The study of the distortion of F- and Ba- sublattices in superionic BaF_2 at elevated temperatures using positron annihilation technique

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Abstract. There is a general misunderstanding regarding the creation of Frenkel pairs in the vicinity of the observed critical temperature T_c in superionic materials. The measured conductivity increases sharply at a temperature coinciding with the deviation of temperature-dependent lattice constant from 6.2086 A. Frenkel pairs responsible for superionic conduction are gradually generated well below the critical temperature and this is informed by the calculation of S-parameter through the measurements of Doppler Broadening at various temperature points. It is interesting to note that the lattice constant plays a pivotal role in the superionic conductivity threshold. Positron annihilation spectroscopy, through the determination of positron lifetime and Doppler broadening, reveals that the generation rate of Frenkel pairs becomes prominent at 113 K below the critical temperature of 693 K. The average lifetime component at 693 K is found to be 267.7 ps with intensity of 62.3 %. This is also a clear indication of continuous disordering of fluorine sublattice noticeable at a temperature of 580 K. The fact that the defect or the second positron lifetime is constant in the temperature range (300 – 900) K confirms a non-distortion of Ba-sublattice.

1. Introduction

Flourites including BaF_2 are class-II ionics in which the transition to a highly ionic conducting material is not accompanied by any structural change in the crystal lattice but associated with anomaly in the heat capacity. The diffuse transition temperature T_d is associated with the temperature well below the melting point at which a peak in the heat capacity occurs [1, 2] and at which negative deviation from the Arrhenius behaviour occurs [3, 4].

Positrons upon entering a sample can have several states associated with different kinds of defects each of which gives a characteristic lifetime. The positron lifetime spectrum is thus the sum of exponential decay components given by

$$-\frac{\mathrm{d}n(t)}{\mathrm{d}t} = \sum_i I_i \lambda_i \mathrm{e}^{-\lambda_i t} \qquad (1)$$

where I_i are relative intensities, $n(t)$ is the probability that a positron is still alive at time t after its emission from the source and λ_i are the annihilation rates at various positron states. Doppler broadening of the annihilation line shape, characterized by the S-parameter, which is defined as the area under the central part of the annihilation photo-peak divided by the total area [5], is a measure of the electron momentum at the annihilation site. If the vacancy charge is positive, and is the only defect-type, we would be observing Frenkel pairs rather than Schottky defects since only one type of interstitials are formed.

The objective of the present work is to determine the temperature value at which interstitials responsible for superionic conductivity, specifically for BaF_2 crystal, are created and to investigate the distortion of both F- and Ba- sublattices in the temperature range. .

2. Experiment

The positron source, with activity of 10.5 μCi, was achieved by evaporating a few drops of sodium solution on a thin (7 μm) nickel foil. The salt was then covered by another identical nickel foil. The foiled source was then sandwiched between two identical silicon BaF_2 crystals (each of size 10×8×2 mm). Two high purity Germanium (HPGe) detectors with energy resolution of 1.2 keV (FWHM) at 511 keV were used to obtain Doppler Broadening profiles of the annihilation radiation. The samples were annealed at different selected temperature points up to 400 K.

The lifetime measurement was carried out using standard coincidence setup by employing two fast scintillator detectors (XP2020) for the start (1275 keV) and stop (511 keV) signals. Samples were kept under the pressure of 10^{-5} Torr. The time resolution of the positron lifetime coincidence-setup used for the measurements was of the order of 220 ps at FWHM. The 1.27 MeV gamma should not exhibit any broadening, see figure 1, since it is not associated with annihilation but with the birth of a positron during a β^+-decay of ^{22}Na into ^{22}Ne. The peak position of 1.27 MeV should be used as a measure of how stable the electronics as shown in figure 2.

