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Vibrational spectra of magnesium oxalates

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ABSTRACT

The infrared and Raman spectra of anhydrous MgC_2O_4 as well as those of the two polymorphic forms of the dihydrated oxalate, α-$MgC_2O_4{\cdot}2H_2O$ and β-$MgC_2O_4{\cdot}2H_2O$, were recorded and discussed on the basis of their structural peculiarities and in comparison with the spectra of natural α-$MgC_2O_4{\cdot}2H_2O$ (the mineral glushinskite). Some comparisons between these polymorphs and with other, previously investigated, oxalate complexes were made. The IR spectra of partially deuterated samples of α-$MgC_2O_4{\cdot}2H_2O$ were also discussed, reinforcing some of the performed assignments.

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1. Introduction

Crystalline metallic oxalates are widely distributed in nature. They have been observed in rocks, soil, and among a variety of living organisms, including plants and animals. They are usually classified by mineralogists as "organic crystals" [1,2] and most of them exist as biominerals, produced through complex physiological mechanisms by different forms of life [2–5]. Calcium oxalate is by far the most widely distributed biomineral of this type and is specially common in the plant kingdom [2,3,6,7]. Other metallic oxalate deposits have also been found during biodeterioration processes of minerals by the action of fungi or lichens [2,8,9]. On the other hand, most of the sparingly soluble oxalates are interesting as precursors in preparative solid state chemistry [10].

As part of our studies of oxalate biominerals [2] and biomineralization processes in plants [2,7], we have initiated different studies to attain a wider insight into the general physicochemical properties of metallic oxalates [11–13]. In this paper we report the results of an investigation of the vibrational spectroscopic behavior of magnesium(II) oxalates.

We have recently reported the presence of the dihydrated magnesium(II) oxalate, α-$MgC_2O_4{\cdot}2H_2O$, the biomineral glushinskite, in the cactaceae species *Opuntia ellisiana* [14]. The same biomineral has also been found in the lichen thallus and at the lichen-rock interface of magnesium rich silicates colonized by *Lecanora atria* [15]. Besides, glushinskite and other magnesium biominerals have also been detected during the initial stages of decay of the saguaro cactus (*Carnegiea gigantea*) [16].

On the other hand, and on the basis of their structural peculiarities [2] this type of oxalate complexes may be promising materials for the photoinduced nonlinear absorption [17,18]. Also for this reason the study of their vibrational spectra is of special interest.

2. Experimental

2.1. Synthesis of the investigated compounds

All the compounds were obtained following known procedures [19]. The α-$MgC_2O_4{\cdot}2H_2O$ modification (synthetic glushinskite) precipitates after mixing concentrated aqueous solutions of magnesium chloride and oxalic acid, in stoichiometric proportions. The corresponding β-$MgC_2O_4{\cdot}2H_2O$ form can be obtained either by leaving a suspension of α-$MgC_2O_4{\cdot}2H_2O$ in contact with 1 M HCl during six months at room temperature, or by heating this suspension in distilled water at boiling temperature during three days. Anhydrous MgC_2O_4 is obtained by isothermal dehydration of α-$MgC_2O_4{\cdot}2H_2O$ at 200 °C during 48 h.

Partially deuterated samples of α-$MgC_2O_4{\cdot}2H_2O$ were obtained suspending the anhydrous oxalate in D_2O during a few minutes and drying rapidly the product in a vacuum exsiccator.

The purity of all the compounds was checked by X-ray powder diffractometry using a Philips PW 1710 diffractometer and Cu-K_α radiation (λ = 1.5425 Å). In all cases excellent agreement of the obtained powder diagrams with the published data [19,20] was observed.

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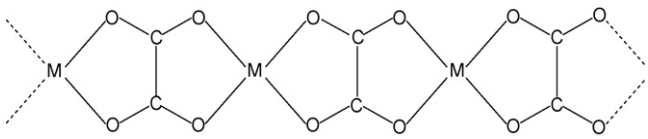

Fig. 1. Schematic drawing of the infinite chain arrangement present in M^{II}-oxalates of composition $M^{II}C_2O_4{\cdot}2H_2O$.

