



# Formation of Single Phased Mixed Crystals from Aqueous Solutions - an Overview

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## Abstract

Single phased mixed crystals are normally formed from two or more isomorphous end member crystals with some conditions. However, in some circumstances, it is possible that such mixed crystals can be formed/prepared/grown from aqueous solutions even when the end member crystals are not isomorphous with each other. An overview of various studies made in this direction is presented in this article focusing the results reported by the present author's research group.

**Keywords:** Aqueous solutions; Crystal growth from solution; Mixed crystals; Quasi mixed crystals; Solid solutions

## Introduction

Single crystals are solids with regular (three dimensionally periodic) arrangement of the constituent atoms, ions or molecules into some fixed and rigid pattern known as a lattice. So, formation/preparation/growth of single crystals means careful arrangement of atoms, ions or molecules in a particular three-dimensional order. There are four major categories of crystal growth methods, viz. solid-state growth, vapor growth, melt growth and solution growth. Solution and melt growth methods are treated separately because solution growth methods differ from methods used for pure melt growth. Crystal growth from solution, an ancient as well as a more advantageous method, is classified into two, viz. low temperature solution growth and high temperature solution growth. If suitable solvents are available, low temperature solution growth can very well be used for the crystal growth of materials which decompose on heating and/or which exhibit any structural transformation while cooling from the melting point. The required super saturation may be obtained by evaporation of solvent by cooling the solution or by a transport process in which the solute is made to flow from a hotter to a cooler region. Evaporation is permissible into the atmosphere for non-toxic solvents such as water. Photonic and dielectric crystals are mainly grown by adopting the melt and solution (mostly aqueous) methods.

It is a known fact that naturally occurring crystals are scarce or imperfect or having less tunable properties and nature's enormous laboratory is unable to meet the demands of developing

technology. Also, it is known that there are several factories available where various crystals ranging in size from small to large crystals are grown. However, further research in the preparation and characterization of crystalline materials and growth of large size crystals is very much necessary for our social requirements. The most important question now is: How to tune or stimulate the physical (optical, mechanical, electrical, magnetic, etc.) properties of crystals? For many applications, it is required to control and alter the functionalities and properties of crystalline materials with greater flexibility and possibility. The most important approach in this regard is to form hybrid material crystals that have properties different from that of single component material crystals. In order to meet the increasing demand of new materials with good optical and electrical properties, formation of new hybrid (doped and/or mixed) crystals has become an interesting and important investigation in crystal growth. A single phased mixed crystal is normally formed by crystallizing together two or more isomorphous crystals with comparable lattice volumes. If the end member crystals are not isomorphous with each other, it is expected to form multi phased mixed crystals. However, in certain circumstances, it is possible for us to form single phased mixed crystals even if the end member crystals are not isomorphous with each other. In this article (a brief overview), we consider mainly the conditions for the formation of single phased mixed crystals from aqueous solutions focusing the results reported by the present author's research group.

## Mixed Crystals

On forming a mixed crystal, the added (guest or solute) ion goes to substitutional position or interstitial position which is determined by the ionic radius of the added ion and electronic configuration of the lattice (host or solvent) ion. Three different kinds of mixed crystals (solid solutions) can be grown (or formed/prepared), viz. substitutional, interstitial and defect solid solutions [1]. In the case of substitutional solid solutions, some of the normal lattice sites in the solvent crystal are occupied by the solute atoms without changing the structure of the solvent crystal. In interstitial solid solutions, the solute atoms occupy the interstitial positions of the solvent crystal without changing its structure. Some sites in the lattice of one component remain vacant in the case of defect solid solutions. A mixed crystal (single/multi phased) may have its physical properties analogous to those of the end member (pure) crystals. The mixed crystal composition varies from system to system and the properties may change in a linear or nearly linear manner. For several properties, the composition dependence is highly nonlinear and, in some cases, the magnitude of the property for the mixed crystal even exceeds that for the end member crystals. So, once the trend in mixed crystal composition dependence is established, we have tailor-made new crystals for our use with desired values for the given properties.

