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Search for a novel zero thermal expansion material: dilatometry of the AgI-CuI system

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AgI is a well-known superionic conductor possessing a negative thermal expansion (NTE) coefficient while CuI is a *p*-type semiconductor possessing a positive thermal expansion coefficient. Pellets of X-Ray Diffraction (XRD) characterized compositions in the AgI–CuI system namely, β AgI, γ AgI, $Ag_{0.5}Cu_{0.5}I$, $Ag_{0.25}Cu_{0.75}I$, $Ag_{0.10}Cu_{0.90}I$, $Ag_{0.05}Cu_{0.95}I$ and γ CuI have been examined by quartz pushrod dilatometry measurements in order to look for a zero thermal expansion material. It is found that the systematic displacement of Ag by Cu gradually reduces the NTE anomaly in AgI. The composition $Ag_{0.25}Cu_{0.75}I$ apparently exhibits near-zero thermal expansion. The results are discussed qualitatively in terms of relevant models.

1. Introduction

Among the unusual and interesting properties of silver iodide is the occurrence of anomalous thermal expansion characteristic of marginally covalent compounds. Over an extended temperature range (-180 to $+150\,^{\circ}$C) the coefficient of linear thermal expansion of both wurtzite (β) and zincblende (γ) phases of AgI is fairly constant and negative (negative thermal expansion or NTE) [1–3]. At the W/ZB to bcc structural phase transition to the superionic conducting bcc or α-phase with a disordered Ag^{+} sublattice (around 147 °C) a sharp and deep anomaly finally settling to the pretransition state of NTE. By contrast CuI which has a stronger covalent bond associated with the tetrahedral CuI_4 building unit shows phase transitions at much higher temperatures (around 369 and 417 °C) to the unstable pseudo-wurtzite and the more cation-disordered zincblende superionic phases respectively but possesses a positive thermal expansion and a PTE anomaly.

Thus the thermal expansion $(\alpha) = [\Delta L/(L\Delta T)]\ K^{-1}$. For $(\Delta L/L) > 0$ one has positive thermal expansion as in CuI while $(\Delta L/L) < 0$ for negative thermal expansion as in AgI.

These simple criteria offer an alluring prospect of looking for a zero thermal expansion (ZTE) material in the AgI-CuI system with potential for sensor/battery applications. The present paper focuses on the systematic dilatometric measurements on solid solutions in the mixed iodide system with the aim of realizing a ZTE material with potential for electrochemical sensing. ZTE would be an important requirement in such devices which need to operate at higher than ambient temperatures. Also such a study would enable a deeper understanding of the occurrence of negative thermal expansion which has a bearing on defects, anharmonicity and cation disorder present in AgI and CuI. Indeed these aspects make these soft materials with continuous solid solubility as we have reported in a recent study of nanophase synthesis by mechanochemical reaction involving Ag and Cu powders and I flakes [4].

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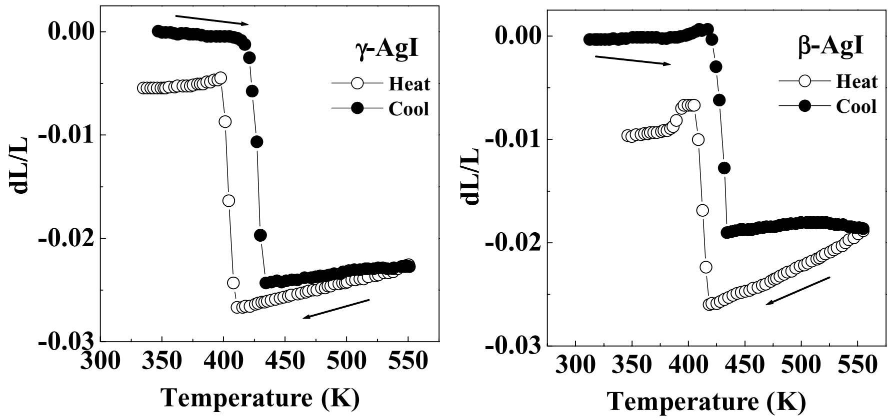

Figure 1 Thermal strain or fractional dilatation of γ-AgI and β-AgI drop sharply as they undergo the superionic phase transition. Note that d$L/L<0$ throughout. Also note the hysteresis.

