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THERMAL DECOMPOSITION STUDIES OF NEODYMIUM PRASEODYMIUM OXALATE DECAHYDRATE CRYSTALS

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Abstract

Neodymium praseodymium oxalate decahydrate crystals were grown using silica gel technique by the controlled reaction of rare earth nitrates with oxalic acid. The grown crystal were characterized using X-ray powder diffraction and thermogravimetric analysis. The thermal decomposition process of the crystals is in good agreement with the proposed crystal structure.

Keywords: $NdPr(C_2O_4)_3 \cdot 10H_2O$, oxalate crystals, X-ray

Introduction

Rare earth compounds have attracted considerable attention on account of their interesting electric, magnetic and luminescent properties [1]. Of the various rare earth compounds, the oxalate family of rare earth stands out because of their intriguing applications [2]. Some recent investigations on the fluorescence of europium oxalate [3] suggest that the rare earth oxalate groups are potential candidates for optical applications. Rare earth oxalates are also used as precursor for the preparation of the corresponding superconducting oxides [4]. The advantage of this method over the conventional solid state reaction technique is that crystals of a wide range of stoichiometric ratio having a high degree of homogeneity can be prepared easily [5].

Since most of the oxalate crystals are insoluble in water and decompose before melting, it is difficult to adopt slow evaporation or melt technique to grow these crystals. The gel technique [6] is in fact a suitable method for the growth of crystals with low aqueous solubility and high thermal decomposition behaviour. This paper reports the thermal decomposition process of neodymium praseodymium oxalate crystals grown in hydrosilica gel.

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Experimental

Hydrosilica gel was prepared from sodium metasilicate solution with required amount of oxalic acid as the inner reactant. Supernatant solution comprises equal volumes of neodymium nitrate and praseodymium nitrate solutions, mixed with concentrated nitric acid. After the proper setting of the gel the supernatant solution was slowly added over the gel to enable the crystallization. As the ions slowly diffuse into the gel column, impregnated with the cations of oxalic acid, well defined crystals of neodymium praseodymium oxalate were formed out of the following chemical reaction.

$$Nd(NO_3)_3+Pr(NO_3)_3+3H_2C_2O_4 \longrightarrow NdPr(C_2O_4)_3 \cdot nH_2O+6HNO_3$$

Depending on the pH, concentration of the reactants and the acidity of the feed solution, the nature of crystallization varied from microcrystals to single crystals, and the largest crystal obtained was about 5×3×1 mm in size. The grown crystals were of different morphology but mainly hexagonal in shape. The details of the growth process and characterisation of these crystals have already been reported [7]. The X-ray powder diffraction pattern of the crystal were recorded on a Rigaku D/max *c* X-ray diffractometer with CuK_α radiation with a scan speed, 1° min^{-1}. The thermal decomposition of the grown crystals were studied using a Shimadzu thermal analyser DT-40 in the temperature range 30–800°C.

Results and discussion

X-ray diffraction analysis

Recently Sheng Hua Hang *et al.* [8] have reported the growth of single crystals of lanthanum oxalate and its detailed crystal structure analysis. They arrived at the stoichiometric formula $La_2(C_2O_4)_3 \cdot 10H_2O$ and suggested that it crystallizes in the monoclinic system having space group $P2_1/c$, and with a=11.382Å, b=9.624 Å, c=10.502 Å, β=114.52° and z=2. The structure is composed of two dimensional networks of edge sharing 1:5:3 coordination polyhedra matching the (020) set of planes. Each Lanthanum atom being surrounded by three chelating oxalate groups and three aqua ligands. The intervening space is filled by lattice water molecules disordered over seven major sites. Ollendorff *et al.* [9] have reported the X-ray diffraction studies of neodymium oxalate decahydrate and praseodymium oxalate decahydrate and found that they also crystallise in the monoclinic system with space group $P2_1/c$ and the cell parameters are identical with that of $La_2(C_2O_4)_3 \cdot 10H_2O$. Since the ionic radii of Nd and Pr are comparable one can expect identical crystal structure for the double rare earth oxalate crystals as that of the single component ones.

Figure 1 shows the X-ray powder diffractogram of $NdPr(C_2O_4)_3 \cdot 10H_2O$. The diffraction peaks are indexed assuming that it crystallises in the monoclinic sys-

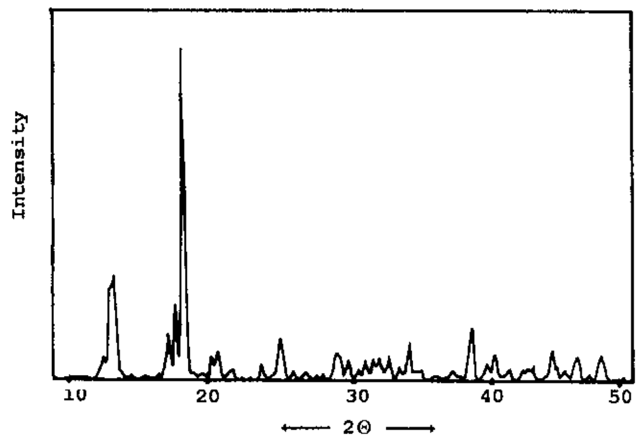

Fig. 1 X-ray diffractogram of NPO crystal

tem with space group $P2_1/c$ as in the case of single rare earth. Based on this the lattice parameters are evaluated.

