

## Thermal properties of high order crystalline dielectric mixtures

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Through experiments the heat capacity is determined at constant volume in ternary and quaternary  $\text{KCl}_{0.5}\text{KBr}_{0.25}\text{RbBr}_{0.25}\cdot\text{Eu}^{2+}$  and  $\text{KCl}_{0.25}\text{KBr}_{0.25}\text{RbCl}_{0.25}\text{RbBr}_{0.25}\cdot\text{Eu}^{2+}$  single crystals. The results are compared with calculated values using the low temperature approximation of the Debye Model, in which the Debye temperature is obtained by applying a Kopp-Neumann relation. It is shown that the  $C_v$  values obtained by the Debye model are in good agreement with the measured ones which demonstrates that the Kopp-Neumann law used for metals and other solids can also be applied to ternary and quaternary alkali halide crystals, that is also an element that strengthens the diffractogram of the quaternary mixture which shows that the crystal has a single phase, thus being a solid solution.

**Keywords:** Dielectric crystals; alkali halide mixtures; Debye solid; heat capacity.

Se determina experimentalmente la capacidad calorífica a volumen constante en un cristal ternario y un cuaternario:  $\text{KCl}_{0.5}\text{KBr}_{0.25}\text{RbBr}_{0.25}\cdot\text{Eu}^{2+}$  y  $\text{KCl}_{0.25}\text{KBr}_{0.25}\text{RbCl}_{0.25}\text{RbBr}_{0.25}\cdot\text{Eu}^{2+}$ . Los resultados se comparan con valores calculados usando el modelo de Debye en la aproximación a baja temperatura, para lo cual la temperatura de Debye se obtiene aplicando la relación de Kopp-Neuman. Se muestra que los valores de  $C_v$  obtenidos por el modelo de Debye están en buena concordancia con los valores medidos, lo cual demuestra que la ley de Kopp-Neuman utilizada para metales y otros sólidos puede también ser aplicado a cristales ternarios y cuaternarios de una sola fase, además es un elemento que refuerza la medida difractiva obtenida del cristal cuaternario que demuestra que el cristal es de una sola fase siendo así una solución sólida.

**Descriptores:** Cristales dieléctricos; mezclas de halogenuros alcalinos; sólido de Debye; calor específico

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### 1. Introduction

There is interest in the study of thermal properties of alkali halide ternary and quaternary mixed crystals (or high order: most components of a binary) with full miscibility. In a precedent work, possible changes of heat capacity in a ternary crystal saturated with F centers were studied [1]. In several papers, the optical and structural studies of ternary and quaternary crystals with full miscibility at all concentrations have been published [2-6]. Also recently, thermally stimulated luminescence of alkali halide mixtures has been studied [7].

Heat capacity is one of the most fundamental properties of matter. From the heat capacity of a crystal, other thermodynamic quantities can be obtained, and these can be used to understand the conditions for thermodynamic equilibrium, including chemical reactivity and thermodynamic stability. Furthermore, knowledge of heat capacity is important for many applications of materials, from energy storage to heat conduction. For example, in investigations of new thermoelectric materials, knowledge of heat capacity is required to convert thermal diffusivity (the quantity usually measured) to thermal conductivity [8].

Although thousands of new compounds are reported each year, heat capacity is not known in all. Traditional calorimetric methods can provide accurate heat capacity data, but this relies on availability of both suitable apparatus and sam-

ples [8]. In general any process that uses energy emits or absorbs heat. The heat capacity of the material involved is very important. It is well known that non metallic crystalline solids at room temperature have a heat capacity  $C_v$  more or less constant and equal to  $3R$ . It was established that the  $C_v$  of some simple metals measured at room temperature was approximately  $25 \text{ J/mol K}$  [9]. This value agrees with the value predicted by the equipartition theorem of classical thermodynamics:  $3Nk_B$ , where  $N$  is the number of atoms in the solid and  $k_B$  the Boltzmann constant. Although the Dulong-Petit law fits the prediction of the equipartition theorem, at low temperatures this rule fails and it is necessary to abandon the classical statistical mechanics and study the problem from the quantum point of view.

The Dulong-Petit law was extended to compounds, leading to the Kopp-Neumann law, which states that the heat capacity of a solid compound is the sum of the heat capacities of the elements from which it is composed [10]. The Kopp-Neumann law can be used for some simple solids as well as binary compounds or alloys. The Kopp-Neumann law is based on additivity of the properties of the elements. Another approach consideration of thermodynamic contributions from the “constituent groups” of a compound has been used with considerable success to estimate thermodynamic properties of complex inorganic compounds, especially the standard-state entropies of mineral oxides [11].

