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Debye temperature calculation from various experimental methods for $Na_x K_{1-x} Cl$ grown from aqueous solution

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Abstract: *Mixed crystals of alkali halides find their applications in optical, opto-electronics and electronic devices. In the present study the pure and ZnS added mixed crystals $Na_x K_{1-x} Cl$ were grown from the aqueous solution. The grown crystals were characterized by taking XRD, TG / DTA and Vicker's micro hardness measurement. The Debye temperature is an important parameter of a solid. Several methods of evaluating Debye temperature are available. In the present study Debye temperatures were calculated from the Debye-waller factor, melting point and microhardness. The results were compared with the Kopp Neumann relation.*
Key words *: Mixed crystals, Alkali halides, Debye temperature, Debye frequency*

I. Introduction

The Debye temperature is an important parameter of a solid. Several methods of evaluating the Debye temperature are available. Alers (1965) reviewed number of these. In the present paper deals with four different methods of calculating Debye temperature. The methods considered here are (a) from melting point (b) from Debye-waller factor (c) from microhardness (d) from Kopp-Neumann relation. The comparison of the results by the first three methods with those the last one enables one to judge the accuracy of the various methods.

Mixed crystals of alkali halides find their applications in optical, Opto electronics and electronic devices. So, the grow of alkali halide mixed crystals are interesting and important today. In this present study totally fourteen crystals (5 pure mixed, 5 doped mixed, 2 pure end members and 2 doped end members).

II. Materials and Methods

2.1. Growth of Sample Crystals

Analytical Reagent (AR) grade NaCl and KCl substance along with doubly distilled water were used for the growth of single crystals. An aqueous solution of the salt with desired molecular ratio was prepared at supersaturated concentration and seed crystals were used to grow the sample crystals. The temperature and volume were kept constant respectively at 32°C and 25ml for all the crystals. IN solution of 2.5ml ZnS was added to the 25ml supersaturated solution. In the present study total of fourteen crystals (five pure mixed crystals, five doped mixed crystals, two pure end members and two doped end members) for various values X viz. 0.2, 0.4, 0.5, 0.6 and 0.8 were grown in identical conditions.

2.2. Estimation of Composition

The composition of pure and ZnS added crystals were accurately calculated from the EDAX spectrum taken by scanning electron microscope (Model FEI Quanta FEG 200). The concentration of Zn and S atom also calculated for the doped system.

2.3. Debye temperature Calculation

Debye temperature of the crystals can be determined from various experimental measurements like melting point, Debye waller factor, hardness number, Kopp-Newmann relation etc.

2.3.1. From melting point

Debye temperature can be estimated from the melting point (Tm) of the crystal using the formula [1]

$$\theta_m = C \left[\frac{T_M}{MV^{\frac{2}{3}}}\right]^{\frac{1}{2}}$$

where C is a constant depending on the X-ray intensity data structure. The formula unit volume was estimated from the lattice constant. A value of 450 has been used for C as the structure is of NaCl type. This value is the average of the values evaluated from the known values of Debye temperature for the end member crystals. The melting point of all the grown crystals were determined from TG / DTA curve recorded on seiko TG/DTA 6200 system at heating ramp of 10°C C/min. Nitrogen was used as purge gas at a flow rate of 500ml/min. The powder sample was encapsulated in platinum pass and the sample pan material was also platinum.

2.3.2. From Debye waller factor

The mean Debye waller factor was determined from the XRD data taken by using PAN analytical, diffractometer with scintillation counter and monochromated CuK_α ($\lambda = 1.5406$ A°) radiation. The reflections were indexed following the procedures of Lipson and Steeple [2].

Analysis of the X-ray diffraction peaks by the available methods [3] shows that for the mixed crystals, all the X-ray diffraction peaks can be indexed with two F.C.C. phases instead of one which shows the existence of two F.C.C. phases one phase nearly corresponds to pure NaCl and the other phase nearly corresponds to pure KCl.

The mean Debye-waller factor for all the fourteen grown crystals were determined by a method similar to that followed by Mahadevan and his co-workers [1, 4 -10]. As the number of reflections are limited, only a common Debye-waller factor was determined for all the atoms in every system by using Wilson theory [11].