2.2. Spectroscopic studies

The infrared spectra in the spectral range between 4000 and 400 cm^{-1} were recorded as KBr pellets with a FTIR-Bruker-EQUINOX-55 spectrophotometer. Raman spectra were obtained with the FRA 106 Raman accessory of a Bruker IFS 66 FTIR instrument, using the 1046 nm line of a solid state Nd:YAG laser for excitation.

3. Results and discussion

3.1. Structural characteristics of the compounds

It is well established that dihydrated oxalates of different divalent metal cations are dimorphic, adopting either the α-$M^{II}C_2O_4{\cdot}2H_2O$ (M^{II} = Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}) form, or its derived β-$M^{II}C_2O_4{\cdot}2H_2O$ form [2,21]. The prototype of the most stable form, α-$M^{II}C_2O_4{\cdot}2H_2O$, is the mineral humboldtine (α-$FeC_2O_4{\cdot}2H_2O$). It belongs to the monoclinic space group *C*2/*c* with *Z* = 4. The metal cations and the oxalate groups generate an infinite chain arrangement as depicted in Fig. 1, whereas the oxalate acts as a tetradentate ligand. Each M^{II} cation is additionally coordinated to two water molecules, generating a distorted octahedral MO_6 environment. These chains generate ordered sheets lying perpendicularly to the *c* axis of the unit cell [21,22].

For the derived β-modification usually a closely related structure of orthorhombic symmetry has been admitted, with a certain degree of disorder in the piling of successive sheets [21,22] but only in the case of β-$MgC_2O_4{\cdot}2H_2O$ this suggestion has been recently confirmed by a complete single-crystal diffractometric study [23]. This form crystallizes in the orthorhombic Fddd space group with *Z* = 8. The close structural relationship between both crystalline modifications is supported by the fact that the space group *C*2/*c* is a translational subgroup of the group Fddd [23].

For the anhydrous oxalate a monoclinic structure has been suggested but not more structural details are available [20].

3.2. Vibrational spectra of the two polymorphic forms of $MgC_2O_4{\cdot}2H_2O$

The "free" uncoordinated oxalate anion presents a staggered D_{2d} configuration [24–26]. Considering only the two oxalate anions bonded to the cation in a planar arrangement, as found in the present cases, the molecular point group of the 13 atoms unit will be D_{2h} and the irreducible representation is given by $\Gamma = 6A_g + 2B_{1g} + 2B_{2g} + 5B_{3g} + 3A_u + 6B_{1u} + 6B_{2u} + 3B_{3u}$. Due to the presence of a symmetry center, the exclusion principle becomes operative. Therefore, phonons with g-parity are only Raman active and those with u-parity are only IR active.

Besides, note that the given representation differs from that previously published for the same arrangement [26] which, although not explicitly stated, refers to a 15 atoms set, surely including the oxygen ligands corresponding to the two water molecules located at equal distances above and below the cation.

The IR and Raman spectra for both crystalline modifications of $MgC_2O_4{\cdot}2H_2O$ are practically identical, confirming the strong structural similarities between them. To illustrate the general spectral pattern for both samples, those of α-$MgC_2O_4{\cdot}2H_2O$, in the spectral range between 2000 and 400 cm^{-1}, are shown in Fig. 2.

