OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 6, No. 11-12, Nov. – Dec. 2012, p. 1170 - 1173

Optical band gap, extinction coefficient and refractive index of $K(NO_3)_{1-x}(ClO_3)_x$ films

R. K. NKUM*, E. K. K. ABAVARE, K. AMPONG, F. BOAKYE

Department of Physics, College of Science, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana

The optical band gap, extinction coefficient and refractive index of $K(NO_3)_{1-x}(ClO_3)_x$ films have been investigated from absorbance and transmittance measurements. The absorption in $K(NO_3)_{1-x}(ClO_3)_x$ solid solutions is found to be due to an allowed direct transmission from the top of the valence band to the bottom of the conduction band at the centre of the Brillouin zone. The band gap of the $K(NO_3)_{1-x}(ClO_3)_x$ solid solutions studied in this work decreases with increasing chlorate concentration. Thus as the concentration of the chlorate ions increases, the absorption edge is shifted to lower energies. The extinction coefficient is lowest for the pure potassium nitrate sample. The introduction of chlorate ions results in an increase in the extinction coefficient and hence the conductivity of the films. It is also observed that the refractive index of the films at photon energy = E_g increases with increasing chlorate ion concentration. With higher chlorate content the band gap shrinks and the refractive index shifts towards longer wavelength.

(Received August 8, 2011; accepted October 30, 2012)

Keywords: Films; Optical properties; Solid solution; $K(NO_3)_{1-x}(ClO_3)_x$

1. Introduction

Ferroelectric thin films have received a great deal of attention because of their device applications [1–5]. Substances in the thin-film form having optical transparency are critical for flat-panel display, photovoltaic cells, light-emitted diodes, energy-efficient windows, and other applications [6, 7].

Thin films of potassium nitrate also have received some attention. In the bulk form, potassium nitrate (KNO_3) has aragonite structure [8] at room temperature (phase II) and is rhombhohedral [9] at 130^o C (phase I). On cooling, phase I does not go directly to phase II, but changes first into a ferroelectric phase III [10] at about 120^o C and then to phase II at a lower temperature around 110^o C. These transitions do not depend upon the nature and history of the material, the heating and the cooling rates, etc. It has been observed that in the thin-film form of KNO_3, the ferroelectric phase III exists over a wide range of temperature down to 0^o C. The thin films of KNO_3 are ferroelectric at room temperature provided they are kept dry [11–13].

New interesting research possibilities in ferroelectricity in potassium nitrate were opened by substituting the NO^{3-} ions with ClO^{3-} ions in the $K(NO_3)_{1-x}(ClO_3)_x$ solid solutions grown from aqueous solutions [14]. The ferroelectric phase in such a system appeared not only on cooling but also on heating in contrast to pure KNO_3, which shows ferroelectricity only on cooling. The temperature range of the ferroelectric phase was found to be broadened drastically by the addition of $KClO_3$. Nkum et al.[15] have recently observed that thick films and bulk samples of melt-quenched $K(NO_3)_{1-x}(ClO_3)_x$ solid solution are ferroelectric even at room temperature.

In this work, the optical properties of melt-quenched $K(NO_3)_{1-x}(ClO_3)_x$ films have been investigated. Since this solid solution is ferroelectric, its films could offer various optical and optoelectronic applications. The absorbance and transmittance are measured from which the optical energy gap, the extinction coefficient and the refractive index are determined.

2. Experimental methods

Analytical grade powders of KNO_3 and $KClO_3$ were used as the starting materials. Powders with the nominal composition $K(NO_3)_{1-x}(ClO_3)_x$ ($0 \le x \le 0.10$) were mixed with acetone and ground in an agate mortar for about 30 min. The resultant mixture was then heated slowly in an alumina crucible till it melted. The melt was stirred to ensure homogeneity. Pre-cleaned glass slide was dipped into the melt and quickly removed. Films were formed on the glass slides. The actual thicknesses of the films were determined by the interference method.

