

Temperature-Dependent Raman Study of $\text{CaCu}(\text{HCOO})_4$ and $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ Crystals

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Unpolarized Raman spectra of polycrystalline samples of calcium (II)–copper (II) formate $[\text{CaCu}(\text{HCOO})_4]$ and dicalcium (II)–copper (II) formate $[\text{Ca}_2\text{Cu}(\text{HCOO})_6]$ were recorded and analyzed in the temperature range from 30 to 300 K. The observed modes at 300 K were assigned on the basis of formate group vibrations and correlations with previous data reported for other formate compounds. The splitting of the internal HCOO modes agrees with the group theory predictions. No changes either in the wavenumber or intensity of Raman modes were observed when the temperature of the samples was cooled to 30 K. This indicates that these compounds do not exhibit any phase transformation in the temperature range investigated.

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1. INTRODUCTION

Renewed interest in formate crystals has been taken place in recent years because they present very interesting properties, such as piezoelectricity, piroelectricity, antiferroelectricity, and antiferromagnetism. There is a large number of works reporting on the Raman investigations of hydrated (1–6) formate and anhydrous single-formate crystals (7–9). Recently, we have studied the room temperature phonon spectrum of mixed $\text{Ba}_2\text{Cu}(\text{HCOO})_6$ formate crystals (10).

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This compound belongs to the family of so-called mixed formates, which have an important application as precursors in obtaining high T_c superconductors (11–15). As a continuation of this study, here we present the investigation on the fundamental vibration spectrum of the anhydrous calcium (II)–copper (II) formate $[\text{CaCu}(\text{HCOO})_4]$ and dicalcium (II)–copper (II) formate $[\text{Ca}_2\text{Cu}(\text{HCOO})_6]$ compounds in the temperature range of 30 to 300 K. The well-known wavenumbers of the free HCOO molecule and correlations with other formate compounds were used to propose a general assignment of the vibration modes of $\text{CaCu}(\text{HCOO})_4$ and $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ at 300 K.

2. EXPERIMENTAL

Anhydrous calcium (II)–copper (II) $[\text{CaCu}(\text{HCOO})_4]$ and anhydrous dicalcium (II)–copper (II) formate $[\text{Ca}_2\text{Cu}(\text{HCOO})_6]$ polycrystals were synthesized following the procedure described in Ref. (16). Raman spectra were excited with a 514.5-nm line of Spectra Physics 170 Argon ion laser operating at 50 mW. The scattered light in the backscattering geometry was dispersed and recorded using a triple spectrometer (Jobin-Yvon T64000) with spectral resolution of $\pm 2 \text{ cm}^{-1}$ equipped with a N_2 -cooled charge device diode (CCD) system. All spectra were obtained in the backscattering geometry. Low-temperature measurements were carried out using a closed-cycle He refrigeration system in which the temperature could be controlled to $\pm 0.1 \text{ K}$.

3. CRYSTAL STRUCTURE AND FACTOR GROUP ANALYSIS

According to Ref. (16), CaCu(HCOO)₄ belongs to the monoclinic space group C_{2h}^4 ($P2/c$) with two formula units per unit cell whose dimensions are $a = 7.300 \text{ \AA}$, $b = 8.493 \text{ \AA}$, $c = 6.493 \text{ \AA}$, and $\beta = 97.57^\circ$. The Cu and Ca cations occupy $C_2(2)$ site symmetries, while HCOO ions occupy two general $C_1(4)$ site symmetries. On the other hand, Ca₂Cu(HCOO)₆ belongs to the monoclinic space group C_{2h}^6 ($C2/c$) with four formula units per unit cell with dimensions $a = 22.296 \text{ \AA}$, $b = 8.803 \text{ \AA}$, $c = 6.377 \text{ \AA}$, and $\beta = 101^\circ$, where Cu, Ca, and HCOO ions occupy one $C_2(4)$, one $C_1(8)$, and three $C_1(8)$ site symmetries, respectively. For both crystals the structure consists of a tridimensional array formed by Cu and Ca ions bridged through formate bidentate groups. This results in chains of edge-sharing pseudo-octahedra [CuO₆] isolated from each other by chains of Ca ions, that is, a distorted dodecahedron with eight oxygen atoms in the corners in the case of CaCu(HCOO)₄ and a distorted capped trigonal prism with coordination number seven in the case of Ca₂Cu(HCOO)₆. Both Cu and Ca chains run practically parallel to the c axis and alternate along the a axis, with the sequence Cu–Ca–Cu ... Cu–Ca–Cu for CaCu(HCOO)₄ and Cu–Ca–Ca ... Ca–Ca–Cu for Ca₂Cu(HCOO)₆.

