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PHYSICS

Infrared Spectroscopy of the Solid Solution $[Ca_{1-x}(Ba)_x]CO_3$

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Abstract. A complete infrared study of the mixed crystal system $BaCO_3$ and $CaCO_3$ is carried out in the region 4000-600 cm^{-1}. The study includes internal fundamental normal vibrations of the CO_3 ion in the ordered phases of the two carbonates at room temperature) at different values of the barium concentration, the IR spectra, spectral band shape, intensities and frequencies of the internal modes as function of the barium ion concentration.

Introduction

BaCO3 is one of the most important divalent carbonates. The crystal structure of $BaCO_3$ was investigated by many authors [1-3] and they found that $BaCO_3$ has non-quenchable high temperature polymorphic transformation. The orthorhombic phase, stable at ambient conditions, transforms at high temperature to hexagonal phase and at still higher temperature from the hexagonal to cubic structure. Speer [4] and Judd [5] reported a systematic investigation of the compositional dependency of the orthorhombic-hexagonal transformation in the system $BaCO_3$ at one atmosphere. I.R. spectra of calcium carbonate signal crystal and powder have been published [6-8]. No measurements on BaCO3-CaCO3 mixed single crystal have been reported.

In the present work we have studied the effects of $CO^{2-}{}_3$ ion environment (type, change, concentration) and the effects of partial replacement of calcium (0.99A) ions by

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larger divalent cations barium (1.35A) on the characteristic of the ordered phase of $CaCO_3$ and $BaCO_3$ in the mixed crystals system.

Experimental

Mixed crystals of barium carbonate and calcium carbonate were prepared by evaporation of aqueous solutions of barium and calcium carbonates of definite ratio in a desiccator, which was kept at constant temperature for few days.

The produced crystal has 2x2 mm cross sectional area and 5mm length. The infrared measurements were carried out using a Backman G.R. 722 R spectrometer. The prepared samples were 2.5 mg of $[Ca_{1-x} (Ba)_x] CO_3$ mixed with 1mg powder KBr and placed in a cylindrical die of 10 mg diameter after shaking the mixture for about one minute. The die was evacuated insuring dryness and the sample was pressed. A clean disc of approximately 1mm thickness was obtained. The infrared spectra were recorded in the region of 4000-600 cm^{-1} on a graphical paper with scanning time of 30 minutes.

Results and Discussion

The IR analysis of the prepared mixed crystal system $[Ca_{1-x} (Ba)_x] CO_3$ were taken at different values of barium concentration "X". In the following IR results we used Herzberg's notation [9] for the internal fundamental normal vibration of CO_3. Thus ν_1 denotes the totally symmetric C-O stretching mode, ν_2 the bending mode, ν_3 the asymmetric C-O stretching mode and ν_4 is the asymmetric in-plane bending mode. The IR spectra for $CaCO_3$, $BaCO_3$ and 50:50 mixture of $CaCO_3$ and $BaCO_3$ are shown in Fig. 1 for the ordered phase in both compounds. The detailed frequencies and their spectroscopic data assignments are collected in Table 1.

Table 1. Effect of Ca ions on the IR internal modes in the ordered phase II of $BaCO_3$

Modes	$BaCO_3$	x = 0.3	x = 0.5	x = 0.6	x = 0.7	x = 0.8	CaCO
υ_4	690 SP	700 SP	690 SP 710 SP	690 SP 710 SP	690 SP 710 SP	700 SP	710 SP
υ_2	850 VS-SP	860 Sh	850 870	850 870	850 870	870	870
ν_1	1055	1050	1055	1055	1055	---	---
ν_3	1430 BB	1430 BB	1430 BB	1430 BB	1430 BB	1430 BB	1430 B
$\nu_1 + \nu_4$	1740 WBB	1760 WBB	1780 WBB	1780 WBB	1780 WBB	1780 WBB	1790 WBB
$2\nu_1$	2000 Sh	2000 Sh	2000 Sh	2000 Sh	2000 Sh	2000 Sh	2000 Sh
$\nu_1 + \nu_3$	2440 WBB	2500 WBB	2500 WBB	2500 WBB	2440 WBB	2440 WBB	2500 WBB
$2\nu_3$	2800 VW	2840 VW	2860 VW	2860 VW	2840 VW	2840 VW	2850 OV

VW = Very weak; SP = Sharp peak; BB = Broad band; Sh = Shoulder; W = Weak; VS = Very strong.

