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Studies on structural parameters and elastic constants in NaCl and CaCl₂

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ABSTRACT

Crystals of mixtures of calcium chloride in sodium chloride were grown in water and these were characterised using X-ray powder patterns obtained from an X-ray diffractometer. Williamson-Hall plot method was used to compute crystallite size and lattice strains in these mixed crystals. These results were compared with elastic constants computed by measuring the velocities of longitudinal and shear sound waves in these crystals. It is observed that the strength of the sodium chloride crystal decreases with addition of calcium ions.

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INTRODUCTION

Sodium chloride is also known as common salt, table salt or halite, is an ionic compound with formula NaCl. It is the most responsible for the salinity of the ocean and the extra cellular fluid or many multi cellular organisms. As the major ingredient in the edible salt, it is commonly used as condiment and food preservative. Sodium Chloride is currently mass-produced by evaporation of sea water or brine from other sources, such as brine wells and salt lakes and by mining rock salt called halite. Some of the characteristics of Sodium chloride with molecular weight of 58.44g/mol, appears as white crystalline solid, has a density of 2.16 gm/cc. It has a boiling point of 1738K and a melting point of 1074K. It has a solubility of 36% at room temperature. Its refractive index is 1.544 for 589 nm wavelength light source. Its crystal symmetry being Fm3m, which is a cubic system. The larger chloride ions are arranged in a cubic close-packing, while the smaller sodium ions fill all cubic gaps between them.

Each ion is surrounded by six ions of the other kind. This same basic structure is found in many other mineral and is known as the halide structure. This arrangement is known cubic close packed. It can be represented as two interpenetrating face centered cubic (FCC) lattice or one FCA lattice with a two basis. It is most commonly known as the rock salt crystal structure. It is held together with an ionic bond and electrostatic forces. Calcium Chloride is a white odorless salt that reacts with water forming hydrate. Crystals are granules or fused masses (Buduvvari 1896) found in both anhydrous and hydrates forms. Anhydrous forms readily hydrates both the anhydrous salt and hydrate release heat as they pick up water. The heat released is useful in melting ice and snow, and the material is used commercially as a de-icer. Calcium chloride is extremely soluble in water and very concentrated solution are possible. Calcium is also used as dust suppressant on dirt and gravel roads. Some of the characteristics of Calcium chloride are that it has a molecular weight of 110.99g/mol and it crystallises as

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white crystalline solid. It has a density of 2.15 g/cc with a melting point of 1045K and boiling point of 2008K. Its solubility in water is 75%. Its refractive index being 1.544(588nm). Its space group is Fm3m.

Recently there is a continued interest in the use of sodium chloride and calcium chloride in various fields of study especially to modify the properties of polymers both natural and man-made^[1-7]. Here we examine the effect of calcium ions in sodium chloride crystal system in terms of microcrystalline parameters. We have compared our results by measuring one of the physical properties like elastic constants of these mixed crystals.

EXPERIMENTAL

Sodium chloride and calcium chloride used for the preparation is taken from S D fine chem Limited Mumbai, of minimum assay 99.9 and 90.0 respectively. A saturated solution of sodium chloride and anhydrous calcium

chloride are prepared using distilled water in a beaker and was covered with a tissue paper. The solution was allowed overnight to grow crystals at room temperature. Powdered crystals are used for X-ray diffractometer recordings. Crystal are used to measure longitudinal and shear sound velocities. The different saturated solutions of CaCl₂ in NaCl are prepared by varying the weight percentage (10 to 50%) of CaCl₂. For X-Ray Diffractometer Recordings, we have used Rigaku-Denki (Mini-flex-II) powder diffractometer with copper as target material (1.5402 Å). The scanning was carried out from 10 to 60 degrees for all the samples.

Figure 1 shows the X-ray recordings of pure as well as mixtures of CaCl₂ in NaCl. Elastic constants of single crystals of pure and mixed system of calcium chloride in sodium chloride were determined by finding the velocities of longitudinal and shear waves using "Digital Ultrasonic Pulse Echo velocity meter" supplied by a Bangalore based company.