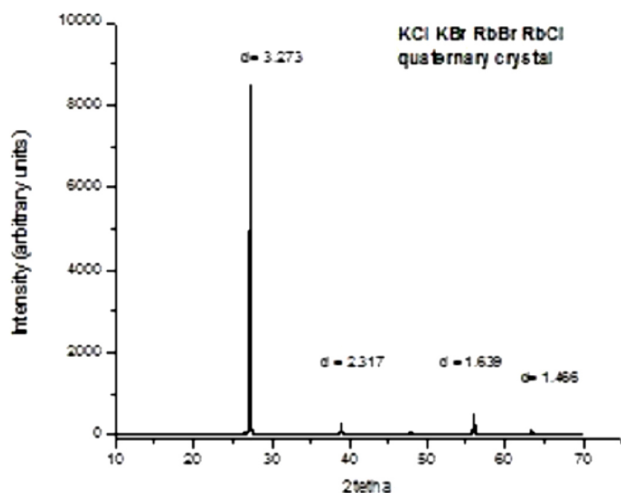


FIGURE 1. Diffractogram of the quaternary crystal.

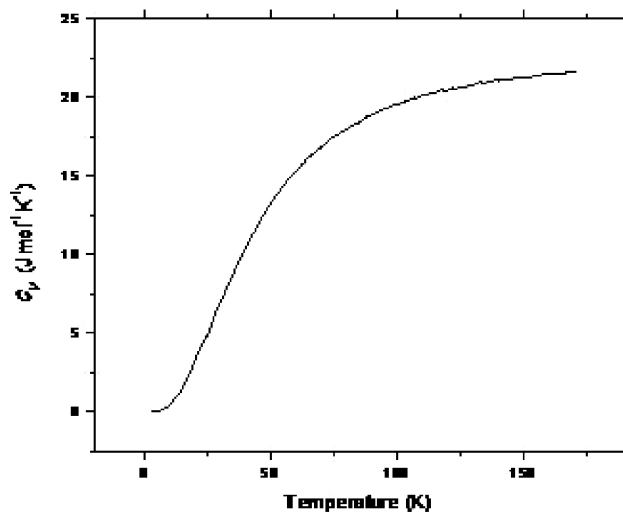


FIGURE 2. Experimental behavior of  $C_v$  of the quaternary crystal.

In this work the molar constant volume heat capacity at low temperature of high order mixtures of crystalline alkali halides is measured and analyzed. These values are predicted by the Debye model if a generalization of the Kopp-Neumann law is used to calculate the Debye Temperatures of the mixtures.

### 2. Experimental

The mixtures  $\text{KCl}_{0.25}\text{KBr}_{0.25}\text{RbCl}_{0.25}\text{RbBr}_{0.25}:\text{Eu}^{2+}$  and  $\text{KCl}_{0.5}\text{KBr}_{0.25}\text{RbBr}_{0.25}:\text{Eu}^{2+}$  were grown by the Czochralski method. In the growth, a KCl seed [12] was used because it has the highest melt point of the components in each mixed material.  $\text{Eu}^{2+}$  was added to the melt as  $\text{EuCl}_2$  in 0.1% molar concentration. The crystals obtained are transparent as a simple alkali halide crystal. Europium impurity is necessary to perform optical studies [7]. The powder diffractometry study was realized in a Bruker Advanced X ray analysis system. Heat capacity at constant volume of samples

of  $5 \times 5 \times 1 \text{ mm}^3$  has been measured in a Physical Properties Measurement System (PPMS) of Quantum Design and Heat Capacity, from approximately the Debye temperature to 2 K.

### 3. Results and Discussion

Figure 1 shows the powder diffractogram of a quaternary sample where it is observed as a solid solution or a crystal with a single phase. In Fig. 2 shows the measurement of  $C_v$  as function of temperature of a quaternary crystal sample. The curve obtained resembles the standard curve of  $C_v$  for solids which is the typical behavior of a single crystal. The results were compared with those of KCl crystals published in Ref. 13. In Fig. 3 the behavior of  $C_v/T$  as function

