–cation complex

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$\text{Cr}^{3+}\text{--M}^{2+}$ ($\text{M} = \text{Ni}, \text{Zn}, \text{Co}, \text{Cu}$) oxalate complexes were obtained by heat treatment of a polyethylene glycol (PEG) solution of a metal nitrate hydrate at 353 K for 6 h. The relation between the cation mole fraction $[\text{M}^{2+}/(\text{Cr}^{3+} + \text{M}^{2+})]$ in the PEG solution and in the precipitate obtained depended on the molecular weight of the PEG. The structure and the cation arrangement in the oxalate precipitate also depended on the molecular weight of the PEG. Two different models for the process of precipitate formation were examined in which it is assumed that Cr^{3+} and M^{2+} coordinate to PEG independently of and cooperatively with each other, respectively. The calculated relation between the M^{2+} mole fraction of the PEG solution and that of the precipitate was compared with the relation obtained from the experimental results. The results obtained from the second model agreed quite well with the experimental results. We therefore conclude that Cr^{3+} and M^{2+} coordinate cooperatively to PEGs.

Introduction

Transition metal oxides show semiconductivity, which can be regulated by doping the different valence cations from the mother oxide cations.¹ The electrical conductivity of the valence-controlled oxide depends on the dispersed state of the doped ions.^{2,3} Furthermore, there are many multicomponent oxides that show both ferroelectric and magnetic properties. In order to obtain multicomponent oxides, the cations in the oxide must be homogeneously dispersed at the atomic level. Many different techniques for preparing homogeneous multicomponent oxides have been developed.^{4,5} Oxalates are considered to be useful precursors for preparing multicomponent oxides,⁶ and oxalates containing different divalent cations can be obtained in a wide compositional range by the coprecipitation method,^{7,8} however, it is difficult to obtain oxalates containing different valence cations. As these oxalates would be good precursors for the preparation of homogeneous multicomponent oxides, it is desirable to develop a straightforward method for their synthesis.⁹

Preparation methods for obtaining multicomponent oxides by the oxidation of polymer–cation complexes have been developed.¹⁰ An important feature of these methods is that the oxides obtained reflect the highly homogeneous dispersion of cations in the polymer–cation complex.¹¹ Thereby, if the oxalates are obtained by oxidation of organic polymer–cation complexes then the cation arrangement in the oxalates reflects that in the polymer–cation complex. The cation arrangement in the polymer–cation complex can be regulated by control of the molecular weight of the polymer,¹² the appropriate oxalate will then be obtained as a precursor of the multicomponent oxides by these methods.

Polyethylene glycol $[\text{PEG HO}(\text{--CH}_2\text{CH}_2\text{O})_n\text{--H}]$ can dissolve many kinds of inorganic salts due to coordination of the PEG ether oxygen atoms to the metal ions. Furthermore, PEG is converted to an oxalic acid by oxidation with nitrate ions.¹³ Consequently, PEG is an appropriate polymer for use

as a multicomponent oxalate precursor in the preparation of oxide ceramics. There are other precipitation methods for the preparation of multicomponent oxalates such as coprecipitation and homogeneous precipitation methods but the precipitates obtained by conventional methods tend to have compositional variations due to differences in the solubility factors of the precipitates. It is expected that precipitation methods that make use of the PEG–cation complex will enable precipitate formation with homogeneous cation dispersion at the atomic level, since the homogeneous cation distribution in the PEG solution is reflected in the PEG–cation complex.

In this study, oxalates containing Cr^{3+} and M^{2+} ($\text{M} = \text{Ni}, \text{Zn}, \text{Co}, \text{Cu}$) were prepared by oxidation of a PEG–cation complex in a PEG solution of the metal nitrate hydrate. The $\text{Cr}^{3+}\text{--M}^{2+}$ oxalate complex was difficult to prepare by the conventional precipitation method. The process for formation of the PEG–cation complex and the precipitate was investigated through the creation of two different models.

Experimental

Preparation of oxalate precipitate

The $\text{Cr}^{3+}\text{--Ni}^{2+}$ oxalate complex was prepared as follows: Chromium(III) nitrate enneahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were added to 10 g of molten PEG having a molecular weight of 1000 (hereinafter referred to as “PEG1000”) and stirred at 333 K. A homogeneous clear solution was obtained. There were 0.012 mol of cations in the PEG solution, and the cation/[PEG monomer] ratio was 0.05. The Ni^{2+} mole fraction $[\text{Ni}^{2+}/(\text{Ni}^{2+} + \text{Cr}^{3+})]$ in this PEG1000 solution is referred to as “ X_s ”. The PEG solution of the metal nitrate hydrate was kept in a Pyrex glass beaker at 353 K for 6 h. The evolution of NO_2 was observed during the heating process. The solution obtained after heat treatment was a complex mixture of

