Inorganica Chimica Acta 362 (2009) 1535-1540



Contents lists available at ScienceDirect

Inorganica Chimica Acta



journal homepage: www.elsevier.com/locate/ica

Crystal structure and thermal characterization of cadmium oxalate $[CdC_2O_4 \cdot 3H_2O]$ and barium-doped cadmium oxalate $[Ba_{0.5}Cd_{0.5}(C_2O_4)_2 \cdot 5H_2O]$ single crystals grown in silica gel

A. Moses Ezhil Raj^{a,*}, D. Deva Jayanthi^b, V. Bena Jothy^b, M. Jayachandran^c, C. Sanjeeviraja^d

^a Department of Physics, Scott Christian College (Autonomous), Nagercoil 629 003, India ^b Department of Physics, Women's Christian College, Nagercoil 629 001, India ^c ECMS Division, Central Electrochemical Research Institute, Karaikudi 630 006, India ^d Department of Physics, Alagappa University, Karaikudi 630 003, India

ARTICLE INFO

Article history: Received 20 February 2008 Received in revised form 16 July 2008 Accepted 24 July 2008 Available online 30 July 2008

PACS: 81.10.-h 61.66.Fn 33.20.Ea 81.70.Pg

Keywords: A. Structural materials D. X-ray diffraction C. Infrared spectroscopy D. Thermogravimetry analysis

1. Introduction

Oxalate crystals have attracted the attention of many researchers due to their interesting physical properties and their suitability in preparing ceramic superconductors and solid solutions [1–4]. The formation of solid solutions of some multi-metal oxalates have been discussed in detail by Schuele [5] and Fischer et al. [6]. Moreover, oxalate ions $C_2O_4^{2-}$ can act as monodentate, bidentate, tridentate or tetradentate donor ligands and therefore, it was found to show a large variety on structural characterizations. In addition, they can form chains, layers and 3-D networks on combining with the metal centers. The water of hydration that links the metal ions and/or loosely bonded to the framework leads to large variety of structural architecture in multi-dimensions [7]. Consequently, concerted attention has been devoted to grow divalent metal oxalates using various techniques. Among the divalent metal ions studied,

ABSTRACT

Pure cadmium oxalate trihydrate (COT) and barium added cadmium oxalate (BCO) single crystals were grown by controlled diffusion of Cd^{2+} and Ba^{2+} ions in silica gel at ambient temperature. A single test tube technique coupled with gel aging conferred maximum size crystals by controlling the nucleation rate. It was found that the pH and age of the gel greatly influenced the crystal quality, their size and transparency. Grown crystals $CdC_2O_4 \cdot 3H_2O$ and $Ba_{0.5}Cd_{0.5}(C_2O_4)_2 \cdot 5H_2O$ were characterized by X-ray diffraction, Fourier transform infrared spectroscopy and thermal analysis. Effect of barium dopant on the growth and morphology of cadmium oxalate was studied. Pure cadmium oxalate crystallized in triclinic system and the barium-doped cadmium oxalate crystallized in hexagonal system with massive changes in their unit cell parameters. The infrared spectrum revealed the presence of oxalate ligands and water of hydration in both the pure and barium-doped crystals. Thermal analysis showed that the grown crystals were dehydrated thermally even from lower temperatures and the doped crystals were found more stable.

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Cd and Ba ions have attracted a great deal of interest because it has rather simple chemistry and coordination geometry [8–13].

The effect of doping on gel-grown crystals has been extensively studied by Dishovsky and Boncheva-M Ladenova [14] and Dennis and Henisch [15]. Mixed crystals are reported to be harder than pure ones [16,17]. In addition to growth parameters, additives such as PSMA (poly-styrene-alt-maleic acid) [18], PSSS (poly sodium 4-styrene-sulfonate) [19] and sodium carboxylate [20] on oxalate crystal matrix have been studied to identify the phase and structural modifications. In an ongoing investigation of the crystal chemistry of oxalates [21–24], the present study is aimed to crystallize cadmium oxalate trihydrate (COT) and barium-doped cadmium oxalate (BCO) mixed crystals in gel media in order to study the effect of gel parameters on nucleation, structural modifications and thermal decomposition behavior.

