

# Growth and X-Ray Characterization of $Pb_xSr_{1-x}(NO_3)_2$ Mixed Crystals

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**ABSTRACT:**  $Pb(NO_3)_2$  and  $Sr(NO_3)_2$  belong to a family of isomorphous alkaline earth nitrates with cubic structure. As these crystals are used in stimulated Raman studies and optical filters, numerous investigations were carried out on their various physical properties. A Series of  $Pb_xSr_{1-x}(NO_3)_2$  with  $x = 0$  to 1 single crystals in the size of  $(16 \times 16 \times 4)$  mm<sup>3</sup> were grown by solution growth slow evaporation technique. All crystals were characterized for its chemical composition by ICP-AES and phase formation by XRD. XRD studies revealed all grown crystals were single crystalline phase with cubic structure and from measurement of Bragg angles, integrated intensities, lattice constants, mean Debye Waller factors, Debye temperatures are determined. Their lattice constants follows Vegard's law. The mean Debye-Waller factor and Debye temperature show non-linear composition dependence with positive and negative deviations from linearity respectively. it is found that  $Pb^{+2}$  was enriched in all 111 sectors.

**KEYWORDS:** X-ray Diffraction, Debye temperature, Debye Waller factor, lattice parameter, Divalent Nitrates

## 1. INTRODUCTION

Lead nitrate, strontium nitrate and barium nitrate are molecular cubic crystals with space group Pa3 [1]. These crystals have applications in stimulated Raman studies and optical studies [2-4]. The crystallisation behaviour of  $Pb_xSr_{1-x}(NO_3)_2$  and  $Ba_xSr_{1-x}(NO_3)_2$  solid solutions was studied by Wu et al [5-7]. For both the systems, the mixed crystals were grown over all compositions and no miscibility problem was reported. They reported Vegard's law behaviour for lattice constants. The crystal growth aspects and study of physical properties of  $Ba_xSr_{1-x}(NO_3)_2$  system in the entire composition range is carried by Hussain et al [8-9].

In the present paper the results of a systematic X-Ray study of the  $Pb_xSr_{1-x}(NO_3)_2$  mixed crystal system is reported. From the measurement of Bragg angles and integrated intensities lattice constants, mean Debye Waller factors and Debye temperatures for different compositions ( $x$  of lead) are determined and the composition dependence of these properties is established; discussed in terms of the degree of disorder of metal ions in the lattice.

## II. EXPERIMENTAL

The  $Pb_xSr_{1-x}(NO_3)_2$  mixed crystals ( $x$  is composition of lead) were grown from solutions by slow evaporation. The starting material were spec pure, from Fluka Chemie AG, CH-9470 Bucha, West Germany. The details of the crystal growth experiments are discussed in a previous communication from this laboratory [10]. Large crystals of size  $(16 \times 16 \times 4)$  mm<sup>3</sup> were successfully grown as shown in figure 1(a,b) and the line diagrams were also shown in figure 1(c,d) respectively. The exact composition of the resulting mixed crystals was estimated by the method of Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). To record X-ray diffractograms, the samples were made

into fine powder and annealed for 4 hours at a temperature of 200°C to reduce the strains. Then the powder was used for the determination of the exact composition and X-ray studies.