2. Experimental

Synthesis of β-AgI, γ-AgI, $Ag_{0.50}Cu_{0.50}I$, $Ag_{0.25}Cu_{0.75}I$, $Ag_{0.10}Cu_{0.90}I$, $Ag_{0.05}Cu_{0.95}I$ and γ-CuI compositions was accomplished by the controlled precipitation of a mixed nitrate solution using 2.5% excess KI solution just below boiling temperature. They were characterized by XRD. Sintered pellets of these compositions were used for Linear thermal expansion coefficient (α) measurements were carried out using Quartz push rod dilatometry (LVDT based)[5] on sintered pellets (10 mm long, 12 mm dia.) in Temperature range: 300–900 K. Samples were taken through Heat-Cool cycles to generate ($\Delta L/L$) Vs T (L-length) data. α Vs T data are finally obtained from the raw data thus generated.

3. Results and discussion

Before we present and discuss the experimental data it would be appropriate to briefly mention the salient characteristics of AgI and CuI: Wurtzite/zincblende (AgI) and zincblende (CuI) structures are all built from rather weak MI_4, M = Ag,Cu tetrahedra resulting in a critical ionicity for AgI and non negligible covalency for CuI. Highly anharmonic interatomic potential arises for AgI even at ambient temperature with considerable cation disorder even at ambient temperature and pressure. Structural phase transitions occur in both AgI and CuI as detailed in the introduction. Damped optical modes and unusually flat optical branches arise for both iodides in their phonon dispersion. Very small elastic constants ($c_{11} = 0.451$, $c_{12} = 0.307$, $c_{44} = 0.182$ for γ-CuI, and, $c_{11} = 0.293$, $c_{12} = 0.213$, $c_{44} = 0.0373$, $c_{13} = 0.196$, $c_{33} = 0.354$, $c_{66} = 0.0399$ for β-AgI, all c's in units of teradynes per cm^2 [6]) are observed implying weak restoring forces which features were recently exploited by us to synthesize AgI and CuI as well as solid solutions by a mechanochemical reaction [4]. Thus disorder, anharmonic phonons and weak restoring forces could be involved in the thermal expansion behaviour of CuI and AgI. Tetrahedrally bonded open crystal structures [7] with critical ionicity such as AgI possess low frequency transverse acoustic, "guitar-string" type modes that give rise to negative thermal expansion even at room temperature. The low temperature heat capacity of AgI also shows non-Debye behaviour [8].

From a fundamental thermodynamic point of view the constant pressure coefficient of thermal expansion of a solid can become negative. The stability conditions on Gibbs free energy do not impose any restrictions on this coefficient [9]

$$\text{Gruneisen Parameter } (\gamma) \text{ defined by } \gamma(\mathrm{T, V}) = [\partial \mathrm{P}/\partial(\mathrm{U/V})]\mathrm{V}$$

where, U = Total thermal energy, V = Volume, P = Pressure and T = Temperature provides a quantitative basis for describing positive and negative thermal expansion γ is dimensionless and can take positive and negative values. $\gamma < 0$ implies that solid contracts with increasing temperature $\gamma \sim -7.5$ for AgI from low frequency Raman mode (17 cm^{-1}) with a large pressure derivative.

Figs 1 and 2 exhibit plots of thermal strain or fractional dilatation as a function of temperature for AgI (both β and γ polymorphs) and γ CuI. The common feature in all the three compounds is the abrupt discontinuous change in dL/L at their respective phase transition temperatures 427(heat) and 405 K(cool) for γ -AgI,432 and 413 K for β-AgI and 654 and 639 K for γ-CuI. Hysteresis associated with the phase transition characterizes it as first order. Most significantly, while γ-CuI shows d$L/L > 0$ over the investigated temperature range indicating positive thermal expansion and an anomaly thereof, both β- and γ-AgI show d$L/L < 0$ signalling a negative thermal expansion and an associated anomaly.