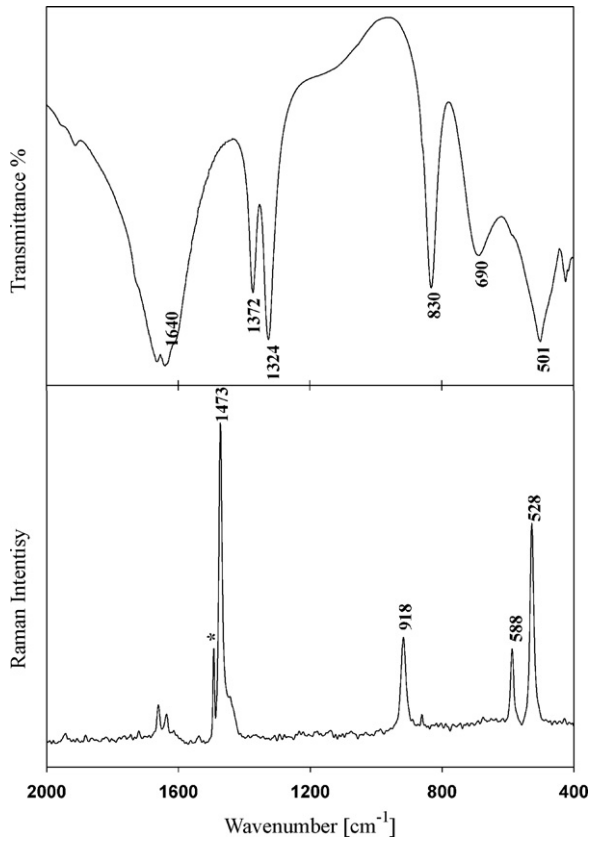

Fig. 2. FTIR (above) and FT-Raman spectra (below) of α-$MgC_2O_4{\cdot}2H_2O$ in the spectral range between 2000 and 400 cm^{-1} (*this band (1492 cm^{-1}) originates in an instrumental noise).

IR and Raman spectra of natural samples of α-$MgC_2O_4{\cdot}2H_2O$ (the mineral glushinskite) have recently been reported and assigned [26,27]. Therefore, in Table 1 we compare these spectroscopic results. And, as can be seen, comparable results are obtained with the synthetic and natural samples. The proposed assignment is based on that reported for the mineral samples [26,27], by comparisons with well-known data from spectroscopic studies of a great variety of metallic oxalates resumed by Nakamoto [28] as well as on the results of our recent studies of the Fe(II) and Mn(II) oxalates [12,13] and of synthetic moolooite, $CuC_2O_4{\cdot}0.2H_2O$ [11], in which the metal cation displays, in the plane, an identical chain structure as that depicted in Fig. 1.

In Table 2 the spectral data for both modifications of $MgC_2O_4{\cdot}2H_2O$ are compared, showing the mentioned strong similarities between these patterns. Besides, the comparison of the IR spectra in the highest frequency region, related to the water stretching motions, does not show significant differences between both crystalline forms. Both complexes present a very strong and broad band centered at about 3380 cm^{-1}, totally similar in their general shape and structure. The bending mode, $\delta(H_2O)$, certainly overlaps with the strong and broad IR band centered at 1640 cm^{-1}.

On the other hand, eventually some differences may be expected in the lower frequency region of the spectra of the two crystalline modifications, related to differences in the lattice modes and MgO_6 vibrations. Although we could not access to the low IR-frequency region, due to instrumental limitations, the Raman spectra of the two polymorphs are also practically identical in this region, showing four bands at 266 (w), 227 (vs), 159 (w) and 99 (vs) cm^{-1}, in both cases.

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Table 1
Comparison of the vibrational spectra of the mineral glushinskite with those of α-$MgC_2O_4 \cdot 2H_2O$ (band positions in cm^{-1}).

Glushinskite [26,27]		α-$MgC_2O_4 \cdot 2H_2O$		Assignment
IR	Raman	IR	Raman	
3389 sh	3391 vs			
3380 vs	3367 w	3385 vs, br	3370 m	ν(OH) (H_2O)
3230 w	3254 w	3233 w		
3126 vw		3130 w		
	1720 vw			
1679 vw				
1660 m	1660 vw	1663 sh	1661 w	
1634 s	1636 w	1640 vs	1635 vw	ν_{as}(C–O)
1603 w	1612 vw		1615 vw	
1580 sh				
	1471 vs		1473 vs	ν_s(C–O) + ν(C–C)
	1454 w, br		1450 vw	ν_s(C–O) + δ(OCO)
1369 m		1372 s		
1322 s		1324 vs		ν_s(C–O) + δ(OCO)
1314 vw				
1169 vw			1160 vw	
	915 m		918 m	ν(C–C)
860 vw	861 w		870 vw	
827 s		830 vs		ν(C–C) + δ(OCO)
803 w				
684 m, br		690 m		ρ(H_2O)
	657 vw			
	585 s		588 m	δ_{ring}
	527 vs		528 s	δ_{ring}
	521 w	501 s		δ_{ring}
		421 m		ν(Mg–O) (?)

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

Table 2
Comparison and assignment of the vibrational spectra of the two crystalline modifications of $MgC_2O_4 \cdot 2H_2O$ (band positions in cm^{-1}).