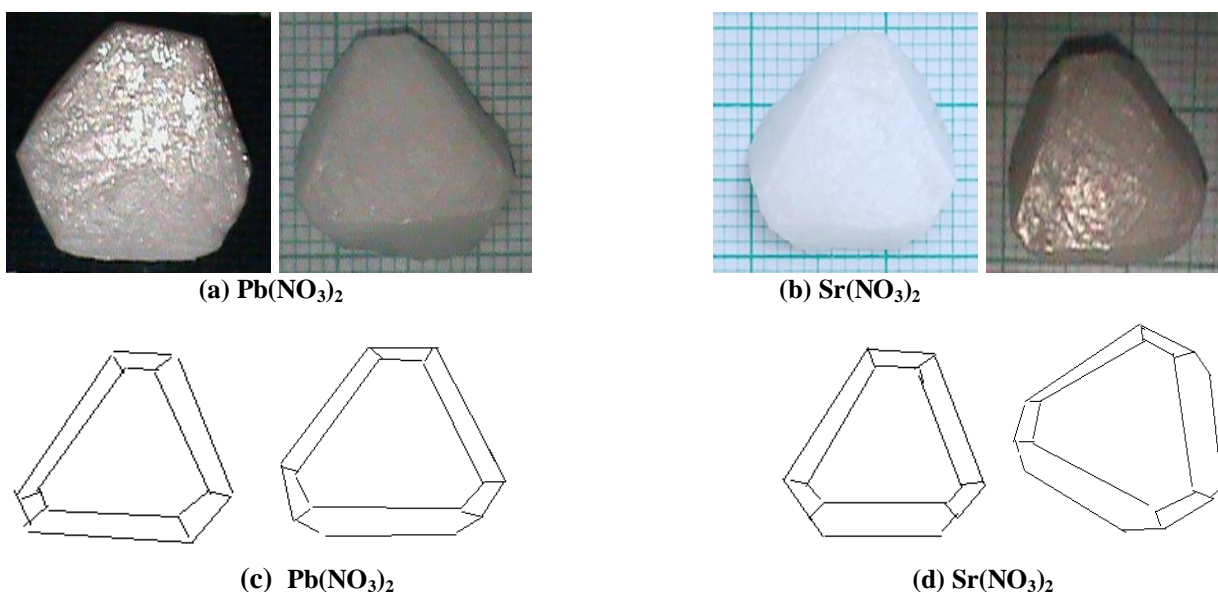


Fig.1. Morphologies of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Sr}(\text{NO}_3)_2$  crystals (Polyhedron  $\{111\}>\{100\}$ )

To check the miscibility and the formation of mixed crystals, X-ray powder diffractograms with the goniometer speed of  $2^\circ/\text{minute}$  were recorded in the angular range  $15 < 2\theta < 80$ . For the determination of accurate lattice constants and thermal parameters the diffractograms were recorded using a JEOL-JDX-8P diffractometer fitted with a scintillation counter. Filtered  $\text{CuK}\alpha$  radiation ( $\lambda=1.54056$ ) was used. The Bragg reflections were recorded in  $\theta$ - $2\theta$  scan with a goniometer speed of  $0.5^\circ/\text{min}$  and a chart speed of  $40 \text{ mm/min}$ , over an angular range of  $2\theta = 15^\circ$  to  $120^\circ$ .

### III. RESULTS AND DISCUSSION

The X-ray powder diffractograms of pure  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$  and six of the  $\text{Pb}_x\text{Sr}_{1-x}(\text{NO}_3)_2$  mixed crystals are shown in figure 2. For all the mixed crystals the diffraction peaks are well defined and sharp indicating the formation of single phase mixed crystals. The integrated intensities have been corrected for thermal diffuse

