

# Growth and thermal behavior of mixed crystals of calcium cadmium tartrate in silica gels

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Received: 1 April 2011 / Accepted: 14 April 2011 / Published online: 1 May 2011  
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**Abstract** In this study, calcium cadmium tartrate single crystals were grown in silica gel at ambient temperature. Effects of various parameters like gel pH, gel aging, gel density, and concentration of reactants on the growth of these crystals were studied. Crystals having different morphologies and habits were obtained. Transparent, diamond-like pyramidal-shaped crystals of calcium cadmium tartrate were obtained. Some of the crystals obtained were faint yellowish, with some milky white crystals being attached to them due to fast growth rate; faces are well developed and polished. The grown crystals were characterized by thermoanalytic techniques (TG, DTA, and DTG), and powder X-ray diffraction (XRD). The crystal system is confirmed to be orthorhombic having lattice parameters  $a = 7.9411 \text{ \AA}$ ,  $b = 7.0396 \text{ \AA}$ , and  $c = 6.7271 \text{ \AA}$  as determined by powder XRD analysis. TG, DTA, and DTG analyses show a remarkable thermal stability. The results of these observations are described and discussed.

**Keywords** Gel technique · Calcium cadmium tartrate · TG · DTA · DTG

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## Introduction

In recent years, the growth of crystals in gel medium has attracted the attention of many investigators [1–5]. The principle of growth is based on the slow migration of crystal constituents (ions) through silica gel so that a very slow reaction occurs with the formation of a sparingly soluble compound. When the concentration of this compound exceeds the solubility limits, crystals will be formed, while the main function of the gel is to control the flow of reacting ions.

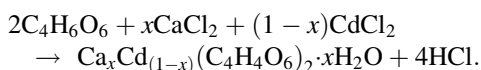
Mixed crystal growth has scarcely been studied by employing the gel technique [6], and the field is in an early stage of development with many opportunities to create new species. Most of the tartrate compounds are insoluble in water and decompose before melting. Hence, single crystals of such type of compounds cannot be grown by either slow evaporation or melt technique. In this situation, gel method is the appropriate one for their growth. The growths of single crystals of calcium tartrate [1, 7] as well as those of strontium tartrate were reported [6]. Thermal studies on tartrate crystals grown by gel method were reported by many investigators [8–10]. Tartrate crystals are of considerable interest, particularly for basic studies, because of some of their interesting physical properties. Some crystals of this family are ferroelectric [11–13].

Mixed crystal of tartrate have several applications in medicine, optics, etc., and, hence, it was thought worthwhile to undertake investigation on the growth of crystals of mixed tartrate and their characterization by different methods. In this article, we report the growth of rare-earth-mixed single crystals of calcium cadmium tartrate grown in silica gel. These crystals are identified and characterized by TG, DTA, and DTG.

## Experimental

Good crystal can be grown in gels in a variety of ways; the single diffusion method was employed in the present study for the growth of calcium cadmium tartrate crystals. The growth process involves the diffusion of mixed calcium chloride–cadmium chloride solution into a gel in which tartaric acid is impregnated beforehand. The silica gel was used as a growth medium. The chemicals used for growth mixed tartrate were  $C_4H_6O_6$ ,  $CaCl_2$ ,  $CdCl_2$ , and  $Na_2SiO_3$ ; all the chemicals were of AR grade. The crystallization apparatus consists of borosilicate glass test tubes of length 20 cm and diameter 2.5 cm placed vertically on wooden stands. Tartaric acid, calcium chloride, and cadmium chloride solution were prepared by dissolving these compounds in an appropriate amount of distilled water to give the required molarities. Gels of required specific gravity were prepared by adding to the solution of sodium metasilicate, a calculated amount of redistilled water, and a stock solution was kept ready for doing further experiments. Tartaric acid solution of particular strength was taken in a 100-mL beaker, and sodium metasilicate solution of a suitable gravity was added dropwise using a tephlon cock burette, constantly stirring the solution in a beaker by magnetic stirrer. Stirring is done to avoid the excessive local ion concentration which may otherwise cause premature local gelling and make the final medium inhomogeneous and turbid. Here, tartaric acid acted as a lower reactant. The systronic digital pH meter model number 335 was employed to measure the pH. The solution after noting the pH values, was allowed to fall freely along the side of a test tube avoiding the formation of the bubbles. Test tubes were then closed with rubber corks or cotton to prevent evaporation, and contamination of the exposed surface of the gel by dust particles from the atmosphere. The solution was found to be strongly dependent on pH. Higher pH value of the gel takes lower time to set than the one with lower pH value, depending on the environmental temperature. After ensuring firm setting by the gel, the saturated mixed solution of calcium chloride and cadmium chloride (supernatant) of particular strength was poured over the set gel by means of a pipette. The solution was allowed to fall freely along the wall of the test tube to prevent the gel surface from cracking. The supernatant ions ( $Ca^{++}$  and  $Cd^{++}$ ) slowly diffused into the gel medium where it reacts with inner reactant.