2. Experimental

In gel technique, silica gel has been used to grow organic and inorganic crystals because of their porous network that permits

^{*} Corresponding author. Tel.: +91 04652 232888; fax: +91 04652 229800. *E-mail address*: ezhilmoses@yahoo.co.in (A.M. Ezhil Raj).

^{0020-1693/\$ -} see front matter @ 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2008.07.025

the diffusion of different ions of any size. Basically silica gel of specific gravity (1.04) was obtained by the neutralization of sodium metasilicate solution with oxalic acid. Gels of different pH (3.5, 4.0 and 4.5) were prepared and the reproducibility was tested by noting the gelation time of gels. After a gel aging of three weeks, growth of cadmium oxalate trihydrate was achieved by allowing controlled diffusion of cadmium ions (Cd^{2+}) through silica gel impregnated with oxalic acid without damaging the gel surface. The tube was kept undisturbed at room temperature and the chemical reaction leads the formation of cadmium oxalate.

$$CdCl_2 + H_2C_2O_4 \rightarrow CdC_2O_4 + 2HCl$$
(1)

Barium added cadmium oxalate crystals were grown by mixing 1.5 M CdCl_2 and 1.5 M BaCl_2 in equal proportion and placed as the supernatant solution and is allowed to diffuse into the gel medium containing oxalic acid. The following chemical reaction was expected in the growth of barium-doped cadmium oxalate (BCO) crystals.

$$0.5BaCl_2 + 0.5CdCl_2 + 2H_2C_2O_4 \rightarrow Ba_{0.5}Cd_{0.5}(C_2O_4)_2 + 4HCl$$
 (2)

Cadmium oxalate crystals were transparent with many facets, whereas on addition of Ba²⁺, spherulite coalesced transparent crystals were harvested (Fig. 1). The maximum sizes of the crystals grown were about 0.44 \times 0.42 \times 0.31 cm in the case of pure cadmium oxalate crystals and 0.33 \times 0.21 \times 0.20 cm in the case of doped oxalate crystals. The optimized growth conditions for the growth of pure and barium-doped cadmium oxalate crystals are summarized in Table 1.

Starting with gelation time and their variation with pH, the growth pattern was observed for undoped and doped crystals.



Fig. 1. (a) Liesegang ring formation in the growth of cadmium oxalate and (b) spherulite crystals of barium-doped cadmium oxalate.

Table 1

Optimized conditions for the growth of pure and barium-doped cadmium oxalate crystals

Parameters	Cadmium oxalate	Barium-doped cadmium oxalate
Concentration of oxalic acid	1 M	1 M
chloride	1.5 M	1.5 M
Concentration of barium chloride		1.5 M
Specific gravity of gel	1.04	1.04
Gel pH	3.5-4.5	3.5-4.5
Gel setting period	10 h	10 h
Gel aging	3 weeks	3 weeks
Period of growth	30 days	30 days
Temperature	RT	RT

Growth rate variations and nucleation control using gel-aging technique were observed. Crystal structure of both COT and BCO were analyzed using an X'pert PRO X-ray diffractometer ($\Delta 2\theta = 10-70^\circ$, 0.2° as increment, integration time 1 s and Cu K α 1 radiation, $\lambda = 1.5406$ Å). FT-IR spectra of the oxalate crystals in the wave number range of 400–4000 cm⁻¹ were recorded on a Bruker Vector 22 spectrometer using KBr pellet technique. The thermal decomposition behavior of the individually precipitated COT and co-precipitated BCO crystals were studied by means of a TA instrument, Model Perkin Elmer, TGA 7 (US) (temperature range: ambient to 700 °C) at the heating rate of 5 °C/min.