The structure factors are calculated using the relations

$$F(h\,k\,l) = 4(f_{Na}^{+} \pm f_{Cl}^{-}) \text{ for NaCl}$$

$$F(h\,k\,l) = 4(f_{k}^{+} \pm f_{Cl}^{-}) \text{ for KCl}$$

$$F(h\,k\,l) = 4\,[x(f_{Na}^{+} \pm f_{Cl}^{-}) + (1-x)(f_{k}^{+} \pm f_{Cl}^{-})] \text{ for mixed system.}$$

Here f_{Na}^{+}, f_{k}^{+} and f_{Cl}^{-} are the respective scattering factors for Na^{+}, K^{+} and Cl ions taken from the literature [12]. x and $(1-x)$ are the composition of NaCl and KCl present in the mixed system. The plus sign for the reflections with even value of h+k+l and minus sign for those with odd values of h+k+l.

The Bragg intensity equation may be written as

$$\left({}^{Ie}/_{Ic}\right) = K \exp\left(\frac{-2B\sin^2\theta}{\lambda^2}\right)$$

The mean Debye-waller factor (Bobs) was obtained by taking a least squares approximation of $\ln\left({}^{Ie}/_{Ic}\right)$ against $\frac{\sin^2\theta}{\lambda^2}$. Ie is experimentally observed (intergrated) intensity. Ic is the calculated intensity, K is the scale factor, θ is the Bragg angle and λ is the wavelength of radiation used.

The presence of mixing of ions creates a static contribution in the case of mixed crystals. Replacement of ions possible only between Na^{+} and K^{+} ions. B_{static} for the mixed crystals was calculated using the relation.

$B_{static} = x(1-x)(r_A - r_B)^2$.

where x and $(1-x)$ are respective mole fractions of NaCl and KCl in the mixed crystals and r_A and r_B are the respective ionic radii of Na^{+} and K^{+}.

Observed Debye-waller factors for the mixed crystals is given by

$B_{observed} = B_{static} + B_{thermal}$

$B_{thermal}$ was calculated from the above relation and the Debye temperature, mean square amplitude of vibration and Debye frequency were determined from the methods followed by Neelakanda pillai and Mahadevan [1].

The Debye temperature (θ_D) was obtained from the Debye-waller theory expressions.

For pure crystals $B_{obs} = \frac{6h^2}{mKT} W(x)$ and for mixed crystals $B_{thermal} = \frac{6h^2}{mKT} W(x)$.

Where m is the mean atomic mass, T is the absolute temperature (298°K) at which X-ray diffraction intensities were measured, h is the plank's constant and K is the Boltzmann's constant. The function w(x) is given by

$$w(x) = \frac{\phi(x)}{x^2} + \frac{1}{4}x$$

Where $x = \frac{\theta_D}{T}$ and $\phi(x)$ is an integral.

$$\phi(x) = \int_0^x \left(\frac{e^y}{1-e^y}\right) dy.$$

The value of $w(x)$ for a wide range of x are tabulated by Benson and Gill [13], θ_D, the Debye temperature was evaluated by using the above expression.

The mean square amplitude of vibration $(< u^2 >)$ was obtained from [1]

$B = 8\pi^2 < u^2 >$. The Debye frequency was obtained from the Debye temperature using the relation [1] $F_D = \frac{\theta_D}{h}$

2.3.3. From microhardness value

Debye temperature can also be estimated from the microhardness value calculated from Vicker's microhardness measurement reported else where [14] using the relation.

$$\theta_H = B\,H^{1/2}\,V^{1/6}\,M^{-1/2}$$

Where B is a constant and its value is 348. Calculated from the known data for the end member

crystals.

2.3.4. From Kopp-Neumann relation

Sirdeshmukh and Srinivas [15] reviewed the data on fourteen alkali halide mixed crystals and concluded that, by and large, the composition dependence of $\theta_D(\text{ie.}\,\theta)$ of alkali halide mixed crystals is well described by the Kopp - Neumann relation given by

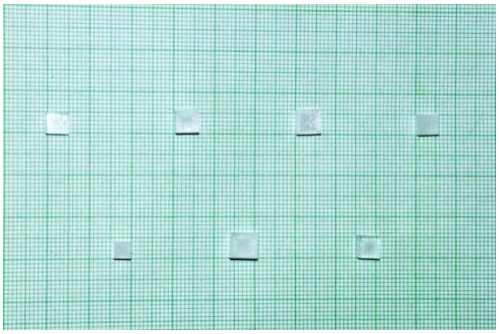
$$\theta^{-3} = x\,\theta_A^{-3} + (1-x)\theta_B^{-3}$$

Where θ_A and θ_B are the temperatures of the end member crystals.