The following reaction is expected to take place in the formation of calcium cadmium tartrate crystals.



The systematic growth experiments were performed by adding  $CaCl_2$ ,  $CdCl_2$ , as feed solution of strength varying

from 0.2 to 1.2 M over the set gel of pH range 4 to 4.5 the gel density range 1.02–1.05  $g/cm^3$ .

## Result and discussion

The various optimal conditions for the growing crystals were found and are given in Table 1.

### Effect of gel density

Gels of different densities were obtained by mixing sodium metasilicate having specific densities ranging from 1.038 to 1.05  $g/cm^3$  with 1.25 M tartaric acid keeping pH 4.2 constant. It was observed that the transparency of the gel decreases as the gel densities increases. Gels with higher densities set more rapidly than the gels with lower densities. It is observed that nucleation density decreases as the gel density increases. A greater gel density implies smaller pore size and poor communication among the pores thus decreasing the nucleation density. It may be noted that single crystals of calcium cadmium tartrate were obtained with sodium metasilicate of specific density 1.04  $g/cm^3$ . Some of them were faint yellowish, and some milky white, with faces being well defined as shown in Fig. 1.

### Effect of concentration of reactant

It was observed that as the concentration of the feed solutions increases, the nucleation density also increases. This may be due to the enhanced availability of  $Cd^{++}$  and  $Ca^{++}$  ions to grow good crystals, for which the suitable concentration of feed solution was 1 M. Similarly, the concentration of tartaric acid suitable for the growth of good quality crystals is 1.25 M as shown in Fig. 2a–c. Table 2 shows the effect of concentration of reactants of habit, quality, and size of  $Ca_xCd_{(1-x)}(C_4H_4O_6)_2$

**Table 1** Optimal condition for the growth of calcium cadmium tartrate

Conditions	Calcium cadmium tartrate
Density of sodium metasilicate solution	1.04 $g/cm^3$
Concentration of tartaric acid	1.25 M
Volume of tartaric acid	7 mL
Volume of sodium metasilicate solution	23 mL
pH of the gel	4.2
Concentration of $CaCl_2$	1 M
Concentration of $CdCl_2$	1 M
Temperature	Room temperature



