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Thermal properties of $Ba_xPb_{1-x}(NO_3)_2$ mixed crystals

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Abstract: *The isomorphous alkaline earth nitrates $Ba(NO_3)_2$ and $Pb(NO_3)_2$ are materials with cubic structure. Mixed crystals of $Ba_xPb_{1-x}(NO_3)_2$ were grown from solution by slow evaporation. Single phase mixed crystals were formed. The capability of mixing the materials and Vegard`s law are tested. Powder diffractometer was employed to record their X-ray patterns. The non-linear dependence of composition with positive and negative deviations from linearity is observed in mean Debye Waller factor and Debye temperatures respectively. Melting temperatures measured also show a non-linear dependence with negative deviations from linearity.*

Keywords: *Vegard`s law, Debye Waller factor, Debye temperature, Bragg reflections, lattice constants, melting temperatures.*

I. Introduction

Among the large number of solid state crystals which exhibit stimulating Raman scattering (SRS) properties, isomorphous alkaline earth nitrates attract attention as one of the interesting class of Raman media. Barium nitrate is the most imminent among them. The infrared and Raman properties of barium nitrate have been studied by many authors [1-9]. Lead, barium and strontium nitrate form an isomorphous series of cubic crystals with space group as Pa3 instead of $P2_13$ [10]. While there is considerable work on these nitrates, there is meager work on their mixed crystals. While the crystal growth aspects of $Ba_xSr_{1-x}(NO_3)_2$ mixed crystal system was studied by Wu et al and Chen et al [11-12]. The $Ba_xSr_{1-x}(NO_3)_2$ system was studied by Tsuchiyama et al, the structural aspects were re-evaluated by Prakash Gopalan and Bart Kahr [13-14]. The nucleation and crystal growth behavior for the solid solutions of Pb_xSr_1-$_x(NO_3)_2$ was also studied by Wu.et. [15].

In the present investigation a systematic X-ray study of $Ba_xPb_{1-x}(NO_3)_2$ mixed crystal system is carried out. From the measurement of Bragg angles lattice constants were determined and Vegard's law is verified. From the data of integrated intensities mean Debye Waller factors have been determined and their characteristic Debye temperatures were calculated. From the recordings of thermograms, thermal stability of these crystals is tested and melting points were determined. The composition dependence of the properties studied is established and discussed.

II. Experimental Method

The mixed crystals of $Ba_xPb_{1-x}(NO_3)_2$ system (x is composition of barium) were grown by evaporation of aqueous solution. Fluka chemie AG, CH-9470 Bucha, West-Germany grade salt was used as starting material. The details of growth process are as discussed [16]. The size of the crystals varied from few millimeters to about one centimeter. The crystalline quality of the crystals degraded with composition of Ba^+. This result is in agreement with lattice distortions caused by Ba^{+2} [10]. Using ICPMAES technique exact composition for the resulting crystals was estimated. The estimated composition is accurate up to 2%.

To check the miscibility and formation of mixed crystals including end members, fast scan X-ray powder diffractograms was recorded using a JEOL-JDX-8P X-ray diffractometer fitted with a scintillation counter in an angular range $15<2\theta<80$. To determine accurate lattice constants and thermal parameters, Bragg reflections were recorded in θ-2θ scan. Goniometer speed of 0.5^o/min and a chart speed of 40mm/min over an agular range of 2θ=10-120 ^{o} and a beta filtered CuKα radiation were used. Integrated intensities have been corrected for thermal diffuse scattering.

Using Mettler Toledo STAR thermo gravimetric analyzer melting temperatures were determined with an accuracy of $\pm$ 1^{o}C.The equipment was standardized for KBr sample whose melting point was determined to be 732^{o}C which is in good agreement with reported value of 734^{o}C[17].