## Single Phased Mixed Crystals

Tobolsky's rule states that, for ionic crystals like alkali halides, complete miscibility is possible only above a temperature  $T_K$  given by  $T = 4.5\delta^2$ ,  $\delta$  being the percentage difference in lattice constants [2,3]. Here,  $\delta$  takes a value of 6% for alkali halides at room temperature. It can be understood that there are available broad miscibility gaps in several binary and ternary systems of alkali halides at room temperature. So, for these systems, single phased mixed crystals are not possible to be prepared by the low temperature solution methods even when these alkali halides have considerable solubility in water. A study made by Mahadevan and his co-workers [4] with  $(\text{NaCl})_x(\text{KCl})_{0.9-x}(\text{KBr})_{0.1}$  solutions evidenced the above. Anandakumari and Chandramani [5] reported that they had grown single phased  $(\text{KBr})_x(\text{NaBr})_{1-x}$  single crystals at room temperature from aqueous solutions. As per Tobolsky's rule, the miscibility is possible for this system at above 488 K. Later, Padma and Mahadevan [6] inferred that the single crystals grown by Anandakumari and Chandramani ought to be multi phased and they would have reported only the total average values of the lattice constants. Moreover, Mahadevan and his co-workers [6-12] have evidenced Tobolsky's rule with alkali halide mixed crystals (both single and poly crystals) grown from melts. In addition, Barrett and Wallace [13] have reported that  $\text{Na}_x\text{K}_{1-x}\text{Cl}$  system does not form a continuous series of single phased mixed crystals. Also, Nair and Walker [14] have reported that for the extreme concentration ranges  $x < 0.3$  and  $x > 0.7$  the  $\text{KBr}_{1-x}\text{I}_x$  crystals could be characterized by single f.c.c. lattice constants, while in the intermediate region three f.c.c. phases characterized by three lattice constants.

It is also interesting to note that Padma and Mahadevan [15] could obtain multi phased mixed poly crystals  $(\text{NaCl-KBr, NaCl-}$

$\text{KBr-KCl}$  and  $\text{NaCl-KBr-NaBr}$ ) grown from miscible  $\text{NaBr}$  and  $\text{KCl}$ . Priya and Mahadevan [16] could obtain multi phased ternary and quaternary mixed poly crystals  $(\text{NaCl-KCl-KBr, NaCl-NaBr-KBr}$  and  $\text{NaCl-NaBr-KCl-KBr})$  grown from miscible  $\text{NaBr}$ ,  $\text{KCl}$  and  $\text{KBr}$ . It should also be understood that  $\text{Na}^+$  has more affinity towards  $\text{Cl}^-$  than  $\text{Br}^-$ . In general, the formation of single phased mixed crystal requires that [17,18]:

- The structures of the two crystals should be of similar type.
- The bonds in the two crystals should be of similar type.
- The radii of the substituent atoms should not differ by more than about 15 % from that of the smaller one.
- The difference between their lattice parameters should be less than 6 %. It is a known fact that potassium di-hydrogen orthophosphate ( $\text{KDP, KH}_2\text{PO}_4$ ) and ammonium di-hydrogen orthophosphate ( $\text{ADP, NH}_4\text{H}_2\text{PO}_4$ ) are hydrogen bonded and nonlinear optically important crystals.

Both KDP and ADP belong to the tetragonal crystal system and are isomorphous with each other. They have the tetra-molecular unit cell dimensions as:  $a=b=7.448$  and  $c=6.977$  Å for KDP [19]; and  $a=b=7.510$  and  $c=7.564$  Å for ADP [19]. It is possible that single phased mixed crystals of KDP with ADP can be prepared as per the above conditions. Moreover, KDP-ADP mixed crystals are interesting particularly due to modification of the hydrogen bonding system in a certain intermediate mixing composition range which leads to significant change in the properties of the crystals [20]. Although there are some reports available on the growth and characterization of  $\text{K}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$  single crystals [20-25], there exists some challenge in obtaining large size mixed crystals in the intermediate mixing composition range.