The coefficient of linear thermal expansion (α) calculated from dL/L vs T data are displayed in Figs 3 and 4 for β- and γ-AgI, and γ-CuI respectively. These plots show deep NTE anomalies in the case of AgI polymorphs and sharp PTE jump in the case of CuI. These phase transition anomalies must be understood in the light of similar

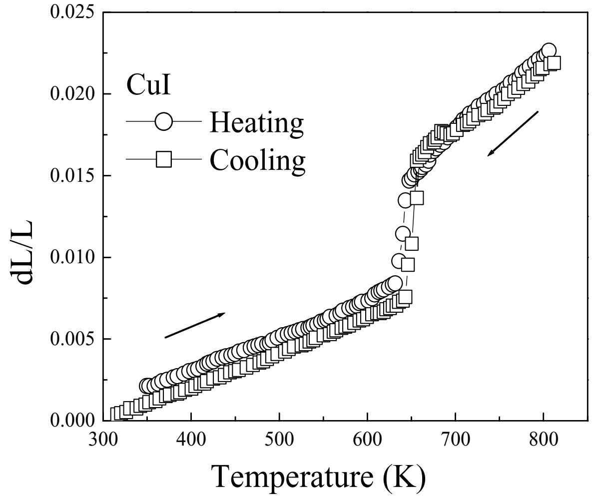

Figure 2 Thermal strain or fractional dilatation in γ-CuI as it undergoes a steep rise at the phase transion to β/α phases. Heating curve and cooling curve are indicated in square and circle respectively. Note that $dL/L > 0$ throughout and the hysteresis.

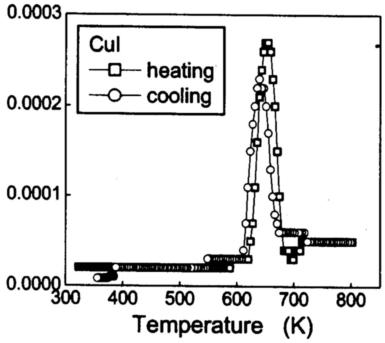

Figure 4 Temperature dependence of the thermal expansion coefficient α during the heating and cooling cycles for β, γ-AgI (Fig. 3) and CuI. Note that before and after the phase transition α remains constant in magnitude. Note the positive thermal expansion at the phase transition temperatures.

anomalies in ionic conductivity and heat capacity among others. The reversibility of the anomalies under Heat-Cool cycle and the hysteresis are apparently characteristic of a first order thermodynamic phase transition. Note however that volume increase as temperature is increased is normal while volume decrease (density increase) upon rise of temperature as observed in AgI is abnormal behaviour. Thus the thermal expansivity of a solid solution of AgI with CuI is expected to change gradually from negative-through –zero-to positive thermal expansion anomaly thus enabling realization of an intermediate composition with nearly zero thermal expansion over an extended range of temperatures.

Fig. 5 displays temperature dependence of fractional dilatation observed for the two Cu-rich compositions $\mathrm{Cu}_{0.95}\mathrm{Ag}_{0.05}\mathrm{I}$ and $\mathrm{Cu}_{0.85}\mathrm{Ag}_{0.15}\mathrm{I}$, the 50:50 composition $\mathrm{Cu}_{0.50}\mathrm{Ag}_{0.50}\mathrm{I}$ and the CuI reference. Even upon a very marginal substitution of Cu by Ag, one notices a reduction in the thermal expansion strongly suggesting the role of Ag in inducing thermal contraction in CuI. The accompanying hysteresis underlines the considerable modification of thermal properties of CuI upon Ag substitution. This modification could include creation of a substantial number of cationic Frenkel defects in the CuI structure which normally does not exhibit ionic conductivity until 473 K.

Of the several models invoked to discuss thermal expansion, we briefly consider two of the more successful ones.

Brown's bond valence model [10] is a semi-quantitative approach to thermal expansion. It considers the temperature dependence of metal-non metal bond. A 'distortion theorem' predicts thermal expansion of inter-atomic bonds. A parameter called bond valance is defined: $S = \exp\,[(R_0 - R)/B$, $R =$ Bond length; R_0, B: experimental constants depending only on the nature of the bond forming atoms. According to this model thermal librations of iodines that destroy local symmetry could account for negative thermal expansion of AgI. Cu substitution probably arrests these librations and makes negative thermal expansion (or thermal contraction) tend towards zero.

Another interesting model was developed by Ishii [11] to explain NTE behaviour as found in AgI (and CuBr). In this cluster-induced distortion model Ishii argues that