III. Results And Discussion

The X-ray powder diffractograms for pure $Pb(NO_3)_2$ and one of the mixed crystals $Ba_{0.47}Pb_{0.53}(NO_3)_2$ are shown in Fig.1

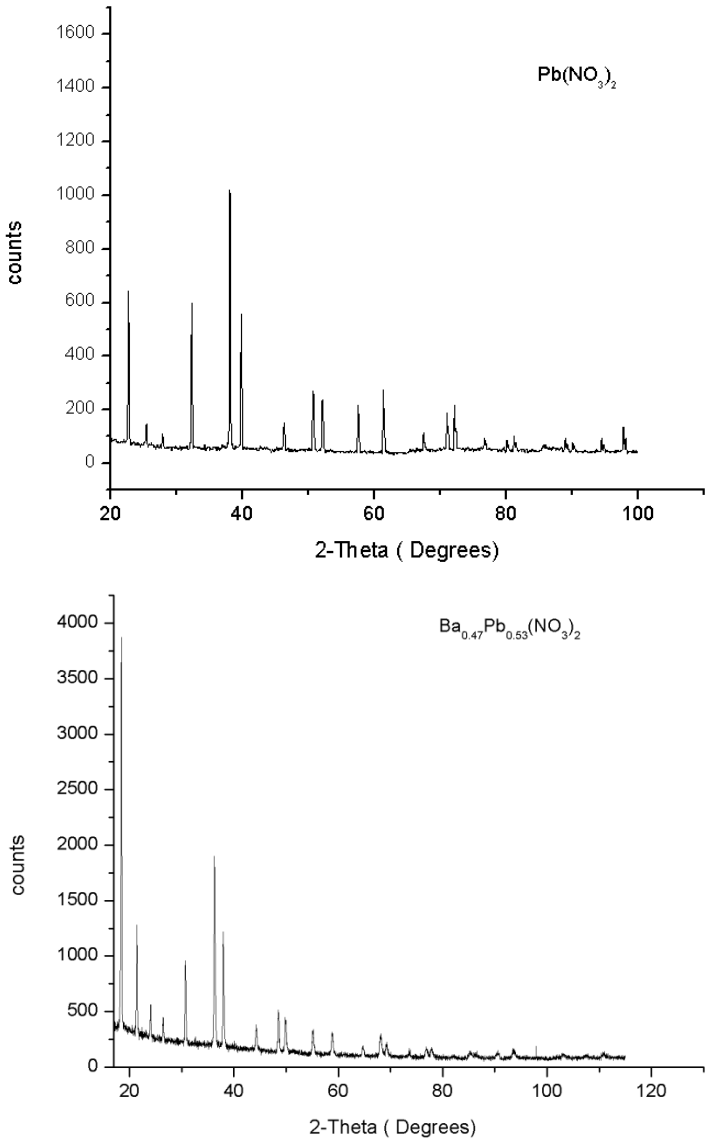

Fig. 1. X-ray diffractograms for pure $Pb(NO_3)_2$ and one of its mixed crystals of $Ba_{0.47}Pb_{0.53}(NO_3)_2$.

3.1 Lattice Constant

A sample extrapolation line for pure $Pb(NO_3)_2$ is shown in figure 2a as an indication to the greater accuracy in lattice constant measurement.