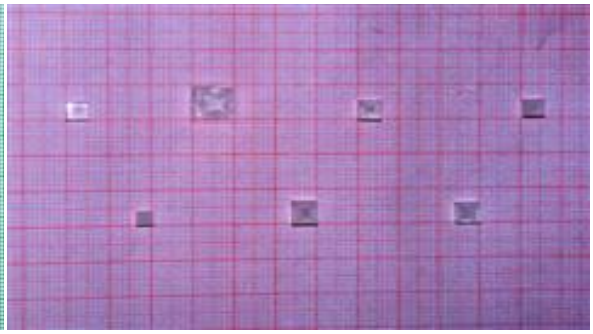
III. Results and discussion

3.1. Growth of sample crystals

Pure and undoped mixed crystals of $Na_xK_{1-x}Cl$ are provided in photograph. 1 and ZnS doped pure and mixed crystals of $Na_xK_{1-x}Cl$ are provided in photograph 2. It is found that all the fourteen crystals grown were stable and transparent. The mixed crystals are found to be harder than the end member crystals and the ZnS added crystals were more harder than the mixed crystals.



Photograph : 1.Undoped $Na_xK_{(1-x)}Cl$ Crystals



Photograph:2. ZnS doped $Na_xK_{(1-x)}Cl$ Crystals

3.2. Estimation of Bulk composition

The composition of all the crystals except the undoped end member crystals were estimated from the EDAX data. The estimated composition along with the weight percentage of Na^+, K^+, Cl^- and Zn^{2+} (for doped crystals only) are provided in Table 1. It is found that the estimated compositions of all the mixed crystals were well agree with the composition taken. EDAX spectrum of undoped $Na_{0.5}K_{0.5}Cl$ is provided in Fig.1. for illustration.

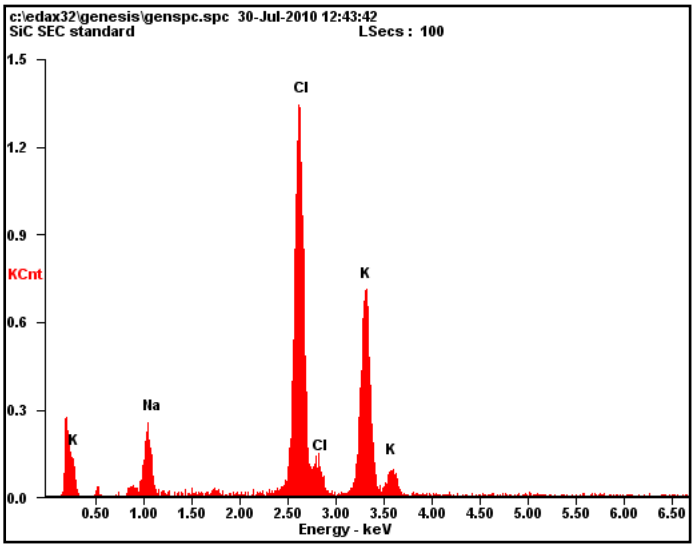


Fig.1. EDAX Spectrum of undoped $Na_{0.5}\ K_{0.5}Cl$

Table .1.Weight percentage and estimated composition values together with the composition taken for pure and ZnS doped crystals.