The absorbance and transmittance of light through the films were measured using CE800 SERIES UV spectrophotometer in the wavelength range of 350–800 nm. To ensure the accuracy of the measurements, a baseline scanning was performed on the glass slide before each sample measurement and a subtraction of the baseline was taken. The absorption and transmission measurements were carried out at room temperature (27^o C). The absorption coefficient for the samples, α, was derived from the absorbance spectrum using the thickness reduced method [16, 17].

3. Results and discussion

3.1. Optical energy gap

The absorption edge of non-metallic materials, crystalline or non-crystalline, is determined by the fundamental absorption [18]. When electron-hole interactions are neglected, the density of states profile is well shaped and proportional to some power of energy. The relation between the absorption coefficient, α, and the photon energy, $h\nu$, is [19]

$$\alpha h\nu = A[h\nu - E_g]^{\gamma} \tag{1}$$

where E_g is the optical energy gap and A is a constant. In a direct transition, γ is equal to 0.5 and 1.5 for allowed and forbidden transitions respectively. For indirect transition, γ is equal to 2 for allowed transitions and 3 for forbidden transitions. The absorption coefficients at the higher energy side of the absorption edge are used to fit the Tauc equation (1).

A plot of $(\alpha h\nu)^2$ as a function of $h\nu$ is shown in Fig. 1 for the x= 0.08 and x = 0.10 films. It is observed that the plot is linear in the strong absorption near the fundamental absorption edge, where the contribution of the absorption coefficient due to other mechanisms is negligible [20]. All the films studied in this work show a similar behaviour. Therefore, the absorption in the $K(NO_3)_{1-x}(ClO_3)_x$ solid solutions is from band to band and is only due to an allowed direct transition from the top of the valence to the bottom of the conduction band at the centre of the Brillouin zone. An extrapolation of the linear portion yields the band gap of 1.87 for the x = 0.08 and1.65 eV for the x = 0.10 sample. Fig. 2 shows that the band gap of the films of $K(NO_3)_{1-x}(ClO_3)_x$ solid solutions studied in this work decreases with increasing chlorate ion concentration following the relation

$$E(x) = -10.0x + E(0) \tag{2}$$

within the range of nominal chlorate ion concentration ($0 \leq x \leq 0.1$), where $E(0)$ =2.65 eV. The value of the band gap for KNO_3 obtained in this work is higher than the theoretical value of 1.76 eV [21] but lower than the experimentally determined value of 4.0 eV [22]. The lower experimental value of the band gap in this work could be due to some amount of impurity levels in the sample.

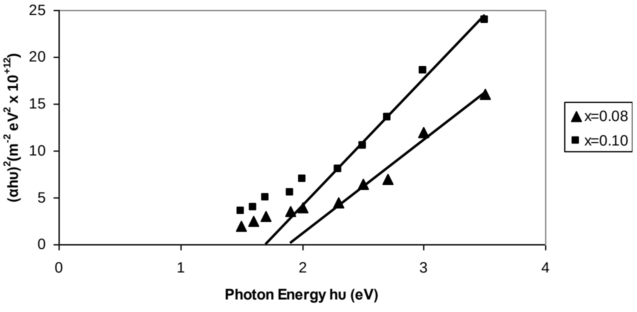

Fig. 1. Dependence of $(\alpha h\upsilon)^2$ on the photon energy for the x = 0.8 and x = 0.10 samples. The intercept on the photon energy axis gives the band gap of the $K(NO_3)_{1-x}(ClO_3)_x$ film.