The frequency asymmetric in-plane bending mode v_4 as shown in Fig. 2, which appeared in the IR spectra as a strong sharp peak in pure $CaCO_3$ exhibited reduction in its intensity and a change in the band contour shape in the room temperature ordered phase of $CaCO_3$. This change depends on the concentration of the added Ba ion "X". For the v_4 band, a distinct splitting is observed at 710 and 690 cm^{-1} for concentration x=0.6 and may be explained as the results of factor group splitting. There is shift in band frequency from 690 cm^{-} to 710 cm^{-1}. The intensity change of his mode, in Fig. 3 shows continuous reduction in relative peak intensity up to x<0.4, after which slight increase is observed. Pobeguin [10] and Dupuis *et al.* [11] observed bands at 705 and 860 cm^{-1} for $CaCO_3$ which is in good agreement with us. The bending mode v_2, shown in Fig. 4, which appeared in IR spectra as a strong sharp peak in pure $BaCO_3$ exhibited reduction in its intensity and a change in the band contour shape in the room temperature ordered phase of $BaCO_3$. This change depends on the concentration of the added Ba ion (X). There is a remarkable shift in band frequency from 850 cm^{-1} to 870 cm^{-1} as the concentration of Ca is increased. The intensity change of this mode, in Fig. 5, shows continuous reduction in