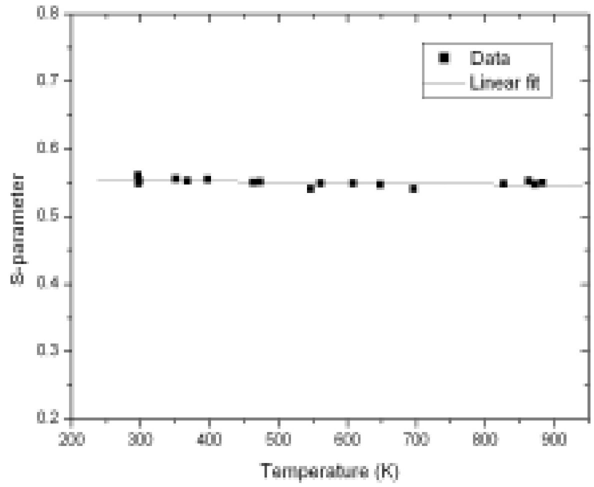

Figure 1. S-parameter of the 1.27 MeV at different temperature points does not exhibit any Doppler broadening variation

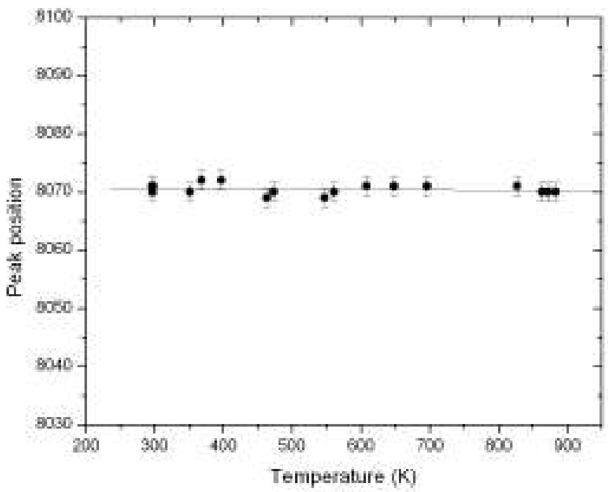

Figure 2. The measured peak positions of 1.27 MeV gamma at various temperature points indicate the stability of the electronics used

The positron annihilation spectra (5×10^5) were accumulated over a temperature range from 300 K to 900 K. The vacancy-type defects act as trapping sites for positrons, and annihilation with low energy valence electrons at these defects results in a narrowing of the photopeak corresponding to an increase in the S-parameter. Since a fraction of positrons, up to (10 – 15) %, annihilate in the source material and source-sample interfaces (foils), it is crucial to subtract these additional lifetime components from the lifetime spectrum. Nickel foil has a lifetime component of 180 ps and the salt NaCl crystal introduces a lifetime of 450 ps. For the foil intensities, the Bertolucci-Zappa empirical formula [6]

$$I_{foil}(\%) = k = 0.324Z^{0.93} \times S^{3.45 \times Z^{-0.4}} \tag{2}$$

was utilized to obtain reliable values of lifetimes and intensities in a sample, where Z is the average atomic number of the sample and S the surface density of the foil (thickness of the foil × density of the foil) in mg cm^{-2}.

3. Results and discussion

The central parameter S is defined as the ratio of the counts in the central region of the annihilation line to the total number of counts under the annihilation curve. From figure 3, it is clear that although there is no appreciable increase in S-parameter from room temperature to about 598 K ($\sim\Delta S = 0.001$) there is a sharp increase of thermal vacancies between 598 K to 877 K ($\sim\Delta S = 0.024$) but a defect lifetime component from room temperature to 700 K, shown in figure 4, remains constant indicating that only positive defects, which are not visible to probing positrons, are created. If negative Barium vacancies were created, a non constant defect lifetime components at various temperature points would have been observed.

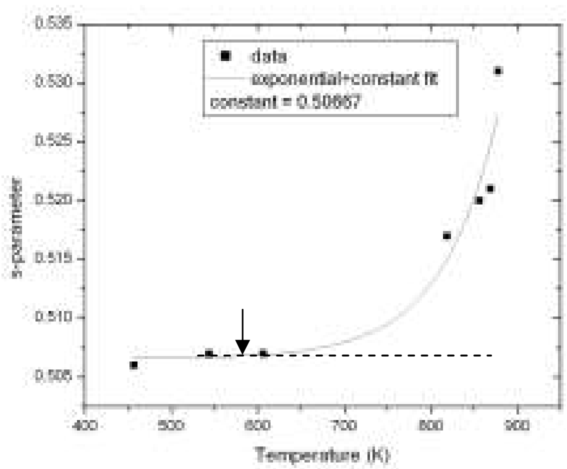

Figure 3. S-parameter versus temperature indicates that the generation of Frenkel defects responsible for superionic region commence earlier at about 580 K

Defect positron lifetime, see figure 4, confirms the non-distortion of Ba sublattice. If Ba++ ions were created, positrons should have been trapped in negative vacancies but, as shown in figure 4, no Ba vacancies were observed in the temperature range.