oxalate, unreacted metal nitrate hydrate and PEG. In order to separate the oxalate, this product was homogeneously dispersed in an 80 wt.% ethanol aqueous solution. The oxalate was separated by centrifugation, followed by drying at 333 K for 3 h. Hereinafter, the Ni^{2+} mole fraction in the obtained precipitate $[\text{Ni}^{2+}/(\text{Cr}^{3+} + \text{Ni}^{2+})]$ is referred to as " X_p ". The above procedures were repeated using either ethylene glycol (EG), triethylene glycol (TEG) or PEG with a molecular weight of 300 (PEG300) and with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ instead of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. All the chemicals used were of reagent grade (Wako Pure Chemical Industries, Ltd.). Hereinafter, the PEG solution of the metal nitrate hydrate and the precipitate obtained from the PEG solution are referred to as $S(n, X_s)$ and $P(n, X_s)$, respectively, with n representing the molecular weight of the PEG used. In this study, EG and TEG are considered to be PEGs.

Characterization

The crystal structures of the resulting compounds were examined using X-ray diffraction (XRD) with $\text{Cu-K}\alpha$ radiation (40 kV 200 mA) and a graphite monochromator (Mac Science Co. Ltd. MXP-18). The cation mole fraction $[X_p = \text{M}^{2+}/(\text{Cr}^{3+} + \text{M}^{2+})]$ in the oxalate obtained was measured by X-ray fluorescence spectroscopy. Differential thermal analysis (DTA) was carried out with the temperature being increased at a rate of 5 K min^{-1} in air (Rigaku Thermoflex). FTIR spectra of the pressed samples with KBr were measured at room temperature (JASCO FT/IR-350).

Results and discussion

Oxalate formation from the PEG1000–cation complex

Fig. 1 shows the relation between the Ni^{2+} mole fraction in the $\text{PEG}-(\text{Cr}^{3+}, \text{Ni}^{2+})$ solution (X_s) and the Ni^{2+} mole fraction in the precipitate (X_p). X_p increased with increasing X_s . It can be seen that coprecipitation of Cr^{3+} and Ni^{2+} occurred in the PEG1000 solution with $X_s \geq 0.2$.

Fig. 2 shows the XRD patterns of the precipitate from the $\text{PEG1000}-(\text{Cr}^{3+}, \text{Ni}^{2+})$ solution. The XRD patterns in Fig. 2(a) and (b) indicate that the precipitates obtained from $S(1000, 0)$ and $S(1000, 0.2)$ are amorphous. The precipitate obtained from the PEG1000 solution, whose X_s was greater than 0.3, showed the same XRD pattern as nickel oxalate hydrate $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, as shown in Fig. 2(c)–(f). The XRD patterns in Fig. 2(c)–(e) are completely different to that of anhydrous NiC_2O_4 , as shown in Fig. 2(g), indicating that the precipitates are not anhydrous oxalate. As shown in Fig. 1, $P(1000, X_s \geq 0.2)$ contains both Cr^{3+} and Ni^{2+} . As a result,

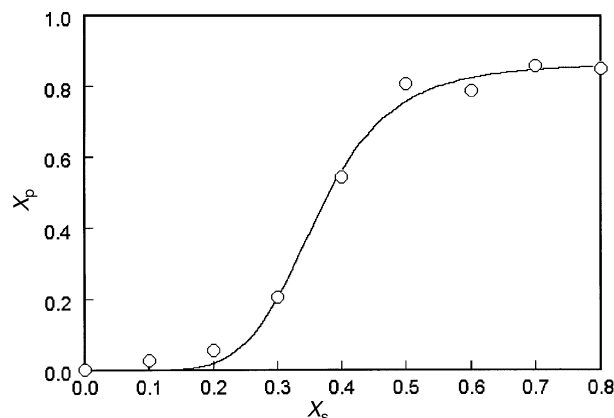


Fig. 1 The relation between the nickel mole fraction of the nitrate hydrate salt solution (X_s) and that of the precipitate (X_p) as determined by X-ray fluorescence spectroscopy.

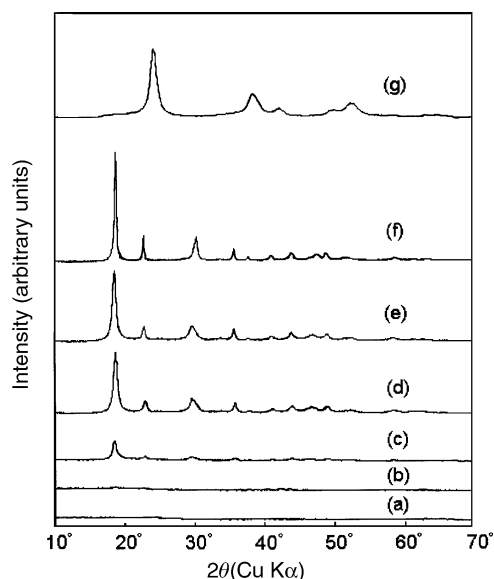


Fig. 2 XRD patterns of the precipitates from the PEG 1000 solutions. The Ni mole fractions $\text{Ni}/(\text{Ni} + \text{Fe})$ of the PEG1000 solutions were: (a) $P(1000, 0)$, (b) $P(1000, 0.2)$, (c) $P(1000, 0.3)$, (d) $P(1000, 0.4)$ and (e) $P(1000, 0.6)$. (f) and (g) are the reference patterns of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and NiC_2O_4 (anhydrous).