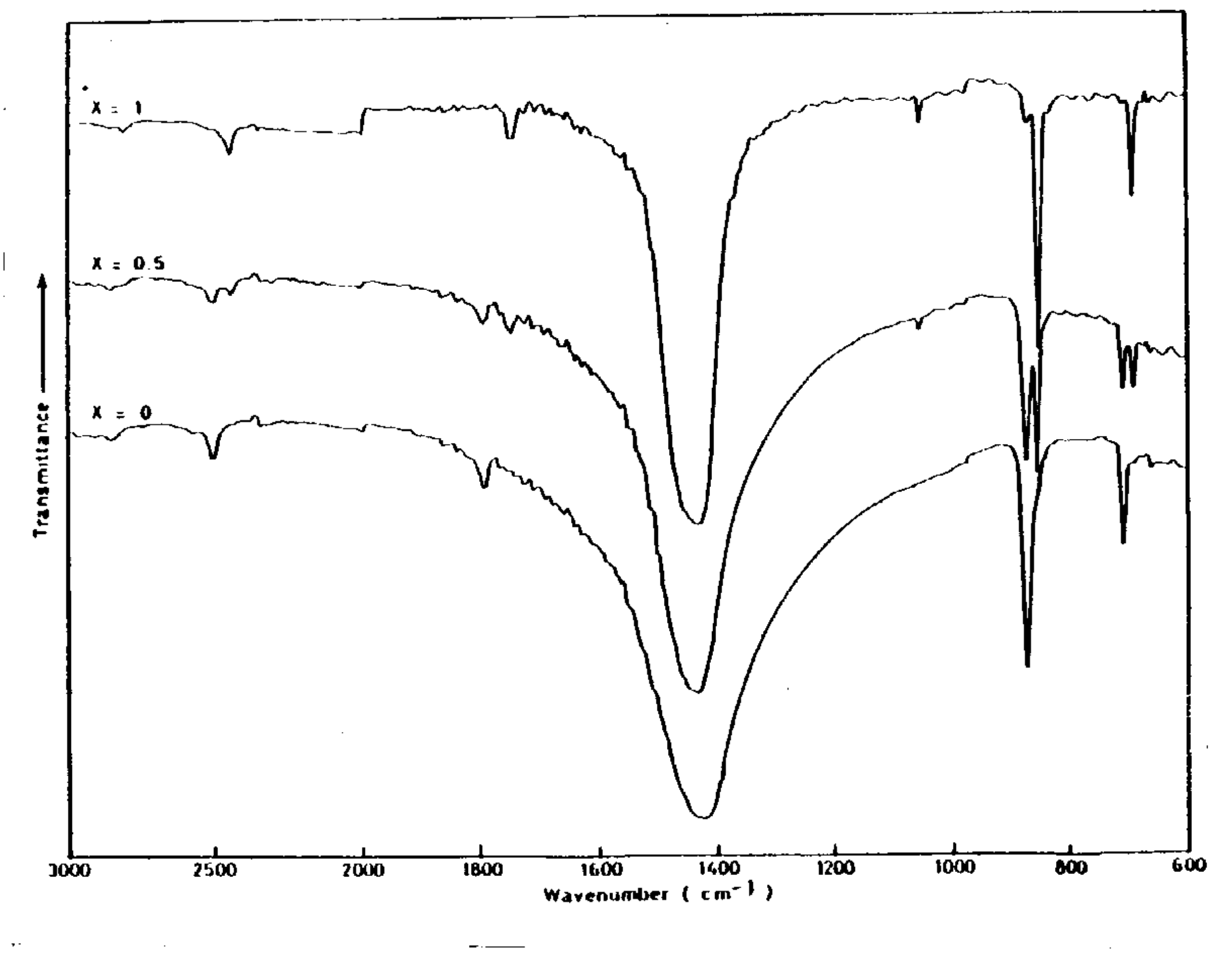

Fig. 1. I.R. Spectra for $BaCO_3$, $CaCO_3$ and (50% $BaCO_3$ + 50% $CaCO_3$ for the ordered phase II (room temperature).

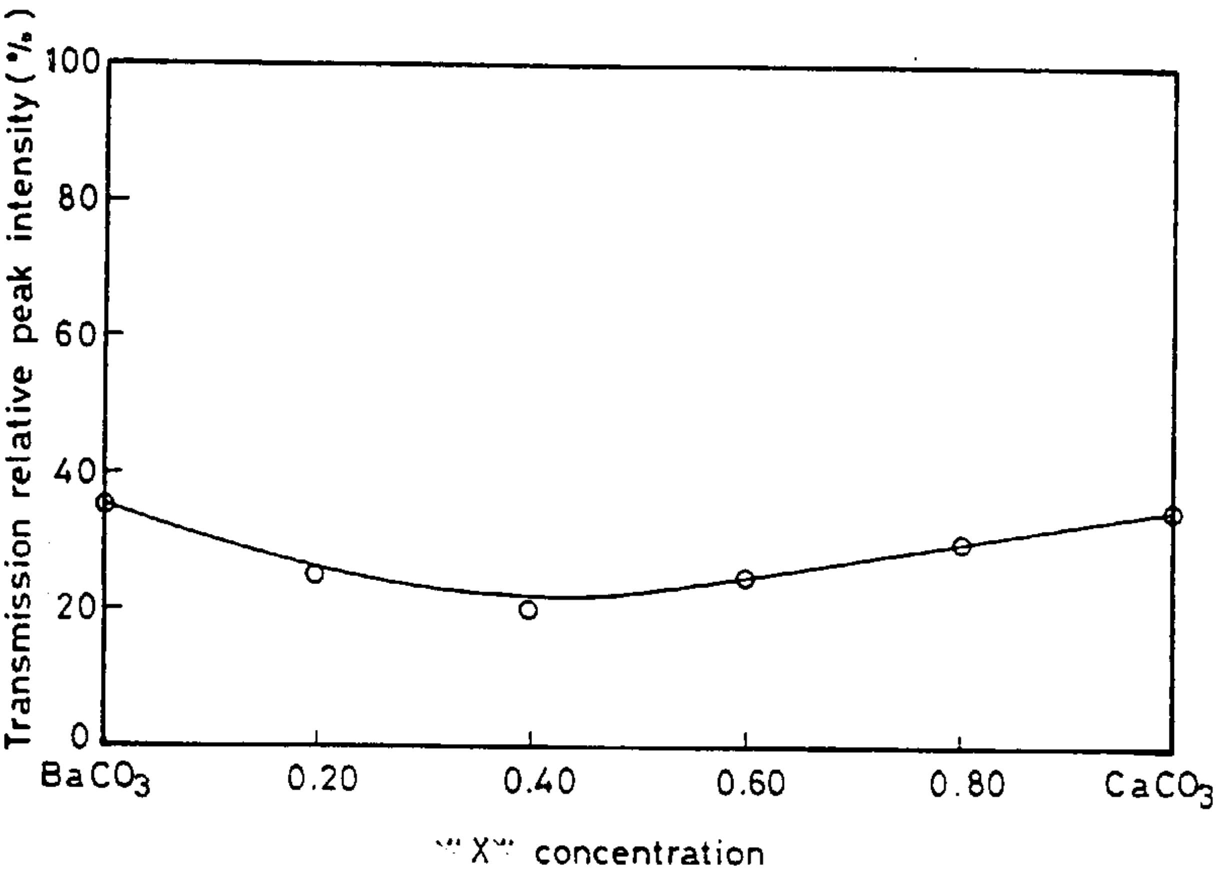

Fig. 3. Variation of transmission relative peak intensity of the υ_4 mode with the concentration of Ba ions in the mixed crystal system.

