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A COMPARATIVE STUDY ON LATTICE DYNAMICS AND SPECIFIC HEAT OF ANTIFLUORITE SUPERIONIC OXIDES Li_2O, Na_2O and K_2O

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Abstract

Superionic oxideslike Li_2O, Na_2O and K_2O are the materials of technological interest, exhibits high ionic conductivity while in solid condition and belongs to the class of fast ion conduction, which allow macroscopic movement of ions through their structure. These superionic conductors find several technological applications. These applications range from miniature light weight high power density lithium ion batteries for heart pacemakers, mobile phones, laptops computers, etc. to high capacity energy storage devices for next generation. Therefore knowledge of the thermal properties of these materials is most significant. Hence in the present study we have studied phonon dispersion relation, phonon density of states and specific heat of Li_2O, Na_2O and K_2O in antifluorite structure by applying lattice dynamical theoretical model. The calculated results are interpreted with existing experimental or theoretical results.

Introduction

Lithium oxide (Li_2O) with its high tritium breeding potential is an attractive candidate fordeuterium–tritium fusion reactors as blanket breeding material [1] and as a lithium ion conductor (solid electrolyte) in solid state batteries [2]. Li_2O exhibits high ionic conductivity while in solid condition and belongs to the class of superionics, which allow macroscopic movement of ions through their structure. This behavior is characterized by the rapid diffusion of a significant fraction of one of the constituent species within an essentially rigid framework formed by the other species. At ambient pressure Li_2O becomes superionic at temperature above 1350 K [3] prior to melting at 1705 K [4]. In the superionic phase, oxygen ion constitutes a rigid framework while lithium ions move from one tetrahedral site to another via octahedral interstitial sites [5, 6]. Technological applications of this material range from miniature light weight high power density lithium ion batteries to high capacity energy storage devices for next generation 'clean' electric vehicles[7]. Other materials of this nature are Na_2O and K_2O, both belongs to the family of superionic conductors, and having similar technological applications. Even then these two materials are rarely studied in literature, may be because of their material formation.Understanding the behavior of Li_2O along with Na_2O and K_2O is, therefore, very useful for its applications as well as a potential aid in understanding the behavior of the hot, dense ice structures which are of such great importance to planetary science, geosciences, and fundamental chemistry [8].Li_2O, Na_2O and K_2O crystallizes in the anti-fluorite structure with a face-centered cubic lattice and belongs to the Fm3m space group [5, 6], lithium, sodium or potassium being in the tetrahedral coordination and oxygen ions arranged in FCC sublattice.

Calculation method

In the present investigation Modified rigid ion model (MRIM) has been used. The MRIM consists of long range electrostatics and short range interactions. The electronic contribution is derived along the line of Kellerman [9]. The electrostatic contribution incorporates an effective charge to include the effect of the polarization which is determined using the Lyddane-Sache-Teller (LST) relation [10]. The short range contribution to the dynamical matrix is derived by using de Launey type angular forces (DAF) [11]. In DAF model, the relative displacement of the reference atom and one of the neighbors is considered. The restoring force on the reference atom is taken to be proportional to the component of the relative displacement perpendicular to the line joining the two atoms at their equilibrium positions. The forces due to all neighbors are calculated separately and summed up together. Different force constants are used for the various categories of neighbors and the net force on the reference atom is obtained by summing over the contribution from all the neighbors. The present calculation involves three central force constants α_1, α_2, α_3, and two angular force constants $\alpha'_1$and α'_2 between O-M_1,M_1-M_2, and M_1- M_1, atoms respectively up to third nearest neighbor (M=Li, Na, K).Since the angular forces are small, they are being accounted for upto two neighbors only. The dynamical matrix of (9X9), thus established is solved at the centre of the Brillouin zone (ZC). The long-wavelength limit method has been used to establish the analytical relation between the force constants and the elastic constants. The expressions for the phonon frequencies at zone centre and the relation between elastic and force constants thus obtained are given as follow.