$P(1000, X_s \geq 0.2)$ is considered to be a mixture of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and the precipitate containing only Cr^{3+} $P(1000, X_s = 0)$ or a compound in which the Ni^{2+} position in the nickel oxalate structure ($\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) is replaced by Cr^{3+} .

The FTIR spectra of the precipitate obtained from the $\text{PEG}-(\text{Cr}^{3+}, \text{Ni}^{2+})$ solution are shown in Fig. 3. The assignments of the absorption peaks are given in the figure. The absorption peak A from 3600 to 3000 cm^{-1} in Fig. 3(a) and (b) can be assigned to the stretching vibration of the hydrogen-bonded OH groups. The absorption peak B around 2800 cm^{-1} in Fig. 3(a) can be assigned to the stretching vibration of the CH_2 group. The absorption peaks E around 1400 cm^{-1} and F around 1100 cm^{-1} in Fig. 3(a) and (b) can be assigned to the stretching vibrations of NO_3^- and the C–O–C bond, respectively.¹⁴ The absorption peaks B and F of $P(1000,$

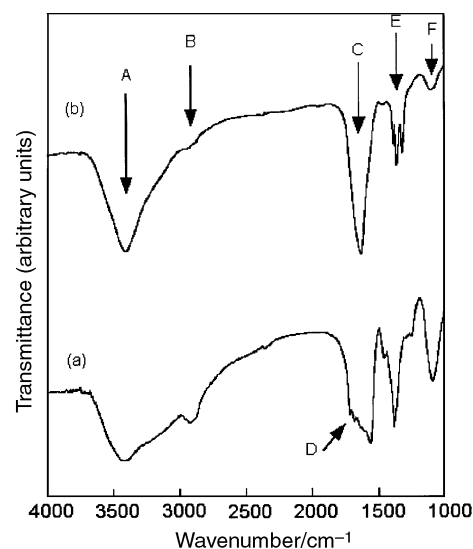


Fig. 3 FTIR spectra of the precipitates: (a) $P(1000, 0)$ and (b) $P(1000, 0.4)$. A: the stretching vibration of the hydrogen-bonded OH group; B: the stretching vibration of the CH_2 group; C: the stretching vibration of the COO^- group; D: the stretching vibration of the C=O group; E: the stretching vibration of NO_3^- and F: the stretching vibration of the C–O–C group.

0.4) in Fig. 3(b) are much weaker than that of P(1000, 0) in Fig. 3(a). It is considered that peaks B, E and F in Fig. 3(a) and (b) correspond to adsorbed PEG on the precipitate. Because an oxalate does not have a $-\text{CH}_2-$ group in its structure the IR absorption of the $-\text{CH}_2-$ stretching vibration of the precipitate can be assigned to that of PEG. PEG is a water-soluble compound so that washing the precipitate with water will remove the weakly adsorbed PEG. Thus it was shown that the absorption peak of $-\text{CH}_2-$ group corresponded to the adsorbed species on the precipitate.

The FTIR spectrum of P(1000, 0) has the absorptions C (at 1570 cm^{-1}) and D (around 1700 cm^{-1}), which we have assigned to the stretching vibrations of the COO^- group and the $\text{C}=\text{O}$ group, as shown in Fig. 3(a). The spectrum of P(1000, 0.4) has only absorption C at 1622 cm^{-1} . The absorption assigned to the $\text{C}=\text{O}$ group cannot be observed in the FTIR spectrum of P(1000, 0.4), as shown in Fig. 3(b). Further, the position of the absorption peak C of P(1000, 0.4) is different from that of P(1000, 0). Hence, it is shown that P(1000, 0.4) is not only a mixture of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and P(1000, 0), which gave a precipitate that included only Cr^{3+} cations. Further, the precipitate P(1000, $X_s \geq 0.3$) had the same structure as $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, so it is considered that the Ni^{2+} site in the nickel oxalate hydrate is replaced by Cr^{3+} . We therefore conclude that the formula of the precipitate is $\text{Cr}_x\text{Ni}_{(1-3x/2)}\text{C}_2\text{O}_4 \cdot y\text{H}_2\text{O}$ due to the electrical charge conservation law.⁸ Accordingly, the oxalate precipitate was formed by heating the homogeneous PEG solution of the metal nitrate hydrate at 353 K. The heating produced oxalate in response to the oxidation of PEG with nitrate ions in the PEG solution at 353 K. Oxidation of the PEG–cation complex by nitrate ions can be assumed based on the evolution of NO_2 gas from the PEG solution during the heat treatment. We can therefore conclude that the precipitation process is one of homogeneous precipitation.