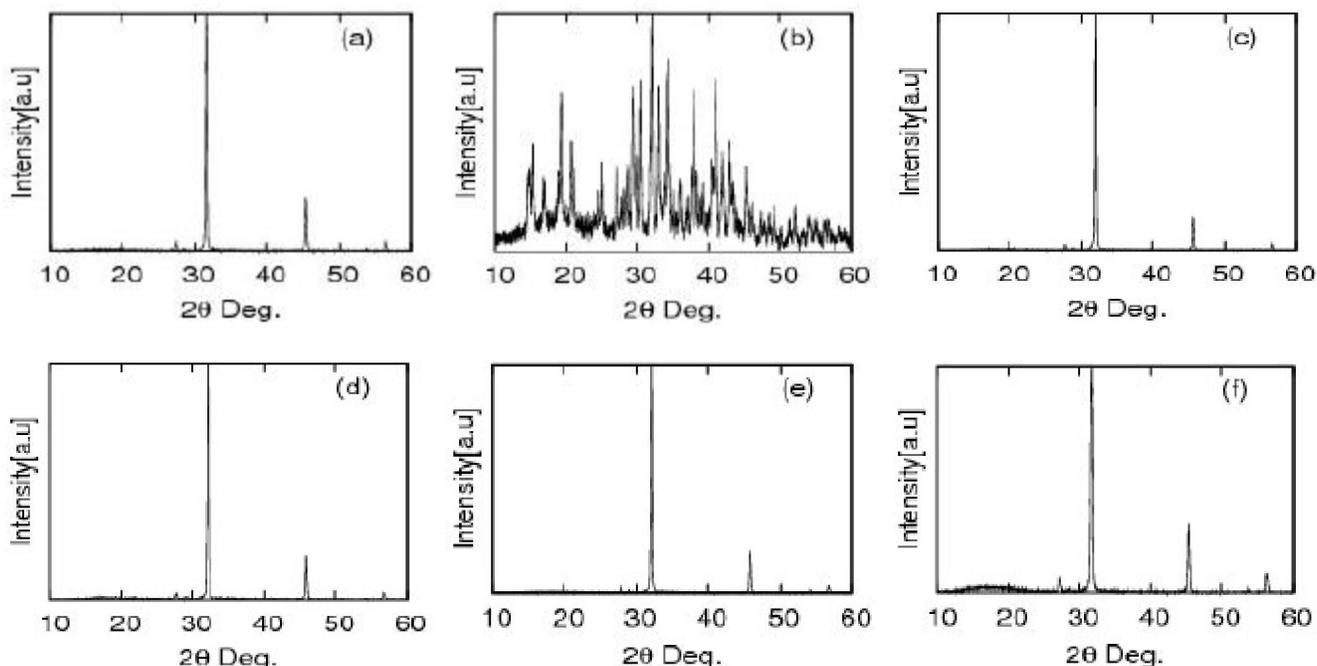


Figure 1 : X-ray diffractometer recordings: (a) NaCl; (b) CaCl₂; (c) 10% CaCl₂; (d) 20% CaCl₂; (e) 30% CaCl₂; (f) 40% CaCl₂

ANALYSIS OF THE DATA

Cell parameters of calcium chloride, sodium chloride and their mixed systems were determined using

TREOR^[8] and CHECKCELL^[9] programs. The goodness of the fit for all the observed Bragg reflections were less than 5% of the mean value. Full width at half maxima (FWHM), peak position and background was determined for all the samples using

PEAKFIT program^[10]. These values are given in TABLE 1.

The crystallite size and lattice strain parameters were computed using the Williamson-Hall plot method^[11-13] and the equation used for this purpose is

$$\beta \cos \theta / \lambda = 1/D + 4 \epsilon \sin \theta / \lambda \quad (1)$$

TABLE 1 : Cell and microcrystalline parameters of NaCl, CaCl₂ and their mixed systems.

Sample	"a" in Å	"b" in Å	"c" in Å	$\langle \epsilon^2 \rangle^{0.5}$	D in Å ³	D* ₍₁₀₀₎ in Å	D* ₍₀₁₀₎ in Å
NaCl	5.66	5.66	5.66	17.970	732.20	189.58	206.23
CaCl ₂	13.71	11.05	6.49	6.087	247.49	138.86	134.73
10% CaCl ₂	6.45	6.45	10.93	4.830	349.48	183.78	92.83
20% CaCl ₂	9.74	9.74	3.63	6.690	471.27	273.10	173.38
30% CaCl ₂	9.75	9.74	3.63	1.005	317.87	268.20	108.55
40% CaCl ₂	9.79	9.79	7.43	8.240	338.75	203.38	83.16
50% CaCl ₂	6.43	6.43	8.37	3.619	318.80	149.42	267.12