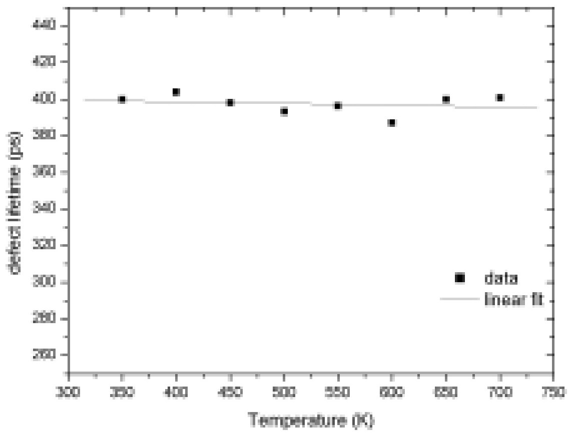

Figure 4. Second positron lifetime component confirms the non-distortion of Ba-sublattice over a temperature range.

The S-parameter and the behaviour of superionic current at different temperatures confirms that although F- sublattice distorts, superionic current, mainly due to high mobility of F^- ions, cannot be established until an appreciable increase of lattice constant reaches at least a threshold value. The linear expansion of the lattice constant *a* reported in [7] is given by

$$a = 6.20[1 + (T - T_m) \times 2.5 \times 10^{-5} / K] \overset{o}{A} \qquad (3)$$

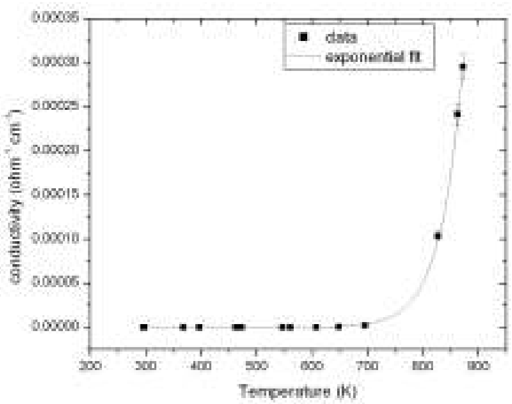

Figure 5. Measured conductivity as a function of temperature. Conductivity enters superionic region at about 693 K.

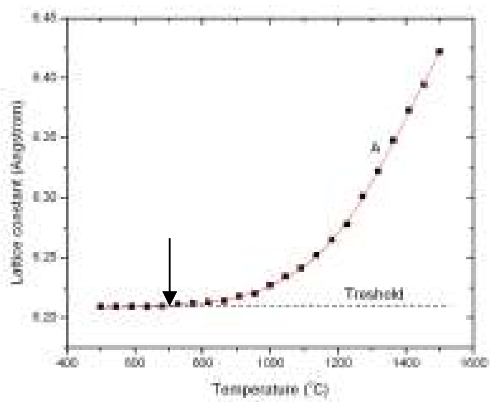

Figure 6. The dependence of the lattice constant BaF_2 on temperature. curve A from [8].

The s-parameter threshold at threshold temperature of 580 K, shown in figure 3, indicates Frenkel defects are generated earlier than the conductivity when current enters superionic region. The threshold temperature (693 K) at which the ionic current enters superionic region, see figure 5, is observed to agree very well with the temperature at which the threshold lattice constant begins to increase beyond 6.20566 Å as shown in figure 6.

4. Conclusion

Positron annihilation lifetime measurement reveals the existence of the distortion of F-sublattice in the temperature range (300 K – 900 K) and that Ba-sublattice stays intact for this temperature range. ΔS in the range (300 – 600) K represents only 4 % of the total change in S-parameter which suggests a non drastic variation in defect creation. In the temperature range from 600 K to 900 K, the 96 % change in S-parameter is a clear indication of the enhanced interstitial space as indicated by both lattice constant curve and conductivity curve in the temperature range from 600 K to 900 K. Since positron lifetime annihilation technique has the capability of detecting point to large defects, the creation of defects in BaF_2 starts at a temperature well below the transition temperature, T_c.(693 K). At the transition temperature, T_c, the generation of defects responsible for superionic region becomes prominent mainly due to the variation of lattice constant with respect to temperature. Therefore a conclusion can be made that defects responsible for superionic conduction are created well below a transitional temperature, T_c.

5. References

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