α-$MgC_2O_4 \cdot 2H_2O$		β-$MgC_2O_4 \cdot 2H_2O$		Assignment
IR	Raman	IR	Raman	
3385 vs, br	3370 m	3380 vs, br	3375 vw	ν(OH)(H_2O)
3233 w		3236 w		
3130 w		3130 w		
1663 sh	1661 w	1663 sh	1671 vw	
1640 vs	1635 vw	1640 vs	1643 w	ν_{as}(C–O)
	1615 vw		1617 vw	
	1473 vs		1472 vs	ν_s(C–O) + ν(C–C)
	1450 vw		1450 w	ν_s(C–O) + δ(OCO)
1372 s/1324 vs		1372 s/1324 vs		ν_s(C–O) + δ(OCO)
	1160 vw		1165 vw	
	918 m		916 m	ν(C–C)
	870 vw			
830 s		830 s		ν(C–C) + δ(OCO)
690 m		690 m		ρ(H_2O)
	588 m		586 m	δ_{ring}
	528 s		527 s	δ_{ring}
501 s		501 s		δ_{ring}
421 m		422 m		ν(Mg–O) (?)

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

In order to attain a better insight into the possible origin of some of the low energy bands we have measured the IR spectra of partially deuterated samples of α-$MgC_2O_4 \cdot 2H_2O$, analyzing the observed band shifts using the Teller–Redlich product rule [28,29]. This analysis is presented in Table 3 and briefly commented, as follows:

- According to the Teller–Redlich product rule, in deuteration experiments the expected ν_H/ν_D-ratio must be close to 1.41, although due to coupling and anharmonicity effects this ratio is usually found to lie between 1.2 and 1.4 [29].

Table 3
Analysis of the band shifts of α-$MgC_2O_4 \cdot 2H_2O$ after partial deuteration (band positions in cm^{-1}).

Normal sample/Table 1	Part. deuterated sample	ν_H/ν_D
3380 vs, br	2553 vs/2476 s	1.32/1.37
ca. 1620 (overlapped)	1189 m	1.36
830 s	821 s	1.01
690 m	470 w	1.47
501 s	502 s	
421 m	416 w	

vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad.

Table 4
Assignment of the vibrational spectra of anhydrous MgC_2O_4 (band positions in cm^{-1}).

Infrared	Raman	Assignment
1692 vs	1681 m	ν_{as}(C–O)
	1502 vs/1463 w	ν_s(C–O) + ν(C–C) + δ(OCO)
1379 s/1329 vs		ν_s(C–O) + δ(OCO)
	928 m	ν(C–C)
803 s	848 w	ν(C–C) + δ(O–C–O)
	640 w	
	556 sh	δ_{ring}
514 s		δ_{ring}
	529 s	δ_{ring}
439 s		ν(Mg–O) (?)

vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

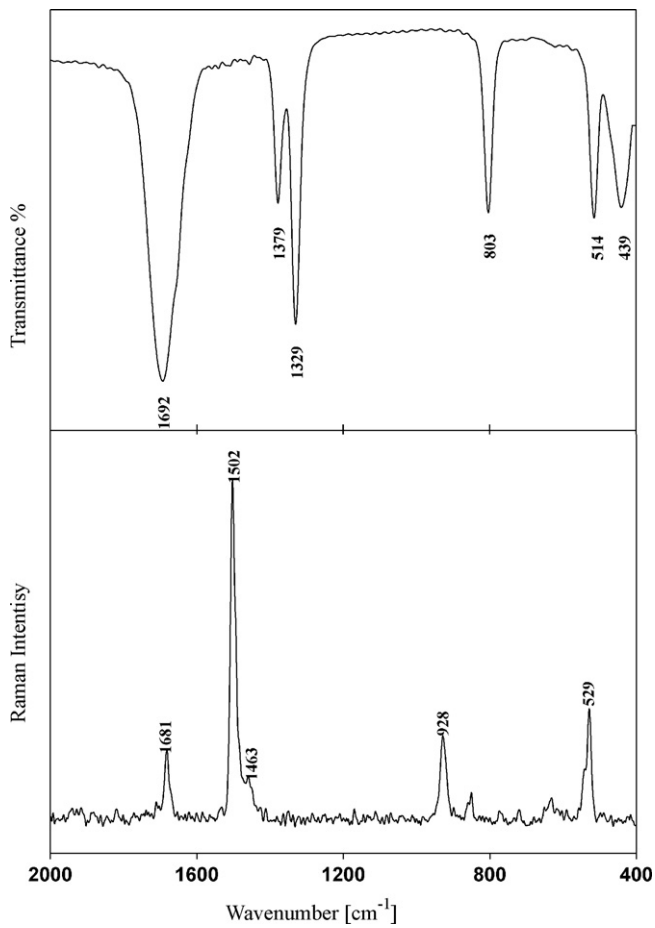

Fig. 3. FTIR (above) and FT-Raman spectra (below) of anhydrous MgC_2O_4 in the spectral range between 2000 and 400 cm^{-1}.

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- After deuteration the ν(O–H) stretching band of the water molecules generates a pair of new relatively strong bands located at 2553 and 2476 cm^{-1} both of which fulfill the above requirement.
- The deformational mode of water appears as a medium intensity band at 1189 cm^{-1}, confirming additionally the assumption that $\delta(H_2O)$ is overlapped by the intense 1640 cm^{-1} oxalate band.
- The medium intensity 690 cm^{-1} band disappears after deuteration, indicating clearly that it must be related to the proposed librational modes of coordinated water. This assignment is reinforced additionally by the fact that no bands in this region are found in the case of $CuC_2O_4{\cdot}nH_2O$ samples, in which water is not coordinated to Cu(II), but is of "zeolitic" nature [11]. Moreover, the fact that the shift of this bands generates a new one at 470 cm^{-1}, with a relatively high ν_H/ν_D-ratio, suggests that this last band probably involves an additional vibrational mode.
- The constancy of the position of the last two bands after deuteration clearly shows that they are not involved in water motions. We have tentatively assigned that at lower energy as being due to a Mg–O stretching vibration.

3.3. Vibrational spectra of anhydrous MgC_2O_4

The anhydrous oxalate, MgC_2O_4, shows much simple spectra than the corresponding hydrated forms, as seen in Fig. 3. These spectra resemble those of synthetic moolooite, $CuC_2O_4{\cdot}0.2H_2O$ [11], a fact that confirms that also after dehydration the compound retains the typical chain structure shown in Fig. 1. The proposed spectral assignment is shown in Table 4.

4. Conclusions

Vibrational spectroscopy constitutes an important tool for the study of biominerals and biomineralization processes [26,27,30,31]. In this context, the detailed spectroscopic characterization of chemically pure oxalates constitutes an aspect of central interest as such information provides the basis for the rapid and sure identification of natural oxalates, generated either as biominerals, as secondary minerals in certain ore deposits, or as a consequence of biodeterioration processes. In the present study, a thorough analysis of the IR and Raman spectra of the two modifications of $MgC_2O_4{\cdot}2H_2O$, as well as those of the anhydrous MgC_2O_4 complex, was performed. The spectral behavior of these compounds closely resembles that of the structurally related Cu(II), Fe(II), and Mn(II) oxalates [11–13] and all these results provide valuable information for the easy characterization of these species in different natural environments.

Finally, it is important to comment that the knowledge of the band gap of this type of complexes is very interesting from the point of view of materials chemistry. Although for oxalate compounds this information remains relatively scarce, in a recent study of the triclinic $CdC_2O_4{\cdot}3H_2O$ the value for this energy gap was estimated as equal to 4.42 eV [32]. This crystal also shows direct and indirect allowed optical transitions across the band gap. The phonons assisting indirect transitions correspond to an internal vibration of 967 cm^{-1} [32]. This vibration may be, essentially, a ν(C–C) stretching mode, and therefore for the investigated magnesium oxalates this phonon lies at around 915–930 cm^{-1}.