System	Weight Percentage of				Estimated composition
	Na	K	Cl	Zn	
Undoped mixed crystals					
NaCl	14.95	00.02	19.15	-	NaCl
KCl	35.38	00.54	64.08	-	KCl
$NaCl_{0.2}\ KCl_{0.8}$	01.46	44.25	54.29	-	$NaCl_{0.135}\ KCl_{0.865}$
$NaCl_{0.4}\ KCl_{0.6}$	02.15	45.64	52.21	-	$NaCl_{0.248}\ KCl_{0.752}$
$NaCl_{0.5}\ KCl_{0.5}$	04.75	42.81	52.44	-	$NaCl_{0.339}\ KCl_{0.661}$
$NaCl_{0.6}\ KCl_{0.4}$	20.08	22.29	57.63	-	$NaCl_{0.602}\ KCl_{0.398}$
$NaCl_{0.8}\ KCl_{0.2}$	39.98	00.28	59.74	-	$NaCl_{0.91}\ KCl_{0.099}$
ZnS doped mixed crystals					
NaCl	37.77	-	54.95	07.28	NaCl
KCl	-	15.11	82.48	00.42	KCl
$NaCl_{0.2}\ KCl_{0.8}$	01.89	13.74	81.88	00.46	$NaCl_{0.191}\ KCl_{0.809}$
$NaCl_{0.4}\ KCl_{0.6}$	04.15	14.28	79.34	00.45	$NaCl_{0.386}\ KCl_{0.614}$
$NaCl_{0.5}\ KCl_{0.5}$	01.16	13.97	82.57	0037	$NaCl_{0.443}\ KCl_{0.55}$
$NaCl_{0.6}\ KCl_{0.4}$	24.62	27.63	46.70	00.22	$NaCl_{0.601}\ KCl_{0.392}$
$NaCl_{0.8}\ KCl_{0.2}$	02.38	14.76	81.14	00.30	$NaCl_{0.697}\ KCl_{0.303}$

3.3. Lattice Parameter

Analysis of the X-ray diffraction peaks of the undoped and doped mixed crystals in the present study by the available methods. It has been found that all the X-ray diffraction peaks can be indexed with two F.C.C. lattices in stead of one, which shows the existence of two F.C.C. phases. The calculated lattice parameters show that one phase nearly corresponds to pure NaCl and the other phase corresponds to pure KCl. The lattice parameters of all the fourteen crystals are provided in Table.2 and the XRD pattern of the sample undoped $Na_{0.5}\ K_{0.5}Cl$ is provided in Fig.2 for illustration.

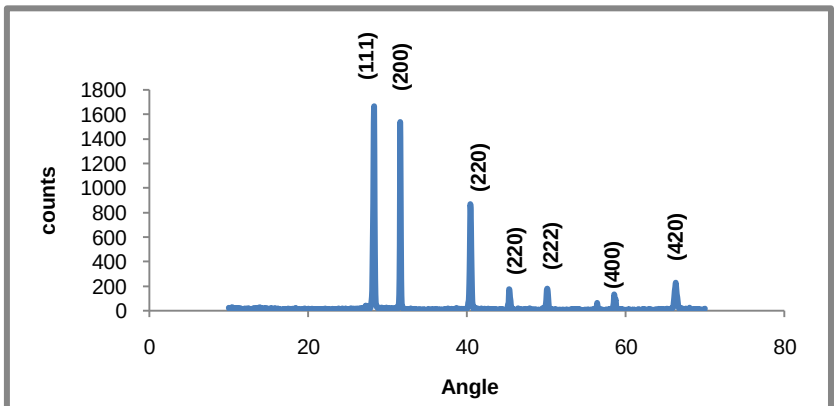


Fig .2. XRD Pattern for the undoped $Na_{0.5}K_{0.5}Cl$

Table .2. Lattice parameters together with the composition taken for pure and doped crystals

System	Lattice Parameter (a)		
	For NaCl Phase	For KCl phase	Average
Undoped mixed crystals			
NaCl	5.633	-	5.633
KCl	-	6.269	6.269
$NaCl_{0.2}\ KCl_{0.8}$	5.656	6.306	5.981
$NaCl_{0.4}\ KCl_{0.6}$	5.643	6.264	5.954
$NaCl_{0.5}\ KCl_{0.5}$	5.652	6.294	5.973
$NaCl_{0.6}\ KCl_{0.4}$	5.641	6.289	5.965

$NaCl_{0.8}$ $KCl_{0.2}$	5.633	6.629	6.131
ZnS doped mixed crystals			
NaCl	5.630	-	5.630
KCl	-	6.311	6.311
$NaCl_{0.2}$ $KCl_{0.8}$	5.641	6.294	5.968
$NaCl_{0.4}$ $KCl_{0.6}$	5.618	6.279	5.949
$NaCl_{0.5}$ $KCl_{0.5}$	5.625	6.289	5.958
$NaCl_{0.6}$ $KCl_{0.4}$	5.618	6.269	5.944
$NaCl_{0.8}$ $KCl_{0.2}$	5.625	6.248	5.703

3.4. Debye temperature

3.4.1. From melting paint

Molecular weight, lattice parameter, melting point and the calculated Debye temperature are provided in Table. 3 for all the systems. It is found that the Debye temperature calculated from the melting point vary non-linearly with composition. The melting point of the end member crystals determined well agree with the literature value which is provided in the bracket.