Magnesium sulfate heptahydrate ( $\text{MSH, MgSO}_4 \cdot 7\text{H}_2\text{O}$ , Epsomite), nickel sulfate heptahydrate ( $\text{NSH, NiSO}_4 \cdot 7\text{H}_2\text{O}$ , Morenosite) and zinc sulfate heptahydrate ( $\text{ZSH, ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , Goslarite) crystals are isomorphous with each other and crystallize in the orthorhombic crystal system. They have the tetra-molecular unit cell dimensions as:  $a = 11.86$ ,  $b = 11.99$  and  $c = 6.858$  Å for MSH [19];  $a = 11.86$ ,  $b = 12.08$  and  $c = 6.81$  Å for NSH [19]; and  $a = 11.779$ ,  $b = 12.050$  and  $c = 6.822$  Å for ZSH [26,27]. As these three materials are not only isomorphous with each other but also with comparable lattice constants (or lattice volumes), single phased mixed (both binary and ternary) crystals can easily be grown by the solution method. Mahadevan and his co-workers have already reported the growth and characterization of single phased  $\text{Mg}_x\text{Zn}_{1-x}\text{SO}_4 \cdot 7\text{H}_2\text{O}$  [28,29],  $\text{Ni}_x\text{Mg}_{1-x}\text{SO}_4 \cdot 7\text{H}_2\text{O}$  [30] and  $\text{Ni}_x\text{Zn}_{1-x}\text{SO}_4 \cdot 7\text{H}_2\text{O}$  [27] crystals. All the above metal sulfate heptahydrate mixed crystals have been grown by the slow (free) evaporation of solvent method from aqueous solutions. The lattice volumes obtained through X-ray diffraction analysis have been found to be nearly additive with the mixed crystal composition and obey the relation:

$$V = xV_1 + (1-x)V_2,$$

Which is similar to Retger's rule applied to cubic system [26,30]. Here,  $V$  is the lattice volume of the mixed crystal and  $V_1$  and

$V_2$  are the lattice volumes of the end member crystals. L-histidine hydrochloride (LHCl) and L-histidine hydrobromide (LHBr) single crystals are found to be isomorphous with each other and are expected to form single phased mixed crystals [31]. Suja Rani et al. [32, 33] have formed LHCl-LHBr mixed crystals by the slow evaporation of solvent method by mixing equimolar proportion of L-histidine and acid ( $\text{HCl}x\text{Br}1-x$  with  $x = 0.0, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$  and  $1.0$ ). X-ray diffraction analysis confirmed the formation of single phased mixed crystals belonging to the orthorhombic crystal system with non-centrosymmetric space group of  $P212121$ . Here, in the formation of end member and mixed crystals, a reaction takes place and the product is crystallized. The acid molecules used (HCl and HBr) are isomorphous with each other. That is, molecular isomorphism is present in the reaction. Now, a question arises. When the end member crystals are not strictly isomorphous with each other, can we use the molecular isomorphism of the reactants to form single phased mixed crystals? It has been found that it is possible in the cases of both anionic and cationic substitutions. Moreover, quasi mixed crystals can also be formed in a similar way.