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References

[1] H. Strunz, Mineralogische Tabellen, 7th ed., Geest & Portig, Leipzig, 1978.
[2] E.J. Baran, P.V. Monje, in: A. Sigel, H. Sigel, R.K.O. Sigel (Eds.), Metal Ions in Life Sciences, vol. 4, J. Wiley, Chichester, 2008, pp. 219–254.
[3] S. Weiner, P.M. Dove, in: P.M. Dove, J.J. De Yoreo, S. Weiner (Eds.), Reviews in Mineralogy & Geochemistry, vol. 54, Mineralogical Society of America/Geochemical Society, Washington, DC, 2003, pp. 1–29.
[4] A. Veis, in: A. Sigel, H. Sigel, R.K.O. Sigel (Eds.), Metal Ions in Life Sciences, vol. 4, J. Wiley, Chichester, 2008, pp. 1–35.
[5] E.J. Baran, Química Bioinoirgánica, McGraw-Hill Interamericana de España S.A., Madrid, 1995.
[6] S.R. Khan (Ed.), Calcium Oxalate in Biological Systems, CRC-Press, Boca Raton, 1995.
[7] P.V. Monje, E.J. Baran, in: A. Hemantaranjan (Ed.), Advances in Plant Physiology, vol. 7, Scientific Publishers, Jodhpur, 2004, pp. 395–410.
[8] P. Adamo, P. Violante, Appl. Clay Sci. 16 (2000) 229–256.
[9] J. Chen, H.P. Blume, L. Beyer, Catena 39 (2000) 121–146.
[10] C.N.R. Rao, J. Gopalakrishnan, New Directions in Solid State Chemistry, Cambridge University Press, Cambridge, 1989.
[11] M.C. D'Antonio, D. Palacios, L. Coggiola, E.J. Baran, Spectrochim. Acta 68A (2007) 424–426.
[12] M.C. D'Antonio, A. Wladimirsky, D. Palacios, L. Coggiola, A.C. González-Baró, E.J. Baran, R.C. Mercader, J. Braz. Chem. Soc. 30 (2009) 445–450.
[13] N. Mancilla, V. Caliva, M.C. D'Antonio, A.C. González-Baró, E.J. Baran, J. Raman Spectrosc. 40 (2009) 915–920.
[14] P.V. Monje, E.J. Baran, Phytochemistry 66 (2005) 611–614.
[15] M.J. Wilson, D. Jones, J.D. Russell, Mineral. Mag. 43 (1980) 837–840.
[16] L.A.J. Garvie, Am. Mineral. 88 (2003) 1879–1888.
[17] I.V. Kityk, A. Majchrowski, E. Michalski, D. Kasprowicz, M. Drozdowski, J. Kisielewski, T. Likasiewicz, B. Sahraoui, J. Phys. Chem. B 110 (2006) 9090–9094.
[18] Y. Wu, J. Liu, P. Fu, J. Wang, H. Zhou, G. Wang, C. Chen, Chem. Mater. 13 (2001) 753–755.
[19] L. Walter Lévy, J. Perrotey, Bull. Soc. Chim. Fr. (1970) 1697–1704.
[20] L. Walter Lévy, J. Perrotey, J.W. Visser, Bull. Soc. Chim. Fr. (1971) 757–761.
[21] J.P. Lagier, H. Pezerat, J. Dubernat, Rev. Chim. Minèr. 6 (1969) 1081–1093.
[22] R. Deyrieux, A. Peneloux, Bull. Soc. Chim. Fr. (1969) 2675–2681.
[23] X.-A. Chen, F.-P. Song, X.-A. Chang, H.-G. Zang, W.-Q. Xiao, Acta Crystallogr. E64 (2008) m863.
[24] K.M. Begun, W.H. Fletcher, Spectrochim. Acta 19 (1963) 1343–1349.
[25] A.R. Hind, S.K. Bhargava, W. van Bronswijk, S.C. Grocott, S.L. Eyer, Appl. Spectrosc. 52 (1998) 683–691.
[26] R.L. Frost, M.L. Weier, J. Raman Spectrosc. 34 (2003) 776–785.
[27] R.L. Frost, Anal. Chim. Acta 517 (2004) 207–214.
[28] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 6th ed., J. Wiley, New York, 2009.
[29] H. Siebert, Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie, Springer, Berlin, 1966.
[30] E.J. Baran, in: A. Hemantaranjan (Ed.), Advances in Plant Physiology, vol. 8, Scientific Publishers, Jodhpur, 2005, pp. 365–392.
[31] H.G.M. Edwards, I.R. Lewis, Spectrochim. Acta 50A (1994) 1891–1898.
[32] K.M. Chauhan, S.K. Arora, Cryst. Res. Technol. 44 (2009) 189–196.