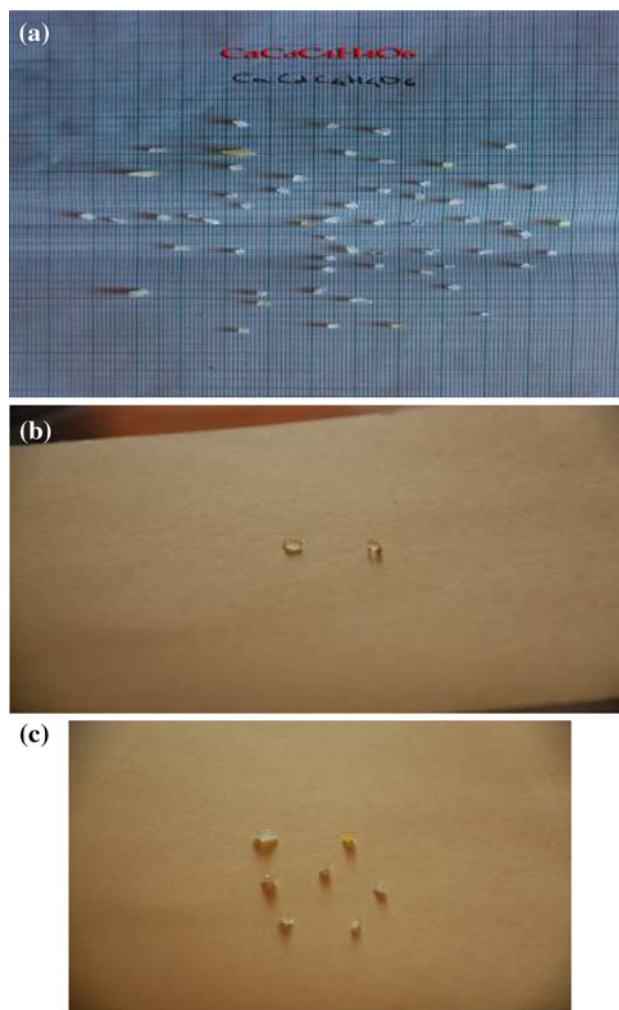
**Fig. 1** Prismatic transparent, semitransparent, and well-defined crystals of calcium cadmium tartrate In gel of density  $1.04 \text{ g/cm}^3$

#### Effect of pH of gel

It was found that the initial pH values in the range of 4–4.5 give the optimal condition for the growth of calcium cadmium tartrate crystals. When the pH value was increased above 4.5 irregularly shaped and opaque dendrites crystals were obtained along with the interface of gel. It was observed that as the pH increased, the transparency of the gel decreased. In the present study, good crystals are obtained at pH of 4.2. The crystals growing at higher pH values were not transparent and well defined. This was due to the contamination of the crystals with silica gel, because as the pH increased, the box-like network structure of the gel changed to a loosely bound platelet structure which lacked cross-linkages; the cellular became less distinct [2], and it was observed that as the pH of gel increased, the number of the crystal decreased.

#### Effect of aging of gels

Gels were allowed to age for different periods before adding the feed solutions. It was found that as aging time of gel increased, the number of crystals decreased. This is because gel aging reduces the cell size and consequently the rate of diffusion of ions into the gel [5]. Gel aging has no pronounced effect on the size or the quality of the crystals. In the present study, pH of the gel was kept constant at 4.2.



**Fig. 2** a Faint yellowish, milky white, transparent, semitransparent, needle-shaped well-defined crystals of calcium cadmium tartrate. b Prismatic transparent crystals of calcium cadmium tartrate. c Translucent diamond-like pyramidal-shaped crystals of calcium cadmium tartrate

#### Characterizations

Mixed tartrate crystals grown were characterized by TG, DTA, and DTG.

#### Thermal analysis

Thermogravimetric analysis (TG), and Differential thermal analysis (DTA) techniques are widely used for thermal studies of organic and inorganic compounds. Modern commercial thermo balances with variable heating rates, variable gaseous media, with vacuum or high-pressure facilities, and with continuous recording facilities eliminated satisfactorily the possible sources of errors in thermal studies of samples under study. As a result, numbers of possible analytical precipitates are mentioned in the

**Table 2** Effect of concentration of reactants on properties, quality, and size of  $\text{Ca}_x\text{Cd}_{(1-x)}(\text{C}_4\text{H}_4\text{O}_6)_2$ 

Conc. of reactant in gel	Conc. of reactant above gel	Habit	Quality	Size/mm
$\text{C}_4\text{H}_6\text{O}_6$ 1 M (7 mL, pH 4.2)	$\text{CaCl}_2$ , $\text{CdCl}_2$ 1 M (15 mL)	Prismatic	Opaque	$2 \times 5 \times 1$
$\text{C}_4\text{H}_6\text{O}_6$ 1.25 M (7 mL, pH 4.2)	$\text{CaCl}_2$ , $\text{CdCl}_2$ 1 M (20 mL)	Prismatic	Good	$3 \times 6 \times 2$
$\text{C}_4\text{H}_6\text{O}_6$ 2.25 M (7 mL, pH 4.2)	$\text{CaCl}_2$ , $\text{CdCl}_2$ 1 M (25 mL)	Dendrite	Poor	$5 \times 10 \times 4$

literature. Thermal studies on tartrate crystals grow by gel method were reported by many investigators [5, 9, 14, 15]