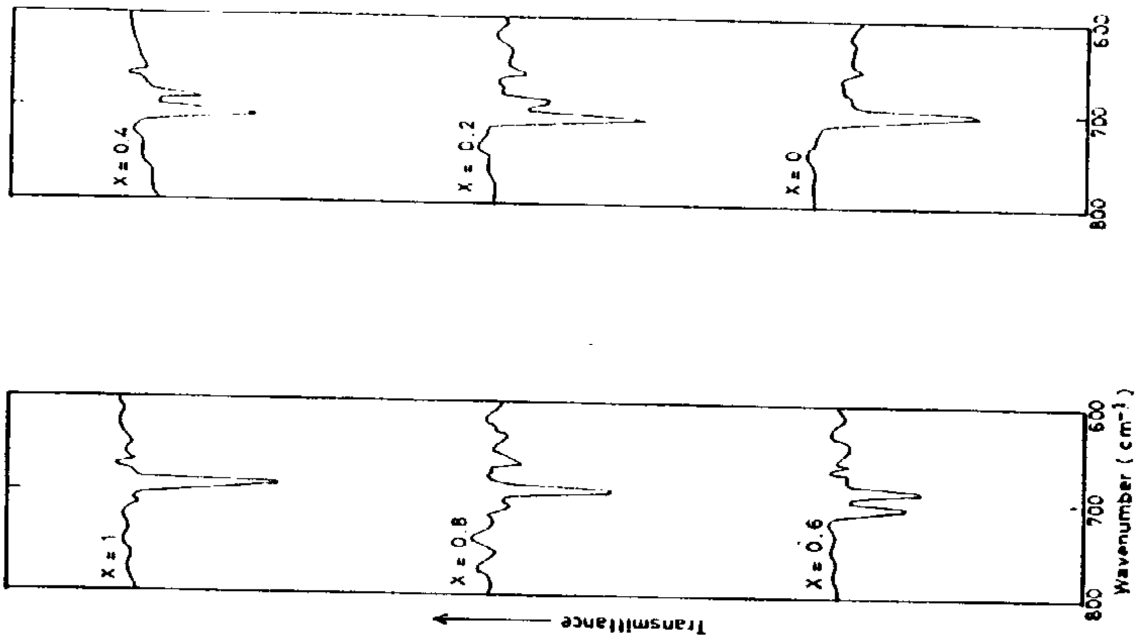

Fig. 2. Variation of the I.R. band contour of the υ_4 mode with the concentration of Ba ions in the mixed crystal system.