It is observed that as the concentration of the chlorate ions increases, the absorption edge is shifted to lower energies. The introduction of chlorate ions in the system may lead to impurities or defects. Widths of energy gaps depend on concentration of defects. The increase of defect concentration diminishes the width of the energy gap. The decrease in the energy gaps may be connected either with a change in lattice parameters or with impurity bands in the system with high concentration of defects. A decrease in the energy gap is also observed when pressure is applied on α-$ZrMo_2O_8$ [20]. The introduction of impurities could result in increased pressure at the grain boundaries [23]. It can therefore be speculated that the substitution of chlorate ions for the nitrate ions could alter the centres of the conduction and valence bands as well as the bandwidths, leading to the overall decrease in the band gaps of the solid solutions. The band gap is within the range of 1.65 to 2.65 eV which falls in the range of semiconductors. The materials in the thin film form could serve in photocell and also in solid-state detectors application, which works on the same principle.

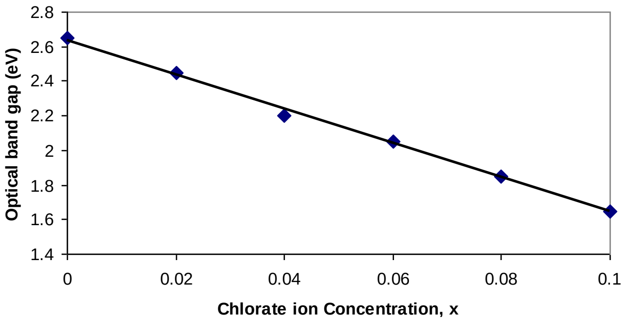

Fig. 2. The dependence of the energy gap of the $K(NO_3)_{1-x}(ClO_3)_x$ films on the chlorate ion concentration.

3.2 Extinction coefficient

The velocity of propagation of electromagnetic wave through a solid is given by the frequency-dependence complex refractive index $N = n - ik$, where n, the refractive index, is related to the velocity, and k, the extinction coefficient is related to the decay, or damping of the oscillation amplitude of the incident electromagnetic wave. The extinction coefficient k can be obtained from the absorption coefficient using the expression [24]

$$k = \frac{\alpha\lambda}{4\pi}. \tag{3}$$

The extinction coefficient is therefore described as being proportional to the penetration of radiation into a solid. It is observed that the extinction coefficient of the films studied in this work generally decreases smoothly with increasing photon energy, as indicated in Fig. 3. A kink is, however, observed at 3.06 eV in the plot for x = 0.08. The extinction coefficient is lowest for the pure potassium nitrate sample. The introduction of chlorate ions increases the extinction coefficient, as in Fig. 3. This indicates that the conductivity of the solid solutions increases with increasing chlorate ion concentration. The films are not very reflective and the radiation through the films experiences a loss which increases with the chlorate ion concentration.

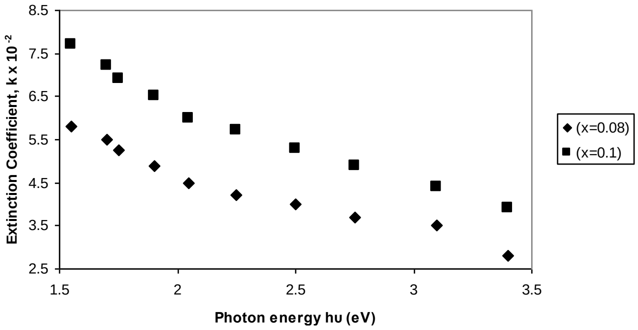

Fig. 3. Dependence of the extinction coefficient of $K(NO_3)_{1-x}(ClO_3)_x$ films on photon energy for x = 0.0.8 and x = 0.10.

3.3 Index of refraction

Knowing the transmittance, *T*, and the absorption, *A*, the reflectance, *R*, can be calculated from the relation

$$A + T + R = 1. \tag{4}$$

For normal-incidence, the refractive index of the films could be calculated from the expression

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \tag{5}$$

for each photon energy. Generally the refractive index of the films studied in this work increases with photon energy, as shown in Fig. 4. It is also observed in Fig. 5 that the refractive index at photon energy $=E_g$ of the films increases with increasing chlorate ion concentration. With higher chlorate content, the band gap shrinks, as already explained, and the refractive index shifts towards longer wavelengths. The value of the refractive index of the chlorate-doped samples is a little higher than the value of 1.50 for pure KNO_3 [21]. The increase of the refractive index of the films is consistent with the increase in the dielectric polarisation of films of the same system [15]. Calculations of the refractive index and the extinction coefficient were made around the absorption edge and the energy gap. The measured refractive index might be slightly affected by grain boundary effects [25]. The high values of the refractive index make this material suitable for the manufacture of capacitors in industry. In the thin-film form, such materials could be used for multi-layer capacitors which will enhance further miniaturisation.