Thermal studies on mixed crystals of Calcium Strontium tartrate grown by gel method using calcium chloride and strontium chloride format mixed with formic acid as the supernatant solution was reported by [16]. The thermal decomposition study of calcium cadmium tartrate involves simultaneous TG, DTA, and DTG of the compound under ambient conditions.

#### TG, DTA, and DTG

The curves were obtained using Diamond TG/DTA/DTG thermal analyzer available at the National chemical laboratory of Poona. Recrystallized alumina sample holders were used, and the heating rate was 10 °C/min. The curves were recorded in the temperature range from 30 to 1000 °C. The experiment was carried out under a flow rate of 60 mL/min of nitrogen atmosphere. Microcrystalline (powdered) samples of Calcium Cadmium tartrate crystal were taken for thermal studies and the mass of the sample was 24.505 mg. The sample was held for 1.0 min at 30 °C to evaporate water arising from moisture and then heated from 30 to 1000 °C at 10 °C/min. The curves (TG, DTA, and DTG) of calcium cadmium tartrate crystal is shown in Fig. 3a–c. The percentages of the mass loss in the different stages of decomposition of Calcium Cadmium tartrate are presented in Table 3. There is a good agreement between the observed and calculated mass losses.

Calcium Cadmium tartrate is water-coordinated compound. Therefore, there is a possibility that this crystal may lose some of its water molecules while heating. TG of calcium cadmium tartrate showed clearly four stages of decomposition as expected: (1) dehydration, (2) calcium cadmium tartrate to calcium cadmium oxalate, (3) calcium cadmium oxalate to calcium carbonate and cadmium carbonate, (4) calcium carbonate and cadmium carbonate to calcium oxide and cadmium oxide. Similar observations are found from the literature on Rochelle salt and rare earth tartrates [9, 14, 15].