The elementary cell of CaCu(HCOO)₄ contains two formula units leading to a total of 108 vibrational modes. In terms of irreducible representations of the C_{2h} point group this mode can be decomposed as

$$\Gamma = 26A_g + 26A_u + 28B_g + 28B_u, \quad [1]$$

which results in 54 Raman active optical vibrations.

The 162 vibrational modes of Ca₂Cu(HCOO)₆ are decomposed in terms of the irreducible representations of the C_{2h} factor group as

$$\Gamma = 40A_g + 40A_u + 41B_g + 41B_u, \quad [2]$$

leading to 81 active optical modes in Raman spectroscopy.

TABLE 1
Internal Modes of the Free HCOO Molecule

Classification	Type	$\bar{\nu}/\text{cm}^{-1}$
C–H stretch (ν_1)	A_1	2860
O–C–O asymmetric stretch (ν_4)	B_1	1588
C–H in plane bend (ν_5)	B_1	1382
O–C–O symmetric stretch (ν_2)	A_1	1372
C–H out of plane bend (ν_6)	B_2	1069
O–C–O symmetric deformation (ν_3)	A_1	792

TABLE 2
Correlation Diagram Showing How the Internal Modes of Free HCOO Molecule are Distributed in Terms of the Irreducible Representations of C_{2h} Factor Group

Free ion symmetry C_{2v}	Site symmetry C_1	Unit cell symmetry C_{2h}	Vibrational modes
			$A_g \quad \nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6$
			$A_u \quad \nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6$
			$B_g \quad \nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6$
			$B_u \quad \nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6$

The normal vibrational modes of the formate group appear in the region $0-3000 \text{ cm}^{-1}$. Assuming that formate ion has a symmetry close to C_{2v} , the Raman positions for internal modes of free HCOO molecule are showed in Table 1 (17).

To get a better understanding of the spectra obtained, it is helpful to know how the internal HCOO vibrations shown in Table 1 are distributed in terms of the irreducible representations of the C_{2h} point group. This is obtained through the use of the correlation diagram calculated by using the method of molecular site group analysis described in Ref. (18) and displayed in Table 2. For both compounds, the HCOO ions occupy general C_1 site symmetries, which implies that their internal vibrational modes are equally

TABLE 3
Factor Group Analysis for CaCu(HCOO)₄ at Room Temperature

C_{2h}^4	n	R' (HCOO) ⁻	T'			T	
			Ca ²⁺	Cu ⁺	(HCOO) ⁻		
A_g	12	6	1	1	6	—	R
A_u	12	6	1	1	6	1	IR
B_g	12	6	2	2	6	—	R
B_u	12	6	2	2	6	2	IR

Note. n , number of internal modes; R' , number of rotational lattice modes; T' , number of translational lattice modes; T , number of acoustic modes; R, Raman active, and IR, infrared active.

TABLE 4
Factor Group Analysis for $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ at Room Temperature

C_{2h}^6	n	R' (HCOO^-)	T'			T	
			Ca^{2+}	Cu^+	(HCOO^-)		
A_g	18	9	3	1	9	—	R
A_u	18	9	3	1	9	1	IR
B_g	18	9	3	2	9	—	R
B_u	18	9	3	2	9	2	IR

Note. n , number of internal modes; R' , number of rotational lattice modes; T' , number of translational lattice modes; T , number of acoustic modes; R, Raman active, and IR, infrared active.

distributed among all irreducible representations of the C_{2h} factor group. For this reason, the splitting of the internal modes is only due to the number of nonequivalent site symmetries. Therefore, for $\text{CaCu}(\text{HCOO})_4$ compound each internal mode is expected to be split into two modes, while for the $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ compound a threefold splitting is expected. In Tables 3 and 4 we summarized the results of the factor group analysis (19) for the $\text{CaCu}(\text{HCOO})_4$ and $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ compounds.