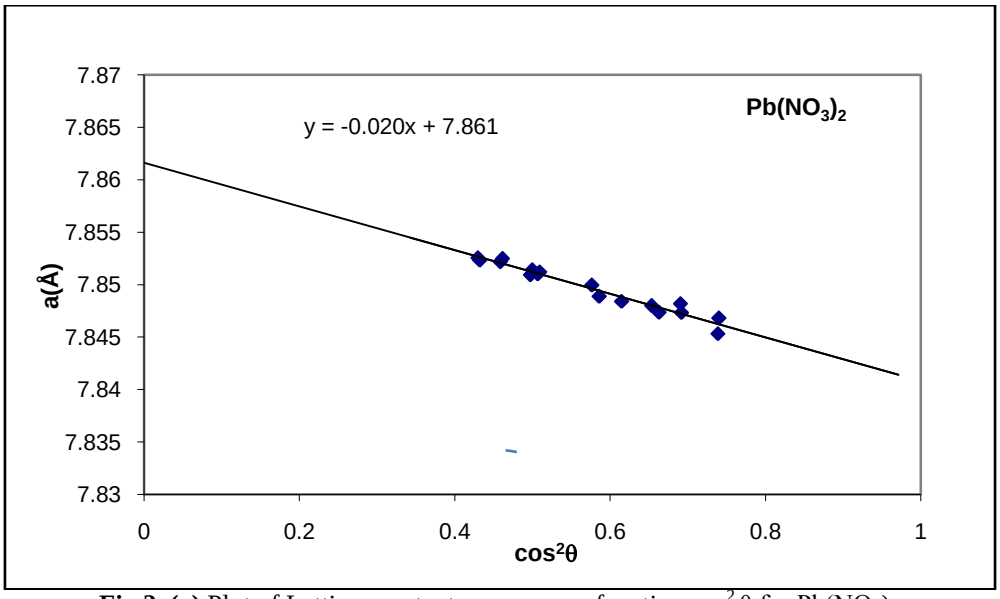

Fig 2. (a) Plot of Lattice constant versus error function $\cos^2\theta$ for $Pb(NO_3)_2$

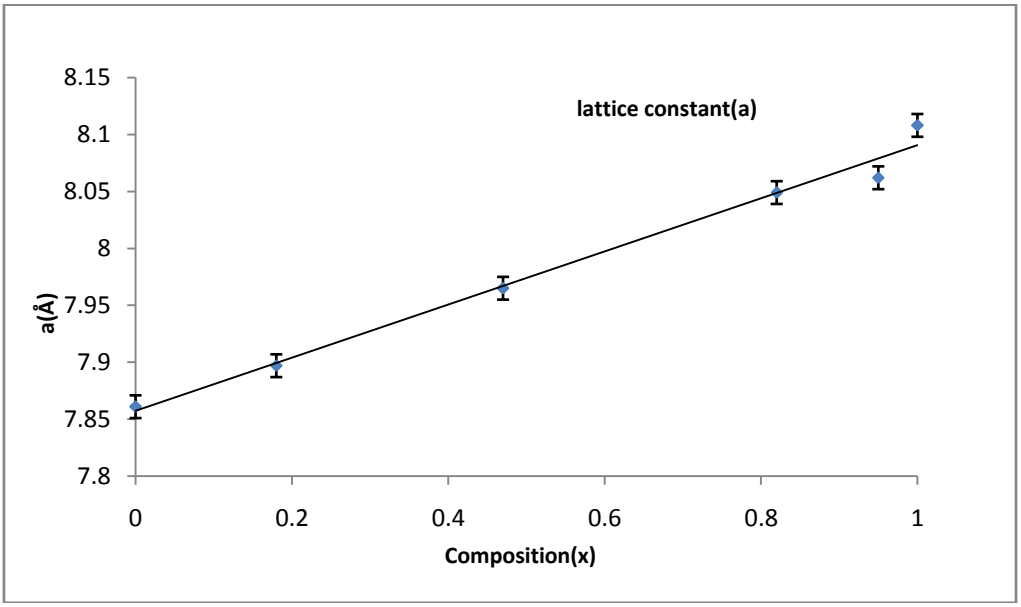

Fig Fig 2. (b) Composition dependence of lattice constant for $Ba_xPb_{1-x}(NO_3)_2$ crystals

The measured lattice constants obtained in this study of $Ba_xPb_{1-x}(NO_3)_2$ mixed crystals are plotted against composition in figure 2(b). The lattice constants for pure $Ba(NO_3)_2$ and $Pb(NO_3)_2$ are 8.119 Å and 7.86 Å which are in good agreement with 8.1174 Å and 7.86 Å from NBS circular [18].There is a scattering in the distribution of experimental values of lattice constants. But the deviations are on either side of the line connecting end members. As noticed the lattice parameter depend in a linear way on the composition and accord well to Vegard`s law. The deviations are very small and are of the order of accuracy in the measurement of lattice constants. This result is same as the observation made in the case of $Ba_xSr_{1-x}(NO_3)_2$ and $Pb_xSr_1\text{-}_x(NO_3)_2$ mixed crystal systems[11,15]. The particle size was estimated from the profile of Bragg reflections using the Scherer formula. The crystallite size of the samples varied between 70-90 nm.