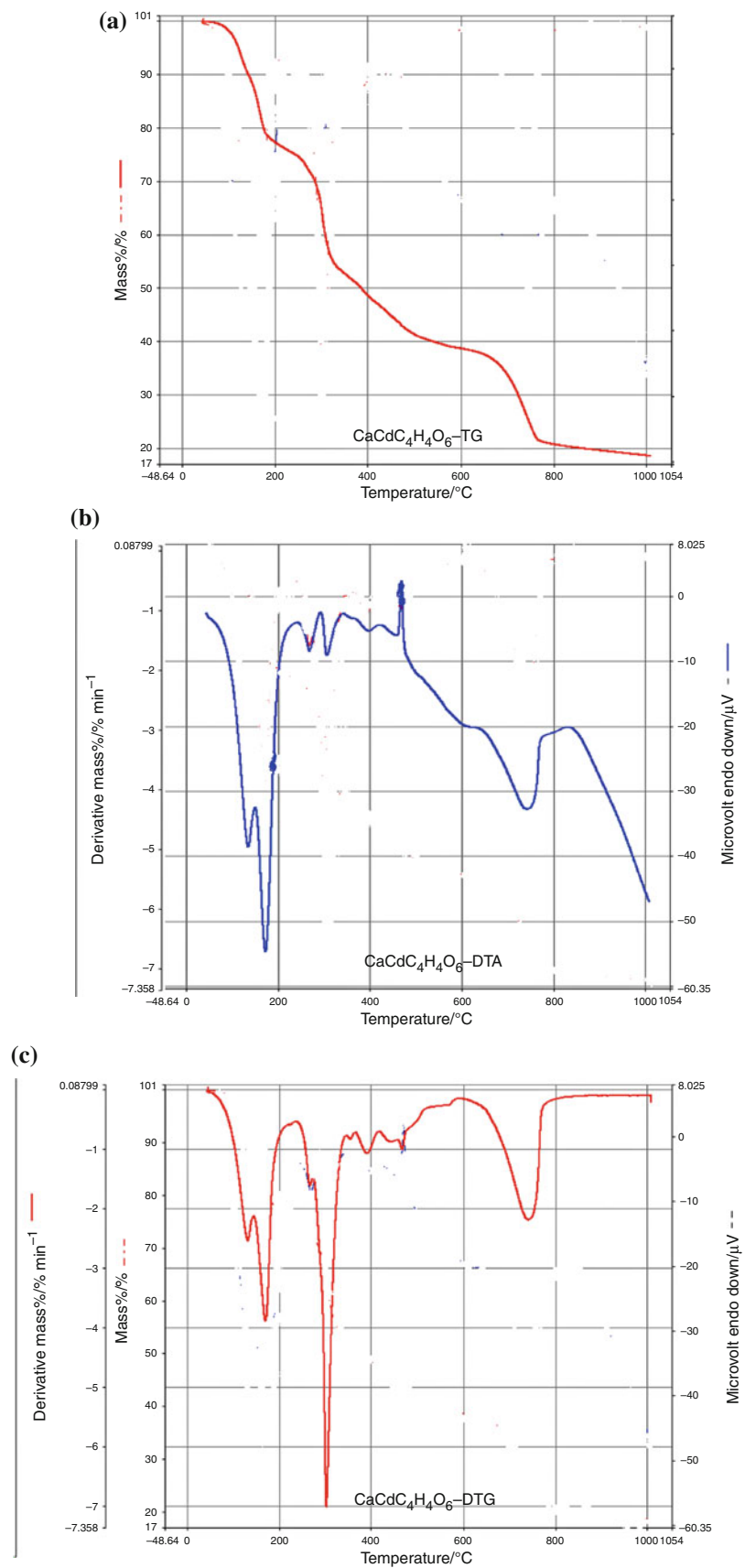
The four stages of the decomposition are described in the following paragraphs. Mass loss calculation clearly indicates that calcium cadmium tartrate crystals have 12 water molecules as water of crystallization. It is noticed that the sample loses water of hydration and becomes anhydrous at 286 °C.

- In the first stage of decomposition, which occurs in the temperature range from 70 to 286 °C, the mass loss of 34.64% is observed which agrees very well with the calculated mass loss of 32.40%. Thus, it is clear that the crystals are hydrated, and the mass loss calculation clearly indicates that calcium cadmium tartrate crystals have 12 water molecules as water of crystallization. It is noticed that the sample loses water of hydration and becomes anhydrous at 286 °C.
- In the second stage of decomposition in the temperature range of 286 to 363 °C, the total mass loss of 17.68% is seen which is due to the loss of 4C and 4H<sub>2</sub>O; this is well in agreement with the calculated mass loss of 18.01%. Then, an anhydrous calcium cadmium tartrate decomposes into calcium cadmium oxalate.
- In the third stage of decomposition, total mass loss 9.672% was observed in the temperature range 450–710 °C which corresponds to the loss of 2CO. This mass loss agrees very well with the calculated mass loss 8.74%. Thus, calcium cadmium oxalate further decomposes into calcium carbonate and cadmium carbonate.
- Finally, in the temperature range of 710 to 840 °C, total mass loss of 13.74% was obtained. This loss is attributed to the loss of 2CO<sub>2</sub>. This is well in agreement with the calculated mass loss of 13.76%. Thus, the calcium carbonate and cadmium carbonate finally turn into calcium oxide and cadmium oxide, respectively, at 784 °C which is confirmed by the residual mass up to the end of analysis as 25.125% of CaO and CdO. This is in good agreement with calculated residual mass of 24.95%.

The various plateaus on the TG curve indicate the formation of stable stoichiometric compounds.