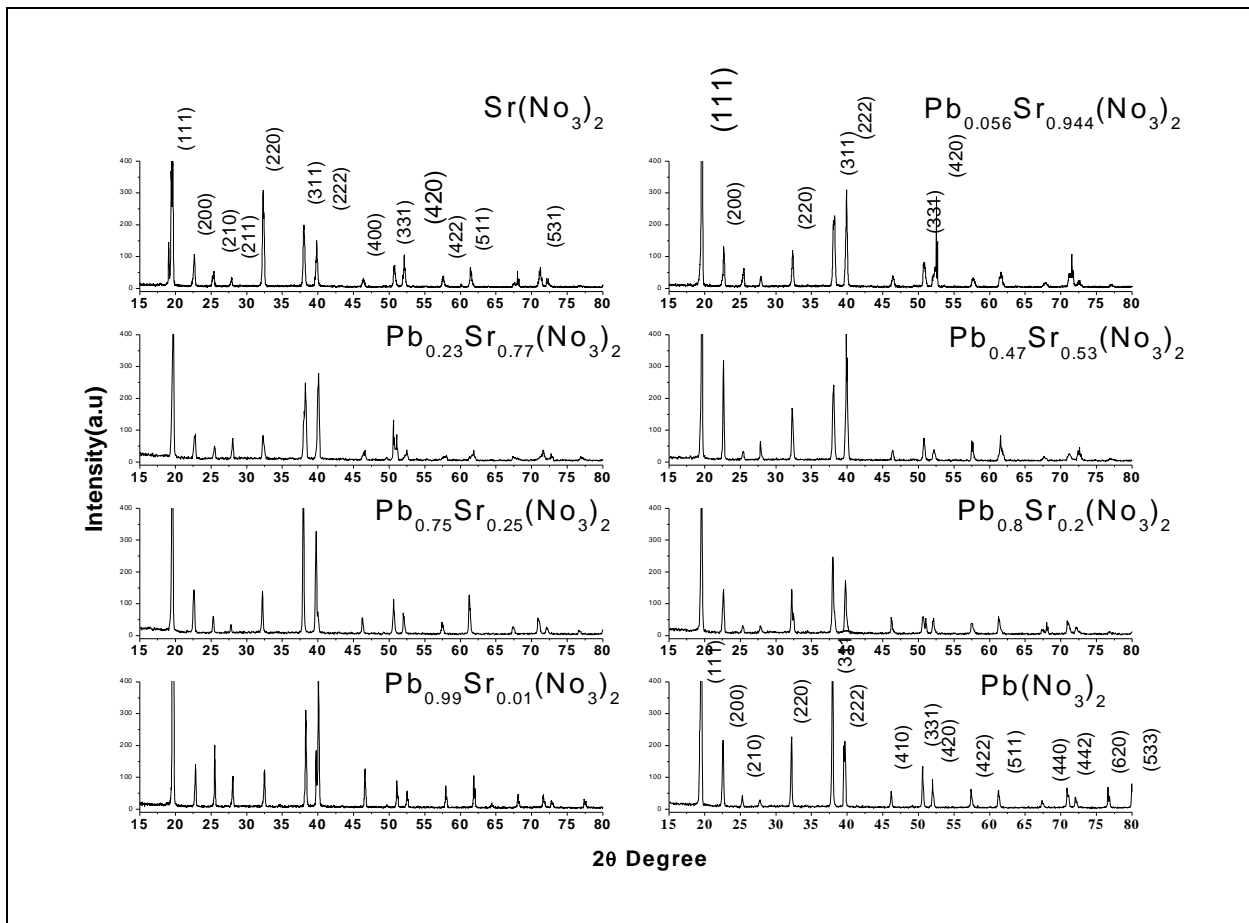


Fig. 2. X-ray diffractograms of  $Pb_xSr_{1-x}(NO_3)_2$  mixed crystal system

scattering (TDS). The average grain size is determined. The values of Full Width Half Maxima (FWHM) of the Bragg profile are measured. The average crystallite size ( $\tau$ ) estimations are generally carried out using XRD measurements by Scherrer formula, the theory of which is available and reproduced below.

$$(\tau) = P \lambda / [ FWHM \cdot \cos \theta ]$$

where  $P$  is shape factor taken as  $0.9$  assuming that all grains are of spherical nature,  $\lambda$  is the wavelength of radiation used ( $\lambda_{CuK\alpha} = 1.540598 \text{ \AA}$ ),  $\theta$  is the Bragg angle, and FWHM is the Full Width-Half-Maximum of the most strongest Bragg peak of the phase under consideration expressed in radians. For this purpose several reflections are used of all the samples. The crystallite size of all the samples including mixed crystals varied between 60-90 nm and it is found that  $Pb^{+2}$  was enriched in all 111 sectors.