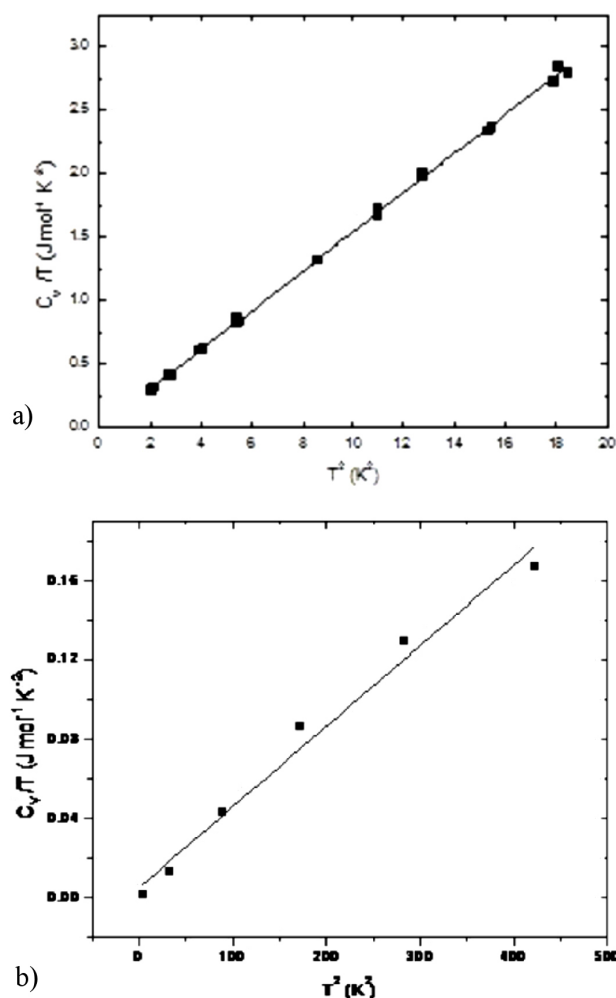


FIGURE 3. Behavior of the experimental  $C_v/T$  vs.  $T^2$  of (a) KCl (taken from Ref. 13) and (b) quaternary crystal at low temperature.

TABLE I. Debye temperature of the components of mixtures [14].

Component	KCl	KBr	RbCl	RbBr
(K)	236.1	172	168.8	136.3

TABLE II. Molar constant volume heat capacity of the quaternary crystal.

$T(K)$	$C_v$ Exp (J/mol K)	$C_v$ Theo (J/mol K)	$T^2$ (K <sup>2</sup> )	$C_v/T$ Exp (J/mol K <sup>2</sup> )	$C_v/T$ Theo (J/mol K <sup>2</sup> )
20.5	3.429	3.860	422.1	0.167	0.188
16.8	2.179	2.009	283.4	0.129	0.119
13.1	1.127	1.003	172.3	0.086	0.076
9.4	0.406	0.364	88.7	0.043	0.039
5.7	0.072	0.083	32.5	0.012	0.014
2.0	0.002	0.003	4.0	0.001	0.002

TABLE III. Molar constant volume heat capacity of the ternary crystal.

$T(K)$	$C_v$ exp (J/mol K)	$C_v$ Theor (J/mol K)	$T^2$	$C_v/T$ Exp (J/mol K <sup>2</sup> )	$C_v/T$ Theo (J/mol K <sup>2</sup> )
22.5	4.350	4.093	504.4	0.193	0.182
17.4	2.240	1.903	302.8	0.129	0.109
12.2	0.764	0.664	150.1	0.062	0.054
7.1	0.090	0.131	51.0	0.013	0.018
2.03	0.002	0.003	4.12	0.001	0.001

of  $T^2$  is displayed in a single KCl and the quaternary crystal. It results a linear function with slope  $s=0.15$  J/mol-K<sup>4</sup>. Using a wider interval of temperature, data of  $C_v/T$  of the quaternary and ternary gives approximately the same slope indicating that at low temperature these types of crystals behave as a one-component alkali halide crystal. The theoretical values were obtained using the low temperature approximation of the Debye model.

The Debye model establish that for a solid at low temperature

$$\lim_{T \rightarrow D} \frac{C_v}{3R} \approx \frac{4\pi^4}{5} \left( \frac{T}{\theta_D} \right)^3 \quad (1)$$

Where is the Debye temperature (DT). At low temperature  $C_v$  is proportional to  $T^3$ . To apply this model to mixed crystals requires knowledge the DT ( $\theta_{DM}$ ) of the mixture, which is calculated using a generalization of the Kopp-Neumann law:

$$\overline{\theta_{DM}^{-3}} = \sum_{i=1}^n x_i \theta_i^{-3} \quad (2)$$

Where  $x_i$  is the molar fraction and  $\theta_i$  the DT of the component  $i$ .  $\theta_i$  values of the components of the quaternary and ternary crystals are listed in Table I. The DTs of the mixtures calculated with the Eq. (2) result 175.2 K for the ternary and 165.9 K for quaternary crystal.