### Mixed Crystals with Non-isomorphous End Members

Bis(thiourea)cadmium chloride (BTCC) is a semi-organic NLO crystal with lattice parameters:  $a = 5.812$ ,  $b = 6.485$  and  $c = 13.106$  Å;  $V = 493$  Å<sup>3</sup> [17,34]. Bis(thiourea)cadmium iodide (BTCl) is a similar metal complex crystal (with chloride replaced by iodide) with lattice parameters:  $a = 10.520$ ,  $b = 7.600$  and  $c = 15.086$  Å,  $\beta = 91.14^\circ$ ;  $V = 1206$  Å<sup>3</sup> [17,35]. The BTCC and BTCl crystals belong to orthorhombic and monoclinic crystal systems respectively and radii of Cl-1 and I-1 for 6 coordination respectively are 1.81 and 2.20 Å [36] (the difference is > 15 %). Prameela Kumari and Mahadevan [17] have formed the  $(\text{BTCC})_x(\text{BTCl})_{1-x}$  crystals from the isomorphous precursors directly even though the end member crystals have lattice mismatching. The crystals were grown by the free evaporation of solvent method at room temperature and the mixed crystals with middle compositions ( $x = 0.6, 0.5$  and  $0.4$ ) were found to be small in size. The molecular isomorphism of cadmium chloride and cadmium iodide was used (anionic substitution). It has been found that, through X-ray diffraction analysis,  $(\text{BTCC})_x(\text{BTCl})_{1-x}$  crystals with  $x = 1.0, 0.8$  and  $0.6$  are orthorhombic in structure with space group  $Pma21$  and that with  $x = 0.5, 0.4, 0.2$  and  $0.0$  are monoclinic in structure with space group  $P21/c$ . Magnesium tris(thiourea)sulphate (MTS) belongs to the monoclinic crystal system with lattice parameters:  $a = 7.67$ ,  $b = 5.48$  and  $c = 8.56$  Å,  $\beta = 131.1^\circ$  [37]. Zinc tris(thiourea)sulphate (ZTS) belongs to the orthorhombic crystal system with lattice parameters:  $a = 11.130$ ,  $b = 7.773$  and  $c = 15.490$  Å [38]. Darlin Mary et al. [39,40], by using the molecular isomorphism (cationic substitution), have formed the ZTS-MTS mixed crystals by the free evaporation of solvent method at room temperature. The lattice parameters obtained through X-ray diffraction analysis show that the grown pure ZTS and mixed ZTS-MTS crystals belong to the orthorhombic crystal system.

The calcium succinate (CS,  $\text{CaC}_4\text{H}_4\text{O}_4$ ) and barium succinate (BS,  $\text{BaC}_4\text{H}_4\text{O}_4$ ) single crystals have been grown and found to have different number of water molecules and different crystal lattices.

The BS crystal grown [41] with one water molecule possesses monoclinic crystal structure with lattice parameters:  $a = 5.20$ ,  $b = 9.02$  and  $c = 5.60$  Å,  $\beta = 91.16^\circ$ . The CS crystal grown [42] with 2.3 water molecules possesses triclinic crystal structure with lattice parameters:  $a = 6.636$ ,  $b = 7.866$  and  $c = 9.420$  Å;  $\alpha = 71.8^\circ$ ,  $\beta = 89.1^\circ$  and  $\gamma = 68.4^\circ$ . Christy et al. [43] have grown, by the free evaporation of solvent method, at room temperature the  $\text{Ba}_x\text{Ca}_{1-x}\text{C}_4\text{H}_4\text{O}_4$  ( $x = 0.2, 0.4, 0.5, 0.6$  and  $0.8$ ) crystals (cationic substitution) using isomorphous precursors (calcium carbonate and barium carbonate). X-ray diffraction analysis indicated that the crystals with  $x = 0.2, 0.4$  and  $0.5$  contain fractional water molecules whereas crystals with  $x = 0.6$  and  $0.8$  contain no water molecule. Jesudurai et al. [44] have reported the growth and characterization of mixed crystals (cationic substitution) based on ammonium pentaborate dihydrate ( $\text{AB}_5$ ) and potassium pentaborate dihydrate ( $\text{KB}_5$ ),  $(\text{NH}_4)_{1-x}\text{K}_x\text{B}_5\text{O}_8$  crystals. The 2 pure and 6 mixed crystals (single phased) grown by them belong to the orthorhombic crystal system and are found to be isomorphous with each other. The mixed crystals grown are found to have more ammonium content than they considered in the solution. Sodium pentaborate dihydrate ( $\text{NB}_5$ ) crystal belongs to the monoclinic crystal system with space group  $P21/c$  and lattice parameters:  $a = 11.114$ ,  $b = 16.437$  and  $c = 13.580$  Å,  $\beta = 111.94^\circ$  [45].  $\text{KB}_5$  crystal belongs to the orthorhombic crystal system with space group  $\text{Aba}2$  and lattice parameters:  $a = 11.043$ ,  $b = 11.177$  and  $c = 9.042$  Å [46]. The lattice mismatching between  $\text{KB}_5$  and  $\text{NB}_5$  could be due to the difference in their ionic radii (for 8 coordination as oxygen atoms are coordinated to K/Na: 1.18 Å for Na+1 and 1.51 Å for K+1 [36]).