$$4/3\ (\alpha_1 + 2\alpha_1') + 4.19\ (Z^2e^2/v_a\varepsilon_\infty) = [m_1m_2 / (m_1 + 2m_2)]\ \omega_{LO}^2 (1)$$
$$4/3\ (\alpha_1 + 2\alpha_1') + 2.095\ (Z^2e^2/v_a\varepsilon_\infty) = [m_1m_2 / (m_1 + 2m_2)]\ \omega_{TO}^2 (2)$$
$$4/3\ (\alpha_1 + 2\alpha_1') + 4(\alpha_2 + 2\alpha_2') = m_2\omega_R^2 (3)$$
$$2aC_{11} = 4/3\ (\alpha_1 + 2\alpha_1') + 4\alpha_2 + 12\alpha_3 + 3.0512\ (Z^2e^2/v_a\varepsilon_\infty) (4)$$
$$2aC_{12} = 4/3\ (\alpha_1 - 4\alpha_1') - 4\alpha_2' + 6\alpha_3 - 5.4046\ (Z^2e^2/v_a\varepsilon_\infty)\ (5)$$
$$2aC_{44} = 4/3\ (\alpha_1 + 2\alpha_1') + 4\alpha_2' + 6\alpha_3 - 1.5256\ (Z^2e^2/v_a\varepsilon_\infty) - [\{4/3\ (\alpha_1 - \alpha_1') - 5.02884\ (Z^2e^2/v_a\varepsilon_\infty)\}^2 / 4/3(\alpha_1 + 2\alpha_1') + 4(\alpha_2 + \alpha_2')]\ \ (6)$$

where v_a is the volume of unit cell (a^2 /4), ε_∞ is the high frequency dielectric constantand –Ze is the charge on oxygen atom and Ze/2 is charge on the metal ion,$m_1$is the mass of oxygen ions and 'm_2' the mass of metal ions Li, Na or K. '$\boldsymbol{\omega}_{LO}$'and '$\boldsymbol{\omega}_{TO}$' represent the infrared optical frequencies whereas '$\boldsymbol{\omega}_R$' is the Raman active mode at the zone centre.The five force constants (α_1, α_2, α_3, α_1', α_2') are calculated by using three elastic constants and three zone centre frequencies.The values of lattice parameters, ZC phonons and Elastic constants from the available results ofNa_2O and K_2O, given in Table 1 are used as input to the above equations, and hence the central and angular force constants thus calculated are listed in table 2

Taking these force constants as input parameters, the dynamical matrix is solvedat the zone center (ZC) as well as along three symmetric directions [k00], [kk0]and [kkk]. The calculated PDC of Na_2O and K_2O with Columbine interactions are given in figure 1 and in figure 2.The phonon dispersion relation for Li_2O is published as Sinha et al. [12], andthe phonon dispersion relations obtained in three symmetric directions for Na_2OandK_2O, without Columbine interaction arepublished as Sinha et al. [13].

The frequency distribution function g(ν) of the normal modes of vibration of a solid is a key property from which specific heat of M_2O (Li, Na, K) have been calculated. We have calculated the phonon density of states (PDOS) of these compounds by applying a sampling method. In the sampling method, one solves for the eigenvalue of the dynamical matrix at the maximum possible number of points that form a mesh in the irreducible section of the first BZ of the reciprocal lattice. A sorting of different frequencies, with proper weighing factors, leads to the evaluation of g(ν). The calculated phonon densities of states (PDOS) are shown in figures3, 4 and 5.

The specific heat at constant volume has been calculated fromthe vibrational spectra at various temperatures by adopting Blackman's techniques. According to Blackman, the specific heat Cv is given by

$$C_v = k \int_0^\infty \frac{x^2e^x}{(e^x - 1)^2} g(\nu)d\nu \ (7)$$

Herex = hν/kT, h being the Planck's constant and 'k' is Boltzmann's constant.Knowing the frequency spectrum the value of Cv can be calculated.

In the present work the frequency spectrum is obtained in terms of 48 different frequency intervals and therefore the above equation (7) reduces to

$$C_v = \sum_1^{48} \frac{Cv(\nu)g(\nu)}{9000} \ (8)$$

Here Cv(ν) is specific heat for the system assuming all the atoms vibrate with constant frequency ν.The value of Cv corresponding to each (hν/kT) is presently determined by applying Einstein's quantum theory of specific heat. According to Einstein, the average energy of an oscillator vibrating with frequency ν is given by hν/ (e^x -1). Accordingly the energy of a gram atom of the solid consisting of Natoms is U = 3N hν/ (e^x -1). We have then,

$$Cv(\nu) = \frac{dU}{dT} = 3R \frac{x^2e^x}{(e^x - 1)^2} \ (9)$$

Using expression (9) the value of Cv(ν) for various x values are calculated. The specific heats are calculatedfor various temperatures ranging from 10K to 330K and are shown in figure 6.