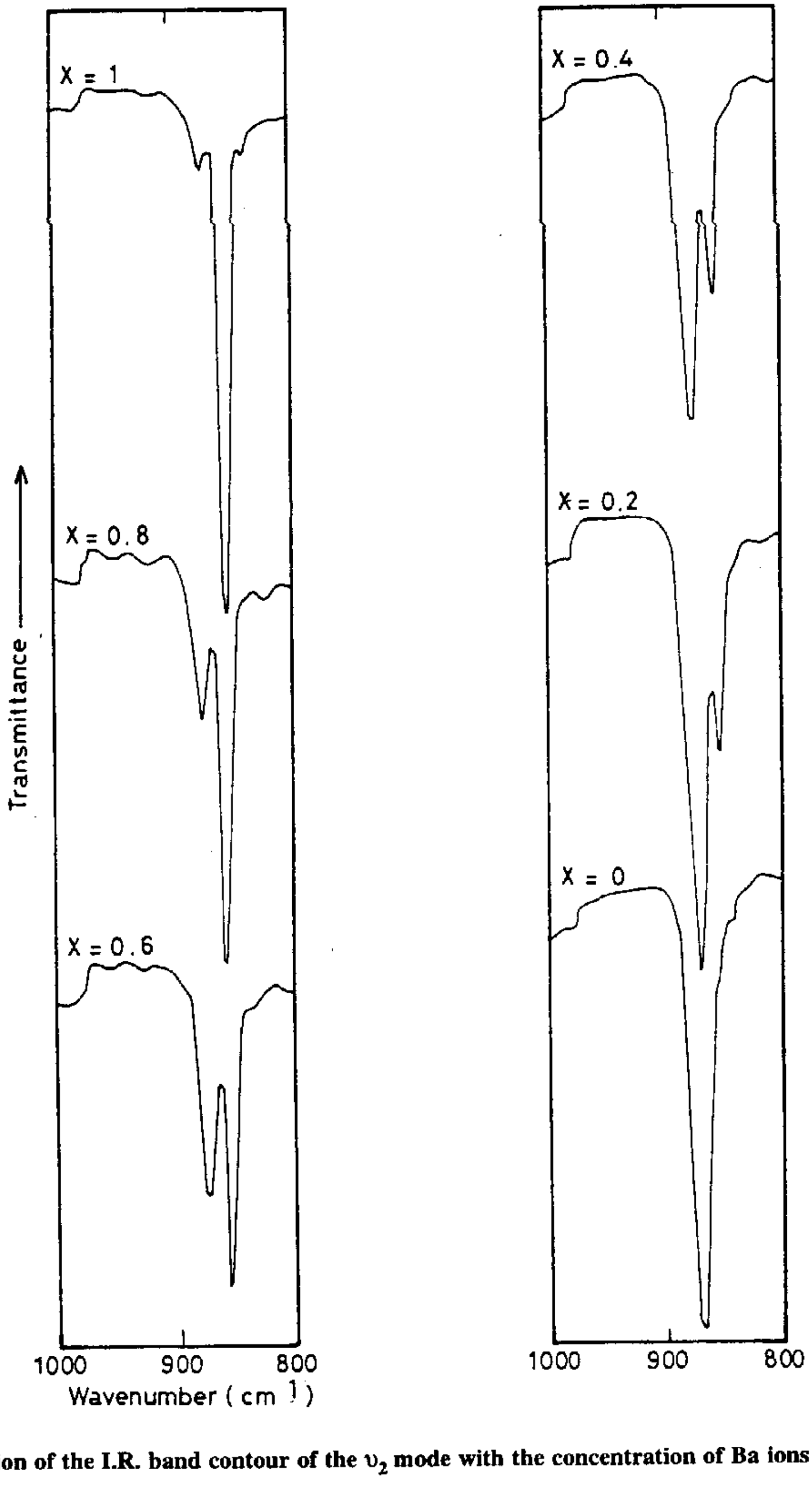

Fig. 4. Variation of the I.R. band contour of the υ_2 mode with the concentration of Ba ions in the mixed crystal system.