Relation between the molecular weight of the PEG used and the precipitate obtained

Fig. 4 shows the relation between the nickel mole fraction of the PEG–(Cr^{3+} , Ni^{2+}) solution (X_s) and that of the precipitate obtained (X_p) through the use of PEGs of different molecular weight. It can be seen that the relation between X_s and X_p depends on the molecular weight of the PEG used for the preparation.

Fig. 5 shows the XRD patterns of the precipitates formed from PEG–(Cr^{3+} , Ni^{2+}) solution with PEGs of different molecular weight. The XRD pattern of P(EG, 0.6) shows a very broad peak due to the amorphous precipitate and the less crystallized oxalate, whose structure is the same as that of

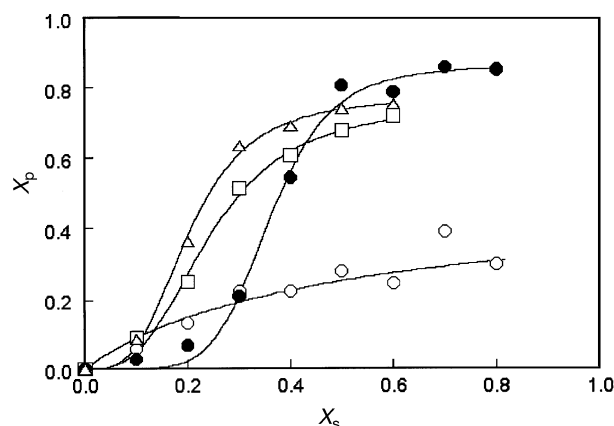


Fig. 4 The relation between the nickel mole fraction of the nitrate hydrate salt solution (X_s) and that of the precipitate (X_p). The glycols used for the nitrate hydrate solutions are: (○), EG; (□), TEG; (△), PEG300 and (●) PEG1000.

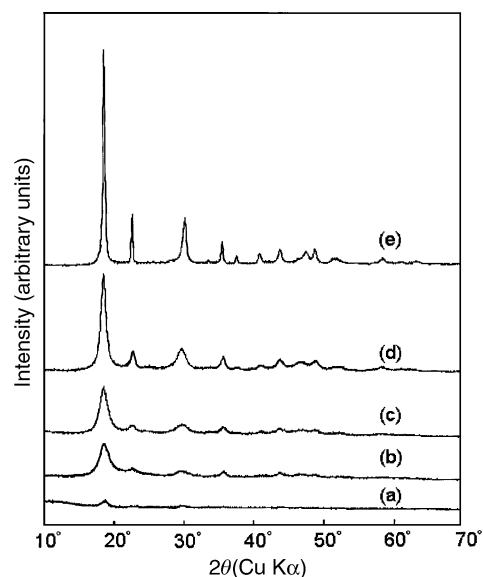


Fig. 5 XRD patterns of the precipitates from the PEG solutions with $X_s = 0.6$. (a) P(EG, 0.6); (b) P(TEG, 0.6); (c) P(300, 0.6); (d) P(1000, 0.6) and (e) the reference pattern of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

nickel oxalate hydrate, as shown in Fig. 5(a). When the molecular weight of PEG was greater than of TEG, the XRD peaks of the precipitate can be observed at the same position as those of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Fig. 5(e)).¹⁵ The intensity and the FWHM of the diffraction peak increased with increasing molecular weight of the PEG. Thus, the structure of the precipitate also appears to depend on the molecular weight of the PEG used.¹⁶

Fig. 6 shows the DTA curves of P(300, 0.5), P(1000, 0.5), obtained from the PEG–(Cr^{3+} , Ni^{2+}) solution and $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The DTA curves of P(300, 0.5) and P(1000, 0.5) have a single exothermic peak at 623 and 546 K, respectively, as shown in Figs. 6(a) and (b). In contrast, the DTA curve of the reference sample $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, which has the same crystal structure as the precipitates, has an exothermic peak at 594 K due to oxidation of the oxalate ion, as shown in Fig. 6(c). $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ also has an endothermic peak at 481 K due to dehydration. Thus, the precipitates obtained from the PEG solution do not have the dehydration endothermic

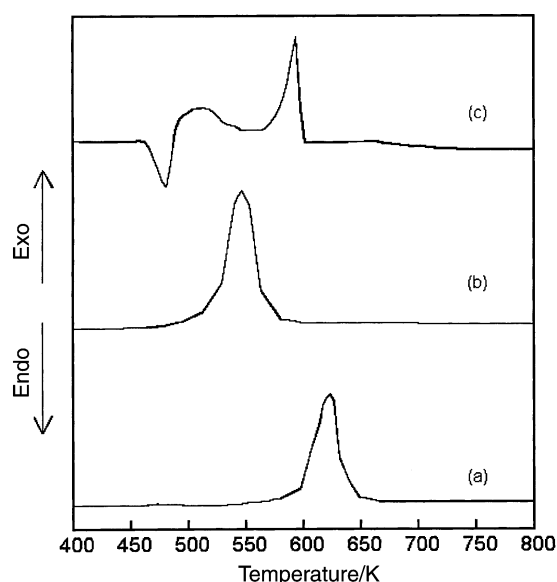


Fig. 6 DTA curves of the precipitates obtained from the PEG solution. (a): P(300, 0.5), (b): P(1000, 0.5) and (c): $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