Results and discussion

Table 2 presents the calculated inter-atomic force constants of Na_2O and K_2O with Columbine interactions. The strongest force constant is α_1, (between metal ion and oxygen) followed by α_2 (between two different metal ions). The larger force constant corresponds to stronger bond give rise to larger value of frequency. Similar result for strong force constant had been reported for Li_2O [12]. Further the strength of the stronger force constant decreases from Li_2O to K_2O. Which is may be because of the increase in atomic mass and size from Li to K. one of the central force constant α_1 between (O-Na_1), and α_2 between (K_1-K_1) is negative. The negative force constant corresponds to motion along modes that lead to energy lowering.

Table 3 presents the calculated and other results for ZC frequencies for Na_2O and K_2O. In case of K_2O, to the best of our knowledge, we had not found T_{1u}(LO) mode in literature, so for the calculation of longitudinal optical zone centre frequency of K_2O the effective charge have been consider to be same as that of Na_2O, because of the same nature of Na and K. Hence, calculated value of the T_{1u} (LO) mode for K_2O at zone centre has been

proposed in this work. It has been found that calculated ZC phonon frequencies are in very good agreement with other results.

The phonon dispersion relations of Na_2O and K_2O calculated along symmetry directions [k00], [kk0] and [kkk] in the Brillouin zone and are shown in figure 1 and figure 2. In these phonon dispersion relations the zone centre phonon of Thompson et al. [15], for Na_2O and zone centre phonon of Dovesi et al. [16] for K_2O have been shown for comparison. The antifluorite Na_2O and K_2O have three atoms per unit cell, so it is obvious to have nine phonon modes for Na_2O and K_2O. In figure 1 and figure 2 at [k00] and [kkk], these phonons are degenerate. At Γpoint theses nine branches are in three fold degeneracy, which is result of LO-TO splitting. This degeneracy is completely removed at[kk0]. Hence, all nine phonon are localized at [kk0]. The set of phonon frequencies at lower value is formed three acoustical branches, which are infrared active. Out of other three set of phonon frequencies, one is infrared active longitudinal optical (at 453.4 cm^{-1} for Na_2O and at 348.2 cm^{-1} for K_2O), and rest two are transverse optical. One of the transverse optical frequencies is infrared, where as the other transverse optical frequency is Raman active. In both the cases the longitudinal optical phonon frequency shows sudden change in [kk0]. The present calculations of eigenvector corresponding to eigen frequencies along the three symmetry direction, it is found that both metal ions and oxygen ions contribute in the entire Brillouin zone. The PDC of Na_2O is found to be in agreement with results of Thompson et al. [15]. It is also observed that metal ions placed at tetrahedral positions are the mobile ions, while the oxygen ions of FCC sub lattice are cage ion. So the superionicity of M $_2$O (M=Li, Na, K) is the result of mobile metal ions of tetrahedral positions. This result for Li_2O is in agreement with Gupta et al.[18].

Figure 3 gives the phonon density of the state for Li_2O, figure 4 is the phonon density of the state for Na_2O and figure 5 is the phonon density of the state for K_2O. The calculations of phonon density of state have been carried out without the splitting of longitudinal and transverse optical phonons. The plot of phonon density of state for Li_2O shows five sharp peaks, along with three small peaks. The complete density of state spans the entire frequency region, the density of state centered around 400 cm^{-1} is sharpens. In the low frequency region the peaks are comparatively small. The peaks below 350 cm^{-1} are the result of longitudinal and transverse acoustical phonon frequencies and the peaks well above 350 cm^{-1} are because of longitudinal and transverse optical phonon frequencies. The plot of phonon density of state for Na_2O andK_2O shows three sharp peaks. For Na_2O the peaks below 300 cm^{-1} are the result of longitudinal and transverse acoustical phonon frequencies and the peaks well above 300 cm^{-1} are because of longitudinal and transverse acoustical phonon frequencies are just below the 225 cm^{-1} and the peaks well above 225 cm^{-1} are the results of longitudinal and transverse optical phonon frequencies. The phonon density of state of Li_2O, Na_2O and K_2O show that phonon in superionic conductors are sensitive to the metal ion atomic radius. There is shift of peak positions and change in their shapes on increasing radius from lithium ion to potassium ion. The numbers of peaks are found to be more in case of Li_2O as comparison to Na_2O and K_2O. Further the sharpen peak shifted towards higher frequencies from Li_2O to K_2O respectively.

