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Innovation The Research Concept

Curie-Temperature variation in Perovskite $SrTiO_3$ containing Pb as Substitutional Impurities

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Abstract

Substitutional impurity Pb dependent Curie-temperature in anharmonic $Pb_xSr_{1-x}TiO_3$ perovskite crystal has been calculated. Double time-thermal Green functions, Fourier-transform and Dyson's equation treatment is used. Change in Curie-temperature occurs due to impurity content lead in the crystal.

Keywords: Curie-temperature retarded Green function, Fourier-transforms, Dyson's equation and Hamiltonian.
PACS: 77.80 Bh

Introduction

Perovskites have been studied extensively not only due to the versatile nature of their structure but more importantly due to their multifunctional properties [1-4]. These exhibit magnetic, dielectric, high temperature super conducting piezoelectric and ferroelectric properties.

$Pb_xSr_{1-x}TiO_3$ crystal belongs to ferroelectric material of (A'A"BO_3 type). Both constituents. $PbTiO_3$ (PT) and $SrTiO_3$(ST) are ferroelectrics. It is well known that there are interesting temperature-dependent properties of perovskites which results from soft mode. Curie-temperature and microwave losses are also affected by substitutional impurities (defects). $SrTiO_3$ is a para electric above 37K. Lead Titanate is a ferroelectric material having a cubic structure with a highCurie-temperature 490°C(763 K). T_c is one of the parameters which is very sensitive to defect concentration [5].

It is easy to control the physical properties like Curie-temperature of the PST ($Pb_xSr_{1-x}TiO_3$) by adjusting [Pb/Sr] ratio. Pure ST is intrinsic quantum para electric.It is known that permittivity peaks (anomalous behavior) can be induced in Strontium Titanate by introducing substitutional impurities into the lattice.

Aim of the Study

This work is aimed at the determination of influence of the ferroelectric components PT and ST on Curie-temperature.

$Pb_xSr_{1-x}TiO_3$ (PST) which is to adopt ABO_3 type solid solution, is a continuous solid solution of $PbTiO_3$ (PT) and $SrTiO_3$ (ST). Over the whole concentration range x = 0 to 1.0, the properties of $Ba_xSr_{1-x}TiO_3$ are known to depend dramatically on composition [6-8].

In the present paper, an expression for the Shift in Curie-temperature in $Pb_xSr_{1-x}TiO_3$ perovskite crystal is summarized using our earlier paper [8] where modified model Hamiltonian (in presence of anharmonicity,defect, mass and force constant changes are taken into account) considering Dyson's equation treatment and Green function method is used. The variation of Curie-temperature (T_c) with impurity concentration (x) of Pb in pure $SrTiO_3$ crystal has been theoretically studied and results are compared.

Theory

Using our previous reference [8], the modified Hamiltonian of a mixed perovskite is given by

$$H'=H + H_D. \quad \ldots\ldots\ldots \quad (1)$$

Here, H and H_D are same as in reference [8]. Equation (10) of this reference leads to soft mode frequency as

$$v^2(\omega)= - (\omega_0^0)^2+Y_1T+ Y_2T^2+\Delta(v_D^2(\omega)) \quad \ldots\ldots\ldots\ldots \quad (2)$$

Here $\Delta(v_D^2(\omega))$ is temperature independent part due to substitution(defect). Y_1 and Y_2 are the temperature dependent part in $v^2(\omega)$

and depend on anharmonic force constant and electric dipole moment terms. Equation (2) can be reduced to

$$v^2(\omega) = Y_1(T-T_c'+\xi T^2) \quad \ldots\ldots\ldots\ldots (3)$$

Where $T_c'=-(\omega_0^0)^2/ Y_1+ \Delta(v_D^2(\omega))/ Y_1$ and $\xi = Y_2/ Y_1$ (non linearity constant)and for ST, ξ is negligible [8].

$$\text{So, } v^2(\omega)= Y_1 (T-T_c'). \quad \ldots\ldots\ldots\ldots\ldots (4)$$

Here $T_c'= T_c + \Delta(T_c)$ is the new Curie-temperature in presence of defect impurity.

$$\text{Hence, } \Delta(T_c)=- \Delta(v_D^2(\omega))/ Y_1. \quad \ldots\ldots\ldots\ldots (5)$$

Thus T_c is one of the parameters which is very sensitive to impurity (x). The above results show that T_c varies linearly with x.

Hence, for PST, the result is approximated as

$$x=a[T_c(x)-37], \quad \ldots\ldots\ldots\ldots (6)$$

where a is constant and it is determined by interpolating the values of $(T_c)_{PT}$ and $(T_c)_{ST}$ from the references[2,5] and comes out to be as $a=1.37741 \times 10^{-3}K^{-1}$

Calculation of Curie-temperature

Using equation (4),Curie-temperature is calculated and summarized in Table 1 and drawn in Fig.(1).