3. Results and discussion

3.1. Crystal growth observations and nucleation control

During the growth of crystals, initial crystallization occurred just below the gel–solution interface. In the beginning, very small crystals without definite shape were found to grow and the crystal nucleation density was high due to higher supersaturation at the interface. In due course, as metal ions diffused deep into the gel and due to the nonavailability of sufficient cations, the number of crystals decreased and large crystals with definite morphology resulted far below the interface. Growth of the crystal was stagnant after 30 days. In order to investigate the exact growth conditions, the experiment was repeated by changing the growth parameters.

3.1.1. Gelation time as a function of pH

The gelation time depends on many parameters such as concentration of ionic species inside the gel, gel pH, and temperature of the gel. In our study, gels were prepared for the pH values 3.5, 4.0 and 4.5, whereas other parameters like concentration of ionic species and crystallization temperature were held constant. On observing the gelation time variation with pH for silica gels, the low pH gels (acidic gels) took more time to set than the high pH gels. Usually polymerization reaction is very fast at the neutralization point and therefore gelation time is very low for the high pH gels. Low pH gels are far from neutralization and therefore the gelation time is high. The observed gelation time was 26.5 h. for the 4.5 pH gel, whereas 40 h for the gel of pH 3.5.

3.1.2. Growth observations

Fig. 1 shows the growth pattern of pure and barium-doped oxalate crystals grown for identical crystallization parameters: gel age, 3 weeks; supernatant solution concentration, 1.5 M; and reactant solution concentration in gel, 1 M. The minimum value of pH for which crystals of cadmium oxalate crystallized was 3.5. In all the experiments, the upper reactant on contact with the gel precharged with lower reactant was observed to form a white precipitate which advanced into almost the entire gel column leaving a small transparent zone at the bottom. The precipitate did not form a continuous band. Instead, the precipitated column was divided into several bands, each thicker band of dense precipitate separated by a partially transparent band of relatively thinner precipitate. As a result, faintly observable rings against the background of the precipitate were obtained. As days advanced, clear transparent zone results because the colloidal particles of the species get condensed into crystals. Finally, Liesegang ring formation is observed and below that, the density of nucleation was highly controlled and isolated nucleation sites were observed as seen in Fig. 1a. As metal ions diffused deep into the gel, the number of crystals decreased and large crystals with definite morphology resulted. Within the gel pH studied, crystallization of cadmium oxalate favors the Liesegang ring formation, whereas on barium doping ring formation is not observed (Fig. 1b).

3.1.3. Growth rate as a function of time

Fig. 2 shows the crystal size variations of the grown pure and barium-doped crystals in gels of pH 3.5. Growth rate curves of both COT and BCO represent a portion of a parabola, which is the char-



Fig. 2. Crystal size variations as a function of time for COT and BCO.



Fig. 3. Number of nuclei (*N*) vs. growth duration.

acteristic of a one-dimensional diffusion control process. However at the early stages of growth, a departure in linearity is observed. This may be due to transient period during which the steady state concentration are established. The linear parabolic middle region reveals the supersaturation of the species needed for the growth process. The self sufficient supply of the required species results in the formation of highly perfect single crystals that confirms the constant surface supersaturation hypothesis [25]. During the final growth stage, the curve deviates from its linearity due to the shortage of the available solute for the formation of the required compound.

3.1.4. Nucleation rate as a function of gel pH

Nucleation rate was estimated during the growth of the crystals. It is clear from Fig. 3 that the pH of gel drastically changes the nucleation rate of the crystals. This variation is attributed to the variation in pore size of the gel matrix. Because of the variations in pore size, the gel structure controls the convective mass flow while allowing the Brownian motion of ions and small clusters through the intra-porous phase. In both the nucleation of cadmium oxalate and barium-doped cadmium oxalate crystals, gels with more acidic pH show less number of nucleation sites. Consequently, it is possible to say that gels with acidic pH have a more homogeneous porous size distribution with small pore radius [26]. Further in homogeneous nucleation, molecules come together and form a stable nucleus that grows in size to form critical nucleation that obeys the homogeneous nucleation theory. It is envisaged that after the formation of critical nucleation, continuous growth is possible only if sufficient solute is available. Supersaturation (S) is required for the formation of crystals and it should obey the energy consideration as given by Gibbs [27,28].