The calculated specific heat of M_2O (M= Li, Na, K) are shown in figure 6. The obtained specific heat curve of Li_2O is found to be similar to other available results [17, 18]. To our knowledge, there are no experimental measurements of the specific heat at constant volume for Na_2O and K_2O. Therefore critical comparison could not be made. On comparison the specific heat curve of Li_2O, Na_2O and K_2O, a very small increase is observed in the value of specific heat at constant volume with temperature. The value of specific heat is maximum for K_2O and minimum for Li_2O at each value of temperature. The nature of specific heat curve for these superionic conductors beyond 300K satisfies the well known relation C_v= 3R.

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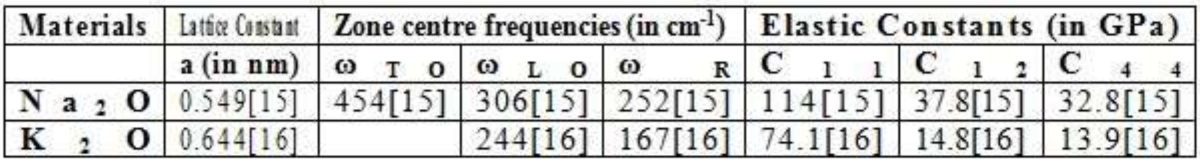
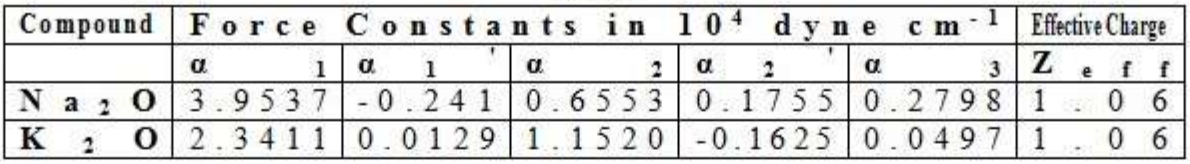
Table 1



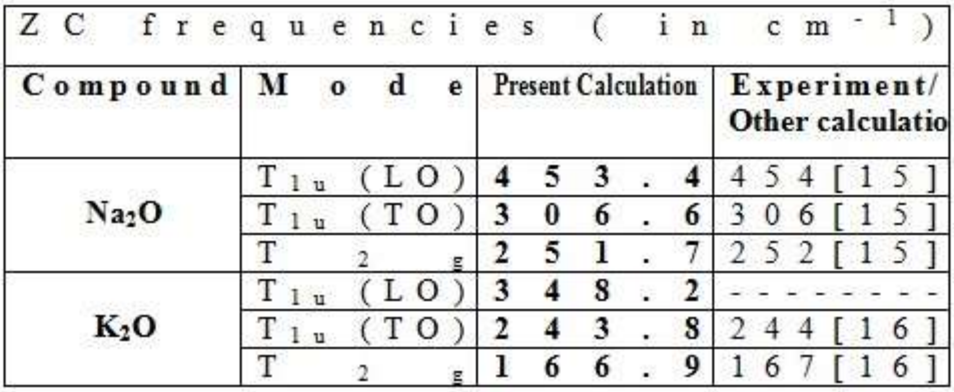
Materials	Lattice Constant	Zone centre frequencies (in cm^{-1})			Elastic Constants (in GPa)		
	a (in nm)	ω_{TO}	ω_{LO}	ω_R	C_{11}	C_{12}	C_{44}
Na_2O	0.549[15]	454[15]	306[15]	252[15]	114[15]	37.8[15]	32.8[15]
K_2O	0.644[16]		244[16]	167[16]	74.1[16]	14.8[16]	13.9[16]

Table 2:



Compound	Force Constants in 10^4 dyne cm^{-1}					Effective Charge
	α_1	α_1'	α_2	α_2'	α_3	Z_{eff}
Na_2O	3.9537	-0.241	0.6553	0.1755	0.2798	1.06
K_2O	2.3411	0.0129	1.1520	-0.1625	0.0497	1.06

Table 3



ZC frequencies (in cm^{-1})			
Compound	Mode	Present Calculation	Experiment/ Other calculatio
Na_2O	T_{1u} (LO)	453.4	454[15]
	T_{1u} (TO)	306.6	306[15]
	T_{2g}	251.7	252[15]
K_2O	T_{1u} (LO)	348.2	--------
	T_{1u} (TO)	243.8	244[16]
	T_{2g}	166.9	167[16]