Table 1: Defect concentration with Curie-Temperature

Defect concentration (x)	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Curie-temperature (T_c)(K)	37.0	109.6	182.2	254.8	327.0	400.0	472.6	545.2	617.1	690.4	763.0

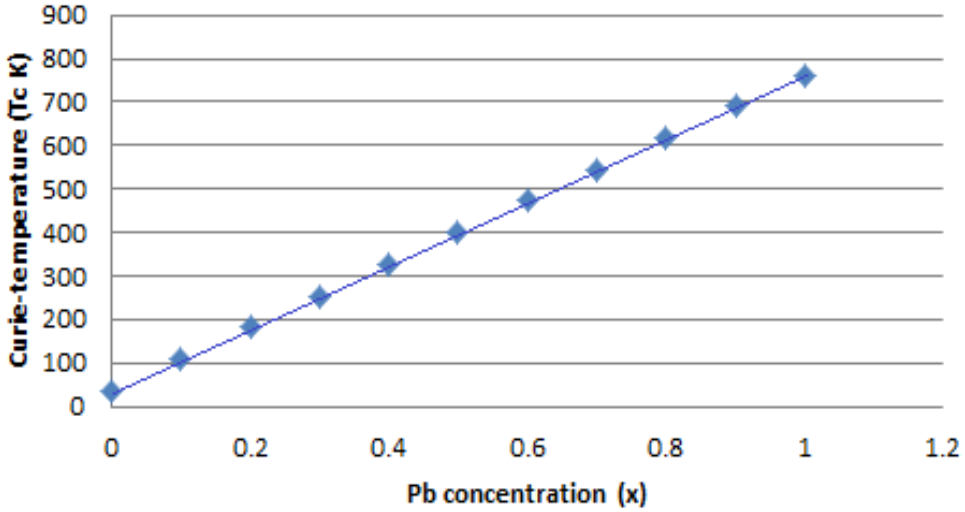

Fig. (1): Curie-temperature vs concentration

Equation (5) shows that the change in Curie-temperature depends on substitutional impurity.

$\Delta(v_D^2(\omega))$ (temperature independent part due to defect) and Y_1(anharmonic coupling constant) and hence ΔT_c is a function of mass change due to defect and anharmonic constants. Here, influence of defects on dipole moment coefficient is neglected. So change in T_c cannot be explained without anharmonicity in perovskite crystals. The calculated results are in good agreement with the experimental results available [9].

Discussion

Our theoretical results show that the Curie-temperature changes due to the presence of defects in anharmonic ferroelectric crystal. Anharmonicity is also necessary in these crystals to observe the Curie-temperature change. ΔT_c caused by an impurity [8] depends on the change in the harmonic force constants between the impurity and host lattice atoms and mass change due to impurity and can be negative or positive.

Our results are in quantitative agreement with the experimental results available elsewhere.

Conclusion

It is easy to control the dielectric properties of PST by adjusting [Pb/Sr] ratio.T_c increases with Pb concentration. The Curie-point varies nearly from 37K to 763K for x= 0. 0to x = 1.0. We have discussed here the impurity dependence of ΔT_c of anharmonic perovskite crystal in a qualitative way. T_c decreases with [Pb/Sr] ratio.The T_c in ST increases approximately 7.26K for each 1% increase in Pb concentration.

References

1. *Deorani S.C., Naithani U.C. andSemwal B.S., "Ultrasonic investigation in $KTaO_3$." Pramana J. Phys. 1990, 35, 181-186.*
2. *Deorani S.C., Naithani U.C.,Semwal B.S., "Microwave losses in ABO_3 type perovskites."Pramna J. Phys. 1990, 35, 361-369.*
3. *Deorani S.C., Naithani U.C.,Semwal B.S.,"Ultrasonic attenuation in $SrTiO_3$ perovskite above the phase transition." Int.J. Phys. Chem. Solids1990, 51, 1277-1280.*
4. *Deorani S.C., Naithani U.C.,Semwal B.S., "Dielectric behavior of ABO_3 type ferroelectric*

perovskites." Indian J. Pure Appl. Phys. 1991, 29, 143-149.

5. *Subramanyam S., "Nucleation of the ferroelectric phase in $Pb_xSr_{1-x}TiO_3$ system."Acta Materials, 1998, 46, 817-822.*
6. *Jeon J., "Effect of $SrTiO_3$ concentration and sintering temperature on micro structure and dielectric constant of $Ba_{1-x}Sr_xTiO_3$." J. Eur. Ceram. Soc. 2004, 24(6), 1045-1048.*
7. *Zhou L.,Vilarinho PM,Baptista J.L., "Dependence of the structural and dielectric properties of $Ba_{1-x}Sr_xTiO_3$ ceramic solid solutions on raw material processing." J. Eur. Ceram. Soc., 1999, 19(11), 2015-2020.*
8. *Yadav M.S. and Deorani S.C., "Composition dependence of soft mode in $Ba_xSr_{1-x}TiO_3$ ferroelectric mixed crystal." Indian J. Theor. Phys.,2010, 58, 179-191.*
9. *Landolt – Born Stein's numerical data and functional relationship in science and technology, ed. T. Mitsui,Springer – Verlag, New York, series III 1998.*