3.2 Debye Waller factor and Debye temperature

The Debye-Waller factor is determined from intensities [19]. For this purpose to calculate the structure factor for pure alkaline earth metal nitrates and their mixed crystals under study, the equation using the data on coordinates of equivalent positions [20] was used. The atomic scattering factors are corrected for anomalous dispersion [21].

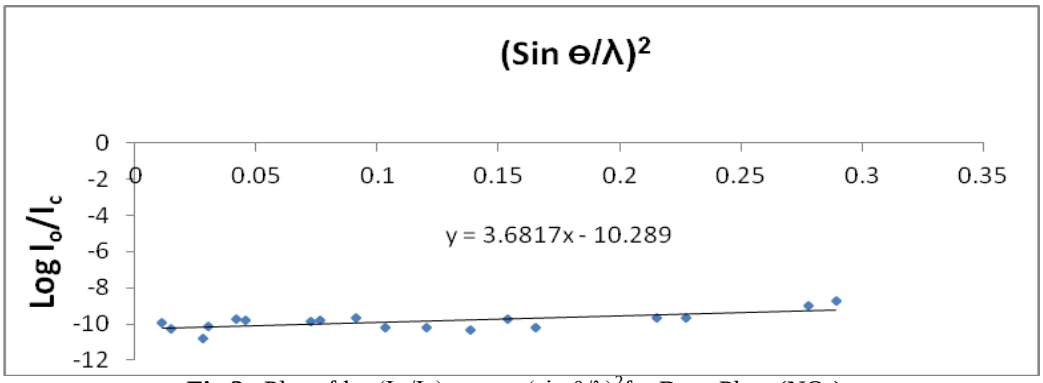

Fig 3. Plot of log(Io/Ic) versus $(\sin \theta/\lambda)^2$ for $Ba_{0.47}Pb_{0.53}(NO_3)_2$

The mean Debye-Waller factor (B) and Debye temperature (θ_M) are determined from least square treatment of data on log(Io/Ic) versus $(\sin \theta/\lambda)^2$. A typical plot is shown in figure 3. The values of B and θ_M evaluated are plotted against composition(x) in figure 4 and found to be nonlinear. The Debye-Waller factors for $Ba(NO_3)_2$ and $Pb(NO_3)_2$ obtained are 0.44 and 0.47 respectively . The exhaustive survey of literature indicates that there is only one report on Debye-Waller factor of $Ba(NO_3)_2$ with a value of 1.67 $(Å)^2$ [22]. In the present work Debye temperatures for $Ba(NO_3)_2$ and $Pb(NO_3)_2$ are 173 K and 149 K which are in agreement with 170 K and161 K reported from X-ray studies [23-24].In addition to X-ray studies, Debye Waller factors for these nitrate end members are also reported from other methods like elastic constants and specific heats [25-26].

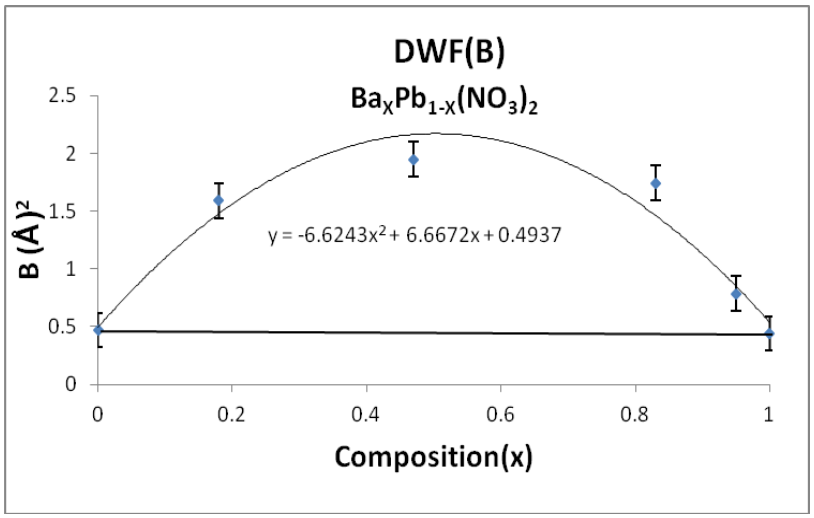

Fig. 4 (a) Composition dependence of Debye-Waller factor (B) for $Ba_xPb_{1-x}(NO_3)_2$ crystals.