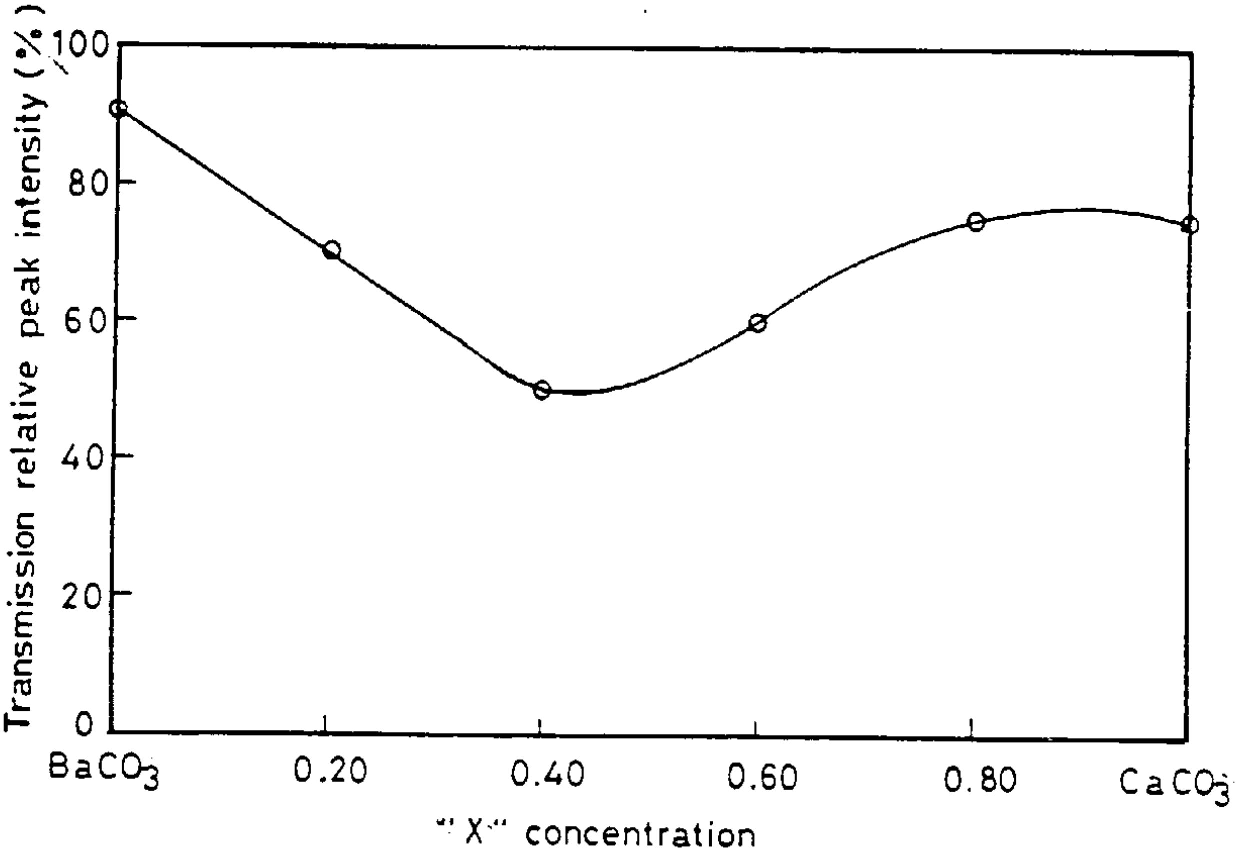

Fig. 5. Variation of the transmission relative peak intensity of the υ_4 mode with the concentration of Ba ions in the mixed crystal system.