#### A. LATTICE CONSTANT

Accurate lattice constant ( $a$ ) was determined by least squares treatment of the values of lattice constants obtained for several reflections and the error function  $\cos^2\theta$ . A typical extrapolation plot is shown in Fig.3. The formation of the single phase mixed crystals is evident from the quality of the peaks. The estimated composition of lead

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in mixed crystals is accurate up to 1%. The values of the lattice constants obtained in this study for  $Pb_xSr_{1-x}(NO_3)_2$  mixed crystals are plotted against the composition in Fig.4. The values of lattice constants for lead nitrate

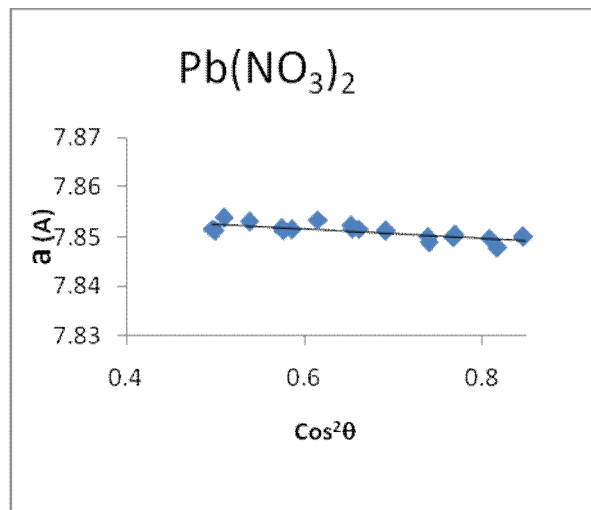


Fig.3. plot of lattice constant (a) versus error function  $\cos^2\theta$  for  $Pb(NO_3)_2$

and strontium nitrate in the present study are 7.857 Å and 7.781 Å. These values are in good agreement with those reported by other workers [12-14]. The lattice constants are accurate up to  $\pm 0.001$  Å. From figure 4 it is clear that the composition dependence follows linear relation and hence Vegard's law.

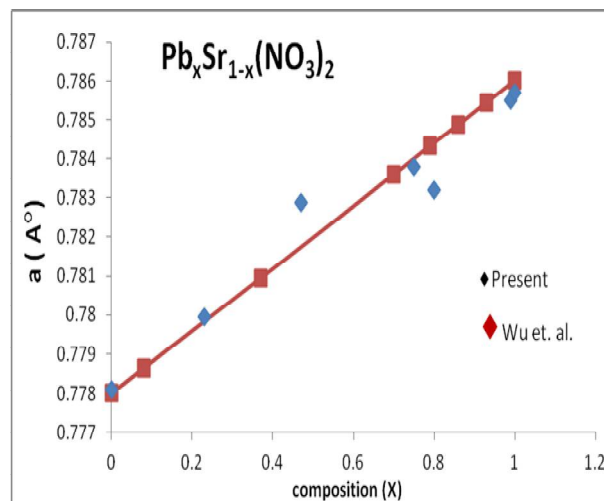


Fig.4. composition dependence of lattice constant (a) for  $Pb(NO_3)_2$

### B. DEBYE WALLER FACTOR AND DEBYE TEMPERATURE

The Debye-Waller factor is determined from intensities. The experimental conditions and procedure of sample preparation are such that errors in intensity due to surface roughness, porosity and extinction are minimized. The integrated intensity  $I_o$  of a Bragg reflection of a powder sample may be written as  $I_o = C I_c \exp(-2B \sin^2\theta/\lambda^2)$ , where

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C is the scale factor, B, the mean Debye –waller factor and  $I_c$ , the calculated intensity which is given by  $I_c = (LP)JF^2$ , where LP is the Lorentz Polarization factor, J the multiplicity factor and F, the structure factor.

For alkaline earth metal nitrate the structure factor can be written using the data of coordinates of equivalent positions [15] as

$$F(hkl) = f_m^o \exp(-M_m) + 8f_N^o \{ \cos(2\pi)hu \cos(2\pi)ku \cos(2\pi)lu \} \exp(-M_N) + 8f_o^o \{ \cos(2\pi)hx \cos(2\pi)ky \cos(2\pi)lz + \cos(2\pi)hy \cos(2\pi)kz \cos(2\pi)lx + \cos(2\pi)hzc \cos(2\pi)kxc \cos(2\pi)ly \} \exp(-M_o)$$

where m, N and O stand for metallic ions (Pb and Sr), nitrogen atoms, and oxygen atoms respectively;  $f_m$ ,  $f_N$  and  $f_o$  are the atomic scattering factors[16]; and u, y, and z are positional parameters[17]. Since the masses of nitrogen and oxygen differ by only two atomic mass units, one can approximately take  $M_N \approx M_O$ . The atomic scattering factors are corrected for anomalous dispersion [18]. The mean Debye - waller factor is determined from a least squares treatment of data on the log ( $I_o / I_c$ ) versus  $(\sin \theta / \lambda)^2$ . A typical plot is shown in fig.5.