Single crystals of  $(\text{NB}_5)_x(\text{KB}_5)_{1-x}$  (with  $x = 1.0, 0.8, 0.6, 0.5, 0.4, 0.2$  and  $0.0$ ) have been grown by the slow evaporation of solvent method using the molecular isomorphism of the precursors. X-ray diffraction analysis indicated the formation of single phased mixed crystals belonging to the orthorhombic crystal system [18,47]. Energy dispersive X-ray absorption and atomic absorption spectroscopic analyses confirmed the presence of Na and K atoms in mixed crystals in proportion with precursors (sodium carbonate and potassium carbonate) taken in solution used for the crystal growth.

### Quasi Mixed Crystals

Sodium and potassium hydrogen phthalates (NaHP and KHP) belong to orthorhombic crystal system with non-centrosymmetric space groups  $B2ab$  and  $Pca21$  respectively. Ramasamy and Meenakshisundaram [48] have grown the  $\text{K}0.78\text{Na}0.22[\text{C}_6\text{H}_4(\text{COO})_2]_2 \cdot \text{H}_2\text{O}$  crystal (NaKP) belonging to the trigonal crystal system with centrosymmetric space group  $P(-3)1c$  at room temperature by the slow evaporation of solvent method using KHP and NaOH as the precursors. This NaKP has been found to exhibit high second harmonic generation (SHG) activity (1.14 times that of KHP which could be explained as due to dislocation of NaKP crystal into KHP and NaHP (both NLO-active materials) leading to local non-centrosymmetry.

Amuthambigai et al. [49] have also grown at ambient conditions by the solvent evaporation method good quality bimetallic (Na

and K) phthalate single crystals but with a different composition ( $\text{Na}_0.51\text{K}_{1.49}[\text{C}_6\text{H}_4(\text{COO})_2] \cdot \text{H}_2\text{O}$ ). This crystal also belongs to the trigonal crystal system with space group  $P(-3)1c$  exhibiting good SHG activity (0.93 times that of KHP). Another bimetallic phthalate ( $\text{Li}$  incorporated KHP,  $\text{C}_{16}\text{H}_{16}\text{KLiO}_{11}$ ) crystal has also been successfully grown from aqueous solution and reported [50]. Zinc cadmium thiocyanate ( $\text{ZCTC}$ ,  $\text{ZnCd}(\text{SCN})_4$ ) is a semi-organic highly efficient NLO material. It belongs to the tetragonal crystal system with lattice parameters:  $a = b = 11.135$  and  $c = 4.376$  Å [51]. The  $-\text{S}=\text{C}=\text{N}-$  bridges between  $\text{Cd}$  and  $\text{Zn}$  atoms in it leads to the formation of an infinite three-dimensional  $-\text{Cd}-\text{S}=\text{C}=\text{N}-\text{Zn}-$  network permitting us to combine the advantages of inorganic crystal with those of organic crystals such as good stability and high nonlinearity [52].