*computed using scherrer method.

where beta is FWHM in radians, theta is the Bragg angle at the peak, D is the crystallite size, and epsilon is the lattice strain. In each crystalline samples, we have observed several Bragg reflections and we have determined the FWHM for all these reflections and for all the samples using PEAKFIT method to determine D and epsilon by fitting a least square line. The computed values of D and lattice strain are given in TABLE 1. For each reflections, we have also determined the crystallite size for various Bragg reflections in each samples using Scherrer equation^[14]. Using cell parameters and computed crystallite values from Scherrer equation, we could project them to 2-dimensional plane and the appropriate D₍₁₀₀₎ and D₍₀₁₀₎ values are also given in TABLE 1.

RESULTS AND DISCUSSION

A cursory glance at the X-ray powder patterns show that there are significant changes with addition of calcium chloride in sodium chloride. There is an increase in the cell volume with addition of calcium chloride. This is also associated with the change in crystal symmetry of the mixed system. Further the crystallite size and lattice strain parameters computed from W-H plot show significant changes. Initially crystallite size increases and decreases above 30% of calcium chloride in sodium chloride. Crystallite size estimated using Scherrer equa-

tion is a bit over estimated because of the fact the Scherrer equation does not consider lattice strain. However, the values obtained from Scherrer equation are projected on a two-dimensional plane as crystallite shape ellipsoid for a better perspective and is shown in Figure 2.

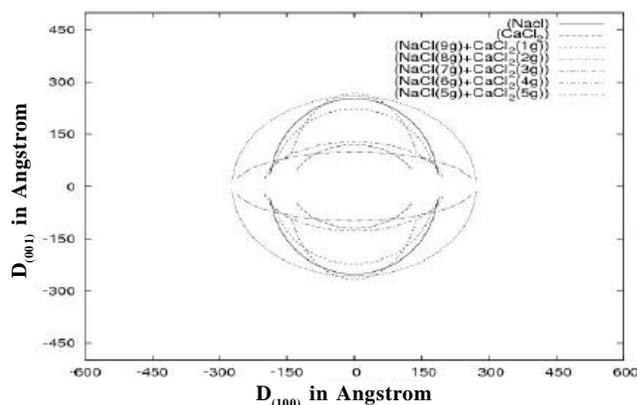


Figure 2 : Crystallite shape ellipsoid computed from scherrer method

The following results emerge from the above calculations:

- 1) In sodium chloride, the crystallite size is more compared to calcium chloride.
- 2) With addition of calcium chloride, we observe that there is a slight increase in the crystallite size and thereafter the size decreases. Essentially, the calcium ion reduces the inter-atomic interactions and hence their binding. This in turn reduces the strength of the crystals that are formed with those of appropriate concentrations of calcium chloride. A cursory glance on the measurement of elastic constants for various concentrations of calcium chloride in sodium chloride justifies the results obtained from X-ray measurements.
- 3) The extent of decrease in the inter atomic interactions can be gauged by the appropriate change in the elastic constant values of mixed crystals.
- 4) Lattice strain is relatively small in sodium chloride crystals compared to calcium chloride crystals. With addition of calcium chloride, the strain increases slightly and decreases after 30% of calcium chloride within the experimental errors. These results indicate that the disorder increases with

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increase in calcium ions, which also lead to an unstable crystalline order.

- 5) A plot of elastic constant with crystallite size and lattice strain indicate that strength of the crystal increases with increase in crystalline order. Here we have quantified in terms of both crystallite size and lattice strain.
- 6) Further, we also observe that with addition of calcium chloride, there is a slight change in the crystal symmetry.
- 7) It is evident from crystallite shape ellipsoid in Figure 2, that with addition of CaCl_2 , the crystalline volume decreases a bit and after 30% of CaCl_2 , it increases.

CONCLUSIONS

With addition of calcium ions, we observe that the crystal symmetry, crystalline order and strength in sodium chloride crystal change indicating that there is an absence of necessary interaction with neighbouring atoms. Such crystal system are more fragile and beyond certain concentration, it is difficult to grow single crystal of the mixed system.

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