4. RESULTS AND DISCUSSION

In Figs. 1a and 1b we show the room temperature Raman spectra for $\text{CaCu}(\text{HCOO})_4$ and $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ polycrystals, respectively. Following the usual procedure, the assignments are discussed in four regions, namely: (i) high-wavenumber region ($2500\text{--}3000\text{ cm}^{-1}$); (ii) medium-wavenumber region ($1200\text{--}1700\text{ cm}^{-1}$); (iii) low-wavenum-

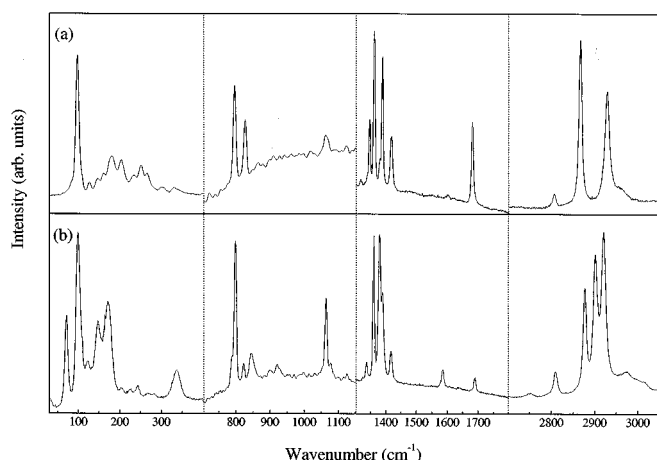


FIG. 1. Room temperature Raman spectra of (a) $\text{CaCu}(\text{HCOO})_4$ and (b) $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ polycrystal samples.

ber region ($700\text{--}1000\text{ cm}^{-1}$); and (iv) lattice-vibration region (below 400 cm^{-1}).

4.1. High-Wavenumber Region

In this wavenumber region besides the $\nu_1(\text{HCOO})$ modes, vibrations related to some combinations and overtones of other $\nu(\text{HCOO})$ modes are expected to be observed. From Fig. 1a, we identify two different wavenumbers at 2926 and 2864 cm^{-1} , which were assigned to ν_1 , while from Fig. 1b we identify three different wavenumbers at around 2919 , 2900 , and 2876 cm^{-1} , which we also assigned to ν_1 , as predicted by the factor group analysis. The remaining mode appearing in Fig. 1a was assigned to the combination of ν_4 and ν_5 modes at 2957 cm^{-1} and to the overtone $2\nu_5$ mode at 2804 cm^{-1} , while from Fig. 1b the vibrations at 3000 , 2972 , 2809 , and 2749 cm^{-1} were assigned to the combination of ν_1 with a translation of (HCOO^-) ion, a combination of ν_4 and ν_5 modes, and the overtones $2\nu_5$ and $2\nu_2$, respectively. These results agree well with those presented in Ref. (20) for $\text{Cd}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$, in Ref. (21) for $\text{Ni}(\text{HCOO})_2$ and in Ref. (6) for $\text{BaCd}(\text{HCOO})_4 \cdot 2\text{H}_2\text{O}$.

4.2. Medium-Wavenumber Region

In this wavenumber region we expect to observe the $\nu_2(\text{HCOO})$, $\nu_4(\text{HCOO})$, and $\nu_5(\text{HCOO})$ modes. From Fig. 1a, we assigned the vibrations at 1680 and 1600 cm^{-1} as two ν_4 , while from Fig. 1b we assigned as three ν_4 the vibrations observed at 1690 , 1637 , and 1585 cm^{-1} . There are some discrepancies in the current literature relating to the assignment of the $\nu_2(\text{HCOO})$ and $\nu_5(\text{HCOO})$ modes. Some authors assign as ν_2 the most intense modes in this wavenumber range (3, 9, 22), while other authors attribute to ν_5 the most intense modes (4, 17). We have decided to take into account the criteria used in Refs. (6, 20, 23), where the highest wavenumbers were assigned as the $\nu_5(\text{HCOO})$ vibrations. In this way, the modes observed in Fig. 1a at 1416 , 1386 , and 1377 cm^{-1} were assigned as the ν_5 and those at 1360 , 1345 , and 1315 cm^{-1} as the ν_2 . Following the same criterion, we have assigned the six vibrations observed in Fig. 1b as: (i) three ν_5 oscillating at 1417 , 1389 , and 1378 cm^{-1} and (ii) three ν_2 oscillating at 1360 , 1336 , and 1324 cm^{-1} .

4.3. Low-Wavenumber Region

In this wavenumber region we should observe the appearance of the $\nu_6(\text{HCOO})$ and $\nu_3(\text{HCOO})$ modes. From Fig. 1a we observe just one ν_6 -type mode oscillating to 1062 cm^{-1} and two ν_3 -type modes at 825 and 794 cm^{-1} , while from Fig. 1b we assign two ν_6 -type vibrations at 1070 and 1063 cm^{-1} and four ν_3 -type modes at 845 , 825 , 797 , and 785 cm^{-1} . A very low intensity mode oscillating at

TABLE 5
Spectral Data and Band Assignments at Room Temperature for $\text{CaCu}(\text{HCOO})_4$ and $\text{Ba}_2\text{Cu}(\text{HCOO})_6$ Crystals

