Thermomechanical studies on phase transition of $\text{KNO}_2\text{--H}_3\text{BO}_3$ binary

M L N MADHU MOHAN*[†] and C HARANADH

Physics Department, Nagarjuna University, Nagarjunanagar 522 510, India

[†]Present address: Inter University Consortium for D.A.E Facilities, Khandwa Road, Indore 452 001, India

MS received 23 November 1994; revised 15 February 1996

Abstract. Thermomechanical properties like thermal expansion (α_c) and electrostriction along with ΔH and transition temperature are reported for the $\text{KNO}_2\text{--H}_3\text{BO}_3$ binary phase. The transition is classified as second order phase transition. Some of these properties were compared with those of its pure compound. On the basis of thermodynamic properties it is predicted that binary phase is more stable rather than its pure phase.

Keywords. Electrostriction; phase transition; thermal expansion.

1. Introduction

$\text{KNO}_2\text{--H}_3\text{BO}_3$ binary phase is reported by us (Madhu Mohan and Haranadh 1994) to be hexagonal. In this paper we report the thermodynamic and electro-mechanical properties of this binary phase.

2. Experimental

8.51 g of KNO_2 (BDH Chemicals) and 6.18 g of H_3BO_3 (BDH Chemicals) were weighed and dissolved in triple distilled water. The aqueous solution with equimolar proportions of KNO_2 and H_3BO_3 was kept in desiccator and maintained at a constant temperature of 30°C. The naturally grown seedlings in the desiccator were carefully separated with a clean forceps and were suspended in the equimolar solution by a torsion less thread. Transition temperatures and ΔH values were obtained using Perkin and Elmer DSC-7 while thermal expansion (Madhu Mohan 1993) and electrostriction coefficients were studied using an optical interference set-up (Madhu Mohan and Haranadh 1995) described elsewhere. The experimental resolution of this set-up is $\pm 2700 \text{ \AA}$. The electrostriction coefficients were measured using a dc voltage source, the experimental accuracy being $0.002 \times 10^{-18} \text{ m}^2/\text{V}^2$.

3. Results and discussion

3.1 DSC studies

It is reported (Roy 1956) that KNO_2 exhibits a phase transition at 313 K. Our DSC studies (figure 1) revealed that the $\text{KNO}_2\text{--H}_3\text{BO}_3$ binary phase too exhibits a transition. The onset of transition is at 312.4 K while the offset of transition is at 316.2 K. The ΔH value of the binary phase is calculated to be 9.4 J/g while the ΔH value for KNO_2 is reported (Rapport 1966) to be 24.6 J/g. When compared to its pure sample, interestingly, $\text{KNO}_2\text{--H}_3\text{BO}_3$ binary phase possesses a large difference in the

Figure 1. DSC chart of $\text{KNO}_2 - \text{H}_3\text{BO}_3$ binary.

ΔH value and marginal difference in the transition temperature. The large difference in the ΔH value in the binary phase in comparison to its pure one testifies that the binary phase has lower Helm-Holtz energy and thus, is more stable than its pure counterpart. Furthermore, it may be pointed out that the binary phase is not hygroscopic and stable while its pure compound is hygroscopic and unstable (Rao and Rao 1966).

3.2 Thermal expansive measurements

Dilatometric studies on the binary have yielded information about thermal expansion coefficient α_c along c-axis. The α_c of KNO_2 and its binary $\text{KNO}_2 - \text{H}_3\text{BO}_3$ have been determined by using this set-up. The thermal expansion coefficient of the KNO_2 at 28°C is $149 \times 10^{-6}/^\circ\text{C}$ and it has concurred with the reported data (Hellwedge 1975). The variation of α_c with temperature for the binary phase is illustrated in figure 2, α_c of binary phase is measured to be $146 \times 10^{-6}/^\circ\text{C}$. An anomaly has been observed at the transition temperature and correspondingly the thermal expansion coefficient has decreased to $138 \times 10^{-6}/^\circ\text{C}$. The discontinuity in α_c suggests the transition to be of second order. The α_c value of the binary phase at room temperature (28°C) may be compared with that of its pure phase. The magnitude of lattice constant c at 28°C for KNO_2 ($10.253 \text{ \AA}$) (JCPDS) is slightly more than that of binary phase ($10 \text{ \AA}$) at the same temperature (Madhu Mohan and Haranadh 1994), which is in concurrence with the

Figure 2. Thermal expansion coefficient α_c as a function of temperature.

value of α_c for pure ($149 \times 10^{-6}/^\circ\text{C}$) and binary phase ($146 \times 10^{-6}/^\circ\text{C}$) at 28°C respectively.

3.3 Electrostriction studies

It may be pointed out that in the hexagonal crystal system out of the seven point groups (C_6 , C_{3h} , C_{6h} , D_{3h} , C_{6v} , D_6 and D_{6h}), the former three point groups evolve eight independent electrostrictive coefficients while the latter four contribute six independent electrostrictive coefficients (Narasimhamurthy 1981). $\text{KNO}_2\text{--H}_3\text{BO}_3$ binary phase is reported earlier by us (Madhu Mohan and Haranadh 1994) to belong to one point group which exhibits six independent electrostrictive coefficients. They are $R_{1111} = R_{2222}$, $R_{1122} = R_{2211}$, $R_{1133} = R_{2233}$, $R_{3311} = R_{3322}$, R_{3333} and R_{2323} .

Out of these the values of $R_{1122} = R_{2211}$ and $R_{1133} = R_{2233}$ have been measured to be $6.5 \times 10^{-18} \text{ m}^2/\text{V}^2$ and $4 \times 10^{-18} \text{ m}^2/\text{V}^2$ respectively.

4. Conclusions

- (I) The binary phase of $\text{KNO}_2\text{--H}_3\text{BO}_3$ exhibits a second order phase transition nearly at the same temperature as that of its pure sample but ΔH value decreases nearly three fold to that of its pure sample.
- (II) Thermal expansion coefficient α_c of the binary phase at room temperature is marginally higher than that of its pure compound justifying the lattice constant c data obtained from X-ray results.

Acknowledgements

One of the authors (MLNMM) gratefully acknowledges the financial support provided in the form of SRF by CSIR, New Delhi.

References

- Hellwedge K H 1975 *Numerical data and functional relationships in technology* (New York: Springer) p. S135
- Joint committee on powder diffraction standards, data card (card 840 from set 22) for Potassium nitrite
- Madhu Mohan M L N and Haranadh C 1994 *Pramana-J. Phys.* (communicated)
- Madhu Mohan M L N 1993 *X-ray and optical investigations in electro-optic binary crystalline compounds*,
Ph D thesis, Nagarjuna University, Nagarjunanagar
- Madhu Mohan M L N and Haranadh C 1995 *Bull. Mater. Sci.* **18** 599
- Narasimhamurty T S 1981 *Photoelastic and electrooptic properties of crystals* (New York: Plenum Press)
p. 662
- Rao K J and Rao C N R 1966 *Br. J. Appl. Phys.* **17** 1653
- Rapport E J 1966 *J. Phys. Chem.* **45** 2721
- Roy J O and Ra Ogg 1956 *J. Phys. Chem.* **60** 1599