It is evident that as the droplet density increases, the supersaturation decreases, which will lead to a decrease in nucleation density. This case favors the controlled growth of crystals in low pH gels. Moreover, the nucleation rate increases rapidly during the early stages of observation and then it ceases at the end stages and move towards saturation. Comparatively the nucleation rate is approximately five times more in barium-doped cadmium oxalate than pure cadmium oxalate crystals.

3.1.5. Nucleation control using gel aging

Control of nucleation is of great importance because crystals that grow in any particular gel system compete with one another for solute. The competition reduces their size, perfection and



Fig. 4. Variation of nucleation on gels of different age.

purity. By adopting gel-aging technique, the nucleation sites can be controlled by placing the overhead solution after a predefined period above the set gel. A typical variation of nucleation with gel aging is shown in Fig. 4 for both the COT and BCO crystals. As seen, the nucleation rate decreases as the age of the gel is increased. This may be due to syneresis, during which the pore size gets reduced further so that less amount of reactant is transported through the gel for the formation of crystals that leads to controlled growth with less number of nucleation sites. In the present study, purity of the crystal is retained only by adopting the gel-aging technique and by optimizing the pH of the gel.

3.2. Structural characterization

The XRPD (powder XRD) pattern of COT and BCO crystal are shown in Fig. 5. The pattern (Fig. 5a) shows that the sample is essentially in single phase and the lines are indexed on the basis of triclinic structure of pure COT according to the Joint Committee on Powder Diffraction Standards (JCPDS Card No. 53-0085) and the reported results [29,30]. However, X-ray diffractogram obtained for BCO presents coincident d_{hkl} values with Ba_{0.5}Cd_{0.5}(C₂O₄)₂ · 5H₂O (JCPDS Card No. 45-0743). The XRD data prove that the

crystal is hexagonal in structure and the observed lattice parameters are in good agreement with the reported values [28]. The crystal data of both COT and BCO crystals are given in Table 2. The microstrain (σ) [31] and dislocation density (δ) [32] of COT crystal in its preferred orientation (010) is found to be 2.9 × 10⁻³ and 9.67 × 10¹⁴ lines/m², respectively. Whereas, 2.6 × 10⁻³ and 4.35 × 10¹⁴ lines/m² are the respective values of ' σ ' and ' δ ' of barium-doped cadmium oxalate crystals in its (101) lattice plane. It is interesting to note that the crystal structure of pure COT changes from triclinic to hexagonal when barium is added in 1:1 (Cd:Ba) ratio in the supernatant precursor solution.

3.3. Infrared spectral studies

FT-IR vibrational spectra of $CdC_2O_4 \cdot 3H_2O$ (Fig. 6a) and $Ba_{0.5}Cd_{0.5}(C_2O_4)_2 \cdot 5H_2O$ (Fig. 6b) crystals grown in silica gel exhibits strong absorption peaks in between 3400 and 3500 cm⁻¹, which is due to OH stretching vibrations of water. On adding barium as dopant, the shift in the band from its usual position to the lower wave number side is observed, which may be due to the OH bond weakness caused by the interaction of the additionally added metal ion Ba^{2+} in the crystal lattice. The bands at approximately



Fig. 5. XRPD pattern of (a) COT and (b) barium-doped COT crystal.



Fig. 6. FT-IR spectra of (a) cadmium oxalate and (b) barium added cadmium oxalate.