DTA peak, which seems to indicate that the obtained precipitate is anhydrous nickel oxalate. However, as shown in Fig. 2, the obtained precipitates are not anhydrous oxalates. From Fig. 6, we can also see that the precipitates P(300, 0.5) and P(1000, 0.5) are not merely a mixture of nickel oxalate hydrate $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and a precipitate containing only Cr^{3+} , since the endothermic peak due to the nickel oxalate hydrate ($\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) was not observed. Furthermore, the DTA peak position of P(300, 0.5) is different from that of P(1000, 0.5). Both P(300, 0.5) and P(1000, 0.5) have almost the same Ni^{2+} mole fraction (X_p) and show almost the same XRD diffraction peaks. This result seems to indicate that the cation arrangement (Cr^{3+} and Ni^{2+}) in P(300, 0.5) is different from that in P(1000, 0.5). The difference in the cation arrangement in the precipitate causes the cation–cation and the cation–anion interactions in the precipitates to be different, which explains why the DTA peak position was different. Thus, the cation arrangement in the precipitate also depends on the molecular weight of the PEG used.

Fig. 7 shows the relation between X_s and X_p of the precipitate obtained from the PEG1000–(Cr^{3+} , M^{2+}) solution ($\text{M} = \text{Zn}, \text{Co}, \text{Cu}$). The coprecipitation of Cr^{3+} and M^{2+} was obtained from the PEG solution with $X_s > 0$. The XRD measurement of the precipitates with $X_s \geq 0.3$ showed the same spectra as those of the oxalate hydrate salts. Thus, when both Ni^{2+} and the other divalent ion M^{2+} ($\text{M} = \text{Zn}, \text{Co}, \text{Cu}$) were used, a Cr^{3+} and M^{2+} oxalate complex was obtained.

Models of the homogeneous precipitation process from PEG solution

In this section, the relation between X_s and X_p is derived from models of the homogeneous precipitation process from the PEG–(Cr^{3+} , M^{2+}) solution. The formation process for the precipitate from the PEG solution will be investigated by means of a comparison between the experimental results and those obtained from the models.

Here, we examine the models, which are based on the following three assumptions: [1] A complex between PEG and cations [PEG–(Cr^{3+} , M^{2+}) complex] is formed in the PEG solution of the metal nitrate hydrate ($\text{M} = \text{Ni}, \text{Zn}, \text{Co}, \text{Cu}$). [2] An oxalate precipitate is formed by oxidation of the PEG–(Cr^{3+} , M^{2+}) complex with nitrate ions (NO_3^-). [3] The M^{2+} mole fraction X_p [$\text{M}^{2+}/(\text{M}^{2+} + \text{Cr}^{3+})$] in the precipitate is the same as the M^{2+} mole fraction of the PEG–(Cr^{3+} , M^{2+}) complex in the PEG solution.

Assumption [1] corresponds to the solvation of cations in the solution.¹⁷ Assumption [2] was derived from our finding that the precipitate contains both Cr^{3+} and M^{2+} . Here, if assumption [3] holds, the relation between X_s and X_p

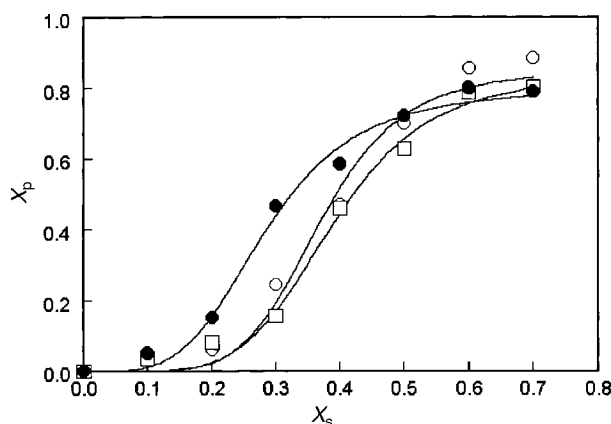


Fig. 7 Relation between the nickel mole fraction of the nitrate hydrate salt solution (X_s) and that of the precipitate (X_p). The divalent ions (M^{2+}) in the PEG1000–cation complex are: (□) Zn^{2+} ; (○) Co^{2+} ; and (●) Cu^{2+} .