Table . 3. Molecular weight, lattice constant, melting point and Debye temperature together with the composition taken for pure and doped crystals.

System	Molecular weight	Lattice constant	Melting pt	Debye Temperature
Undoped mixed crystals				
NaCl	58.44	5.633	1081.3	253
KCl	74.56	6.269	1051.1	206
$NaCl_{0.2}$ $KCl_{0.8}$	72.38	5.981	1032.6	214
$NaCl_{0.4}$ $KCl_{0.6}$	70.56	5.954	1038.3	218
$NaCl_{0.5}$ $KCl_{0.5}$	69.10	5.973	977.7	213.5
$NaCl_{0.6}$ $KCl_{0.4}$	64.86	5.965	942.7	218.4
$NaCl_{0.8}$ $KCl_{0.2}$	60.56	6.131	1055.6	235
ZnS doped mixed crystals	58.44	5.630	1083.8	249.3
NaCl	74.56	6.311	1049.2	209.1
KCl	72.38	5.968	1047.1	216
$NaCl_{0.2}$ $KCl_{0.8}$	70.56	5.949	1032.	217.4
$NaCl_{0.4}$ $KCl_{0.6}$	69.10	5.958	1045.6	221.01
$NaCl_{0.5}$ $KCl_{0.5}$	64.86	5.944	938.4	216.28
$NaCl_{0.6}$ $KCl_{0.4}$	60.56	5.703	939.5	227.07
$NaCl_{0.8}$ $KCl_{0.2}$				

3.4.2. Debye Waller factor

The Debye-waller factors (B_{sta}, B_{ob} and B_{ther}) and the Debye temperature are given in Table.4 for all the systems. The reported value of Debye temperature for the end member crystals are provided in bracket. It is found that the observed value for the end member crystals well agreed with the reported value given in bracket. The bulk composition dependence of Debye-waller factor is highly non-linear. The observed Debye temperature is also independent of the composition of the mixed crystals.

Table . 4. Debye waller factors (B) and Debye temperature (θ_D) together with the composition taken for pure and doped crystals.

System	$B_{sta}(A°)^2$	B_{obs}	$B_{ther} = B_{obs} - B_{sta}$	(θ_D)	$f_D 10^{12}$Hz
Undoped mixed crystals	-	2.5565	2.5565	152	1.432
NaCl	-	-0.5455	0.5455	294	3/166
KCl	0.0168	4.979	4.962	138.6	6.123
$NaCl_{0.2}$ $KCl_{0.8}$	0.0269	-1.564	1.5909	249.45	3.887
$NaCl_{0.4}$ $KCl_{0.6}$	0.0323	3.0765	3.0442	181.5	5.195
$NaCl_{0.5}$ $KCl_{0.5}$	0.0348	2.6375	2.603	202.8	4.224
$NaCl_{0.6}$ $KCl_{0.4}$	0.0130	1.926	1.913	261	3.418
$NaCl_{0.8}$ $KCl_{0.2}$					
ZnS doped mixed crystals	-	5.7	5.7	144	2.116
NaCl	-	6.01	6.01	124	1.487
KCl	0.0212	3.7545	3.733	164.1	3.418
$NaCl_{0.2}$ $KCl_{0.8}$	0.0341	-4.886	-4.9201	143.3	2.985
$NaCl_{0.4}$ $KCl_{0.6}$	0.0355	1.479	1.4435	268.35	5.589
$NaCl_{0.5}$ $KCl_{0.5}$	0.0345	-1.843	-1.8775	239.4	4.986
$NaCl_{0.6}$ $KCl_{0.4}$	0.0304	-1.222	-1.2524	297.9	6.204
$NaCl_{0.8}$ $KCl_{0.2}$					

3.4.3. From microhardness

The measured hardness value and the Debye temperature calculated are provided in Table.5. It is found that here also the Debye temperature shows non-linear variation with composition.