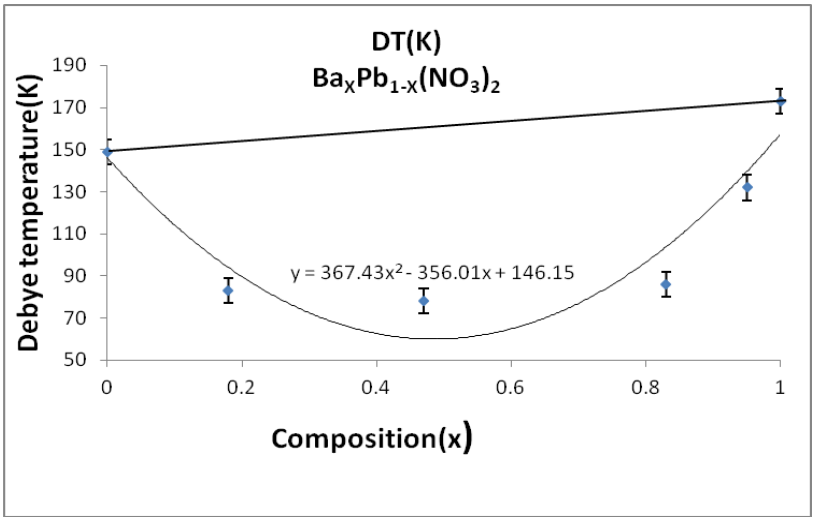

Fig. 5 (b) Plot of Debye temperature (θ_M) for $Ba_xPb_{1-x}(NO_3)_2$ crystals.

The mean Debye-Waller factor varies nonlinearly with composition and the deviation is positive from linearity, whereas Debye temperature also varies nonlinearly with composition and the deviation is negative from linearity. Since the alkaline earth nitrates are ionic in nature, the results in the present case can be compared with those of alkali halide mixed crystal systems. There is only one report on the study of composition dependence of Debye Waller factors and Debye temperatures for alkaline earth nitrate mixed crystals systems [22]. The results in the present study are similar to those reported earlier.

In all the alkali halide mixed crystal systems the Debye Waller factor vary nonlinearly with composition and a positive deviation from linearity. The composition dependence of Debye temperature is non linear with negative deviations from linearity [27]. The deviations from linearity in the present study are much larger than the experimental error whereas the deviations reported in case of alkali halide mixed crystal systems were of order of the experimental error. The nature of lattice vibrations in $Ba_xPb_{1-x}(NO_3)_2$ lattice is not the same as that of alkali halide mixed crystal systems. The larger difference between experimental and calculated values of B and θ_M also reflects the degree of the disorder of the arrangement of metal ions in the lattice. Further the large difference in ionic radii between barium nitrate and other two nitrates namely strontium and lead is also responsible for the larger deviation. Therefore it is concluded that the in $Ba_xPb_{1-x}(NO_3)_2$ lattice is more disordered than that in alkali halide mixed crystals.

3.3 Melting point.s

A typical thermogram for $Ba(NO_3)_2$ is shown in figure 5(a).The thermal stability up to about 500^{o}C indicates no water of hydration in the crystals. The experiments were performed for $Ba(NO_3)_2$, $Pb(NO_3)_2$ and the mixed crystals of $Ba_xPb_{1-x}(NO_3)_2$ systems. The melting point of $Ba(NO_3)_2$ obtained in the present work is 566.65^{o}C which is not in good agreement with the earlier reported value of 590^{o}C[17]. Kenneth et al mentioned that the commercial sample of $Ba(NO_3)_2$ melts at 552 **^{o}C.** [28]. However, in the case of $Pb(NO_3)_2$ the melting point reported in the literature is 470 **^{o}C** [17] and it decomposes before melting at 400 **^{o}C**, unlike for $Ba(NO_3)_2$ and $Sr(NO_3)_2$ which do not decompose before melting. The same feature is observed for $Pb(NO_3)_2$ from present experiments.