depends on the formation process of the PEG–cation complex (assumption [1]). We therefore study assumption [1] in detail. The precipitate P(PEG, $X_s > 0$) contains both Cr^{3+} and M^{2+} . It is not necessary to consider the possibility that only Cr^{3+} and PEG form the PEG– Cr^{3+} complex nor is it necessary to consider the possibility that only M^{2+} and PEG form the PEG– M^{2+} complex. Further, there are two cases in which the cations coordinate to the coordination site in PEG independently and cooperatively, respectively. The word “independently” means that the coordination of Cr^{3+} to PEG and that of M^{2+} do not influence each other. The word “cooperative” means that the coordination of the cation to PEG affects the coordination at the other PEG coordination sites. This type of cooperative coordination is characteristic of these polymer complexes.^{18,19} Based on the above model, two different cases were considered. One involved a case in which the cations independently coordinate to the PEG coordination site (model 1) and an other in which the cations cooperatively coordinate to the PEG coordination site (model 2).

We examined the relation between X_p and the heating time (0.5, 1, 2, 3 and 6 h). No dependence of X_p on the heating time was observed. Showing that formation of the PEG–cation complex is more rapid than oxidation of the PEG–cation complex. Thereby, before oxidation of the PEG–cation complex, the equilibrium of the cation mole fraction in the PEG–cation complex was established. Thereby, it is considered that the kinetics of the precipitation process is not important.

The relation between X_s and X_p derived from model 1

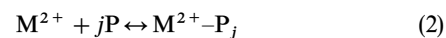
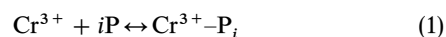
In this section, model 1, which consists of the following assumptions, is studied. Coordination of the cations occurs independently at each coordination site.

[1] When the PEG–(Cr^{3+} , M^{2+}) complex is formed, cation coordination follows assumptions [1-1] and [1-2]. [1-1] The coordination of Cr^{3+} to PEG is not affected by the condition of the other PEG coordination sites. [1-2] The coordination of M^{2+} to PEG is not affected by the condition of the other PEG coordination sites.

[2] The oxalate precipitate is formed by the oxidation of the PEG–(Cr^{3+} , M^{2+}) complex with nitrate ions (NO_3^-).

[3] The M^{2+} mole fraction [$\text{M}^{2+}/(\text{M}^{2+} + \text{Cr}^{3+})$] in the precipitate (X_p) is the same as the M^{2+} mole fraction of the PEG–(Cr^{3+} , M^{2+}) complex in the PEG solution.

According to assumptions [1-1] and [1-2], the formation of the PEG–(Cr^{3+} , M^{2+}) complex can be represented schematically as:



where P represents the coordination site of PEG (the ether oxygen atom); i and j are the coordination numbers of the PEG coordination site, which is required for the coordination of Cr^{3+} and M^{2+} , respectively; and $\text{Cr}^{3+}\text{-P}_i$ and $\text{M}^{2+}\text{-P}_j$ represent the complexes between the PEG coordination site and the cations. Here, eqn. (3) and (4) can be derived.

$$[\text{Cr}^{3+}\text{-P}_i] = K_1[\text{Cr}^{3+}][\text{P}]^i \quad (3)$$

$$[\text{M}^{2+}\text{-P}_j] = K_2[\text{M}^{2+}][\text{P}]^j \quad (4)$$

where K_1 and K_2 are the equilibrium constants of reactions (1) and (2), and $[\text{Cr}^{3+}\text{-P}_i]$, $[\text{M}^{2+}\text{-P}_j]$, $[\text{Cr}^{3+}]$, $[\text{M}^{2+}]$ and $[\text{P}]$ are the mole fractions in the solution. As a result, X_p [$=\text{M}^{2+}/(\text{M}^{2+} + \text{Cr}^{3+})$] can be expressed from assumption [2].

$$X_p = \frac{[\text{M}^{2+}\text{-P}_j]}{[\text{Cr}^{3+}\text{-P}_i] + [\text{M}^{2+}\text{-P}_j]} \quad (5)$$

When eqn. (3) and (4) are substituted into eqn. (5), eqn. (6) is obtained.

$$X_P = \frac{K_2[M^{2+}][P]^j}{K_1[Cr^{3+}][P]^i + K_2[M^{2+}][P]^j} \quad (6)$$

Here, there is excess PEG for the cations in the PEG solution. As a result, $[Cr^{3+}]$, $[M^{2+}]$, $[Cr^{3+}-P_i]$, $[M^{2+}-P_j] \ll [P]$ applies, because the mole ratio of cation/ $[P] = 0.05$, as pointed out in the Experimental section. Then, $[P] = 1$ is a good approximation. When $[P] = 1$ is substituted into eqn. (6), eqn. (7) applies.

$$X_P = \frac{K_2[M^{2+}]}{K_1[Cr^{3+}] + K_2[M^{2+}]} \quad (7)$$

When the amount of Cr^{3+} and M^{2+} in the PEG solution is assumed to be in large excess in relation to the PEG-cation complex, the change in the cation composition in the solution can be ignored during the precipitation process. As a result, $[Cr^{3+}] + [M^{2+}]$ is considered to be constant throughout the precipitation process.

$$X_S = \frac{[M^{2+}]}{[Cr^{3+}] + [M^{2+}]} \quad (8)$$

$$[Cr^{3+}] \cong k(1 - X_S), [M^{2+}] \cong kX_S \quad (9)$$

where k is the proportionality constant. When eqn. (9) is substituted into eqn. (7), we obtain eqn. (10).

$$X_P = \frac{X_S}{\alpha + (1 - \alpha)X_S} \quad (10)$$

where $\alpha = K_1/K_2$. In this way, eqn. (10), which describes the relation between X_S and X_P , can be obtained from model 1.