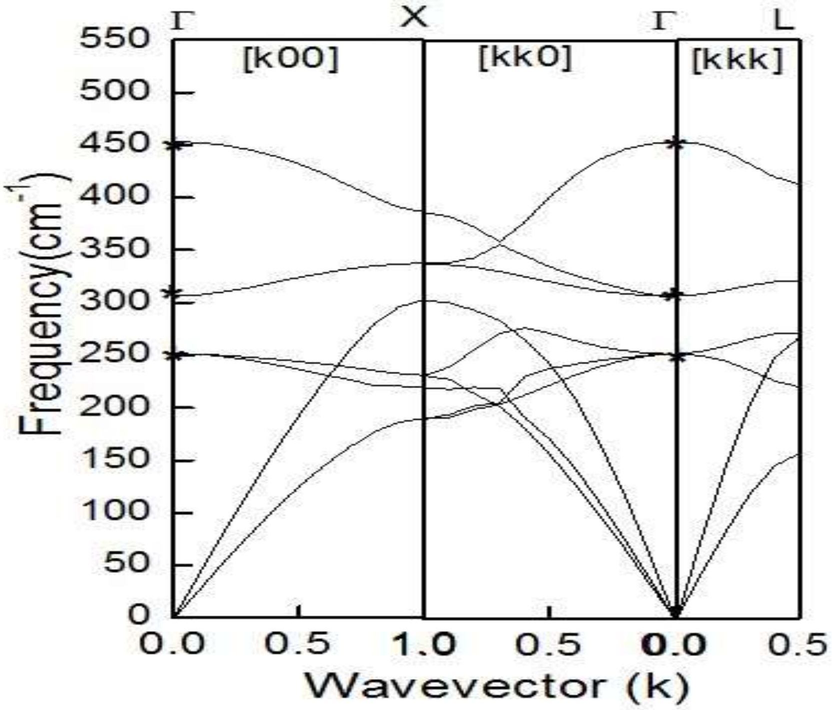


Fig. 1 Phonon dispersion curve of Na_2O

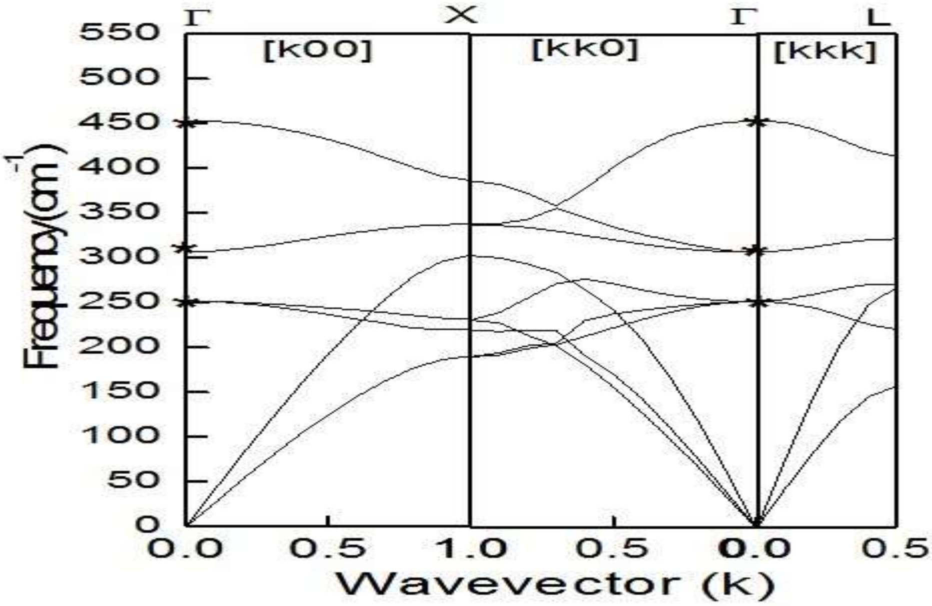


Fig. 2 Phonon dispersion curve ofK_2O

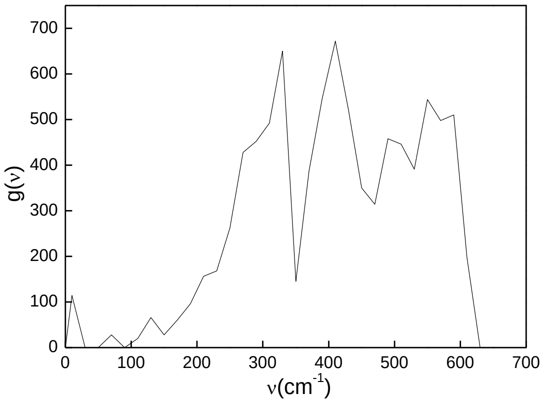


Fig.3 Phonon density of state of Li_2O