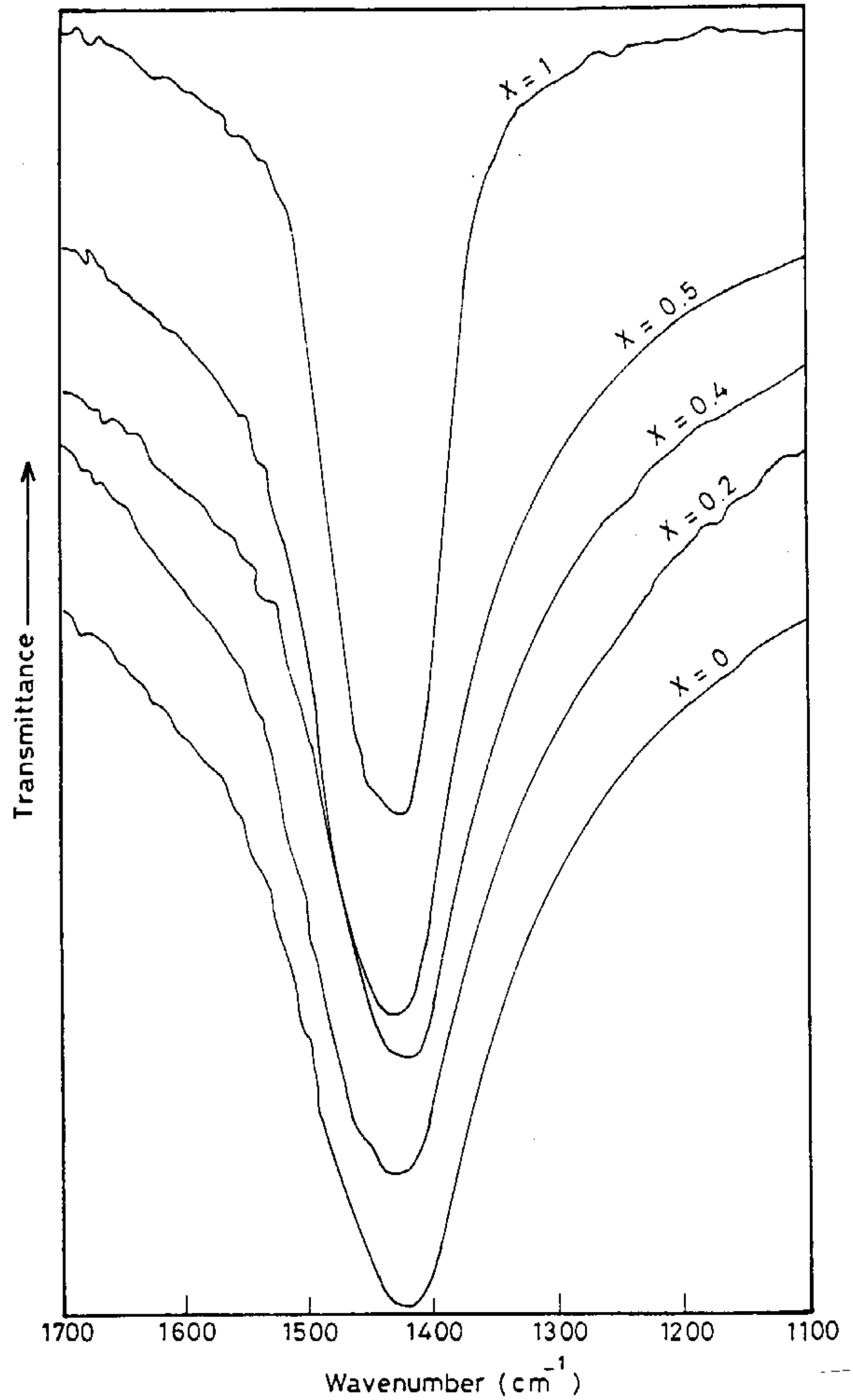

Fig. 6. Variation of the I.R. band contour of the asymmetric stretching mode υ_3 at various concentration of Ba ions in the mixed crystal system.

relative peak intensity up to x>0.4, after which a slight increase is observed. The (υ_2 bands has been interpreted by Sterzel and Chorinsky [12] and by Sterzel [13] as being due to the ν_2 mode of $C^{13}CO^{-2}_3$ originating from the natural abundance of the $C^{13}C$ isotope.

The asymmetric stretching mode ν_3 is affected by the presence of the added barium cation in the mixed system, as shown in Fig. 6. Careful examination of the strong band absorption in the $1600^{-1}1400$ cm^{-1} region at room temperature indicates that this mode loses some of its broadening features in the presence of Ba ions. For this band, no distinct splitting is observed. However, no remarkable shift in band frequency could be detected.