Wavenumbers		Assignments
$\text{CaCu}(\text{HCOO})_4$	$\text{Ca}_2\text{Cu}(\text{HCOO})_6$	
—	3000 br	ν_1 + translation (HCOO)
2957 br	2972 br	$\nu_4 + \nu_5$
2926 vs	2919 vvs	ν_1
—	2900 vvs	ν_1
2864 vvs	2876 vvs	ν_1
2804 m	2809 s	$2\nu_5$
—	2749 w	$2\nu_2$
1600 vs	1690 vvs	ν_4
—	1637 w	ν_4
1680 w	1585 s	ν_4
1416 s	1417 s	ν_5
1386 vvs	1389 vs	ν_5
1377 s	1378 vvs	ν_5
1360 vvs	1360 vvs	ν_2
1345 s	1336 s	ν_2
1315 w	1324 w	ν_2
—	1070 w	ν_6
1062 w	1063 w	ν_6
—	919 w	
—	845 w	ν_3
825 w	825 w	ν_3
794 w	797 vs	ν_3
—	785 m	ν_3
332 m	336 vs	Cu–O stretch
329 m	—	Cu–O stretch
301 s	—	Cu–O stretch
266 m	—	Ca–O stretch
250 s	—	Ca–O stretch
232 s	242 s	Ca–O stretch
204 s	—	
184 s	—	
176 s	172 vvs	HCOO wagging
160 m	161 sh	HCOO wagging
147 m	147 vs	HCOO twisting
—	142 sh	HCOO twisting
126 m	121 m	HCOO twisting
107 sh	106 sh	HCOO translation
97 vs	98 vvs	HCOO translation
84 sh	85 sh	HCOO rocking
—	70 vs	HCOO rocking

Note. The relative intensities are vvs, very very strong; vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; and br, broad.

919 cm^{-1} was also observed. The observed wavenumbers, relative intensities, and the proposed assignment for the vibrations of $\text{CaCu}(\text{HCOO})_4$ and $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ compounds at room temperature are summarized in Table 5.

From results summarized in Table 5, we observe that there is a good agreement between the predictions of the factor group theory analysis and the phonons observed for

both crystals. The observation of three $\nu_5(\text{HCOO})$ and $\nu_2(\text{HCOO})$ vibrations for $\text{CaCu}(\text{HCOO})_4$ instead of two, and of four $\nu_3(\text{HCOO})$ vibrations for $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ instead of three, should be due to a superposition between A_g and B_g modes, once we have performed unpolarized Raman measurements.

4.4. Lattice-Vibration Region

In this wavenumber region we expect to identify the translational, rocking (ρ), twisting (τ), and wagging (ω) librational modes of the HCOO molecule as well as the Ca–O and Cu–O vibrations. By considering the hierarchical sequence obeyed by the librational modes in formate-like compounds, i.e., $\rho < \tau < \omega$ [6], we have assigned for $\text{CaCu}(\text{HCOO})_4$ the following vibrations: (i) two ω at 176 and 160 cm^{-1} , (ii) two τ at 147 and 125 cm^{-1} , and (iii) one ρ at 84 cm^{-1} . We attributed the intense mode at 97 cm^{-1} and the mode appearing at 107 cm^{-1} to HCOO translations, while the bands at 330 and 300 cm^{-1} are identified as Cu–O stretch and those at 266 , 250 , and 232 cm^{-1} as Ca–O stretch. For the $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ compound we have assigned the mode appearing at 336 and 242 cm^{-1} as Cu–O