The TG curve did not show the appreciable mass change in the temp. range of 30–70 °C indicating that the calcium cadmium tartrate crystals are thermally stable in this range and that no transformation took place. It was observed that the decomposition started at 85 °C, and the crystals were unstable beyond 85 °C. A small plateau observed in the temp. range from 160 to 190 °C signals the loss of first 7H<sub>2</sub>O; the plateau between 210 to 260 °C indicates the formation of stable anhydrous calcium cadmium tartrate; the plateau in the temperature range 320 to 400 °C indicates the formation of stable calcium cadmium oxalate; the

**Fig. 3** **a** TGA curve of calcium cadmium tartrate crystal. **b** DTA curve of calcium cadmium tartrate crystal. **c** DTG curve of calcium cadmium tartrate crystal



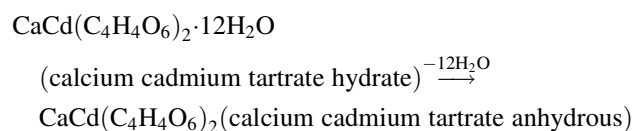
**Table 3** TG Data

Stage	Temperature range/°C	Observed mass loss/%	Calculated mass loss/%	Loss of molecule in stage
I	70–286	34.64	32.40	12H <sub>2</sub> O
II	286–363	17.68	18	4C and 4H <sub>2</sub> O
III	363–491	10	8.42	2CO
IV	600–765	13.62	13.22	2CO <sub>2</sub>

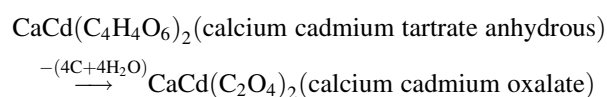
plateau between the temperature 510 to 655 °C is attributed to the stable calcium carbonate and cadmium carbonate; and beyond 840 °C up to the end of analysis, there is a stable CaO and CdO.

Following is the stoichiometry of the different intermediates involved in the decomposition process of calcium cadmium tartrate hydrate.

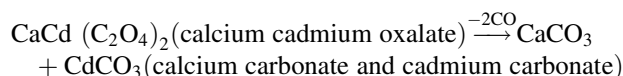
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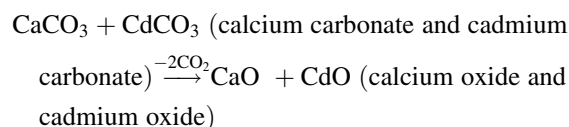
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3.



4.



## Conclusions

From the experiments on the growth of calcium cadmium tartrate crystals in the system CaCl<sub>2</sub>–CdCl<sub>2</sub>–Na<sub>2</sub>SiO<sub>3</sub>–C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>, the following conclusions may be drawn.

1. The growth of calcium cadmium tartrate crystals is accomplished by allowing diffusion of calcium chloride, cadmium chloride through silica gel impregnated with tartaric acid in a single-gel–single-tube system.
2. The crystals exhibit transparent, diamond-like pyramidal-shaped morphology even under varied conditions of growth. The maximum size of the growth crystal under optimum conditions was 2–6 mm in length.

3. Different habits of calcium cadmium tartrate crystals can be obtained by changing parameters such as gel density, gel aging, pH of gel concentration of reactants, concentration of impurities, etc.
4. It is found that well-developed single crystals of calcium cadmium tartrate are obtained at 1 M concentration of feed solution with the pH range of 4–4.5 for the gel.
5. XRD analysis reveals that calcium cadmium tartrate crystals belong to orthorhombic system.
6. The thermo gravimetric analysis suggests that the grown calcium cadmium tartrate is associated with 12 molecules of water of hydration.
7. From the curve it was concluded that the grown crystals are thermally unstable beyond 85 °C, and decompose into calcium oxide and cadmium oxide through many stages of dehydration.
8. The decomposition reactions show exothermic as well as endothermic peaks.

**Acknowledgements** The authors are grateful to Dr. L. A. Patil, and Prof. S. A. Patil, the Department of Physics, Pratap College, Amalner, for their providing the laboratory facilities. The authors wish to thank the authorities of the North Maharashtra University, Jalgaon; the Physics Department, Poona University, Poona; and the NCL, Pune for their help in the analytic study. One of the authors, D. K. Sawant, expresses his thanks to the Principal, J. E. S<sup>s</sup>. College Nandurbar for his continuous encouragement

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