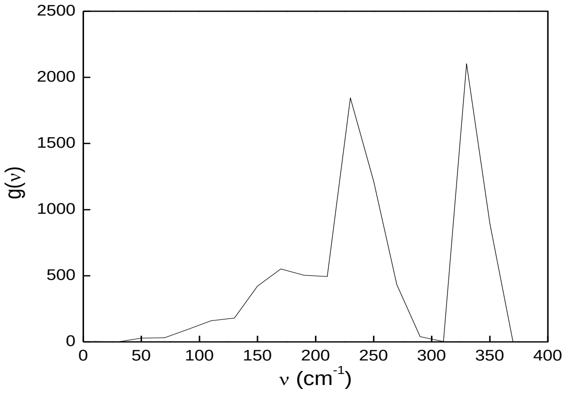


Fig.4 Phonon density of state of Na_2O

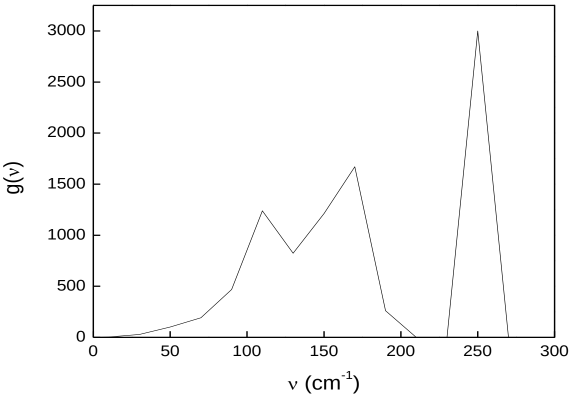


Fig.5 Phonon density of state of K_2O

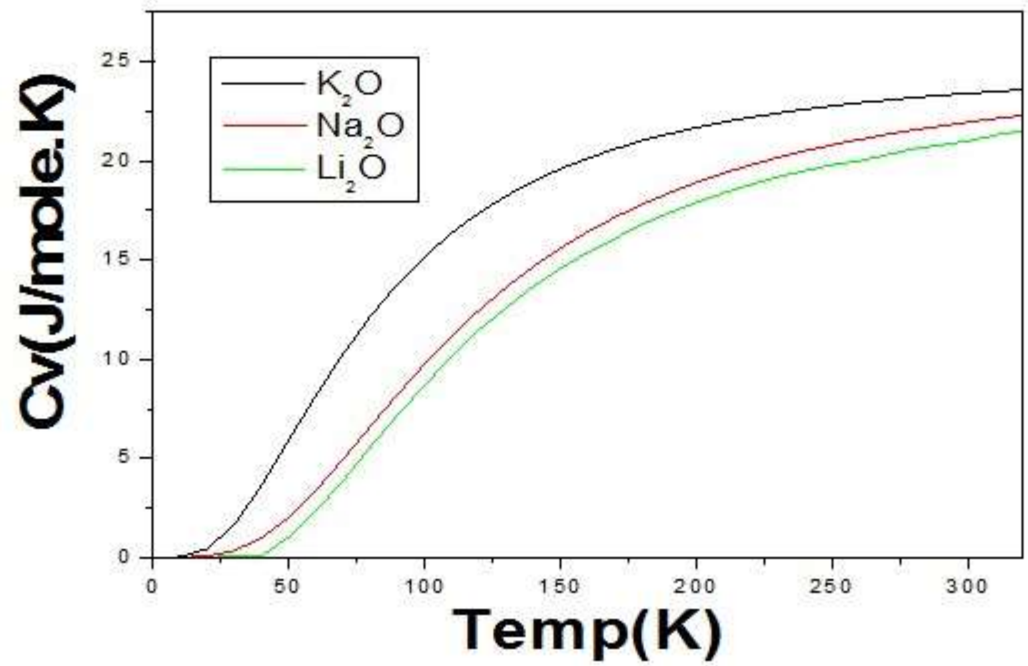


Fig.6 Specific heat curve ofM_2O(M = Li, Na, K)