In order to understand the effect of forming hybrid crystals by quasi mixing on the physicochemical properties of the basic material crystal, Latha et al. [53] have attempted to grow, by the free evaporation of solvent method at room temperature,  $\text{Zn}_x\text{Cd}(2-x)(\text{SCN})_4$  (with  $x = 0.0, 0.4, 0.8, 1.0, 1.2, 1.6$  and  $2.0$ ) single crystals. They could grow single crystals with  $x = 0.0$  (leading to  $\text{Cd}(\text{SCN})_2$ ) but not when  $x = 2.0$  (leading to  $\text{Zn}(\text{SCN})_2$ ). The crystal with  $x = 1.0$  is the normal  $\text{ZnCd}(\text{SCN})_4$  crystal. X-ray diffraction analysis indicated that the  $\text{ZnCd}(\text{SCN})_4$  crystallizes in the tetragonal crystal system;  $\text{Zn}_x\text{Cd}(2-x)(\text{SCN})_4$  with  $x = 0.0, 0.4$  and  $0.8$  crystallize in the orthorhombic crystal system; and  $\text{Zn}_x\text{Cd}(2-x)(\text{SCN})_4$  with  $x = 1.2$  and  $1.6$  crystallize in the hexagonal crystal system. This study indicated a decrease of dielectric constant and SHG efficiency when quasi mixing is done. However, this study has shown the possibility of obtaining a new class of bimetallic thiocyanate single crystals.  $\text{A}_3\text{MX}_5 \cdot n\text{H}_2\text{O}$  (where  $\text{A}$  is a univalent cation,  $\text{M}$  is a divalent metal and  $x$  is a halogen) crystals are found to exhibit unusual physical properties.

These crystals are normally prepared by mixing  $\text{AX}$  and  $\text{MX}_2 \cdot n\text{H}_2\text{O}$  in 3:1 molecular ratio. However, varying stoichiometries have been found to occur in these mixed compound crystals and, due to that, they exhibit unusual physical properties. Mahadevan and his co-workers [54-56] have prepared, from aqueous solutions by the slow evaporation of solvent method,  $\text{K}_3 \cdot 088\text{Ba}0.912\text{Cl}_4.912.1.369\text{H}_2$  (KBC, from  $3\text{KCl} + \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  solution),  $\text{K}_3 \cdot 611\text{Ca}0.389\text{Cl}_4.389.1.177\text{H}_2\text{O}$  (KCC, from  $3\text{KCl} + \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  solution) and  $\text{Na}_3 \cdot 665\text{Ca}0.335\text{Cl}_4.335.0.153\text{H}_2\text{O}$  (NCC, from  $3\text{NaCl} + \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  solution) single crystals and characterized. The temperature dependence of DC electrical conductivity observed by them indicated that KBC is a dielectric material while the others (KCC and NCC) are ionic conductors. Less non-stoichiometry retains the dielectric nature (usual for ionic substances) and higher non-stoichiometry leads to ionic conduction. X-ray diffraction analysis indicated that all the above three crystals belong to the triclinic crystal system with lattice parameters:  $a = 6.286$ ,  $b = 6.294$  and  $c = 6.309$  Å,  $\alpha = 90.04$ ,  $\beta = 90.03$  and  $\gamma = 90.30^\circ$ ,  $V = 249.61$  Å<sup>3</sup> for KBC;  $a = 6.267$ ,  $b = 6.282$  and  $c = 6.319$  Å,  $\alpha = 89.90$ ,  $\beta = 90.73$  and  $\gamma = 90.58^\circ$ ,  $V = 248.71$  Å<sup>3</sup> for KCC; and  $a = 5.633$ ,  $b = 5.641$  and  $c = 5.624$  Å,  $\alpha = 90.16$ ,  $\beta = 89.93$  and  $\gamma = 90.56^\circ$ ,  $V = 178.71$  Å<sup>3</sup> for NCC.

## Conclusion

The validity of Tobolsky's rule put forward for ionic crystals like alkali halides and the general conditions put forward in the preparation of single phased mixed crystals has been proved by several reports available in the literature. Also, it has been understood that single phased normal as well as quasi mixed crystals can be prepared from aqueous solutions even when the end member (or mixing) crystals do not obey the general conditions. However, this is found to be possible when the mixed crystals are grown (the product crystallizing in a reaction) by using the molecular isomerism of the precursors involved in the reaction.

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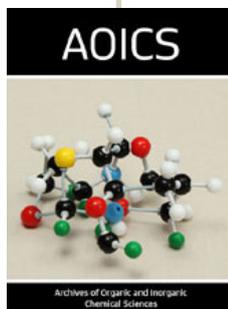
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