Figure 5(b) shows the composition dependence of melting points for the mixed crystal system under study. The plot shows a non-linear behavior with negative deviations from linearity. This is similar to the observation of Sirdeshmukh et al [29] for KCl-KBr and Subhadra and Hussain [30] for $NaClO_3$-$NaBrO_3$ mixed crystals. The maximum deviation from linearity is 15^{o}C and occurs at about the equimolar composition. This deviation is larger than the accuracy in the measurement.

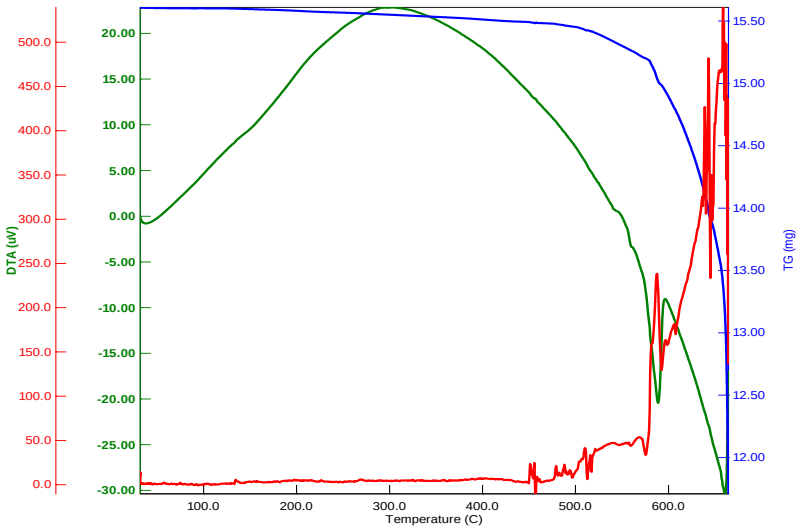

Figure 5(a) Thermogram of pure $Ba(NO_3)_2$ crystal.

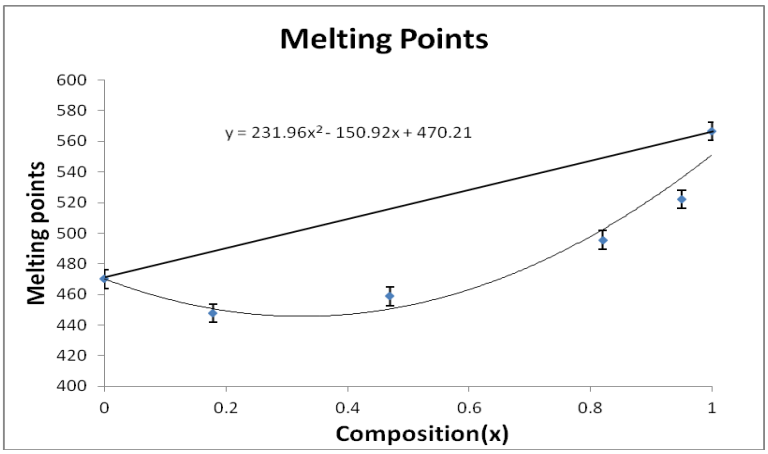

Figure 5(b) Composition dependence of melting points for $Ba_xPb_{1-x}(NO_3)_2$ mixed crystals.

IV. Conclusions

A detailed X-ray study of $Ba_xPb_{1-x}(NO_3)_2$ mixed crystal system has been carried out. Lattice constants, Debye-Waller factors and Debye temperatures have been determined from X-ray powder diffraction studies. Melting points were determined from TG studies. The composition dependence of lattice constant obeys Vegard`s law. The composition dependence of Debye-Waller factor shows non-linear behavior with positive deviations and Debye temperature shows negative deviations from linearity. The composition dependence of melting temperature shows non-linear behavior with negative deviations from linearity. The results are discussed in terms of disorder of the lattice due to larger difference between the ionic size of barium and lead compared to that of lead and strontium.

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