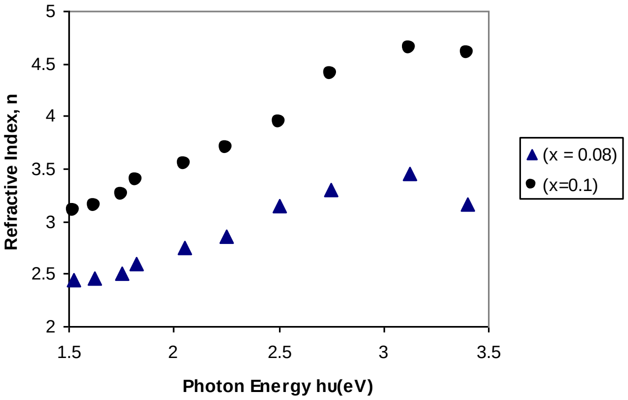

Fig. 4. Dependence of the refractive index of $K(NO_3)_{1-x}(ClO_3)_x$ films on photon energy for x = 0.08 and x = 0.10.

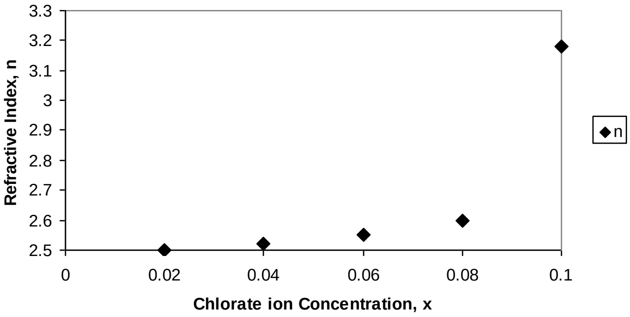

Fig. 5. Dependence of the refractive index at E_g on the chlorate ion concentration of the $K(NO_3)_{1-x}(ClO_3)_x$ thin films.

4. Conclusions

The optical properties of $K(NO_3)_{1-x}(ClO_3)_x$ solid solution have been investigated from the absorbance and transmittance measurements. The absorption in $K(NO_3)_{1-x}(ClO_3)_x$ solid solutions is from band to band and is only due to an allowed direct transition from the top of valence band to the bottom of the conduction band at the centre of the Brillouin zone. The band gap of the films of $K(NO_3)_{1-x}(ClO_3)_x$ solid solutions studied in this work decreases with increasing chlorate ion concentration within the range of chlorate ion concentration $(0 \leq x \leq 0.10)$ investigated. Thus as the concentration of the chlorate ions increases the absorption edge is shifted to the lower energies. The introduction of chlorate ions in the system may lead to impurities or defects. The increase of defect concentration diminishes the width of the energy gap.

The extinction coefficient is lowest for the pure potassium nitrate sample. This indicates that the pure sample is a poor conductor and is essentially loss-free. The introduction of chlorate ions increases the extinction coefficient and hence the conductivity of the films. It is also observed that the refractive index of the films, at photon energy = E_g, increases with chlorate ion concentration. With higher chlorate content, the band gap shrinks and the refractive index shifts to longer wavelengths

Acknowledgement

One of the authors (R.K.N.) thanks the Swedish International Development Cooperation Agency (SIDA) and the Abdus Salam International Centre for Theoretical Physics for the support given him under the Associates Scheme during his visit to the Centre as a Senior Associate. They are also grateful to the Department of Chemistry for the use of the UV Spectrophotometer.

