Electrical Properties of Some New Pyrochlores

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Summary Electrical properties of a new series of compounds $A^+A^{3+}B_2^{5+}O_7^{2-}$ ($A^+ = Li^+, Na^+, K^+, A^{3+}$ = a rare-earth cation, and $B^{5+} = Nb^{5+}, Ta^{5+}$, and V^{5+}) crystallising with pyrochlore structure are reported.

Recently[1] the crystallographic properties of a new type of compound of the general formula $A^+A^{3+}B_2^{5+}O_7^{2-}$ ($A^+ = Li^+, K^+, Na^+, A^{3+}$ = a rare-earth cation, and $B^{5+} = Nb^{5+}, Ta^{5+}, V^{5+}$) crystallising with the pyrochlore structure have been reported. This paper deals with their electrical conductivity, dielectric constant, and loss tangent.

The compounds were prepared by the method reported.[1] The electrical conductivity was measured on circular pellets of 12 mm diameter and 1—2 mm thickness pressed in a Carver press at a pressure of 3000 kg cm^{-2}, the densities of the resulting pellets being 92% of the X-ray densities. Electrical contacts were made by means of Du Pont silver paste baked at 600 °C. Electrical resistivities (ζ) both AC/DC were measured on these pellets from 25—800 °C employing Leeds and Northup precision Jones conductivity bridge using Wheatstone's principle. AC resistivities were recorded at the sonic frequencies of 2000 Hz. Dielectric constants (ϵ) and loss tangents (tan δ) were obtained with the GR-716C capacitance bridge at 1 kHz and 50 V cm^{-1} across the sample up to 500 °C in a sample holder designed in this laboratory.[2]

The resistivities (DC) dielectric constants, tan δ and activation energy (as deduced from the slope of the log ζ *vs.* $1/T$ graph) are given in the Table for some of the series. The ϵ and tan δ values exhibit a linear variation with temperature, possibly indicating the para-electric nature of these samples. The resistivities, however, obeyed the exponential law, $\zeta = \zeta e^{\Delta E/kT}$, and the plot of log ζ *vs.* $1/T$ therefore gave straight lines for all the compositions. The slope giving the value of the energy of activation (ΔE) depends upon the nature of both the A^{3+} and B^{5+} ions. For the same rare-earth ion it decreases in the sequence V^{5+}, Nb^{5+}, Ta^{5+}. However, for the same B^{5+} ion, it decreases with increasing atomic number of the rare-earth cation, provided the A^{+} cation is the same. It is known[3] that the conductivities in polycrystalline samples depend to a large extent on imperfections such as porosity, surface states, inhomogeneities *etc.* The activation energy values ΔE are, however, reproducible and are representative of the nature of the semi-conductor. Our values of resistivities ($1{\cdot}2$—8×10^5 ohm cm) are much lower than those reported by Brixner[4] for the rare-earth titanates. This may be ascribed to (i) presence of Li^+, Na^+, or K^+ at the 16*d* site and (ii) replacement of Ti^{4+} by Nb^{5+}, Ta^{5+}, or V^{5+} at the 16*c* site in the pyrochlore structure.

Room temperature (25 °C) *resistivities, dielectric constant, and loss tangent values of* $A^+A^{3+}B_2^{5+}O_7^{2-}$ *compounds*

Composition	DC resistivities /ohm cm × 10^5	ϵ	tan δ/ %	ΔE/eV
$LaLiNb_2O_7$	2	150	2·1	0·32
$LaLiTa_2O_7$	5	100	1·6	0·22
$LaLiV_2O_7$	7	80	1·2	0·43
$YNaV_2O_7$	3	90	1·1	0·45
$GdNaTa_2O_7$	1·8	200	2·1	0·30
$DyKNb_2O_7$	2·2	180	3·2	0·18
$SmKV_2O_7$	1·2	70	1·0	0·20

The order of the resistivities indicates the presence of the same metal ion in different ionization states at similar crystallographic sites. These compounds are, however, normal valence compounds, the ground state (cationic valence band) configurations involving no excited or incompletely ionized states. One could therefore think of a 'transient' configuration of the A^+, A^{3+}, or B^{5+} ions at the 16*d* and 16*c* sites, respectively. Since the A–A distance in the pyrochlore structure is larger[5] than the B–B distance, conduction would be favoured at the B site only. A band transport mechanism by an exchange process through the anion given by

$$O^{2-} + B^{5+} = O^{-} + B^{4+}$$

could be envisaged as the excitation process of minimum energy. Further work on the measurements of thermo-e.m.f. and Seebeck effect measurements is in progress to clarify if the conduction is due only to a cation–cation hopping mechanism and not to a O^{2-} positive hole band process. The decrease of the energy of activation in the sequence $V^{5+} > Nb^{5+} > Ta^{5+}$ is perhaps indicative of the difference between the 5th ionization potential of these ions, that for the V^{5+} being the largest.[6]

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[1] V. S. Chincholkar, *J. Inorg. Nuclear Chem.*, in the press.
[2] V. S. Chincholkar, Ph.D. Thesis, Poona University, August, 1966.
[3] C. G. Koops, *Phys. Rev.*, 1965, **83**, 121.
[4] L. H. Brixner, *Inorg. Chem.*, 1964, **3**, 1065.
[5] H. D. Megaw, 'Ferroelectricity in Crystals,' Methuen, London, 1957, p. 143.
[6] G. Blasse, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1191.