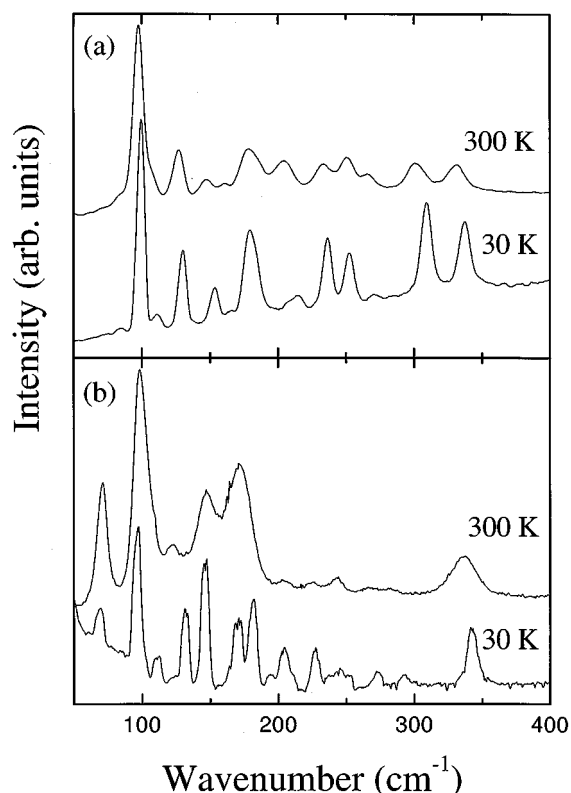


FIG. 2. Low-frequency region of the Raman spectra of (a) $\text{CaCu}(\text{HCOO})_4$ and (b) $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ polycrystals. Upper and lower spectra in each part are related to $T = 300\text{ K}$ and $T = 30\text{ K}$, respectively.

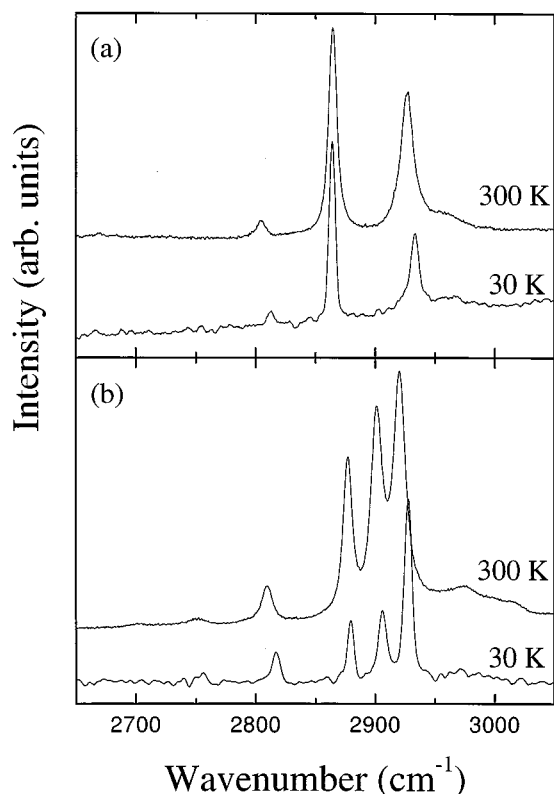


FIG. 3. High-frequency region of the Raman spectra of (a) $\text{CaCu}(\text{HCOO})_4$ and (b) $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ polycrystals. Upper and lower spectra in each part are related to $T = 300$ K and $T = 30$ K, respectively.

and Ca–O stretching vibrations, respectively. The modes appearing at 172 and 161 cm^{-1} were attributed to ω , while those at 147 , 142 , and 121 cm^{-1} were assigned as τ . Two ρ modes were observed at 85 and 70 cm^{-1} . Finally, the modes at 106 and 98 cm^{-1} were assigned as translations of $(\text{HCOO})^-$ ion.

Next, let us present the results concerning the study of the phonon spectrum of $\text{CaCu}(\text{HCOO})_4$ and $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ polycrystals as a function of temperature in the range from 30 up to 300 K. Figures 2 and 3 display the Raman spectrum at 30 and 300 K for $\text{CaCu}(\text{HCOO})_4$ and $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ polycrystals in the wavenumber range of external and ν_1 modes, respectively. A detailed investigation of these spectra shows that there is no appreciable modifications either in the relative intensity or in the wavenumber of the phonons observed. These results indicate that the room temperature phase of $\text{CaCu}(\text{HCOO})_4$ as well as that of $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ are stable in the temperature range studied. It was somewhat expected, in accordance with Ref. (7), that anhydrous formate crystals do not undergo any phase transitions when the temperature is varied in the range 30 – 300 K. Indeed, only hydrated formate crystals do undergo low-temperature phase transition due to the ordering of water molecules.

5. CONCLUSIONS

Raman scattering study of $\text{CaCu}(\text{HCOO})_4$ and $\text{Ca}_2\text{Cu}(\text{HCOO})_6$ polycrystal compounds have been carried out in the temperature range from 30 to 300 K. A general assignment of the vibrations observed at room temperature was proposed on the basis of HCOO group vibrations and correlations with other formate compounds. The observed splitting of some internal HCOO modes for both crystals indicates that the spectra agree well with the predictions of the factor group analysis. The spectra of these compounds at various temperatures in the range 30 – 300 K were taken. The results show that the low-, medium-, and high-wavenumber Raman modes do not exhibit variations either in the wavenumber or in the intensity, indicating that their monoclinic phase at 300 K does not undergo any transition when the temperature is cooled down to 30 K.

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