Lattice parameters of NPO crystals:

Chemical formula	$NdPr(C_2O_4)_3\cdot 10H_2O$
Space group	$P2_1/c$
Cell dimensions	a=11.2189 Å
	b=9.6349 Å
	c=10.2916 Å
	β=114.399°
	z=2
Volume	1013.1 $Å^3$

The lattice parameters of NPO crystals are found to be identical with that of single component systems. This suggests that the mixed rare earth oxalate crystals are formed by the simple substitutional exchange of the two rare earth ions. From a comparative study of the lattice parameters of single and mixed oxalates of Nd and Pr with that of La, it can be concluded that the NPO crystals have the same structure as that of $La_2(C_2O_4)_3\cdot 10H_2O$.

Thermal analysis

The mechanism and chemical intermediates associated with the thermal decomposition of the trivalent lanthanide oxalates have been studied extensively [10–12]. The interest in these decomposition process derives largely from the importance of the insoluble oxalates in the separation of lanthanides from other metals by precipitation and for preparing the oxides of the lanthanides. Most of the results reported in the literature for the decomposition of the hydrated trivalent lanthanide oxalates are consistent with stepwise dehydration, followed by the thermal decomposition of the anhydrous oxalate to the sesquioxide via a dioxycarbonate intermediate [3, 13]. However, Glasner and coworkers [14, 15] have suggested a decomposition mechanism for anhydrous rare earth oxalate via a divalent intermediate. Gallagher *et al*. [16] used Mössbauer, emission and IR spectroscopies and various thermal analysis techniques to characterize the decomposion in the case of europium oxalate. They found no evidence for a divalent europium intermediate. The observations made on the thermal decomposition process of gel grown crystals of neodymium praseodymium oxalate discussed below is in confirmation with the results obtained for Gibson [3] and Gallagher [16].

TG and DTA curves showing the decomposition stages of praseodymium samarium oxalate decahydrate crystal are shown in Fig. 2. Taking the initial weight as standard, the course of decomposition is analysed from the proportionate mass loss at each stage.

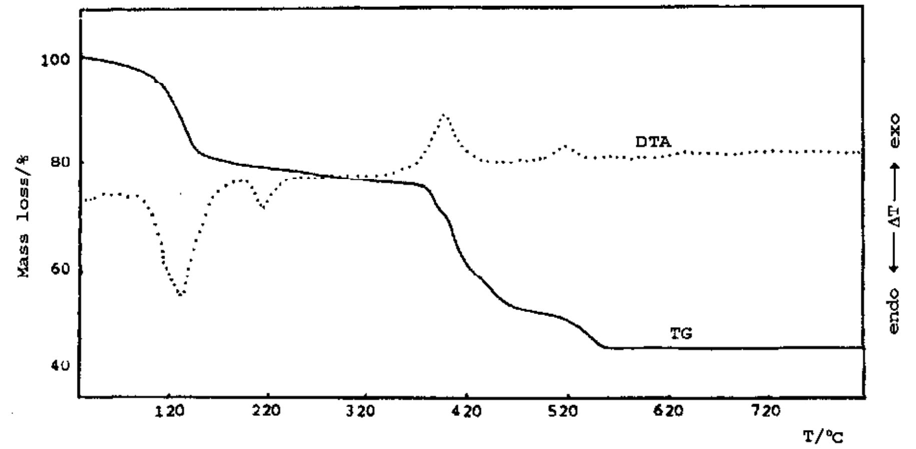

Fig. 2 TG and DTA traces of NPO crystal. Sample mass – 8.48 mg; heating rate – 10°C min^{-1}; atmosphere – O_2

As indicated by the TG, the material starts decomposing at about 60°C and the process is completed at about 590°C, and is reduced to the oxide form. The process of decomposition involves four different stages. The first stage which is a dehydration step continues up to 150°C and results in the elimination of seven water molecules. In the second stage, 150–350°C, the rest of the water molecules are lost, leading to the formation of anhydrous neodymium praseodymium oxalate. The first two endotherms in the DTA curve correspond to these dehydration stages.

The anhydrous $NdPr(C_2O_4)_3$ is unstable and decomposes in the next stage which extends up to 460°C. In this transition the crystal loses two CO_2 molecules and three CO molecules from its carboxylic group. This intermediate dioxy carbonate is stable only for a narrow range of temperature (~20°C) and is reduced to $NdPrO_3$ in the fourth stage of decomposition extending up to 590°C. The DTA curve in the region 350–590°C is characterized by two exothermic peaks. The first exotherm is typical of oxalate decomposition in air. The final exothermic reaction is also well established for oxalate decompositions and is attributable to the decomposition of an intermediate carbonate. Dollimore and Griffith [17] have postulated that the highly exothermal behaviour of the oxalate decomposition in air is either due to the internal solid product or due to the oxidation of the carbon monoxide formed. Since the rare earths would not form oxidizable solid intermediates during oxalate decomposition, the carbon monoxide oxidation is the most likely reason for exothermic peak.