References

[1] M. H. Francombe, in M. H. Francombe, J. I. Vossen (Eds), Physics of Thin Films*:* Mechanic and Dielectric Properties, Academic Press, San Diego, CA, 1995.
[2] K. Yamakawa, S. Trolier-McKintry, J.P. Dougherty, S. B. Krupanidhi, Appl. Phys. Lett. **67**, 2014 (1995).
[3] I. Kanno, S. Hagashi, M. Kitagawa, R. Takayama, T. Hirao, Appl. Phys. Lett. **66**, 145 (1975).
[4] K. K. Li, F. Wang, H. H. Haertling, J. Mater. Sci. **30**, 1386 (1995).
[5] G. R. Bai, H.L.M. Chang, D.J. Lam, Y. Gao, Appl. Phys. Lett. **62**, 1754 (1993).
[6] A. Wang, J. R. Babcock, N.L. Edleman, A.W. Metz, M. A. Lane, R. Asahi, V. P. Dravid, C. R. Kannewurf, A. J. Freeman, T. J. Marks, Proc. Natl. Acad. Sci USA, **98**, 7113 (2001).
[7] D. R. Krammler, D. D. Edwards, B. J. Ingram, T. O. Mason, G. B. Palmer, A. Ambrosini, K. R. Poppelmeier, Proc. Electrochem. Soc. **99-11**, 68 (1999).
[8] D. E. Edwards, Z. Krist. **80,** 154 (1931).
[9] P. E. Tahlonen, Ann. Acad-Sci. Fenn. Ser A **1**, 44 (1947).
[10] S. Sawada, S. Nomura, S. Fuji, J. Phys. Soc. Japan **13**, 1549 (1947).
[11] J. P. Nolta, N.W. Schrubring, R. A, Dork, in: E. F. Weller (Ed), Ferroelectricity, Elsevier, Amsterdam, 1967.
[12] J. P. Nolta, N. W. Schrubring, R. A. Dork, J. Chem. Phys. **42**, 508 (1965).
[13] J. P. Nolta, N. W. Schrubring, R. A. Dork, J. Appl. Phys. 38 (1967) 1671.
[14] Y. Takeuchi, Ferroelectrics **165,** 263 (1995).
[15] R. K. Nkum, T. T. Annan, M. Fudlurrahman, F. Boakye, Mater. Chem. Phys. **93**, 277 (2005).
[16] R.K. Nkum, A.A. Adimado, H. Totoe, Mater. Sci. Eng. B **55**, 102 (1998).
[17] W. G. Driscoll, W. Vaughan, Handbook of Optics, McGraw Hill, New York, 1978.
[18] J. M. Gonzales, in: Bol. Soc. Esp. Cerám. Vidris **36**, 282 (1997).
[19] J. Tauc (Ed), Amorphous and Liquid Semiconductor, Plenum Press, New York, 1974, p. 159.
[20] D. V. S. Muthu, B. Chen, J. M. Wrobel, A. M. Krogh Andersen, S. Carlson, M. B. Kruger, Phys. Rev. B **65**, 064101 (2002).
[21] B. Erdinc, H. Akkus, Phy. Scr. **79**, 025601 (2009)
[22] V. K. Pak, V. A. Nevostruev, High Energy Chem **34**, 246 (2000)
[23] M. E. Lines, A. M. Glass, Principle and Applications of Ferroelectric and Related Materials, Oxford University Press, 1977.
[24] H. S. Soliman, J. Phys. D: Appl. Phys. **31**, 1516 (1998).
[25] T. Peng, J. Piprek, G. Qiu, J. O. Olowolafe, K. M. Unruch, C. P. Swann, E. F. Schunbert, Appl. Phys. Lett. **71**, 2439 (1997).

---

*Corresponding author: rknkum.cos@knust.edu.gh
rknkum@gmail.com