Table .5. Hardness number Hv and Debye temperature θ_H together with the composition taken for pur and doped crystals.

System	Hardness number for 25gm	θ_H
Undoped mixed crystals		
NaCl	9.515	253
KCl	7.285	206
$NaCl_{0.2}$ $KCl_{0.8}$	6.650	195.7
$NaCl_{0.4}$ $KCl_{0.6}$	15.150	298.49
$NaCl_{0.5}$ $KCl_{0.5}$	7.705	215.45
$NaCl_{0.6}$ $KCl_{0.4}$	15.950	319.74
$NaCl_{0.8}$ $KCl_{0.2}$	15.800	333.89
ZnS doped mixed crystals		
NaCl	17.750	345.22
KCl	13.850	285.84
$NaCl_{0.2}$ $KCl_{0.8}$	15.550	298.93
$NaCl_{0.4}$ $KCl_{0.6}$	9.585	237.32
$NaCl_{0.5}$ $KCl_{0.5}$	16.700	316.79
$NaCl_{0.6}$ $KCl_{0.4}$	6.485	203.52
$NaCl_{0.8}$ $KCl_{0.2}$	17.750	341.32

3.4.4. Comparison of Debye temperatures calculated with Kopp-Neumann relation

Debye temperatures observed from all the three methods of the mixed crystals are provided in Table.6. It shows a non-linear variation with composition, Debye temperature observed from the melting point of the mixed crystals well agree with those calculated from the Kopp-Neumann relation, while observed from the Debye-waller factor are less than the values observed from the Kopp-Neumann relation except for some crystals. After analysing the data on the Debye temperatures of a large number of mixed crystals, Sirdeshmukh and Srinivas [15] concluded that the observed values of Debye temperatures from the Debye-waller factor are lower than those calculated from composition. The deviation of Debye temperature from the Kopp-Neumann relation may be due to increase in Vibrational entropy.

Mahadevan and his co-workers [1,4-10] observed the Debye temperature for ternary mixed crystals of alkali halide crystals, they have also reported that the Debye temperature varies non-linearly with composition.

Ahtee and Koshi made similar observation in the case of $KCl - KBr$ mixed crystals and attributed the enhancement of the Debye-waller factors to an increase in the vibrational entropy.

Table .6. Debye temperature calculated from melting point θ_H and Kopp-Neumann relation $\theta_K$together with the composition taken for pure and doped crystals.

System	Debye Temperature			
	θ_M	θ_D	θ_H	θ_K
Undoped mixed crystals				
NaCl	253	152	253	253
KCl	206	294	206	206
$NaCl_{0.2}$ $KCl_{0.8}$	214	138.6	195.7	210.4
$NaCl_{0.4}$ $KCl_{0.6}$	218	249.45	298.49	214.5
$NaCl_{0.5}$ $KCl_{0.5}$	213.5	181.5	215.45	218
$NaCl_{0.6}$ $KCl_{0.4}$	218.4	202.8	319.74	229.5
$NaCl_{0.8}$ $KCl_{0.2}$	235	261	333.89	245.6
ZnS doped mixed crystals				
NaCl	249.3	144	345.22	253
KCl	209.1	124	285.84	206
$NaCl_{0.2}$ $KCl_{0.8}$	216	164.1	298.93	212.4
$NaCl_{0.4}$ $KCl_{0.6}$	217.4	143.3	237.32	219.9
$NaCl_{0.5}$ $KCl_{0.5}$	221.01	268.35	316.79	222.2
$NaCl_{0.6}$ $KCl_{0.4}$	216.28	239.4	203.52	229.4
$NaCl_{0.8}$ $KCl_{0.2}$	227.07	297.9	341.32	234.3

IV. Conclusion

In the present study the Debye temperature of all the pure and ZnS added crystals were determined from the experimental values of melting point, Debye-waller factor and microhardness. Of these, Debye temperature calculated from the melting point temperature for all the grown crystals well agree with the Debye temperature calculated from the Kopp-Neumann relation. From this study it is concluded that the Debye temperature calculated from the melting point is more accurate and when doped the accuracy gets increases further.

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