The decomposition pattern of NPO crystal is in good agreement with that reported for other rare earth oxalates [3, 16]. The proposed chemical formula and hydration number for these crystals are found to fit well as evidenced from the thermal studies. Two distinct stages in the dehydration process in steps of seven and three water molecules are in agreement with the structure proposed from the X-ray studies. The three coordinated water molecules take longer time to leave the sample. On the other hand the other seven water molecules which are distributed at random in the intervening lattice space leave the crystal faster.

Based on TG and DTA results, the following tentative mechanisms have been proposed for the thermal decomposition of neodymium praseodymium oxalate decahydrate crystals.

$$NdPr(C_2O_4)_3{\cdot}10H_2O \xrightarrow[60\text{–}150^\circ C]{-7H_2O} NdPr(C_2O_4)_3{\cdot}3H_2O$$

$$NdPr(C_2O_4)_3{\cdot}3H_2O \xrightarrow[150\text{–}350^\circ C]{-3H_2O} NdPr(C_2O_4)_3$$

$$NdPr(C_2O_4)_3 \xrightarrow[350\text{–}460^\circ C]{-(3CO+2CO_2)} NdPrO_2CO_3$$

$$NdPrO_2CO_3 \xrightarrow[480\text{–}590^\circ C]{-CO_2} NdPrO_3$$

A summarized analysis of different stages associated with the thermal decomposition of the material, observed in the thermogram along with the calculated and observed mass losses are given in Table 1 .

Conclusions

The X-ray diffraction studies of the gel grown NPO crystals show that they are structurally identical with the single rare earth crystals. The decomposition pattern of NPO crystal is in good agreement with that reported for the other rare earth oxalates [16]. The proposed chemical formula and crystal structure for these crystals are found to fit well as evidenced from the thermal studies. Two

Table 1 Thermal analysis results of $NdPr(C_2O_4)_3 \cdot 10H_2O$

Stage	$T_{decomp. reg.}$/°C	Loss of material	Mass loss/%		Nature of reaction
			observed	calculated	
1	60–150	$7H_2O$	18.03	17.28	endo dehydration
2	150–350	$3H_2O$	7.70	7.40	endo dehydration
3	350–460	$3CO+2CO_2$	24.30	23.58	exo decomposition
4	480–590	CO_2	6.27	6.00	exo decomposition

distinct stages in the dehydration process in steps of seven and three water molecules are in agreement with the general structure proposed. The three coordinated water molecules take longer time to leave the sample. On the other hand the other seven water molecules which are distributed at random in the intervening lattice space leave the crystal faster.

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References

1 L. Eyring, 'Progress in Science and Tehcnology of Rare Earths', Pergamon Press, New York 1964.
2 D. E. Morris and D. E. Hobart, J. Raman Spectroscopy, 19 (1988) 231.
3 J. K. Gibson and N. A. Stump, Thermochim. Acta, 226 (1993) 231.
4 R. C. Vickery, 'Analytical Chemistry of Rare Earths', Pergamon Press, Oxford 1966.
5 Wang Fan and Lauri Niinisto, Mater. Res. Bull., 29 (1994) 451.
6 H. K. Henisch, 'Crystals in Gels and Leisegang Rings', Cambridge University Press, Cambridge 1988.
7 C. Joseph, G. Varghese and M. A. Ittyachen, Cryst. Res. Tech., 30 (1995) 159.
8 Huang Sheng-Hua, Gong-Du Zhou and Thomas, C. W. Mak, 1. Crystallographic and Spectroscopic Research, 21 (1991) 127.
9 W. Ollendorff and F. Weigel, Inorg. Nucl. Chem. Lett., 5 (1969) 263.
10 M. J. Fuller, and J. Pinkstone, J. Less Common Metals, 70 (1980) 127.
11 M. Shymala, S. R. Dharwadkar and Chandrasekharaiah, Thermochim. Acta, 56 (1982) 135.
12 K. Nagase, H. Yokobayashi, K. Muraishi and M. Kikuchi, Thermochim. Acta, 177 (1991) 273.
13 E. Birnbaum, Handbook of Inorganic Chemistry, Springer-Verlag, New York, Vol. D5, 1984.
14 A. Glasner, E. Levy and M. Steinberg, J. Inorg. Nucl. Chem., 25 (1963) 1415.
15 A. Glasner, E. Levy, M. Steinberg, and W. Bodenheimer, Talanta, 11 (1964) 405.
16 P. K. Gallagher, F. Schrey and B. Prescott, Inorg. Chem., 9 (1970) 215.
17 D. Dollimore and D. Griffiths, J. Thermal Anal., 2 (1970) 229.