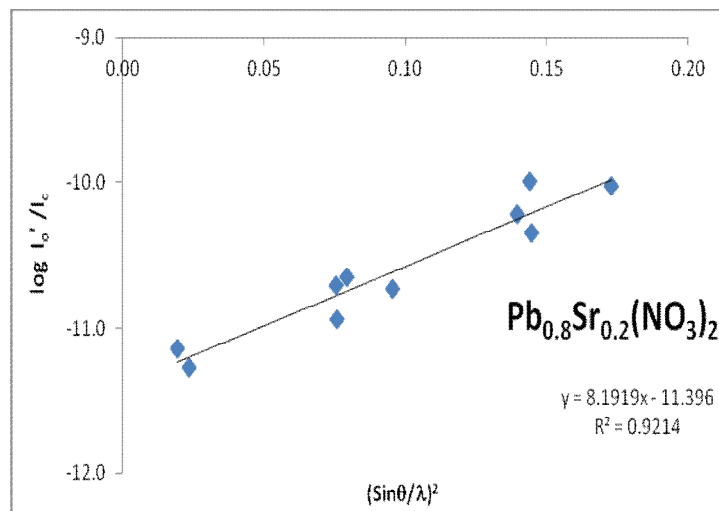


Fig. 5. Plot of  $\log ( I_o / I_c )$  vs.  $\sin^2 \theta / \lambda^2$  for  $Pb_{0.8}Sr_{0.2}(NO_3)_2$

For the mixed crystals the Debye-Waller factor thus determined ( $B_{obs}$ ) is the sum of the true thermal Debye –Waller factor ( $B_{thermal}$ ) and a static component ( $B_{static}$ ) due to the presence of two types of metallic ions in the mixed crystal.  $B_{thermal}$  is obtained from  $B_{obs}$  by applying a correction for  $B_{static}$  [19]. The theoretical details are discussed in a previous publication [8]. From the Debye –Waller theory, for a cubic crystal ‘B’ may be expressed as  $(6h^2/mKT)W(x)$ , where m is the mean mass, T is the absolute temperature, ‘h’ and ‘k’ are the planck and the Boltzmann constants respectively. The function  $W(x)$ [20] is given by  $[ \Phi(x) / x + 1/4 ]$ , where  $\Phi(x)$  is the Debye function and  $x = \theta_M / T$ ,  $\theta_M$  being the Debye temperature .

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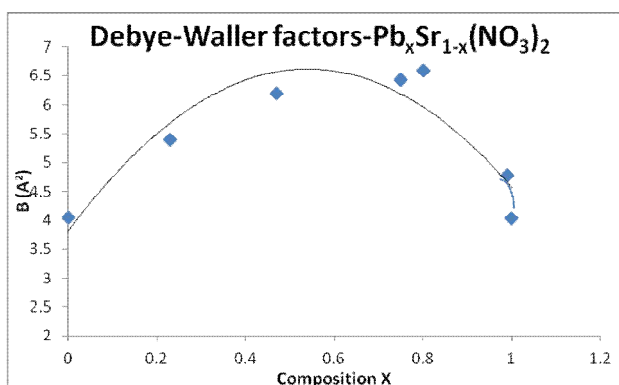


Fig. 6. Composition dependence of Debye Waller factor for  $Pb_xSr_{1-x}(NO_3)_2$  mixed crystals