Table 2

Obtained crystallographic parameters for cadmium oxalate single and compound patterns

Compound	Crystal system	Spatial group	Unit cell parameters		JCPDS standards
			Observed	Standard	
CdC ₂ O ₄ · 3H ₂ O	Triclinic	P1(2)	a = 5.9903(7) Å b = 6.6484(2) Å c = 8.5728(4) Å $\alpha = 73.984(8)^{\circ}$ $\beta = 74.196(4)^{\circ}$ $\gamma = 80.840(2)^{\circ}$	$a = 6.0059 (4) \text{\AA}$ $b = 6.6656(3) \text{\AA}$ $c = 8.4925(6) \text{\AA}$ $\alpha = 74.660(5)^{\circ}$ $\beta = 74.287(6)^{\circ}$ $\gamma = 81.008(6)^{\circ}$	53-0085
$BaCd_2(C_2O_4) \cdot 5H_2O$	Hexagonal		a = 8.358 Å c = 13.19 Å	a = 8.37 Å c = 13.42 Å	45-0743

1600 cm⁻¹ are attributed to the C=O stretch of the carbonyl group and the peaks at around 1300 cm⁻¹ is assigned to C=O symmetric and O-C=O modes [33–37]. Even though C and H molecules are present in the oxalate matrix, the absence of bands in the 1145, 1050, 1006, 816 cm⁻¹ reveals the purity of the grown oxalate crystals without any C-H bonding. The bands below 800 cm⁻¹ are due to metal-oxygen bonds. As seen, barium-doped COT has more number of absorption bands in the lower wave number region (<800 cm⁻¹), which reveals the incorporation of barium ions in the crystal lattice forming additional metal-oxygen (Ba–O) bonding. Table 3 summarizes the FT-IR results of the pure and barium added cadmium oxalate crystals.

3.4. Thermal analysis

In order to elucidate the decomposition behavior of the pure and coprecipitated oxalate crystals, TG/DTG curves of COT and BCO crystals are given together for comparison (Fig. 7). The shape of thermal decomposition curve of $CdC_2O_4 \cdot 3H_2O$ in the temperature range 31–179 °C shows a single step dehydration reaction.

Table 3

Vibrational modes, in wavelength (cm⁻¹), observed in the infrared spectra for the samples $Cd(C_2O_4) \cdot 3H_2O$ and $BaCd(C_2O_4)_2 \cdot 5H_2O$

Vibration modes (cm ⁻¹) observed in Fig. 7		Literature data	Assignment of peaks/ bands
$Cd(C_2O_4) \cdot 3H_2O$	$BaCd_2(C_2O_4)\cdot 5H_2O$		
3542	3482	3502 [28]	γНОН
3496	3429	1620 [29]	δH ₂ O
1613	1586	1393 [30]	$\gamma(CO) + (CC)$
1381	1348	1314 [28]	$\gamma(CO) + \delta(O-C=O)$
1314	1301	804 [29]	
777	791	545 [28]	$\delta(O-C=O) + \gamma(MO)$
519	532		γ(MO)
	479		



Fig. 7. TGA of (a) Cadmium oxalate and (b) barium added cadmium oxalate crystals.



Fig. 8. DTA of (a) cadmium oxalate and (b) barium added cadmium oxalate crystals.

The measured weight loss for this decomposition stage is about 20.79% of the total weight (calculated loss: 21.24%) resulting in the elimination of three water molecules. Corresponding to this dehydration step, there is only one endotherm in DTA (Fig. 8a). In the second stage (179–390 °C), dehydrated cadmium oxalate is reduced to carbonate and DTA confirms the carbonate formation followed by the exothermic disproportionation [38]. In the third and the final stage (not shown in figure), the material is reduced to cadmium oxide (>700 °C).