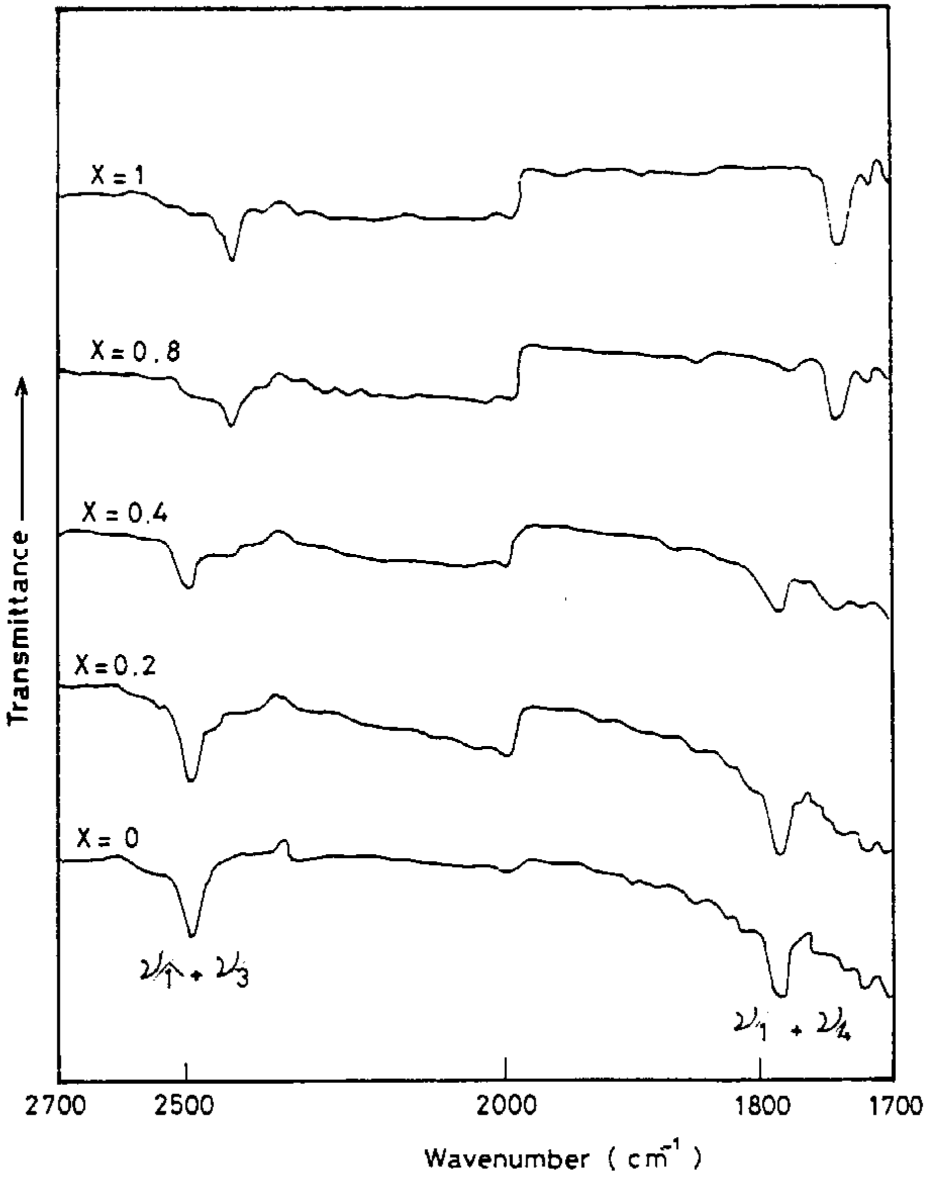

Fig. 7. Variation of the I.R. band contour of the combination modes $\upsilon_1 + \upsilon_4$ and $\upsilon_1 + \upsilon_3$ mode with the concentration of Ba ions in the mixed crystal system.

On the other hand, the intensity of this mode is increased slightly as the barium ion concentration is increased. The paper by Sato and Matsuda [14] shows a nice split band in the region 1500-1400 cm^{-1}, the frequencies of two component bands being 1490 and 1420 cm^{-1}, for $CaCO_3$. The high intensities of the v_3 modes of the crystalline system have been attributed to covalent interaction [15].

The combination mode (v_1+v_4), shown in Fig. 7 was found to be affected by the presence of the added barium ion. Also, the same behavior could be observed for the combination mode (v_1+v_3) with clear shift as the concentration of Ba is increased. Porto *et al.* [16] reported the frequencies of the two combination bands v_1+v_3 and v_1+v_4 observed at 2510 and 1800 cm^{-1}, respectively, which is in perfect agreement with our values of 2500 and 1790 cm^{-1} for $CaCO_3$. The variation of relative peak intensities may be attributed to difference in polarizability arising from the cationic atom sphere ground CO^{-2}_3 [17] (i.e. due to variations in the numbers of Ba and Ca ions with changes in the overall composition).

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دراسة مادتي كربونات الباريوم وكربونات الكالسيوم في المقياس الطيفي للأشعة تحت الحمراء

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ملخص البحث. تمت دراسة كاملة بواسطة جهاز الأشعة تحت الحمراء في الحدود ٤٠٠٠–٦٠٠ سم$^{-1}$ لمخلوط المواد الصلبة من كربونات الباريوم وكربونات الكالسيوم. واشتملت الدراسة على أساس الترددات الداخلية لمادة أيونات الكربون في مخلوط كربونات الباريوم وكربونات الكالسيوم عند درجة حرارة الغرفة، وعند اختلاف تركيز مادة الباريوم في المخلوط في جهاز الأشعة تحت الحمراء، ومن ذلك الشكل الطيفي، الشدة والتردد مع زيادة أيونات الباريوم.