The values of mean Debye Waller factors and Debye temperatures obtained in the present study are shown in table 1. The value of mean Debye Waller factor for  $Sr(NO_3)_2$  is 4.04 which is small compared to only value 1.76 [8] available in the literature. The value of 4.03 for  $Pb(NO_3)_2$  obtained in the present study is the first report. The values of Debye temperatures of 196 K and 161 K obtained in the present study for  $Sr(NO_3)_2$  and  $Pb(NO_3)_2$  respectively are in good agreement with many of the earlier reported values shown in table 1. The composition dependence of mean Debye Waller factors and Debye temperatures for  $Pb_xSr_{1-x}(NO_3)_2$  mixed crystal system is shown in figure 6 and 7 respectively. The composition dependence of mean Debye Waller factor is nonlinear with positive deviations from linearity and for Debye temperature is nonlinear with negative deviations from linearity. The magnitude of the deviation is much larger than the uncertainty in determination of mean Debye Waller factor and Debye temperature.

Table 1. Values of the mean Debye Waller factors (B) and Debye temperature ( $\theta_M$ ) for  $Pb_xSr_{1-x}(NO_3)_2$  mixed crystals

$Pb_xSr_{1-x}(NO_3)_2$ crystalsl. No.	Composition (x)	Debye Waller Factor (B)(Å <sup>2</sup> )	Debye ( $\theta_M$ ) K
1	0.00	4.04 1.76[8]	196 K 237 K [8] 195 K [21] 290 K [22] 304 K [23] 197 K [24]
2	0.23	4.39	189 K
3	0.47	6.19	152 K
4	0.75	6.42	142 K
5	0.8	6.58	177 K
6	0.99	4.78	159 K
7	1	4.03	161 K 167 K [21] 197 K [22] 227K [23] 107K [25]

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This behaviour of  $Pb_xSr_{1-x}(NO_3)_2$  mixed crystal system is similar to that of  $Ba_xSr_{1-x}(NO_3)_2$  [8] mixed crystal system and alkali halide mixed crystal systems. In alkali halide mixed crystal systems the magnitude of deviation is of the order of

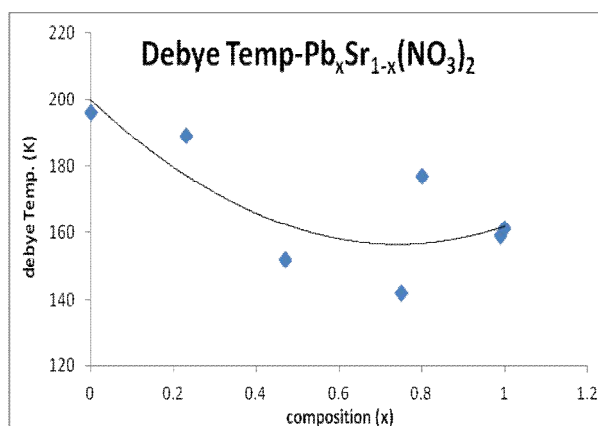


Fig. 7. Composition dependence of Debye temperature for  $Pb_xSr_{1-x}(NO_3)_2$  mixed crystals

the experimental uncertainty, whereas in alkaline earth nitrate mixed crystal systems the magnitude of deviation is much larger. In this sense the mixed crystal system under study is more disordered in the distribution of metal ions in the lattice and the nature of lattice vibrations when compared to the alkali halide mixed crystal systems. In individual difference between the  $Ba_xSr_{1-x}(NO_3)_2$ ,  $Pb_xSr_{1-x}(NO_3)_2$  and  $Ba_xPb_{1-x}(NO_3)_2$  mixed crystal systems in their thermal behaviour will come to the fore only when the data on these properties is available. For this to happen the experiments underway for the study of  $Ba_xPb_{1-x}(NO_3)_2$  system in this laboratory should be completed.

### IV. CONCLUSIONS

A detailed X-ray study of  $Pb_xSr_{1-x}(NO_3)_2$  mixed crystal system is carried out. Lattice constants, mean Debye Waller factors and Debye temperatures are determined. Their composition dependence is established and discussed in terms of the degree of disorder in the distribution of metal ions in the lattice and compared with that in the case of alkali halide mixed crystal systems. In the present mixed crystal system, the lattice constants followed Vegard's law, mean Debye Waller factors varied nonlinearly with positive deviations from linearity and Debye temperatures varied nonlinearly with negative deviations from linearity.

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