The relation between X_S and X_P derived from model 2

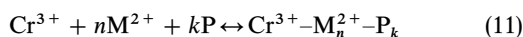
In model 2, it is assumed that the cations coordinate to PEG by a cooperative process. When Cr^{3+} and M^{2+} coordinate to the PEG coordination site, the coordination of Cr^{3+} and M^{2+} occurs cooperatively.

[1] When the PEG- (Cr^{3+}, M^{2+}) complex is formed, the coordination of the cations follows assumptions [1-3] and [1-4]. [1-3] The coordination of Cr^{3+} to PEG is not affected by the condition of the other PEG coordination sites. [1-4] One Cr^{3+} ion coordinates to PEG together with n M^{2+} ions. The coordination of only the M^{2+} ions can be considered to be negligible.

[2] The oxalate precipitate is formed by oxidation of a PEG- (Cr^{3+}, M^{2+}) complex with nitrate ions (NO_3^-).

[3] The Cr^{3+} mole fraction $[Cr^{3+}]/([M^{2+}] + [Cr^{3+}])$ in the precipitate (X_P) is the same as the Cr^{3+} mole fraction of the PEG- (Cr^{3+}, M^{2+}) complex in the PEG solution.

The coordination of Cr^{3+} to PEG is much stronger than that of M^{2+} . (For example, the stability constants $\log \beta_1(\text{EDTA})$ of Cr^{3+} and Ni^{2+} are 23 and 18.6, respectively.²⁰) When cations with greatly different stability constants coordinate to PEG, the cooperative coordination process described in [1-4] makes possible an increase in the number of divalent cations in the precipitate compared with the precipitation process described in model 1. It is reasonable to accept assumption [1-4] in order to explain the coprecipitation of Cr^{3+} and M^{2+} . Assumptions [1-3] and [1-4] can be expressed as the equilibrium eqn. (1) and (11), respectively.



$Cr^{3+}-M_n^{2+}-P_k$ represents the complex formed by the coordination of Cr^{3+} and M^{2+} to PEG. When K_3 is the equilibrium constant of eqn. (11), we obtain eqn. (3) and eqn. (12).

$$[Cr^{3+}-M_n^{2+}-P_k] = K_3[Cr^{3+}][M^{2+}]^n[P]^k \quad (12)$$

According to eqn. (3), eqn. (12) and assumption [3], X_P can be expressed as follows:

$$X_P = \frac{n[Cr^{3+}-M_n^{2+}-P_k]}{[Cr^{3+}-P_i] + (n+1)[Cr^{3+}-M_n^{2+}-P_k]} \\ = \frac{nK_3[Cr^{3+}][M^{2+}]^n[P]^k}{K_1[Cr^{3+}][P]^i + (n+1)K_3[Cr^{3+}][M^{2+}]^n[P]^k} \quad (13)$$

Here, $[Cr^{3+}]$, $[M^{2+}]$, $[Cr^{3+}-M_n^{2+}-P_k]$, $[Cr^{3+}-P_i] \ll [P]$ holds, so we can approximate $[P] = 1$. When $[P] = 1$ is substituted into eqn. (13), eqn. (14) is obtained.

$$X_P = \frac{nK_3[M^{2+}]^n}{K_1 + (n+1)K_3[M^{2+}]^n} \quad (14)$$

When eqn. (9) is substituted into eqn. (14), eqn. (15) is obtained.

$$X_P = \frac{nX_S^n}{\beta + (n+1)X_S^n} \quad (15)$$

where β is the constant described as eqn. (16).

$$\beta = \frac{K_1k^{-n}}{K_3} \quad (16)$$

Accordingly, the relation between X_S and X_P follows eqn. (15) when model 2 applies.

A comparison between models 1 and 2

We examine here whether or not the relation between X_S and X_P derived from the experimental data follows eqn. (10) derived from model 1. Eqn. (10) can be transformed to eqn. (17).

$$X_P^{-1} = (1 - \alpha) + \alpha X_S^{-1} \quad (17)$$

If model 1 applies, eqn. (17) indicates that the relation between X_S^{-1} and X_P^{-1} follows a linear plot. Fig. 8 shows the plot of X_S^{-1} vs. X_P^{-1} of the precipitates obtained from the various molecular weights of PEG shown in Fig. 4. According to Fig. 8, the relation between X_S^{-1} and X_P^{-1} does not follow a linear relation. Therefore, model 1, which assumes that the cations independently coordinate to PEG, does not appear to be appropriate for describing the PEG- (Cr^{3+}, M^{2+}) complex and the formation of the oxalate precipitate.