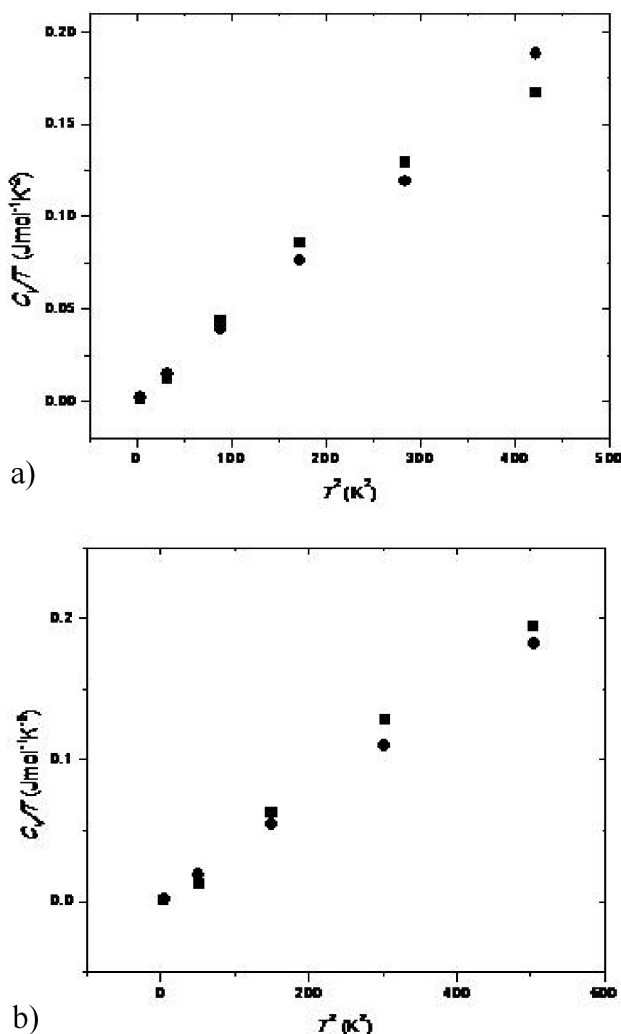


FIGURE 4. Comparison between experimental (full squares) and theoretical (full diamonds) values of  $C_v/T$  vs.  $T^2$  of (a) the quaternary crystal and (b) the ternary crystal.

Applying Eq. (1) for temperatures in the range 2 to 25 K, the  $C_v$  and  $C_v/T$  values of ternary and quaternary crystals have been calculated. The results are listed in the third and fifth columns, respectively, of the Tables III and IV. The calculated data are plotted in the Fig. 4. In it is compared the  $C_v/T$  vs  $T^2$  experimental and theoretical values of the ternary and quaternary crystals.

As can be seen in these figures, the theoretical values present a very similar behavior to those obtained from the measurements for both ternary and quaternary crystals. These results indicate that the way the Debye temperature is calculated is appropriate and therefore, it means that the generalization of the Kopp-Neumann law to this type of materials is valid.

Summarizing, the  $C_v$  of ternary and quaternary alkali halide crystals behaves as that of a single alkali halide crystal. At low temperatures, a good agreement between experimental and theoretical values is obtained by using the Debye model for which the Debye temperature is obtained through

a Kopp-Neumann relation. As can be seen the Europium impurity has not effect in the heat capacity which was expected, since this is a similar situation to the case of F centers [1]. According with these results, the generalization of the Kopp-Neumann law is valid to be applied to mixtures of three and four components of alkali halides. Characterization of these higher-order mixed systems of ionic crystals is important because it opens new perspectives for research and applications. The values for  $C_v$  here reported provide valuable information for the application areas of mixed alkali halide crystals.

Would be interesting know the  $C_v$  behavior in crystals of two and three phases. Actually there are structural and optical studies in two phases ternary KCl:KBr:KI [15], structural studies in two phases, in

the sexenary crystal; KCl:KBr:KI:RbCl:RbBr:RbI [16] and structural studies in three phases, in the quinary crystal; KBr:KI:RbCl:RbBr:RbI [6].

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