Co-precipitated $Ba_{0.5}Cd_{0.5}(C_2O_4)_2 \cdot 5H_2O$ has the first stage of dehydration (32-333 °C), which consist of three sub-stages in the temperature ranges 32-118 °C, 118-197 °C and 197-333 °C (Fig. 8b). These dehydration stages are occurred at higher temperatures than the dehydration of pure $CdC_2O_4 \cdot 3H_2O$ which reveals the stability criterion of the doped crystals [16,17]. The first substage (32-118 °C) is due to loss of one H₂O molecule and the second sub-stage (118-197 °C) results in the elimination of two water molecules from the material. In the third and final sub-stage (197-333 °C), remaining two water molecules are ejected out. The total measured weight loss in the stage (32-333 °C) is about 14.33%, resulting in the elimination of five water molecules. Corresponding to these dehydration steps, three endothermic peaks are observed in DTA (Fig. 8b), at 78, 175 and 221 °C, respectively. In the second stage, the mass loss between 333 and 425 °C corresponds to the formation of carbonates from anhydrous mixed oxalate by the evolution of CO. As evidenced from DTA, this decomposition stage also has two sub-stages. The exotherm at 386 °C can be attributed to the partial decomposition of the Ba + Cd oxalate into barium carbonate followed by the decomposition of the remaining mixed oxalate into a homogeneous mixed Ba + Cd carbonate at 452 °C. Knaepen et al. [39] and Dharmaprakash and Mohan Rao [40,41] have already reported similar observation for the decomposition of Ca + Sr oxalate crystals. These results revealed a fact that partial segregation takes place during the decomposition process. On heating further above 700 °C, partially segregated mixed carbonate decomposes to the final products CdO and BaO (not shown in the thermogram).

4. Conclusions

Pure and barium added cadmium oxalate single crystals were grown by the gel method. The optimized crystallization conditions were: gel pH, 3.5; specific gravity of the gel, 1.04, gel age, 3 weeks; lower reactant concentration, 1 M: upper reactant concentration. 1.5 M: 1.5 M CdCl₂ + 1.5 M BaCl₂, mixed in 1:1 ratio. The growth kinetic studies revealed the dependence of nucleation density. morphology and ultimate size of crystals on growth parameters like gel concentration, gel age, gel pH, and concentration of lower and upper reactants. The decrease in supersaturation resulted less nucleation in aged gels. X-ray power diffraction has revealed the crystallinity of the material. On adding barium, the triclinic structure of the COT transformed to hexagonal structure. Presence of water of crystallization and the oxalate phase formation was identified from the FT-IR band assignments. The thermogravimetric analysis hinted that the gel-grown cadmium oxalate had three molecules of water of hydration and the barium added crystals had five molecules of water of hydration. The chemical formulae $CdC_2O_4\cdot 3H_2O$ and $Ba_{0.5}Cd_{(0.5)}(C_2O_4)_2\cdot 5H_2O$ were established from the experimental evidences.

References

- E. Knaepen, J. Mullens, J. Yperman, L.C. Van Poucke, Thermochim. Acta 284 (1996) 213.
- [2] J. Mullens, A. Vos, A. De Backer, D. Franco, J. Yperman, L.C. Van Poucke, J. Therm. Anal. 40 (1993) 303.
- [3] S.I. Hirano, T. Hayashi, Thermochim. Acta 174 (1991) 169.
- [4] A. Michaelides, S. Skoulika, J. Cryst. Growth 94 (1989) 208.
- [5] W.J. Schuele, J. Phys. Chem. 63 (1959) 83.
- [6] S. Fischer, H. Langbein, C. Michalk, K. Knese, U. Heinecke, Cryst. Res. Technol. 26 (1991) 563.
- [7] B. Chapelet-Arab, G. Nowogrockia, F. Abrahama, S. Grandjean, J. Sol. State Chem. 177 (2004) 4269.
- [8] S.M. Dharma Prakash, P. Mohan Rao, J. Mater. Sci. Lett. 8 (1989) 167.