Next, it is considered whether or not the relation between X_S and X_P derived from the experimental data follows eqn.

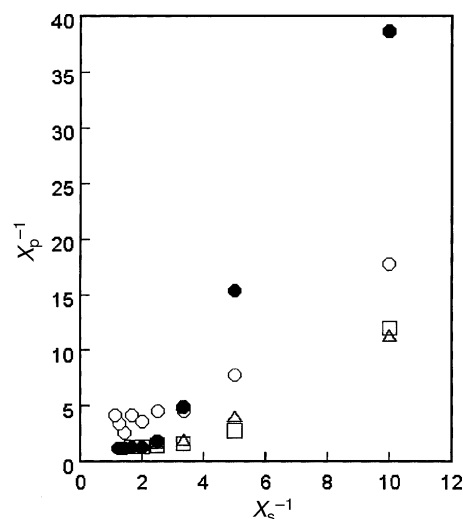


Fig. 8 The X_S^{-1} vs. X_P^{-1} plot for the precipitate obtained from the PEG solution of Cr^{3+} and Ni^{2+} . The glycols used for the nitrate hydrate solutions are: (○) EG; (◻) TEG; (◻) PEG300; and (●) PEG1000.

Table 1 The relation between the parameter n in eqn. (15) and the molecular weight of PEG

Molecular weight of PEG	n
62 (EG)	0.97
150 (TEG)	3.03
300	3.38
1000	6.13

(15) derived from model 2. The parameters β and n in eqn. (15) were adjusted by the least-square method in order to obtain the best fit between the experimental curve in Fig. 4 and Fig. 7 and the calculated curve. The solid lines in Fig. 4 and 7 are the curves obtained by the curve-fitting of eqn. (15). According to Fig. 4 and 7, the calculated curve agrees well with the experimental data, indicating that model 2 reproduces the experimental data accurately. Thus, the precipitation process from the PEG-(Cr³⁺, M²⁺) solution (M = Ni, Zn, Co, Cu) can be described by model 2.

Table 1 shows the relation between the molecular weight of PEG in the PEG-(Cr³⁺, Ni²⁺) solution and the parameter n in eqn. (15) derived from model 2. Here, the parameter n is not an integer because n is the average value. The parameter n increased with increasing molecular weight of PEG, as the coordination sites in PEG that can be cooperatively coordinated by the cations increase in number when the molecular weight is increased. This result, shows that the cation arrangement in the PEG-cation complex is different, which is in agreement with the discussion regarding Fig. 6. It is considered that model 2 is appropriate to explain the coordination of the cations to PEG and the precipitation process. The strength of Cr³⁺ coordination to PEG is much stronger than that of Ni²⁺. When Cr³⁺ is coordinated to PEG, the steric structure of PEG changes from a random coil structure in the molten phase to a helix structure in the PEG-cation complex.²¹ The helix structure in the PEG-cation complex shows a chelate effect for the coordination of Ni²⁺ to PEG. This chelate effect accelerates the coordination of Ni²⁺ to PEG, which explains the cooperative coordination of the cations to PEG. It is considered that the chelate effect becomes strong with increasing molecular weight of PEG. This hypothesis also agrees with the result shown in Table 1. Furthermore, if the molecular weight of PEG is low (EG, TEG), it is considered that the PEGs coordinated with Cr³⁺ are easily oxidized by nitrate ions so that the oxalate ions precipitate Cr³⁺ with the neighboring Ni²⁺. The cooperative coordination of PEG-(Cr³⁺, M²⁺) complex (M = Zn, Co, Cu) also can be described by the above discussion.

Conclusion

Cr³⁺-M²⁺ (M = Ni, Zn, Co, Cu) oxalate complexes were obtained by heating a PEG solution with a metal nitrate hydrate solution at 353 K for 6 h. The relation between the

cation mole fraction $[M^{2+}/(Cr^{3+} + M^{2+})]$ in the PEG solution and that of the precipitate obtained depended on the molecular weight of the PEG used. The structure and the cation arrangement in the oxalate precipitate obtained also depended on the molecular weight of the PEG. This PEG method enables us to prepare multicomponent oxalates with different valence cations. Two different models for the precipitate formation process were proposed. In the first, it is assumed that Cr³⁺ and M²⁺ coordinate to PEG independently of each other. In the second model, it is assumed that Cr³⁺ and M²⁺ cooperatively coordinate to PEG. The calculated relation between the M²⁺ mole fraction of the PEG solution and that of the precipitate was compared with the relation obtained from the experimental results. The results obtained from the second model agreed well with the experimental results. We therefore conclude that Cr³⁺ and M²⁺ coordinate cooperatively to PEGs.

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