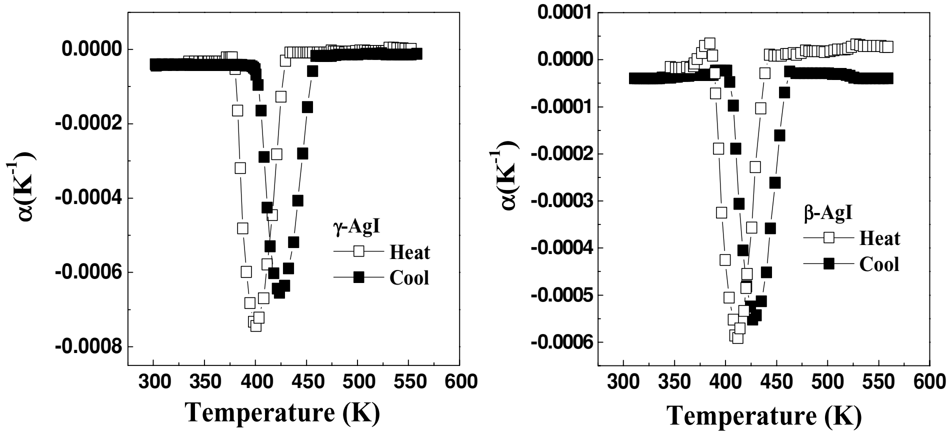

Figure 3 Thermal expansion coefficient (α) vs. temperature plots for β- and γ-AgI through the superionic phase transition. α is negative throughout and anomalous at the phase transition. The anomaly is stronger for γ-AgI.

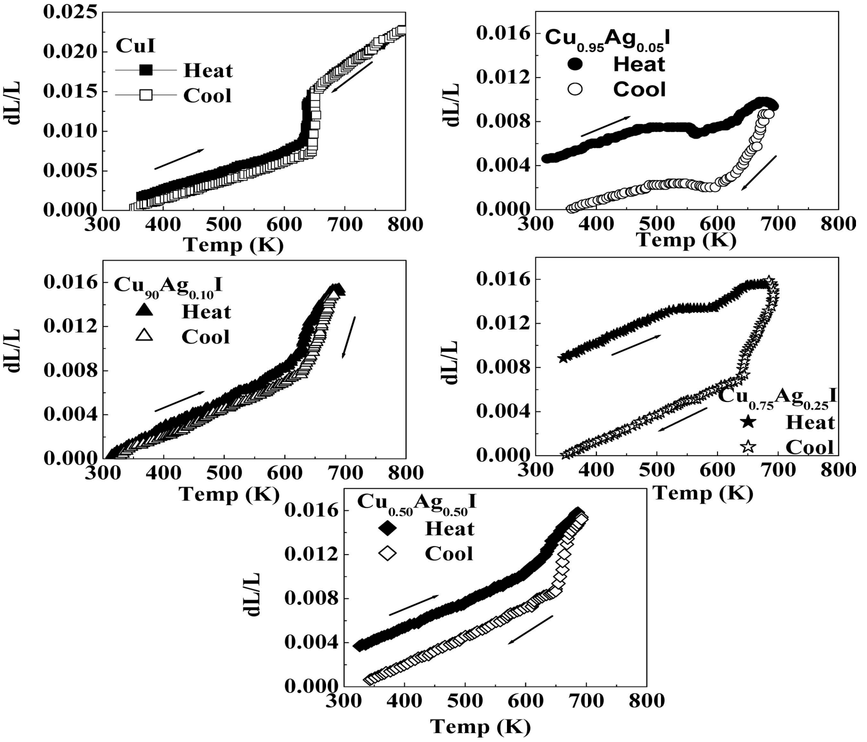

Figure 5 Fractional dilatation dL/L Vs temperature for the Cu-rich solid solutions along with undoped CuI for reference. Note the reduction in expansion as the Ag concentration increases. Hysteresis is observed in all Ag-doped samples during heating and cooling cycles. For the composition $Cu_{0.75}Ag_{0.25}I$ near zero expansion is apparently seen in the heating cycle (slope $= 2.27 \times 10^{-5}\ K^{-1}$) rather than in the cooling cycle with slope $2.8 \times 10^{-5}\ K^{-1}$.

a negative expansion can be induced by a coupling between the pair-cluster of mobile ions (Cu^+ or Ag^+) and the local(static) distortion thereof. This cluster-induced distortion drives the first-order phase transition. Then the Ag-I distance corresponding to the minimum of the pair-potential has the temperature dependence given by

$$R_0(T) = R_0 + \Delta R(T)$$

where, R_0 is a constant at some reference temperature. This model predicts that the local expansion in AgI is negative and the static distortion prevails over the dynamic distortion. Applying this model to the present work, one finds that as more and more Cu substitutes Ag in AgI, one progressively reduces the static distortion until at some stage the static distortion completely disappears resulting in a composition that is expected to show zero thermal expansion. In other words Cu drives the NTE material AgI more and more towards zero thermal expansion (ZTE) material.