- [9] M.R. Shedam, A. Venkateswara Rao, Mater. Chem. Phys. 52 (1998) 263.
- [10] B.P. Agarwal, K.M. Chauhan, M. Mohan Bhadbhade, Indian J. Pure Appl. Phys. 37 (1999) 395.
- [11] M.R. Shedam, A. Venkateswara Rao, Cryst. Res. Technol. 28 (1993) K5.
- [12] C. Bridle, T.R. Lomer, Acta Crystallogr. 19 (1965) 483.
- [13] G.A. Volkova, M. Yu Smirnov, R.A. Zvinchuk, Fiz. Khim. 4 (1985) 98.
- [14] N. Dishovsky, Z. Boncheva-M Ladenova, J. Cryst. Growth 51 (1981) 147.
- [15] J. Dennis, H.K. Henisch, J. Electrochem. Soc. 114 (1967) 263.
- [16] P.N. Kotru, A.K. Razdan, B.M. Wanklyn, J. Mater. Sci. 24 (1989) 2401.
- [17] S.M. Dharma Prakash, P. Mohan Rao, Cryst. Res. Technol. 22 (1987) 1095.
- [18] Jiaguo Yu, Hua Tang, Bei Cheng, Sci. China Ser. B–Chem. 47 (2004) 311.
- [19] Jiaguo Yu, Hua Tang, Bei Cheng, Mater. Chem. Phys. 91 (2005) 134.
- [20] Jiaguo Yu, Hua Tang, Bei Cheng, J. Colloid Interface Sci. 288 (2005) 407.
- S. Radhakrishnan, B.V.R. Chowdari, M. Salagram, J. Chem. Phys. 72 (1980) 1908.
 A.N. Christensen, R.G. Hazell, A.M.T. Bell, A. Altomare, J. Phy. Chem. Sol. 56 (1995) 1359.
- [23] G. Vanhoyland, M.K. Van Bael, J. Mullens, L.C. Van Poucke, Powder Diff. 16 (2001) 224.
- [24] H.S. Potdar, S.B. Despande, A.S. Despande, Y.B. Khollam, A.J. Patil, S.D. Pradhan, S.K. Date, Int. J. Inorg. Mater. 3 (2001) 613.
- [25] M. Liaw, J.W. Faust, J. Cryst. Growth 13/14 (1972) 471.
- [26] H.K. Henisch, Crystals in Gels and Liesegang Rings, Cambridge University Press, Cambridge, 1988.
- [27] J. Willard Gibbs, Collected works, Longman's Green and Co., London, 1928.
- [28] E. Kirkova, M. Djarova, Krystall and Technik 6 (2006) 601.
 [29] Erwann Jeanneau, Nathalie Audebrand, Daniel Louer, Acta Crystallogr., Sect. C
- C57 (2001) 012.
- [30] Lian-xiang Yu, Kui-rong Ma, Yong Fan, Ping Zhang, Rengong Jingti Xuebao 36 (2007) 46.
- [31] S. Veleumani, Sa.Ka. Narayanadhas, D. Mangalraj, Semicond. Sci. Technol. 13 (1998) 1016.
- [32] M. Dhanam, R. Balasundar Prabhu, S. Jayakumar, P. Gopalakrishnan, M.D. Kannan, Phys. Status Solidi (a) 19 (2002) 149.
- [33] S.M. Dharma Prakash, P. Mohan Rao, Cryst. Res. Technol. 23 (1988) K143.
- [34] E.D. Bacce, A.M. Pires, M.R. Davalos, M. Jafelicci Jr., Int. J. Inorg. Mater. 3 (2001)
- 443.[35] G.C. Jones, B. Jackson, Infrared Transmission Spectra of Carbonate Minerals, Springer, 1993.
- [36] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, 1986.
- [37] M. Fujita, Phys. Chem. 61 (1957) 1014.
- [38] A.F. Cesur, Y. Elerman, Physique 28 (1979) 17.
- [39] E. Knaepen, M.K. Van Bael, I. Schildermans, R. Nouwen, J. D'Haen, M. D'Olieslaeger, C. Quaeyhaegens, D. Franco, J. Yperman, J. Mullens, L.C. Van Poucke, Thermo Chim. Acta 318 (1998) 143.
- [40] S.M. Dharmaprakash, P. Mohan Rao, Bull. Mater. Sci. 12 (1989) 465.
- [41] S.M. Dharmaprakash, P. Mohan Rao, Cryst. Res. Technol. 24 (1989) 693.