$BaTiO_3$ merits a comparison to AgI in that the thermal expansion behavior of AgI is somewhat like that of $BaTiO_3$ [12]. $BaTiO_3$ shows $(\Delta L/L) \sim 10^{-6}$ with a NEGATIVE anomalous peak at 110°C coinciding with the paraelectric (cubic) phase ferroelectric I tetragonal) phase transition. Unlike AgI, the high temperature thermal expansion anomaly in $BaTiO_3$ does not exhibit hysteresis. However, the two low temperature phase transitions in $BaTiO_3$ namely ferroelectric I (tetragonal)-ferroelectric II (orthorhombic) transition at 4°C and ferroelectric II (orthorhombic)-ferroelectric III (trigonal) transition at -99°C both exhibit considerable temperature hysteresis (~ 9°C) [13].

The specific heat peak observed in $BaTiO_3$ is identical to the α peak while in AgI the heat capacity shows a positive anomaly while thermal expansion anomaly is deeply negative. As Barron and White [14] have pointed out using the example of CuCl, heat capacity and thermal expansion need not have the same qualitative temperature dependence. Interestingly the ceramic composition $98\%BaTiO_3 + 2\%Al_2O_3 + Fe_2O_3$ dose not seem to exhibit thermal contraction.

The origin of the thermal hysteresis in the reversible phase transitions of both AgI and CuI must be sought in the 'reactions' gamma- or beta-AgI $<=>$alpha AgI and gamma CuI$<=>$ beta CuI$<=>$Alpha CuI. Under arbitrary conditions of thermal cycling, the forward and reverse reactions are characterized by different 'rates' [15] which are exponential functions of activation energies for the respective processes. Kinetically speaking, hysteresis in transition temperatures could be related to different nucleation barriers in the forward and reverse directions which should be large for transitions involving large changes in molar volume. It turns out that the reverse reactions are almost always more sluggish than the forward ones so that $T^{\text{peak}}{}_{\text{heating}} > T^{\text{peak}}{}_{\text{cooling}}$. The observation of temperature hysteresis $\Delta T_h (= T^{\text{peak}}{}_{\text{heating}} > T^{\text{peak}}{}_{\text{cooling}})$ is a necessary consequence of the coexistence of the two phases involved (gamma and alpha or beta and alpha) [16]. Thus the effects of hysteresis seen in high temperature X-ray diffraction measurements are also manifest in the present dilatometry measurements. In the case of both beta and gamma AgI the transition to the alpha phase is accompanied by a large and negative volume change. It is proposed that the hysteresis observed upon cooling from the alpha phase results from an inhibition of the nucleation of the new beta or gamma phase which should proceed by atomic rearrangements involving the silver ions.

Cu partially substitutes for Ag in the AgI lattice altering the thermodynamic properties (heat capacity, compressibility) of AgI nontrivially. At a certain concentration of Cu the number of Frenkel defects per unit volume in AgI becomes so small that the avalanche-type transition that destabilizes the AgI structure does not take place. The disorder contribution to heat capacity and thus thermal expansion considerably decreases. The Gruneisen parameter also becomes less sensitive to temperature especially in the vicinity of the AgI (undoped) phase transition. The effects of cluster-induced distortion referred to earlier is also progressively reduced. Thus neither cation disorder nor anharmonic phonons can intervene to produce any NTE in substantially Cu –substituted AgI. These statements are substantiated by our earlier work on the DSC of AgI-CuI solid solutions obtained by mechanochemical reaction. (Detailed heat capacity measurements are required to further strengthen the validity of these plausible arguments.) In this work it has been established that Cu substitution even by 10% considerably weakens the phase transition in AgI which is accompanied by the NTE anomaly. In a way the elastic properties which assist in the facile synthesis of AgI-CuI solid solutions by the MCR process are also indirectly involved in the gradual change of thermal expansion behavior from NTE to PTE.

4. Conclusions

Dilatometry measurements (300–600 K) on solid solutions between 'NTE' material AgI and 'PTE' material CuI have shown that $Cu_{0.75}Ag_{0.25}I$ has near zero thermal expansion. Cu apparently helps control cation disorder and anharmonicity of phonons in AgI and stabilizes crystal structure through Cu^+ disorder. The composition $Cu_{0.25}Ag_{0.75}I$ has potential applications for chemical sensing and micro battery electrolytes.

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